

Synthesis, Spectral and Antimicrobial Investigation of 2-(Naphthalene-1-ylamino)-2-Phenylacetonitrile and 1, 10-Phenanthroline with Five Divalent Transition Metal Ions

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ABSTRACT

Five new mixed ligand metal complexes have been synthesized by the reaction of divalent transition metal ions (Hg, Ni, Zn, Cu and Cd) with 2-(naphthalen-1-ylamino)-2-phenylacetonitrile (L^1) and 1,10-phenanthroline (L^2). The coordination likelihood of the two ligands toward metal ions has been suggested in the light of elemental analysis, UV-Vis spectra, FTIR, ¹H-NMR, flame atomic absorption, molar conductance and magnetic studies. Results data suggest that the octahedral geometry for all the prepared complexes. Antibacterial examination of synthesized complexes in vitro was performed against four bacteria. Firstly, Gram-negative bacteria namely, *Pseudomonas aeruginosa* and *Escherichia coli*. Secondly, Gram-positive bacteria namely, *Bacillus subtilis*, *Staphylococcus aureus*. Results data exhibit that the synthesized complexes exhibited more biological activity than tetracycline pharmaceutical.

Keywords: 2-(naphthalen-1-ylamino)-2-phenylacetonitrile, divalent transition metal ions, mixed ligand.

INTRODUCTION

Mixed ligand complexes preparation has attracted the awareness of several researchers in the recent past so mixed ligand complexes of transition metals are very useful in so many different areas of chemistry like photochemistry, analytical chemistry, magnetochemistry¹. Furthermore these complexes show interesting properties like antibacterial, antifungal, anticancer^{2,3}. Mixed ligand complexes of some transition elements {Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Hg²⁺} have been got interest in the synthesis and characterization of our study. The utility sides of these complexes have got their share of notice as these have found applications in varied fields. The stability of such complexes and the change in electron delocalization on forming a mixed ligand complex by a ligand exchange reaction have been the main subjects of these studies^{4,5}. Metal complexes with mixed ligand are particularly useful because of their potential to bind DNA via multitude of interactions and to cleave the duplex by virtue of their intrinsic chemical, electrochemical and photochemical reactivity⁶⁻⁹. The main part in this work is the complexation of two ligands L^1 and L^2 and coordinated with some divalent transition metals Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Hg²⁺ will be of much interest in elucidating the structure, reactivity and microbiological study of the complexes. 1, 10-phenanthroline forms strong complexes with most metal ions. Among the metal-ion compounds, those of 1, 10-phenanthroline has pulled in line. L^2 ligand as chelating nitrogen donor ligand is among the most productive miscreants for moving metal particles with which it frames

stable edifices in arrangement¹⁰. The complexes were separated and characterized by FTIR, UV-Vis spectra, hydrogen, and nitrogen elements, electronic spectra of the ligand and complexes were obtained, conductivity measurements, magnetic susceptibility.

Chemicals and methods

Chemicals

The primary ligand (L^1) was synthesized in accordance with the procedure described by Rasheed co-worker¹¹. The secondary ligand, (L^2) was obtained by Fluka. Ethanol and glacial acetic acid were obtained from Carl Roth. Nickel (II) chloride hexahydrate, copper (II) chloride dehydrate, Zinc (II) chloride, Cadmium(II) chloride and Mercury(II) chloride were obtained from Sigma-Aldrich.

Synthesis of the five mixed ligand metal complexes

In 25 mL ethanol, the ligand (L^1)-0.001 mol, 0.258 gm and the ligand (L^2)-1 mmol, 0.198 gm were dissolved, and then the solutions were added dropwise to the different solutions of 1 mmol of divalent transition metal ions (Ni²⁺ = 0.278 gm, Cu²⁺ = 0.170 gm, Zn²⁺ = 0.136 gm, Cd²⁺ = 0.219 gm and Hg²⁺ = 0.271 gm) were dissolved in (25 mL) C₂H₅OH. The different solutions containing metal ions with L^1 and L^2 were stirred under anhydrous conditions using sodium sulfate anhydrous. All mixtures were refluxed at (75-80) °C for 3-5 hrs. After that all solution mixtures were left to be stirred at 3 rpm overnight at room temperature. The precipitates were recrystallized with absolute ethanol and then collected and stored in desiccators. The yield % of five mixed ligand metal complexes was equal to (Ni²⁺-complex=76.3, Cu²⁺-complex

Table 1: Analysis and physical data of L¹ [11] and five mixed ligand metal complexes.

Complexes: Formula M.w.t (gm/mol)	yield %	C % Cal (Found)	H % Cal (Found)	N % Cal (Found)	M % Cal (Found)	Chlo- rine % (Found)	Color	M.P °C
L ¹ : C ₁₈ H ₁₄ N ₂ (258.00)	80.9	83.72 (82.33)	5.42 (5.17)	10.88 (10.07)	-----	-----	Maroon	155- 157
L ² : C ₁₂ H ₈ N ₂ .H ₂ O (198.00)	-----	(72.72)	(5.05)	(14.14)	-----	-----	White- Crystal	100- 102
Complex 1: [NiL ¹ L ² Cl(H ₂ O)]Cl.H ₂ O (621.81)	76.3	58.88 (57.89)	4.58 (4.50)	10.88 (9.00)	10.22 (9.43)	12.0 (11.41)	Pale Blue	288- 292
Complex 2: [Cu L ¹ L ² Cl(H ₂ O)]Cl (599.65)	80.6	61.77 (60.03)	4.21 (4.16)	8.24 (9.33)	11.55 (10.59)	12.87 (11.84)	Green Blue	310 Dec.
Complex 3: [Zn L ¹ L ² Cl ₂] 1.5H ₂ O (619.50)	72.6	59.12 (58.11)	5.11 (4.35)	10.22 (9.03)	11.08 (10.55)	11.88 (11.46)	White	323- 326
Complex 4: [Cd L ¹ L ² Cl ₂] 2H ₂ O (675.52)	80.5	54.11 (53.29)	5.44 (4.14)	8.77 (8.28)	17.90 (16.64)	11.76 (10.51)	Off- White	290 Dec.
Complex 5: [Hg L ¹ L ² Cl ₂] H ₂ (745.70)	75.0	48.77 (48.27)	4.24 (3.48)	8.00 (7.50)	27.11 (26.89)	10.77 (9.52)	Off- White	337 Dec.

Dec. =Decomposition

Table 2: Infrared bands data of the ligand L¹ [11] and the synthesized five mixed ligand metal complexes.

Comp. Molecular Formula	$\nu(\text{N-H})$ cm ⁻¹	$\nu(\text{C-H})$ arom. cm ⁻¹	$\nu(\text{C}\equiv\text{N})$ cm ⁻¹	$\delta(\text{N-H})$ cm ⁻¹	$\nu(\text{C=N})+$ (C=C) cm ⁻¹	$\nu(\text{M-N})$ cm ⁻¹	Others
L ¹ : C ₁₈ H ₁₄ N ₂ (258.00)	3340 w.sh	3064 v.sh	2169 v.s.sh	1650 w.sh	1582 s.sh	-----	$\nu\text{H}_2\text{O}=3475$
L ² : C ₁₂ H ₈ N ₂ .H ₂ O (198.00)	-----	3058	-----	-----	1616,1587,1558, 1504,1446,1137 m.sh	-----	$\nu\text{H}_2\text{O}=3359 -$ 3384
Complex 1: [NiL ¹ L ² Cl(H ₂ O)]Cl. H ₂ O (621.81)	3386 m.br	2988 w.sh	2204 v.sh	1637 m.sh	1542,1515,1458, 1425 w.sh	528 w.br	$\nu\text{H}_2\text{O} = 3444$
Complex 2: [Cu L ¹ L ² Cl(H ₂ O)]Cl (599.65)	3384 m.br	2927 w.sh	2183 v.sh	1647 w.sh	1585,1517,1427 m.sh	432 m.sh	$\nu\text{H}_2\text{O} = 3450$
Complex 3: [Zn L ¹ L ² Cl ₂] 1.5H ₂ O (619.50)	3359 m.br	3020 m.sh	2233 v.sh	1625 w.pr	1584,1519,1494, 1427 w.sh	424 s.sh	$\nu\text{H}_2\text{O} = 3454$
Complex 4: [Cd L ¹ L ² Cl ₂] 2H ₂ O (675.52)	3363 m.br	2988 w.sh	2216 v.sh	1623 m.sh	1571,1507,1488, 1414 s.sh	484 w.sh	$\nu\text{H}_2\text{O} = 3448$
Complex 5: [Hg L ¹ L ² Cl ₂] H ₂ O (745.70)	3355 m.sh	2983 w.br	2138 v.s.sh	1632 m.sh	1519,1510,1400 w.br	428 w.sh	$\nu\text{H}_2\text{O} = 3490$

Where: s=strong, m=medium, w=weak, v=very, br=broad, sh=sharp

80.6, Zn²⁺-complex 72.6, Cd²⁺-complex 80.5 and Hg²⁺-complex 75.0).

RESULTS AND DISCUSSION

The color, elemental analysis data and physical properties of the two ligands and the five mixed ligand metal complexes were summarized in Table [1] below

Infra red spectra

The IR data of ligand L¹ [11] and the prepared metal complexes were exhibited in Table 2. Figure 1 was illustrating the FT-IR spectra of the L¹ ligand. The L¹ ligand show stretching vibration of aliphatic and aromatic (C-H) at (2981 and 3064) cm⁻¹ [11-13]. The stretching vibration of (C≡N) of the free ligand L¹ was appeared at (2169) cm⁻¹ [5,11,14]. The (N-H) stretching vibration appeared at (3330) cm⁻¹ [15-17]. The band assigned to (N-H) deformation appeared at (1650) cm⁻¹ [18,19]. The bands that appeared at

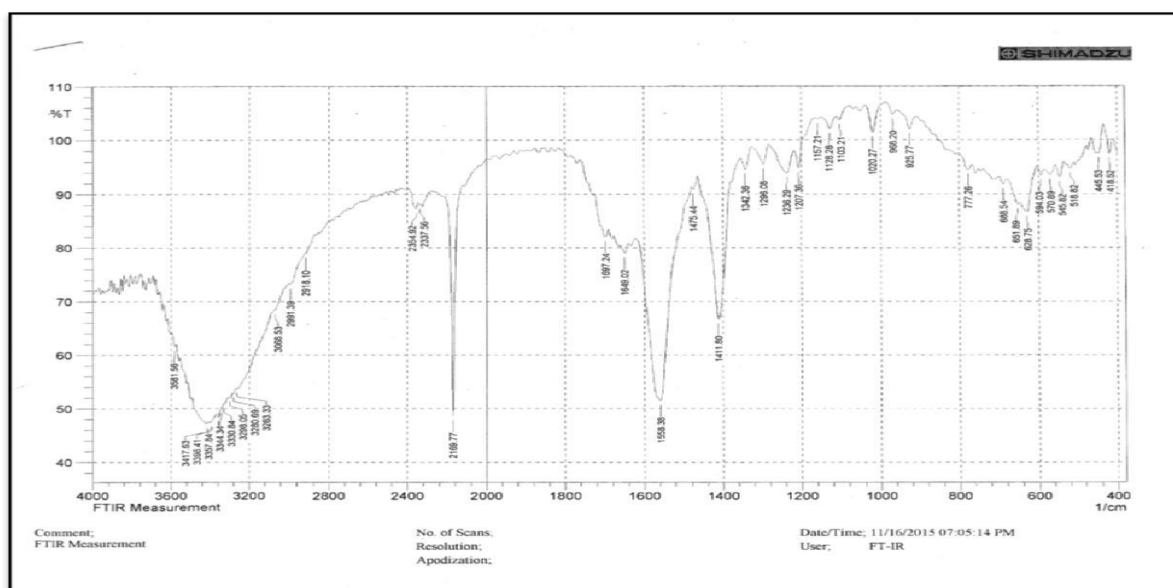

 Figure 1: FT-IR spectrum of L¹ ligand [11].

Table 3: The electronic absorption and molar conductance data of ligands and the five mixed ligand metal complexes.

Compounds: Formula	Wave length (nm)	Wave no. cm ⁻¹	Assignment	Molar Cond. (Ω ⁻¹ cm ² mol ⁻¹)	Magnetic susceptibility μ... eff (B.M)	Suggested Geometry
L ¹ : C ₁₈ H ₁₄ N ₂	355	28169	n→π π→π*	-----	-----	-----
L ² : C ₁₂ H ₈ N ₂ .H ₂ O	269	37174	n→π π→π*	-----	-----	-----
Complex 1: [NiL ¹ L ² Cl(H ₂ O)]Cl.H ₂ O	229	43668				
	958	21505	3A _{2g} →3T _{2g}	38.7	3.31	Octahedral
Complex 2: [Cu L ¹ L ² Cl(H ₂ O)]Cl	670	35842	3A _{2g} →3T _{1g} (F)		(2.82)	
	326	42372	3A _{2g} →3T _{1g} (P)			
Complex 3: [Zn L ¹ L ² Cl ₂] 1.5H ₂ O	669	14947	2E _g →2T _{2g}	32.5	1.88	Octahedral
Complex 4: [Cd L ¹ L ² Cl ₂] 2H ₂ O	325	30769	L → M (CT)	14.8	diamagnetic	Octahedral
Complex 5: [Hg L ¹ L ² Cl ₂] H ₂ O	317	31545	L → M (CT)	10.3	diamagnetic	Octahedral
Complex 5: [Hg L ¹ L ² Cl ₂] H ₂ O	390	25641	L → M (CT)	18.0	diamagnetic	Octahedral

(923-985) cm⁻¹ assigned to lattice water ρ_w (H₂O)¹⁷ and the band that appeared at (3450-3531) cm⁻¹ which assigned to ν(OH) as shown in table (2). The stretching vibration of the (N-H) group of L¹ was appeared at (3340) cm⁻¹ was shifted to (3386, 3384, 3359, 3363 and 3355) cm⁻¹ respectively. This gave an indication that the ligand was coordinated with the metal ions through the nitrogen atom of α-amino group. The stretching vibration at (2169) cm⁻¹ which was assigned to the (C≡N) group of L¹ was shifted to higher frequencies (2204, 2183, 2233 and 2216) cm⁻¹ for (1, 2, 3 and 4 complexes) respectively and to lower frequencies (2138) cm⁻¹ in the spectrum of complex (5) which refers to the linkage of (C≡N) group from nitrogen atom. The spectra of complexes were showed an increase shift in ν (C≡N) stretching vibration towards to higher frequencies and lower frequencies as a result of coordination with metal ion through the lone pair of electrons of nitrogen atom. The δ(N-H) bending vibration of

(N-H) group of L¹ was shifted to (1637, 1647, 1625, 1623 and 1632) cm⁻¹ respectively, this gave further indication that the ligand was coordinated with metal ions through the nitrogen atom of α-amino group and thus supports the complexes formation, Table (2). In the free L² a Strong band at 1137 cm⁻¹ was assigned for stretching vibration of benzene and pyridine ring. This band shows a slight shift to lower or higher frequencies by (18-59) cm⁻¹ as shown in Table 2, which was indicating the coordination of the pyridine nitrogen atoms to the metal ions in a bidentate manner^{20,22}. The appearance a new bands were attributed to ν (M-N) vibration lie in the range from 424-528 cm⁻¹.

Ultraviolet-Visible spectrum and molar conductance of the prepared complexes

The electronic absorption data of the two ligands and the five mixed ligand metal complexes were recorded in C₂H₅OH at room temperature (10⁻⁴ M) as exhibited in Table 3. The spectra of L¹¹¹ and complex [Zn L¹L²Cl₂]

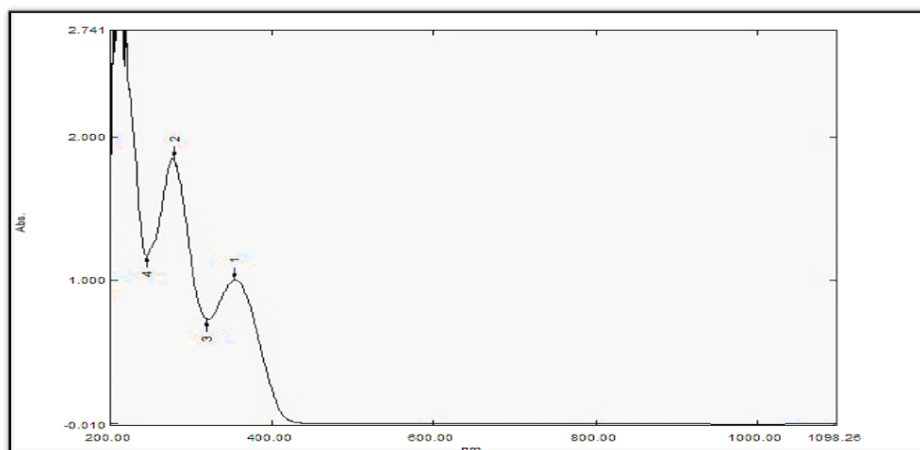
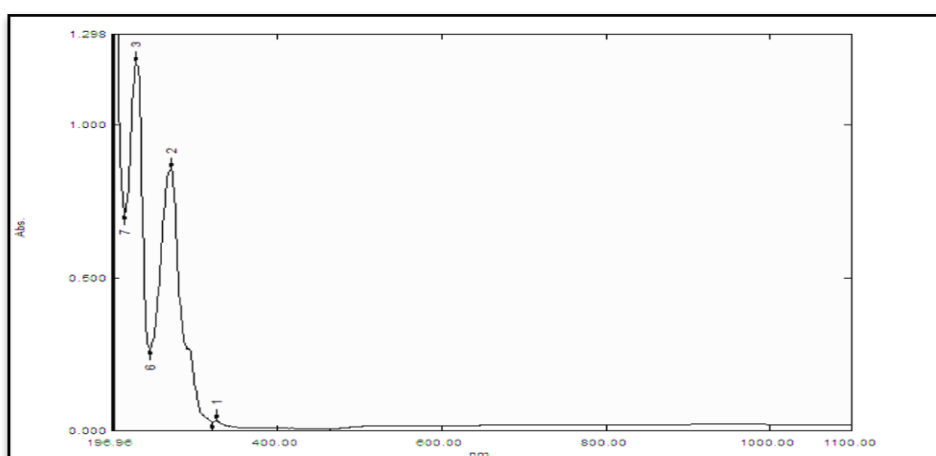

 Figure 3: Ultraviolet-Visible spectrum of L¹ [11].


Figure 4: Ultraviolet-Visible spectrum of Complex 3

 Table 4: ¹HNMR of the L¹[11], L² and the five mixed liand metal complexes.

Compounds: Formula	Groups	Chemical Shifts δ (ppm)
L ¹ : C ₁₈ H ₁₄ N ₂	(-NH)	4.35
	(-CH-C \equiv N)	5.94
	(Ar-H)	6.71-7.98
L ² : C ₁₂ H ₈ N ₂ .H ₂ O	(Ar-H)	7.58-8.83
Complex 1: [NiL ¹ L ² Cl(H ₂ O)]Cl.H ₂ O	(-NH)	4.48
	(-CH-C \equiv N)	5.61
	(Ar-H)	6.61-8.77
Complex 2: [Cu L ¹ L ² Cl(H ₂ O)]Cl	-CH ₃	2.98
	(-NH)	4.21
	(-CH-C \equiv N)	5.87
	(Ar-H)	6.35-8.88
Complex 3: [Zn L ¹ L ² Cl ₂] 1.5H ₂ O	-CH ₃	3.31
	(-NH)	4.45
	(-CH-C \equiv N)	5.58
	(Ar-H)	6.95-8.64
Complex 4: [Cd L ¹ L ² Cl ₂] 2H ₂ O	(-NH)	4.60
	(-CH-C \equiv N)	5.65
	(Ar-H)	6.77-7.83
Complex 5: [Hg L ¹ L ² Cl ₂] H ₂ O	(-NH)	3.98
	(-CH-C \equiv N)	5.71
	(Ar-H)	6.81-8.64

1.5H₂O were shown in Figures 3 and 4. The spectra of the L¹ and L² were exhibited at high intensity bands were become visible in the region (43668, 38461) cm⁻¹ respectively, which were assigned to $\pi \rightarrow \pi^*$ of conjugated system. The bands which appeared in the near UV-Visible region (28168, 37174) cm⁻¹ respectively, were assigned to $n \rightarrow \pi^*$ transition, the intensity and positions of these bands depends on the molecules structure and the kind of the solvent used²³. The electronic spectra of the complexes were offer a new bands, the positions and intensities of these bands are mainly dependent on the ligand field effects, stereochemistry of complexes and electron configuration of the metal ions²⁴. The molar conductance of all the five mixed ligand metal complexes was measured in C₂H₅OH at room temperature. The values of the molar conductance (Table 3) of the five complexes (3, 4 and 5) were indicated that these complexes were non electrolytes, this mean that all the chloride anions are coordinated to the metal ion inside the coordination sphere, while values (Table 3) of the complexes (1 and 2) were indicated that these complexes are weak electrolytes and that for complexes (1 and 2) was one chloride anion coordinated to the metal ion, leaving the other chloride anion outside the coordination sphere.

Proton-Nuclear Magnetic Resonance Spectra

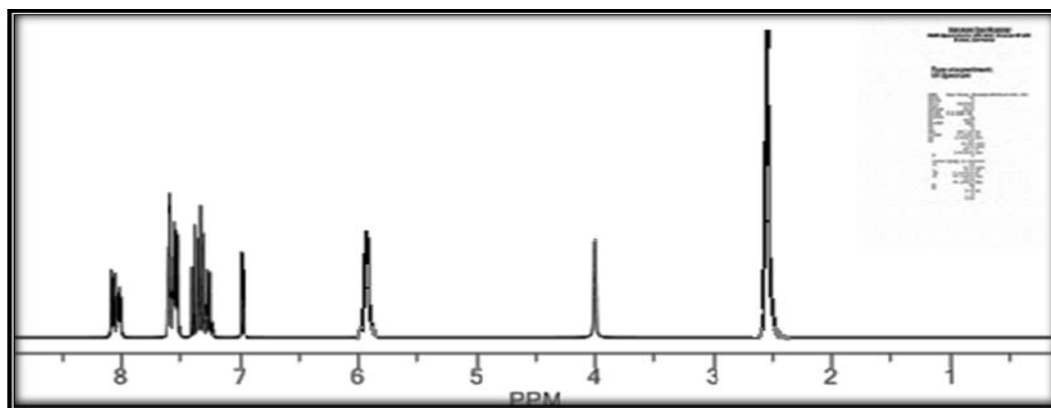
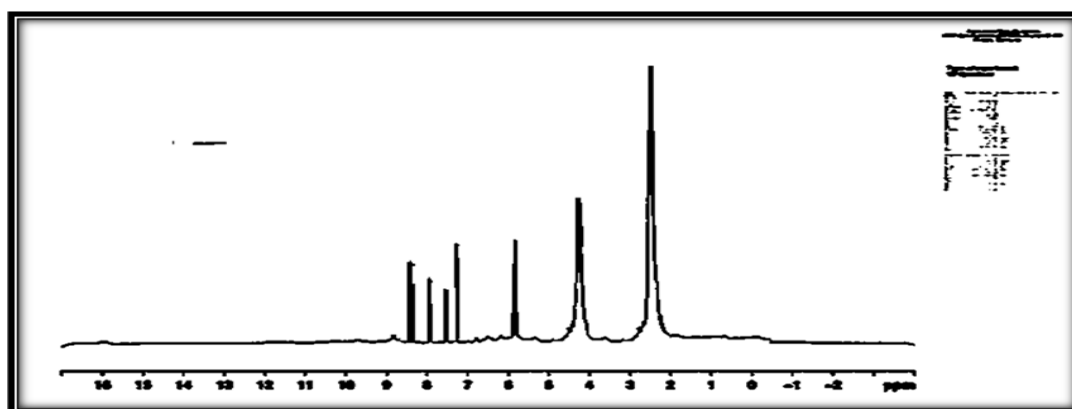

 Figure 5: ^1H NMR spectrum of L^1 [11].

 Figure .6: ^1H NMR spectrum of complex 3.

Table 5: Antibacterial activity of the investigated the five mixed ligand metal complexes to tetracycline antibiotic pharmaceutical.

Compounds	Inhibition-zone (mm)				
	Escherichia coli	Pseudomonas ginosa	aeru-	Staphylococcus aure-us	Bacillussubtilis
DMSO	-----	-----	-----	-----	-----
Tetracycline	-----	-----	-----	15.4	-----
Complex 1: $[\text{NiL}^1\text{L}^2\text{Cl}(\text{H}_2\text{O})]\text{Cl}\cdot\text{H}_2\text{O}$	-----	-----	-----	14	-----
Complex 2: $[\text{Cu L}^1\text{L}^2\text{Cl}(\text{H}_2\text{O})]\text{Cl}$	20	22	-----	21	17
Complex 3: $[\text{Zn L}^1\text{L}^2\text{Cl}_2] 1.5\text{H}_2\text{O}$	-----	-----	-----	10	-----
Complex 4: $[\text{Cd L}^1\text{L}^2\text{Cl}_2] 2\text{H}_2\text{O}$	31	33	-----	32	28
Complex 5: $[\text{Hg L}^1\text{L}^2\text{Cl}_2] \text{H}_2\text{O}$	-----	-----	-----	-----	13

The ligand L^2 was characterized by ^1H NMR spectra, as well as all the five mixed ligand metal complexes as exhibited in Table 4 and Figures 5 and 6. The ^1H NMR spectrum of L^1 [11] exhibited three peaks; firstly was appeared at 4.35 ppm which was assigned to the $-\text{NH}_2$, secondly was appeared at 5.94 ppm which was assigned to the $-\text{CH}_2-\text{C}\equiv\text{N}$ while the thornily was appeared at 6.71-7.98 ppm which was corresponded to the protons of the aromatic $\text{Ar}-\text{H}$. The ^1H NMR spectrum of L^2 was exhibited a peak; which was appeared at 7.58-8.83 ppm was attributed to the protons of the aromatic rig. The ^1H NMR spectra of the five mixed ligand metal complexes were like to that of the two ligands, the only difference were

that in the signal of $=\text{N}-\text{H}$ of the L^1 was shifted in these complexes by (0.13, 1.37, 1.04, 0.25, and 0.37) ppm respectively and the signal of $-\text{CH}_2-\text{C}\equiv\text{N}$ was shifted in these complexes by (0.33, 0.07, 0.36, 0.29 and 0.23) ppm respectively, all these data gave an indication for the five mixed ligand metal complexes formation. Finally, many techniques have been used to illustrate the potential structure of the five mixed ligand metal complexes (Figure 7).

Antibacterial activity of the five mixed ligand metal complexes

All the synthesis compounds have screen antibacterial activities against test bacteria; Bacillus subtilis, Staphylococcus aureus (Gram +ve), Pseudomonas aerugin and

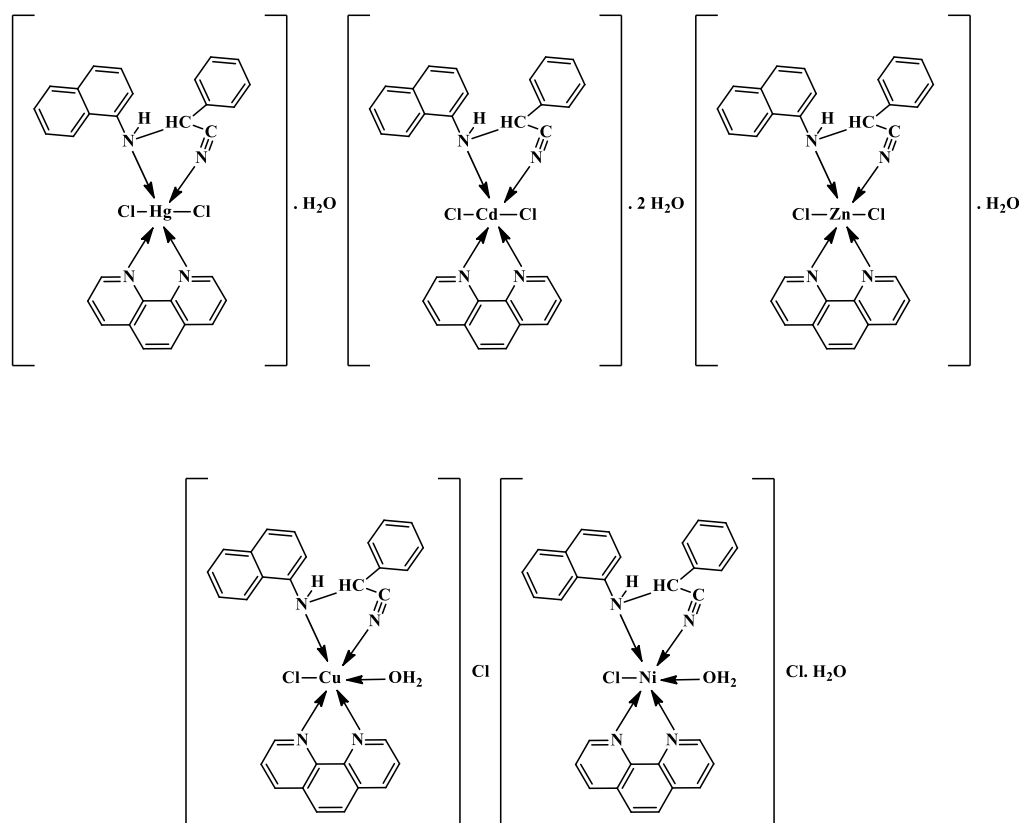


Figure 7: Suggested structure of the five mixed ligand metal complexes.

Escherichia (Gram -ve). Agar (well-diffusion method) was used to detect the activity²⁵. Table 5 was showed the inhibition regions of the synthesis compounds and the solvent that used. Sulphoxide used as solvent and was used as a control (Gram -ve) while Tetracycline was used as a control (Gram +ve). Some compounds (2 and 4) were showed activity against the gram negative bacterium (Escherichia coli), which is the source for so many disease for example; enterotoxigenic strains can produce a toxin in the gut, resulting typically in diarrhea²⁶. The Complexes (2 and 4) were showed activity against the (Gram -ve) bacterium (pseudomonas). The complexes (2 and 4) were showed activity against the gram positive bacterium (Staphylococcus aureus), this bacterium causes food poisoning and was found on the skin²⁷. The complexes (2, 4 and 5) were showed activity against the gram positive bacterium (Bacillus subtilis).

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