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Synthesis, Characterization and Antibacterial Studies of Mixed Ligand Complexes of 2-phenyl-2-(o-tolylamino) Acetonitrile and 1,10-phenanthroline with Some Metal Ions

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ABSTRACT

The bidentate, ligand $L_1=2$ -phenyl-2-(o-tolylamino) acetonitrile was prepared by the reaction of primary amine (o-toluidine) with benzaldehyde in presence of potassium cyanide and acidic media. The metal ion complexes of mixed ligands L_1 and L_2 (1,10-phenanthroline) were prepared by condensation a solution mixture of [VO(II), Cr(III), Mn(II), Fe(II), Co(II) Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II)] metal salts with the ligands (L_1 and L_2) in absolute ethanol with stirring. The complexes were characterized by the Elemental Micro Analysis (C, H, N), Chloride Content, FT-IR, UV-Vis spectra, Thermal Gravimetric Analysis (TGA), flame atomic absorption, molar conductivity as well as magnetic susceptibility measurement. According to the obtained data the probable coordination geometries of these complexes were suggested as octahedral except VO(II) complex was found as square pyramid. Some complexes were found to be non-electrolyte, others were found to be weak electrolyte. The antibacterial activity of the ligands and their metal ion complexes have been studied by screening against various microorganisms, *Staphylococcus aureus*, *Bacillus subtilis* (Gram-positive), *Escherichia* and *Pseudomonas aeruginosa* (Gram-negative). Agar (well-diffusion method) was used to determine the activity. The metal ion complexes gave the formulae: $[VOL_1L_2]SO_4 \cdot 3H_2O$, $[ML_1L_2Cl(H_2O)]Cl$, Where M: (Fe(II), Mn(II) and Cu(II)), $[CrL_1L_2Cl_2]Cl \cdot 2H_2O$, $[CoL_1L_2Cl(H_2O)]Cl \cdot H_2O$, $[ML_1L_2Cl_2] \cdot 3H_2O$. Where M: (Ni(II), Zn(II), Cd(II)) and $[HgL_1L_2Cl_2]H_2O$.

Keywords: 2-Phenyl-2-(o-tolylamino) acetonitrile, Transition metal ions

INTRODUCTION

Strecker, reaction [1] is the oldest known synthesis of α -aminonitriles, since 1850 when Adolph Strecker, interacted an amine, an aldehyde and hydrogen cyanide. α -Aminonitriles synthesis represents one of the simplest and most economical methods, for the preparation of α -amino acids [2,3] for both laboratory and industrial, scales [4]. The synthesis of nitrogen-containing heterocyclic is important such as their no pyrimidine derivatives which have antibacterial and antifungal activities higher than the corresponding antibacterial ampicillin and antifungal nystatin [5,6]. Moreover, among many other applications, they are readily hydrolyzed to diamines and diamine compounds are interest as ligands for Platinum(II) complexes with potential antitumor properties [7]. Complexes with ligands N2-type are of interest not only in theoretical but also from a practical point of view. They have found application as antitumor activity, antibacterial activity [8] and antiviral activity in agriculture field [9]. Phenanthroline (L_2) is a heterocyclic organic compound, as a bidentate ligand in coordination chemistry; it forms strong complexes with most metal ions. In terms of its coordination properties, it is similar to 2, 2'-bipyridine. It has a rigid framework and possesses a super, ability to chelate many metal ions via two nitrogen donors, which shows potential for technological applications, due to their high charge transfer mobility, bright light-emission, and good electro- and photo-active properties [10,11].

EXPERIMENTAL

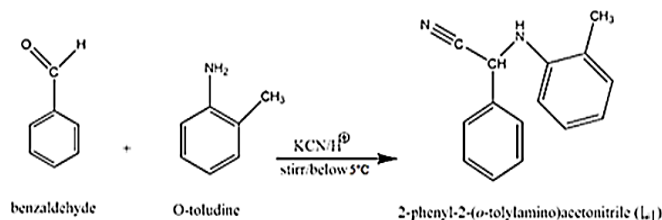
Materials and results

The chemicals used included 1,10-phenanthroline monohydrate, $VOSO_4 \cdot H_2O$, $CrCl_3 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, $FeCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$ (BDH), $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $ZnCl_2$, $CdCl_2 \cdot 2H_2O$, $HgCl_2$ (Merck). The organic solvents which were used (BDH) included ethanol, diethyl ether and Dimethyl Sulphoxide (DMSO).

Synthesis of 2-phenyl-2-(o-tolylamino) acetonitrile [L1]

Potassium cyanide (0.13 g, 0.002 mol) was dissolved in (4 ml) of distilled water and cooled below 5°C. To this solution, benzaldehyde (0.212 g, 0.002 mol) in (25 ml of ethanol) was added [12].

The mixture was stirred maintaining temperature below 5°C. Glacial acetic acid (0.12 g, 0.002 mol) was added with constant. Stirring, keeping temperature below 5°C, this was followed, by the, addition of primary amine [*o*-toluidine (0.214 g 0.002 mol)] in (10 ml of 95% ethanol) and (5 ml) of glacial acetic acid (cooled below 5°C) with continuous, stirring in well ventilated hood. During addition, the temperature was maintained at (15°C). The mixture was stirred for 2 h which, was kept at room temperature for 24 h. The obtained long (pall yellow) needles were washed with diluted hydrochloric acid (0.2 M) to remove any excess of cyanide. The compound was re-crystallized with 95% ethanol. The yield percentage of this procedure was (75.9%). The synthesis route of the ligand was illustrated in reaction below:



Preparation of mixed ligand complexes

The present mixed complexes were prepared by mixing equal amounts (1 mmol) of hot saturated, ethanolic solution of the first ligand [2-phenyl-2-(*o*-tolylamino) acetonitrile] and the second ligand (1,10-phenanthroline) with the same ratio of metal chlorides salts. The mixture was refluxed for 3 h. The resulting complexes were filtered and washed several times with absolute ethanol until the filtrates become clear. The solid complexes then dried in desiccator over anhydrous calcium chloride.

RESULTS AND DISCUSSIONS

Microanalysis

The importance of preparing α -aminonitrile compounds arises from their versatility as starting materials for the synthesis of many compounds. The structures, of the prepared α -aminonitrile with its metal ion complexes were identified, by C, H, N, (Table 1), FT-IR (Table 2) and UV-Visible (Table 3) with some other techniques.

Table 1: Elemental micro analysis and some physical properties of the ligands (L_1 and L_2) and there prepared complexes

Comp.	Formula M.w.t (g/mol)	Yield%	Color	M.P. (°C)	C % Cal. (Found)	H % Cal. (Found)	N % Cal. (Found)	M % Cal. (Found)	Chlorine %
L_1	$C_{15}H_{14}N_2$ (222.00)	75.40	Light-Yellow	128-131	52.87 (52.20)	5.44 (5.13)	10.88 (10.00)	-	-
L_2	$C_{12}H_8N_2 \cdot H_2O$ (198.00)	-	White	100-102	83.72 (82.33)	5.42 (5.17)	10.85 (10.00)	-	-
C_1	$[VOL_1L_2]SO_4 \cdot 4H_2O$ (637.00)	73.50	Light-Green	210-213	50.88 (50.86)	5.75 (4.70)	8.87 (8.79)	8.22 (8.00)	S%=6.22 (6.02)
C_2	$[CrL_1L_2Cl_2]Cl \cdot 3H_2O$ (614.40)	80.63	Yellow-Green	223-225	53.33 (52.73)	5.50 (4.55)	9.33 (9.11)	9.66 (8.46)	17.65 (17.33)
C_3	$[MnL_1L_2Cl(H_2O)]Cl \cdot H_2O$ (564.00)	74.40	Brown	200 Dec.	58.04 (57.44)	4.74 (4.60)	10.70 (9.92)	10.30 (9.73)	13.51 (12.84)
C_4	$[FeL_1L_2Cl(H_2O)]Cl \cdot H_2O$ (564.80)	78.70	Reddish-Brown	230 Dec.	53.36 (52.12)	5.08 (3.98)	8.90 (8.00)	7.07 (6.10)	9.02 (8.09)
C_5	$[CoL_1L_2Cl(H_2O)]Cl \cdot 2H_2O$ (586.00)	86.50	Gerry	210-213	55.67 (53.26)	5.30 (4.76)	9.27 (8.16)	7.80 (6.63)	4.69 (4.04)
C_6	$[NiL_1L_2Cl(H_2O)]Cl \cdot 3H_2O$ (603.69)	83.70	Light-Blue	205-208	55.64 (54.75)	5.43 (4.08)	9.27 (8.83)	7.68 (6.78)	4.63 (3.11)
C_7	$[CuL_1L_2Cl(H_2O)]Cl \cdot H_2O$ (572.54)	87.55	Dark-Blue	233-235	57.94 (56.58)	5.62 (4.54)	9.98 (9.78)	12.87 (11.09)	13.00 (12.40)
C_8	$[ZnL_1L_2Cl_2] \cdot 4H_2O$ (610.39)	83.32	White	255-257	54.18 (53.08)	5.05 (4.91)	10.11 (9.17)	10.40 (9.23)	12.07 (11.63)
C_9	$[CdL_1L_2Cl_2] \cdot 4H_2O$ (657.40)	77.97	Pall-Yellow	270 Dec.	49.88 (49.28)	4.88 (5.62)	8.82 (8.51)	18.70 (17.10)	11.22 (10.80)
C_{10}	$[HgL_1L_2Cl_2] \cdot 2H_2O$ (709.60)	87.00	Off-White	234 Dec.	46.60 (45.65)	4.20 (3.66)	8.65 (7.89)	29.70 (28.26)	10.50 (10.00)

Decomposition

Molar conductance measurement

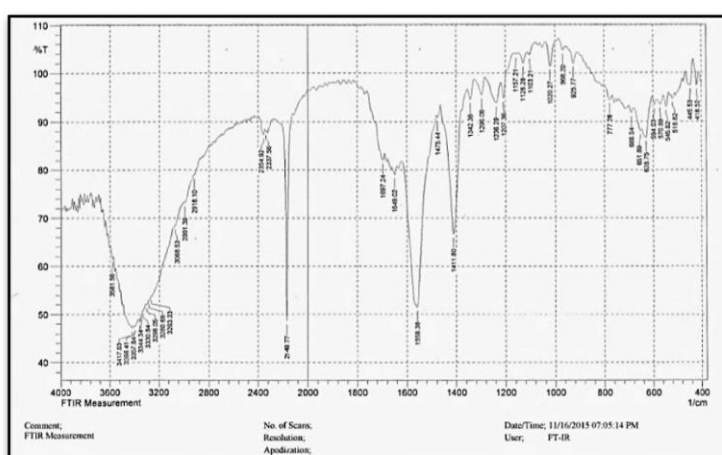
The molar conductance values of the synthetic complexes obtained in ethanol as a solvent at room temperature were listed in Table 3. These results were showed that the Zn(II), Cd(II) and Hg(II) complexes have a molar conductivity value of 17.30, 19.00 and 11.40 respectively, which were indicated the non-ionic nature of these complexes and hence they are non-electrolytic nature [12]. The molar conductivity values of VO(II), Cr(II), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes under investigation were found to be 38.00, 30.50, 25.00, 33.00, 60.00, 35.00 and 23.00 $\Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$, respectively. It is obvious from these data that these complexes are ionic in nature and they are of the type 1:1 electrolytes [13].

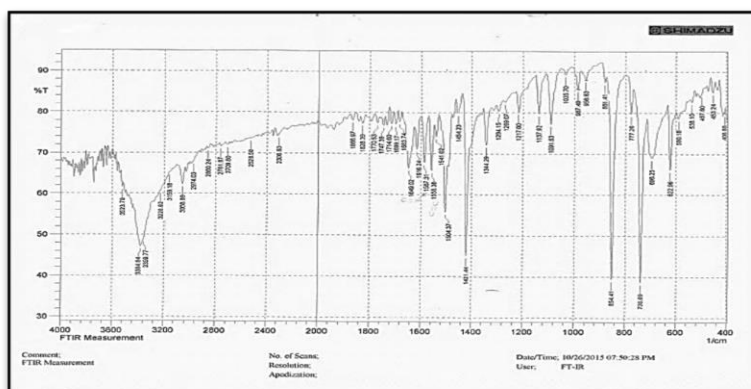
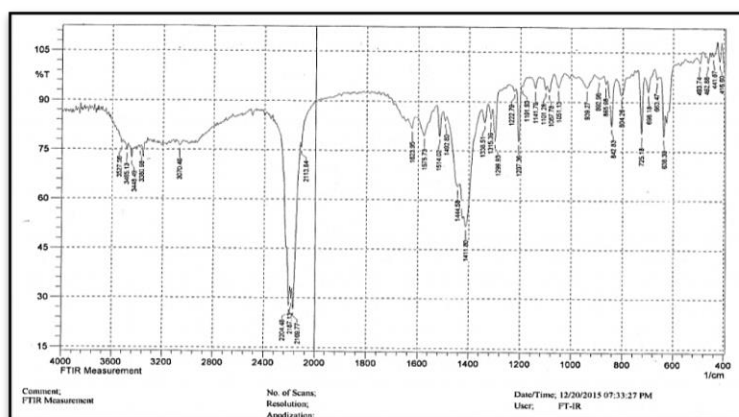
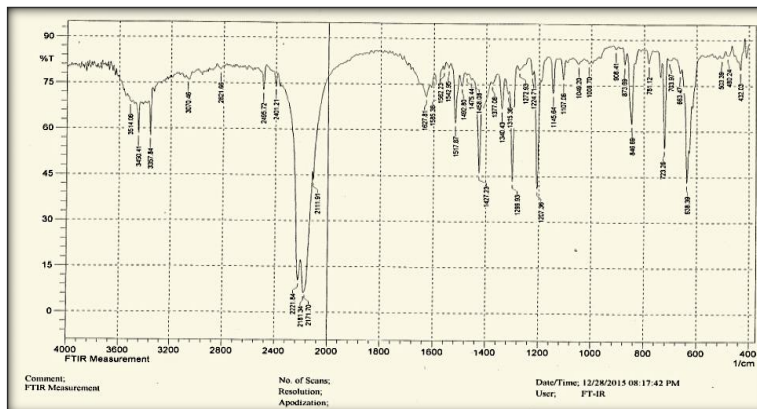
FT-IR spectral studies

Infrared spectroscopy can be used as a good analytical tool to follow the complexation of the metal ions by the organic ligands [14]. [2-phenyl-2-(o-tolylamino)acetonitrile] (L_1) as a bidentate ligand normally coordinates with metal ions through nitrogen of the nitrile group and the nitrogen of the $\nu(N-H)$ group [15,16]. The bands related to $\nu(C\equiv N)$ stretching vibration of the free ligand (L_1) appeared at $(2169) \text{ cm}^{-1}$. The band related to $\nu(N-H)$ stretching vibration appeared at $(3344) \text{ cm}^{-1}$ [17]. The bands related to $\nu(C\equiv N)$ stretching vibrations of the complexes were shifted to higher frequencies (2227, 2196, 2204, 2206, 2221 and 2237) cm^{-1} respectively, in complexes [C_1 , C_3 and C_5-C_8] as a result of coordination with metal ions through the lone pair electrons of nitrogen atom [18], the increase of $\nu(C\equiv N)$ attributed to presence of π -acceptor ligands. The spectra of complexes [C_2 , C_4 , C_9 and C_{10}] were showed shifting to lower frequencies (2167, 2161, 2162 and 2165) which assigned to coordination of $\nu(C\equiv N)$ with metal ions. The decreases were attributed to metal $d\pi$ to ligand $p\pi^*$ back-bonding [19]. The band at $(1649) \text{ cm}^{-1}$ which was assigned to the $\delta(N-H)$ bending vibration of $\delta(N-H)$ group of (L_1) was shifted in the spectra of complexes (C_1-C_{10}) to (1635, 1622, 1625, 1631, 1623, 1629, 1627, 1629, 1623 and 1633) 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. The band ($C=N$) which was characteristic to I, 10-phenanthroline was shifted in all complexes by (14-25) this indicated coordination of (L_2) with the metal ion through two nitrogen atom [20]. New bands were found in the spectrum of the complexes were lie in the range from $(493-561) \text{ cm}^{-1}$ which are not present in the spectrum of the ligand were attributed to $\nu(M-N)$ vibration (Figures 1-4) [21].

Table 2: FT-IR spectra of the ligands (L_1 and L_2) and their metal ion complexes

Comp.	Molecular formula	$\nu(N-H)$ cm^{-1}	$\nu(C\equiv N)$ cm^{-1}	$\delta(N-H)$ cm^{-1}	$\nu(C=N)+$ $(C=C) \text{ cm}^{-1}$	$\nu(M-N) \text{ cm}^{-1}$
L_1	$C_{18}H_{14}N_2$	3344 w.sh	2169 v.s.sh	1649 w.sh	1558,1475,1411 s.sh	-
L_2	$C_{12}H_8N_2 \cdot H_2O$	-	-	-	1616,1587,1558,1541 m.sh	-
C_1	$[VOL_1L_2]SO_4 \cdot 4H_2O$ (637.00)	3332 w.sh	2227 s.sh	1635 w.sh	1517,1492, 1456,1425 m.sh	448 s.sh
C_2	$[CrL_1L_2Cl_2]Cl \cdot 3H_2O$ (614.40)	3355 w.sh	2167 s.sh	1622 w.sh	1466, 1454, 1440 w.sh	426 s.sh
C_3	$[MnL_1L_2Cl(H_2O)]Cl \cdot H_2O$ (564.00)	3357 s.sh	2196 v.sh	1625 m.sh	1573,1512,1492,1463 w.sh	493 W.br
C_4	$[FeL_1L_2Cl(H_2O)]Cl \cdot H_2O$ (564.80)	3382 w.sh	2161 v.sh	1631 m.sh	1566,1508,1411 s.br	568 w.br
C_5	$[CoL_1L_2Cl(H_2O)]Cl \cdot 2H_2O$ (586.00)	3380 w.sh	2204 v.sh	1623 w.sh	1575,1514,1492,1425 m.sh	462 w.sh
C_6	$[NiL_1L_2Cl(H_2O)]Cl \cdot 3H_2O$ (603.69)	3355 m.br	2206 v.sh	1629 m.sh	1542,1515,1458,1425 w.sh	524 w.br
C_7	$[CuL_1L_2Cl(H_2O)]Cl \cdot H_2O$ (572.54)	3357 m.sh	2221 v.sh	1627 s.sh	1517,1492,1458, 1427 s.sh	432 s.sh
C_8	$[ZnL_1L_2Cl_2] \cdot 4H_2O$ (610.39)	3340 w.sh	2237 v.sh	1629 s.br	1515,1492,1425 s.sh	418 s.sh
C_9	$[CdL_1L_2Cl_2] \cdot 4H_2O$ (657.40)	3377 s.sh	2162 s.sh	1623 s.sh	1514,1448,1425 s.sh	416 m.sh
C_{10}	$[HgL_1L_2Cl_2] \cdot 2H_2O$ (709.60)	3373 s.sh	2165 s.sh	1633 s.br	1515,1448,1429 m.sh	424 m.sh

Figure 1: FT-IR spectrum of [L_1]

Figure 2: FT-IR spectrum of [L₂]Figure 3: FT-IR spectrum of [C₃]Figure 4: FT-IR spectrum of [C₇]

Electronic spectra (UV-Visible) studies

The UV-Visible spectra of the two ligands (L₁ and L₂) showed intense bands at (28248, 35714) cm⁻¹ and (37174, 43668) cm⁻¹ which were belong to n→π* and π→π* respectively. The two bands were attributed to conjugate of nitrile group and aromatic ring [22-25], as shown in Table 3. The electronic spectra of the mixed ligand complexes were recorded for their solution in ethanol at room temperature (10⁻⁴ M) in the range (190-1100) nm. The electronic spectrum of VO(II) complex was exhibited three transitions at (15384, 18348 and 24154) cm⁻¹ related to ²B_{2g}→²E_g, ²B_{2g}→²B_{1g} and ²B_{2g}→²A_{1g} respectively suggesting square pyramid complex, Cr(III) complex was exhibited three transitions at (11235, 15503 and 18281) cm⁻¹ assignable to ⁴A_{2g}(F)→⁴T_{2g}(F), ⁴A_{2g}(F)→⁴T_{1g}(F) and ⁴A_{2g}(F)→⁴T_{1g}(P) transitions, respectively, suggesting octahedral environment around Cr(III) ion. The magnetic moment value was found to be (3.87) B.M, which is also agree well with the known values for Cr(III) complex in octahedral geometry [26]. The conductance measurements indicate that complex was to be an electrolyte behavior. The spectrum of the Mn(II) complex was showed two bands the first (d-d) transition observed at (11025) cm⁻¹ and the second was (26525) cm⁻¹ due to charge transfer (M→L). The first band may be assigned to the transition ⁶A_{1g}→⁴T_{1g} (D). The magnetic moment values (6.03) B.M was in accordance with those having octahedral complexes [27]. The spectrum of the Fe(II) complex was showed one band (d-d) transition observed at (14492) cm⁻¹ this band may be assigned to the transition ⁵T_{2g} (D)→⁵E_g (D). The magnetic moment of the complex was (4.95) B.M, indicating paramagnetic nature of the complex and octahedral geometry [27]. The spectrum of the Co(II) complex was showed three bands observed at (10559, 14064 and 18796) cm⁻¹ respectively, these bands may be assigned to the transitions ⁴T_{1g}(F)→⁴T_{2g}(F), ⁴T_{1g}(F)→⁴A_{2g} and ⁴T_{1g}(F)→⁴T_{1g}(P) respectively. The magnetic moment value (4.03) B.M was in accordance with those having octahedral structure [28,29].

The spectrum of the Ni(II) complex was showed three bands observed at (15503, 18281 and 28571) cm^{-1} respectively these bands may be assigned to the transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and C.T. The magnetic moment value (3.31) B.M was in accordance with those having octahedral structure [30]. The electronic spectrum of Cu(II) complex, was exhibited absorption band at (14084) cm^{-1} assignable to ${}^2E_g \rightarrow {}^2T_{2g}$ transition indicating octahedral geometry [31]. The Cu(II) complex showed magnetic moment 1.80 B.M. corresponds to one unpaired electron, which offers possibility of an octahedral geometry [32]. Conductivity measurement was showed the complex to be electrolyte behavior. The Zn(II), Cd(II) and Hg(II) complexes are diamagnetic. According to the empirical formulae, an octahedral geometry was proposed for these complexes (Figures 5-7) [33].

Table 3: Electronic spectra, spectra parameter and magnetic susceptibility molar conductance and suggested stereo chemical of the ligands and their metal ion complexes

Comp.	Assignments	wave no. (cm^{-1})	Wavelength λ (nm)	Geometry Suggested	Meff (B.M)	Molar Cond. $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$
L ₁	$n \rightarrow \pi^*$	28248	354	-----	---	-----
	$\pi \rightarrow \pi^*$	35714	280			
L ₂	$n \rightarrow \pi^*$	37174	269	-----	---	-----
	$\pi \rightarrow \pi^*$	43668	229			
C ₁ VO(II)	${}^2B_{2g} \rightarrow {}^2E_g$	15384	650	Square pyramid	2.33	38.6
	${}^2B_{2g} \rightarrow {}^2B_{1g}$	18348	545			
	${}^2B_{2g} \rightarrow {}^2A_{1g}$	24154	414			
C ₂ Cr(III)	${}^4A_{2g} \rightarrow {}^4T_{2g}$	11235	890	Octahedral	3.87	30.5
	${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$	15503	645			
	${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$	18281	547			
C ₃ Mn(II)	${}^6A_{1g} \rightarrow {}^4T_{1g}(D)$	11025	907	Octahedral	6.03	25.3
	C.T	26525	377			
C ₄ Fe(II)	${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$	14492	680	Octahedral	4.95	40.3
	C.T	25641	390			
C ₅ Co(II)	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	10559	947	Octahedral	4.03	53.4
	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	14064	711			
	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	18796	532			
C ₆ Ni(II)	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	15503	645	Octahedral	3.31	35.0
	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	18281	547			
	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	26354	379			
C ₇ Cu(II)	${}^2E_g \rightarrow {}^2T_{2g}$	15360	651	Octahedral	1.80	23.2
C ₈ Zn(II)	C.T	26737	374	Octahedral	Diamagnetic	17.0
C ₉ Cd(II)	C.T	27397	365	Octahedral	Diamagnetic	19.5
C ₁₀ Hg(II)	C.T	26041	384	Octahedral	Diamagnetic	11.7

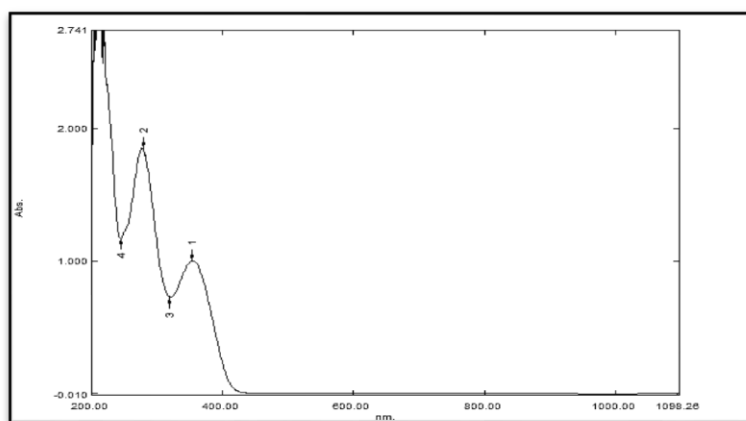
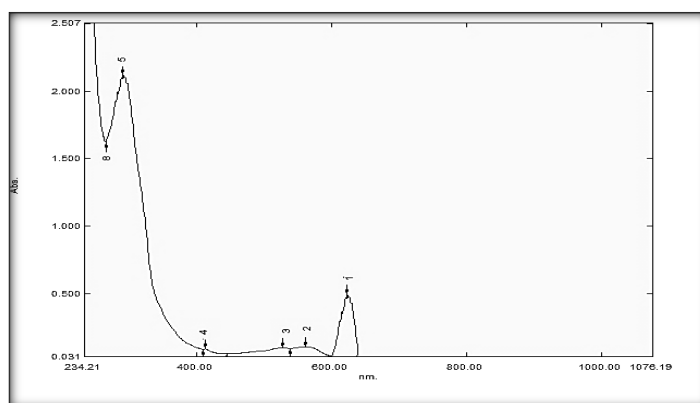
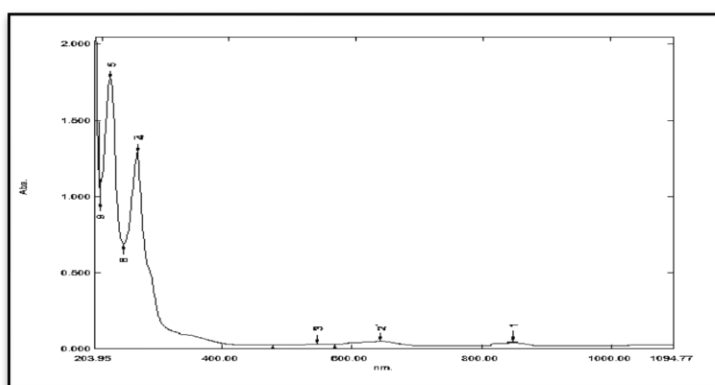


Figure 5: UV-Vis spectrum of [L₁]

Figure 6: UV-Vis spectrum of [C₁]Figure 7: UV-Vis spectrum of [C₂]

X-ray powder diffraction

X-ray powder diffraction pattern of L₁ and L₂ and their metal ion complexes were carried out in the range of $0^\circ < 2\theta < 70^\circ$ in order to give an insight about the lattice dynamics of these complexes. The X-ray powder diffraction obtained reflects a shadow on the fact that each solid represents a definite compound of a definite structure which is not contaminated with the starting materials. The XRD spectra for chelates show that the coordination of L₁ and L₂ to the present metal ions [VO(II), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II)] changes the XRD/pattern of the ligands. This means that the complexes are not fitted in the same phase of L₁ and L₂. In addition, on comparing the XRD spectra of the ternary chelates, with the XRD spectra of the/free ligands it was concluded that all ternary chelates under study can be considered to have a crystalline/structure, as they lack sharp/peaks (Table 4) [34].

Table 4: X-ray powder diffraction pattern of the ligands (L₁ and L₂) and their metal ion complexes

Compound	Formula	Particle size (nm)
L ₁	C ₁₅ H ₁₄ N ₂	193
L ₂	C ₁₂ H ₈ N ₂ .H ₂ O	122
C ₁	[VOL ₁ L ₂]SO ₄ .4H ₂ O (637.00)	122
C ₂	[CrL ₁ L ₂ Cl ₂]Cl.3H ₂ O (614.40)	174
C ₃	[MnL ₁ L ₂ Cl(H ₂ O)]Cl.H ₂ O (564.00)	113
C ₄	[FeL ₁ L ₂ Cl(H ₂ O)]Cl.H ₂ O (564.80)	134
C ₅	[CoL ₁ L ₂ Cl(H ₂ O)]Cl.2H ₂ O (586.00)	110
C ₆	[NiL ₁ L ₂ Cl(H ₂ O)]Cl.3H ₂ O (603.69)	282
C ₇	[CuL ₁ L ₂ Cl(H ₂ O)]Cl.H ₂ O (572.54)	108
C ₈	[ZnL ₁ L ₂ Cl ₂] 4H ₂ O (610.39)	165
C ₉	[CdL ₁ L ₂ Cl ₂] 4H ₂ O (657.40)	177
C ₁₀	[HgL ₁ L ₂ Cl ₂] 2H ₂ O (709.60)	118

¹H-NMR/and ¹³C-NMR spectra

The primary ligand (L₁) was characterized by ¹H-NMR and ¹³C-NMR spectroscopic methods, in addition to ten complexes (C1-C10) using DMSO (d6) as a solvent as shown in Table 5 and Figures 8-11. The ¹H-NMR spectrum of the ligand (L₁) was showed five peaks; the first one appeared at (2.23) ppm which was corresponded to the (-CH₃) protons, the second peak appeared at (2.63) ppm and was assigned to the solvent peak, the third peak was appeared at δ=4.32 ppm was assigned to the (-NH) proton while the fourth peak appeared at δ=5.92 ppm which was corresponded to the (-CH-C≡N). The last peak which was appeared at (6.77-7.98) ppm was attributed to the aromatic, protons [35]. The ¹H-NMR spectrum, of the second ligand (L₂) was showed peaks appeared at (7.58-8.83) ppm was attributed to the aromatic protons [36]. The ¹H-NMR spectra of the complexes (C1-C10) were similar to that of the ligands [L₁ and L₂], the only difference were that the signal of (-NH) of the ligand was shifted in these complexes by (0.10, 0.21, 0.19, 0.20, 0.28, 0.08, 0.12, 0.13, 0.32 and 0.34) ppm respectively and the signal of (-CH-C≡N) was shifted in complexes by (0.11, 0.31, 0.07, 0.14, 0.06, 0.29, 0.08, 0.40, 0.24 and 0.21) ppm this gave an indication for complexes formation.

The ¹³C-NMR spectrum of, the ligand (L₁) was showed four peaks, the first one was appeared at δ=22.50 ppm which was corresponded to the (-CH₃) carbon the second peak appeared at δ(40.00) ppm which was corresponded to the solvent peak (DMSO), the third peak was appeared at δ=60.21 ppm was corresponded to the (-CH-C≡N) carbon and the last peak was appeared at δ=118.6 ppm was assigned to the (-CH-C≡N) carbon atom [37]. The ¹³C-NMR spectra of the complexes, (C1-C10) were similar to that of the ligands [L₁ and L₂], the only difference was that the signal of (-CH-C≡N) carbon of the ligand was shifted in these, complexes by (2.71, 1.67, 2.20, 0.49, 1.44, 2.67, 3.07, 1.33, 2.94 and 0.35) ppm respectively and the signal of (-CH-C≡N) carbon was shifted in these complexes by (1.41, 2.82, 2.37, 2.82, 0.60, 0.90, 2.63, 3.41, 2.52 and 1.58) ppm. The (-HC-N) band of the (L₂) ligand was shifted by (2.2, 1.8, 1.0, 0.8, 1.4, 1.1, 1.0, 0.3, 0.3, 1.1) respectively this gave an indication for complexes formation.

Table 5: ¹H-NMR and ¹³C-NMR data of ligands (L₁ and L₂) and their metal ion complexes

Comp.	Formula	Groups	Chemical Shifts δ(ppm)	Groups	Chemical Shifts δ (ppm)
L ₁	C ₁₅ H ₁₄ N ₂	-CH ₃ (-NH) (-CH-C≡N) (Ar-H)	2.23 4.32 5.92 6.77-7.98	(-CH ₃) (-CH- C≡N) (-CH- C≡N)	22.50 60.21 118.64
L ₂	C ₁₂ H ₈ N ₂ .H ₂ O	(Ar-H)	7.58-8.83	(-HC-N)	121.5-149.9
C ₁	[VOL ₁ L ₂]SO ₄ .4H ₂ O (637.00)	-CH ₃ (-NH) (-CH-C≡N) (Ar-H)	2.10 4.42 5.81 6.73-7.87	(-CH ₃) (-CH- C≡N) (-CH- C≡N) (-HC-N)	20.01 57.50 117.23 122.2-148.4
C ₂	[CrL ₁ L ₂ Cl ₂]Cl.3H ₂ O 614.40)(-CH ₃ (-NH) (-CH-C≡N) (Ar-H)	2.31 4.53 5.61 6.92-8.43	(-CH ₃) (-CH- C≡N) (-CH- C≡N) (-HC-N)	24.01 58.54 115.82 121.8-148.4
C ₃	[MnL ₁ L ₂ Cl(H ₂ O)]Cl. H ₂ O (564.00)	-CH ₃ (-NH) (-CH-C≡N) (Ar-H)	1.86 4.13 5.99 6.23-8.33	(-CH ₃) (-CH- C≡N) (-CH- C≡N) (-HC-N)	21.22 58.01 116.27 120.1-149.5
C ₄	[FeL ₁ L ₂ Cl(H ₂ O)]Cl. H ₂ O 564.80)(-CH ₃ (-NH) (-CH-C≡N) (Ar-H)	2.10 4.52 5.78 6.40-7.98	(-CH ₃) (-CH- C≡N) (-CH- C≡N) (-HC-N)	20.42 59.72 115.82 121.7-148.7
C ₅	[CoL ₁ L ₂ Cl(H ₂ O)]Cl.2 H ₂ O 586.00) (-CH ₃ (-NH) (-CH-C≡N) (Ar-H)	2.07 4.60 5.92 6.72-8.34	(-CH ₃) (-CH- C≡N) (-CH- C≡N) (-HC-N)	23.11 58.77 118.04 122.3-149.3
C ₆	[NiL ₁ L ₂ Cl(H ₂ O)]Cl.3 H ₂ O (603.69)	-CH ₃ (-NH) (-CH-C≡N) (Ar-H)	2.82 4.40 5.63 6.61-8.55	(-CH ₃) (-CH- C≡N) (-CH- C≡N) (-HC-N)	25.21 62.88 117.74 121.5-148.8
C ₇	[CuL ₁ L ₂ Cl(H ₂ O)]Cl. H ₂ O (572.54)	-CH ₃ (-NH) (-CH-C≡N) (Ar-H)	1.98 4.20 5.84 6.31-8.89	(-CH ₃) (-CH- C≡N) (-CH- C≡N) (-HC-N)	23.72 57.14 116.01 122.2-149.6
C ₈	[ZnL ₁ L ₂ Cl ₂]. 4H ₂ O (610.39)	-CH ₃ (-NH) (-CH-C≡N) (Ar-H)	2.31 4.45 5.52 6.95-8.66	(-CH ₃) (-CH- C≡N) (-CH- C≡N) (-HC-N)	26.05 58.88 115.23 120.3-148.4
C ₉	[CdL ₁ L ₂ Cl ₂]. 4H ₂ O (657.40)	-CH ₃ (-NH) (-CH-C≡N) (Ar-H)	2.33 4.64 5.68 6.77-7.89	(-CH ₃) (-CH- C≡N) (-CH- C≡N) (-HC-N)	23.12 63.15 116.12 121.5-149.6
C ₁₀	[HgL ₁ L ₂ Cl ₂]. 2H ₂ O (709.60)	-CH ₃ (-NH) (-CH-C≡N) (Ar-H)	2.38 3.98 5.71 6.81-8.54	(-CH ₃) (-CH- C≡N) (-CH- C≡N) (-HC-N)	18.64 59.86 117.06 121.1-148.4

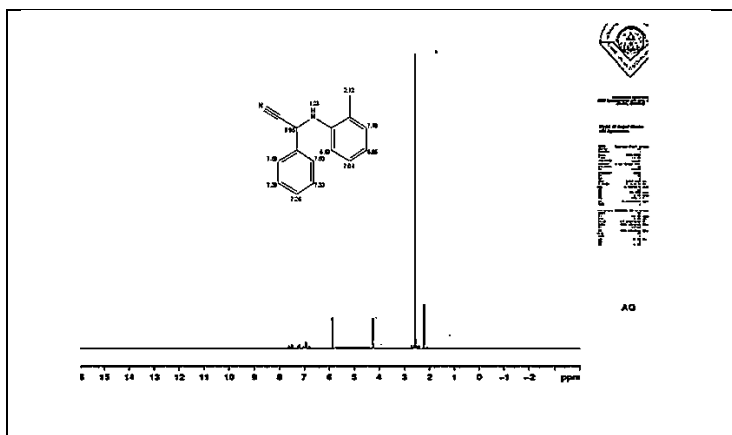


Figure 8: ¹H-NMR spectrum of the ligand [L1]

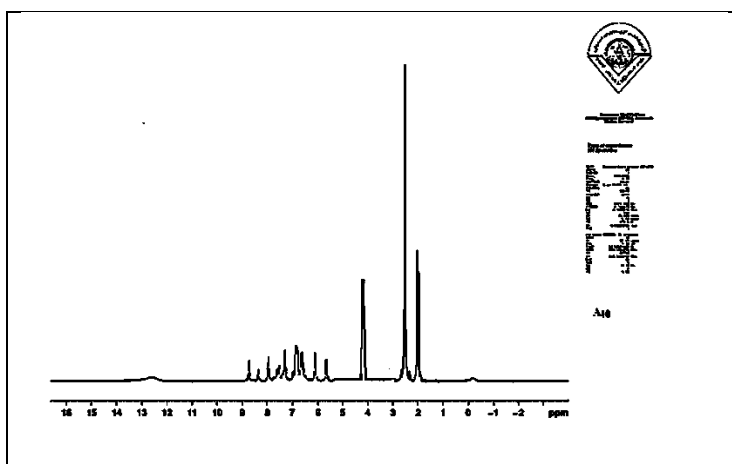


Figure 9: ¹H-NMR spectrum of the complex [C]

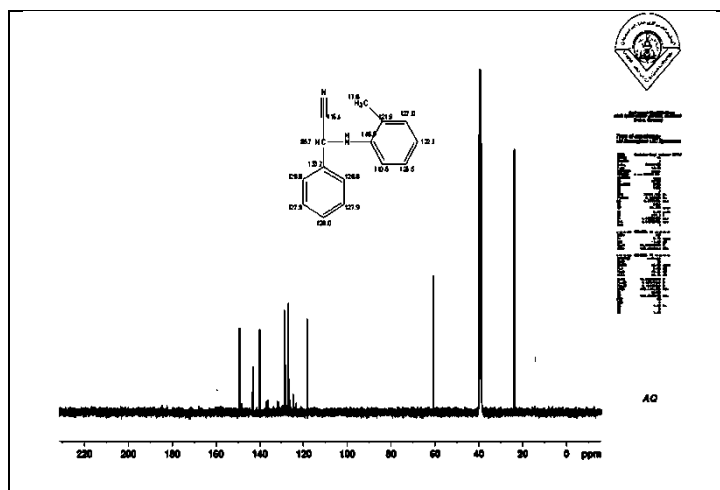


Figure 10: ¹³C-NMR spectrum of the ligand [L1]

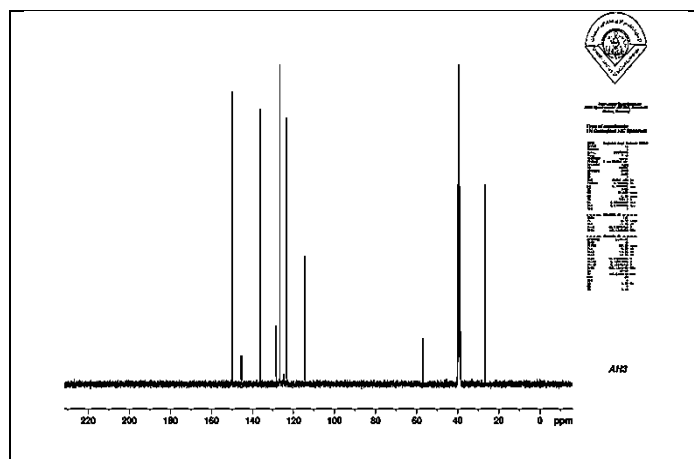

 Figure 11: ^{13}C -NMR spectrum of the complex [C8]

 Table 6: Thermal decomposition data for the metal ion complexes (C₁-C₁₀)

Comp.	Molecular formula	Step	Temperature rang of the decomposition C°	Suggested formula of loss	Mass loss%	
					Cal.	found
C ₁	[VOL ₁ L ₂]SO ₄ .4H ₂ O -637	1	70-120	4H ₂ O	11.3	11.28
		2	120-180	SO ₄	15	14.96
		3	180-420	C ₂₅ H ₂₀ N ₂ O	54.6	54.58
				Residue	18.99	18.96
C ₂	[CrL ₁ L ₂ Cl ₂]Cl.3H ₂ O 614.40))	1	80-130	3H ₂ O	8.78	8.75
		2	130-240	3Cl	17.33	17.31
		3	240-440	C ₂₄ H ₁₇ N ₂	54.19	54.18
				Residue	19.69	19.67
C ₃	[MnL ₁ L ₂ Cl(H ₂ O)]Cl.H ₂ O -564	1	85-110	H ₂ O	3.18	3.16
		2	110-250	2Cl, H ₂ O	15.78	15.76
		3	250-430	C ₂₄ H ₁₇ N ₂	59.04	59.02
				Residue	21.98	21.95
C ₄	[FeL ₁ L ₂ Cl(H ₂ O)]Cl.H ₂ O 564.80))	1	75-130	H ₂ O	3.18	3.17
		2	130-280	2Cl, H ₂ O	15.79	15.75
		3	280-447	C ₂₀ H ₁₇ N ₂ H ₂ O	53.64	53.62
				Residue	32.9	32.88
C ₅	[CoL ₁ L ₂ Cl(H ₂ O)]Cl.2H ₂ O 586.00))	1	70-130	2H ₂ O	6.14	6.12
		2	130-275	2Cl, H ₂ O	15.18	15.17
		3	275-441	C ₂₄ H ₁₇ N ₂ H ₂ O	59.89	59.86
				Residue	17.06	17.04
C ₆	[NiL ₁ L ₂ Cl(H ₂ O)]Cl.3H ₂ O -603.69	1	60-140	2H ₂ O	5.96	5.94
		2	140-220	Cl, 2H ₂ O	11.84	11.82
		3	220-433	C ₁₉ H ₁₅ N ₂ Cl	50.77	50.75
				Residue	33.4	33.38
C ₇	[CuL ₁ L ₂ Cl(H ₂ O)]Cl.H ₂ O -572.54	1	80-120	H ₂ O	3.14	3.13
		2	120-240	2Cl, H ₂ O	15.54	15.52
		3	240-458	C ₂₄ H ₁₇ N ₂	58.16	58.14
				Residue	23.67	23.66
C ₈	[ZnL ₁ L ₂ Cl ₂]. 4H ₂ O -610.39	1	65-150	4H ₂ O	8.84	8.82
		2	150-255	2Cl	14.58	14.58
		3	255-450	C ₂₅ H ₂₀ N ₂	57.01	56.99
				Residue	19.55	19.53
C ₉	[CdL ₁ L ₂ Cl ₂]. 4H ₂ O -657.4	1	57-120	H ₂ O ₂	5.47	5.46
		2	120-276	Cl, 2H ₂ O	10.87	10.85
		3	276-443	C ₂₄ H ₁₇ N ₂ Cl	56.05	56.02
				Residue	25.76	25.75
C ₁₀	[HgL ₁ L ₂ Cl ₂]. 2H ₂ O -709.6	1	73-127	2H ₂ O	5.07	5.03
		2	127-180	2Cl	10	9.97
		3	180-460	C ₂₅ H ₂₀ N ₂ H ₂ O	49.04	49.01
				Residue	35.87	35.84

In vitro antibacterial activity

The antibacterial activities of the ligands (L_1 and L_2) and ternary complexes against *Bacillus subtilis*, *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Escherichia coli* are presented in Table 6. L_1 has no activity towards *Pseudomonas aeruginosa*. This is attributed to its very versatile nutritional capability, adaptability to various hydrocarbons, rings and the possession of pump mechanism which ejects metal ion complexes as soon as they enter the cell [38-41]. In addition, *B. subtilis*, *S. aureus*, *P. aeruginosa* and *E. coli* are sensitive to all the complexes. In all cases, the metal ion complexes are more active than the ligand (L_1) expectedly due to chelation, which reduced the polarity of the metal atom, mainly because of partial sharing of its positive charge with donor groups of the ligand and possible π -electron delocalization, on the aromatic rings. This increased the lipophilic character, favouring, its permeation into the bacterial membrane, causing the death of the organisms. When the antimicrobial activity of metal ion complexes is investigated, the following principal factors [42] should be considered: (i) the chelate effect. of the ligands, (ii) the nature, of the N-donor ligands, (iii) the total charge of the complex, (iv) the existence and the nature of the ion neutralizing the ionic complex and (v) the nuclearity, of the metal center in the complex. In general, all the complexes exhibited better inhibition than free ligand (L_1), against *B. subtilis*, *S. aureus*, *Neisseria gonorrhoeae* and *E. coli*. More specifically, Ni(II) and Cu(II) complexes show the best inhibition among all the complexes in this study and it was more active than L_1 against all the microorganisms used indicating that the coordination of the ligand L_1 to Ni(II) and Cu(II) has enhanced its antimicrobial activity, while (L_2) ligand was showed best inhibition towards all bacterial more than (L_1) but less than some complexes this agreement with that the coordination (L_1 and L_2) with metal ion enhanced their antimicrobial activity (Table 7) [43].

Table 7: Inhibition zones measured in (mm) of DMSO, tetracycline and metal ion complexes

Compound	Inhibition zone (mm) <i>Escherichia coli</i>	Inhibition zone (mm) <i>Pseudomonas aeruginosa</i>	Inhibition zone (mm) <i>Staphylococcus aureus</i>	Inhibition zone (mm) <i>Bacillus subtilis</i>
Control: DMSO	-	-	-	-
Tetracycline	-	-	14.4	-
L_1	10	-	17	12
L_2	21	18	26	16
C_1	23	20	26	28
C_2	29	30	30	26
C_3	18	-	16	-
C_4	20	-	16	-
C_5	12	15	22	26
C_6	37	43	32	27
C_7	20	25	33	24
C_8	-	44	-	19
C_9	-	42	29	-
C_{10}	-	18	22	-

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