Synthesis, Characterization and Antibacterial Activity of Imidazole Derivatives of 1,10-Phenanthroline and their Cu(II), Co(II) and Ni(II) Complexes

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ABSTRACT

Six new CuL^1 (L^1 = 4-bromo-2-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenol), CoL^1, NiL^1, CuL^2 (L^2 = 2-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)-5-methoxyphenol), CoL^2 and NiL^2 complexes were synthesized. L^1 and L^2 ligands were prepared by the condensation of 1,10-phenanthroline-5,6-dione with 5-bromosalicylaldehyde and 2-hydroxy-4-methoxybenzaldehyde, respectively. The structures of the compounds were determined by elemental analyses, IR, UV-visible, ^{1}H-NMR, TGA, magnetic susceptibilities and molar conductance measurements. It is observed that the synthesized complexes have tetragonal and distorted square pyramidal geometrical structures. Antibacterial activity of the ligands and their metal complexes were tested against selected bacteria by disc diffusion method.

KEY WORDS

1,10-Phenanthroline, imidazole, complex, antibacterial activity.

1. Introduction

1,10-Phenanthroline (phen) and its derivations play important roles for supramolecular assemblies because they can also provide bidentate N-donor sites for chelating with metal ions to form bridge ligands.[1–4] Derivatives of phen are very important ligands in organometallic chemistry;[5,6] some of their complexes, for example, bind to DNA.[7–10]

Metal complexes of the type $[M(LL)_3]^{n+}$ where LL is either phen or a modified phen ligand, are particularly attractive species to recognize and cleave DNA.[11–13] Systematic studies of substituted derivatives of phen have been successfully undertaken.[14] 1,10-phenanthroline, as well as some of its derived complexes, do exhibit antimicrobial properties.[15,16] The photocemical and redox properties of complexes can be varied systematically through appropriate substition on the phenanthroline rings.[17,18]

Firstly, we synthesized and characterized Cu(II), Co(II) and Ni(II) complexes with phen imidazole derivatives, which are 4-bromo-2-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenol (L^1) and 2-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)-5-methoxyphenol (L^2) (Fig. 1). Secondly, these compounds were screened for antibacterial activity against such bacterial strains as *A. hydrophila, S. aureus, K. pneumoniae, P. aeruginosa, S. marcescens, E. aerogenes, B. subtilis, E. coli* and *E. faecalis.*

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2. Experimental

2.1. Materials and Physical Measurements

1,10-phenanthroline-5,6-dione was synthesized according to a published method.[19] Ethanol was dried over anhydrous copper (II) sulfate and distilled over metallic sodium. All other chemicals were of analytical grade and were used as purchased.

Elemental analyses (C, H, N) were performed by using a Leco 932 elemental analyzer. ^{1}H NMR spectra were recorded on a Bruker 300 MHz spectrometer in DMSO-d_6. The IR spectra were obtained using KBr discs on an Ati Unicam Mattson 1000 Series FT-IR spectrophotometer. The electronic absorption spectra in the 200–1100 nm range were obtained in DMF on a Shimadzu UV-1700 UV-Visible spectrophotometer. Magnetic susceptibility measurements were carried out by the Gouy method at room temperature using $Hg[Co(SCN)_4]$ as a reference for calibrant. Conductivities of a 10^{-3} M solution of the complexes were measured in DMF at 25 °C using a CMD 750 WPA model

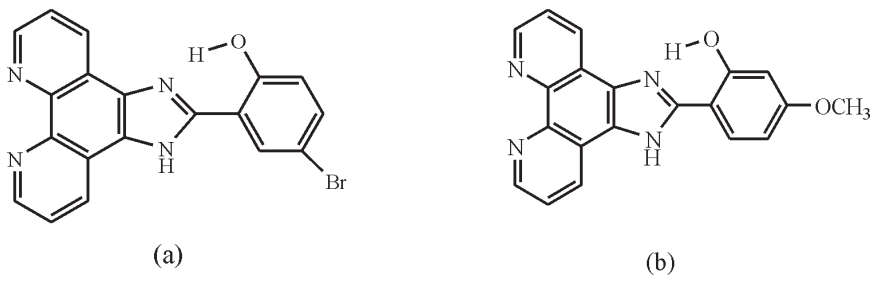

Figure 1 Structure of the (**a**) L^1 and (**b**) L^2 ligands.

conductivity meter. Thermogravimetric analyses (TGA) were carried out by Shimadzu-50 thermal analyzer in a dynamic nitrogen atmosphere in the 20–600 °C range and a heating rate of 20 °C min^{-1}.

2.2. Antibacterial Activity

The *in vitro* antibacterial screening effects of the ligands (L^1, L^2) and their metal complexes were tested against nine bacterial strains, namely *A. hydrophila* ATCC 7966, *S. aureus* ATCC 29213, *K. pneumoniae* ATCC 21541, *P. aeruginosa* ATCC 27853, S. *marcescens* ATCC 21074, *E. aerogenes* ATCC 5402, *B. subtilis* ATCC 6633, *E. coli* ATCC 25922 *and E. faecalis* ATCC 29212 by disc diffusion method using nutrient agar medium for antibacterial activity.[20]

All bacteria were inoculated into Nutrient Broth (Difco) and incubated for 24 h. In the agar well diffusion method (Mueller Hinton Agar (Oxoid) for bacteria), the dilution plate method was used to enumerate microorganisms (10^5 bacteria per mL) for 24 h.[21] Using a sterilized cork borer (6 mm diameter), wells were dug in the culture plates. Metal complexes and ligands were performed at the fixed concentration of 2000 μg mL^{-1} and compounds dissolved in DMF. Compounds dissolved in DMF were added (75 μL) to these wells. The petri dishes were left at 4 °C for 2 h and then the plates were incubated at 37 °C and 30 °C for bacteria (18–24 h). At the end of the period, inhibition zones formed on the medium were evaluated is milimetres. DMF was used as negative control under similar conditions for comparison. Ampicillin (AMP) was used as the reference drug in positive controls. The experiments were performed in triplicate.

2.3. Statistical Analysis

In this study, repeated measures analysis of variance was used to evaluate the data. Ligands and their metal complexes were analyzed antibacterial activity at different temperatures. Statistical significance was determined using Duncan multiple comparison test and Bonferroni multiple comparison test was used for grouping within subject factors. SPSS 15.0, version 8, software was used in the statistical analyses.[22]

2.4. Synthesis of Ligands (L^1, L^2)

Ligands (L^1, L^2) were synthesized by a method similar to one described previously.[18]

4-bromo-2-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenol (L^1)

A mixture of 1,10-phenanthroline-5,6-dione (0.2 g, 1 mmol), ammonium acetate (1.54 g, 20 mmol), 5-bromosalicylaldehyde (0.22 g, 1.1 mmol) and glacial acetic acid (25 mL) was refluxed for 2 h, then cooled to room temperature and diluted with water (50 mL). Dropwise addition of concentrated aqueaus ammonia to neutralize gave a yellow precipitate, which was collected and washed with water. The crude product dissolved in ethanol was purified by filtration on silica gel. The principal yellow band was collected. Evaporation of the solution gave yellow crystals. It was filtered, washed with ethanol and recrystallized from ethanol then dried at 80 °C. Yield: 0.311 g (79 %). IR (ν, cm^{-1}): 3245–2420 (N–H and O–H···N), 1607 (C=N imidazole ring), 1574, 1563, 1539, 1503 (C=C aromatic and C=N phenanthroline ring); δ_H (300 MHz, DMSO-d_6): 13.6 (1H, s, OH), 12.82 (1H, s, NH), 8.97–8.91 (2H, d, C_{Ar} – H), 8.63–8.56 (2H, dd, C_{Ar} – H), 8.18–8.13 (1H, d, C_{Ar} – H), 7.71–7.61 (2H, dd, C_{Ar} – H), 7.46–7.39 (1H, dd, C_{Ar} – H) and 6.98–6.92 ppm (1H, d, C_{Ar} – H); UV-Vis (in DMF, nm): 277, 286, 303, 324, 337, 357, 407 and 552.

2-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)-5-methoxyphenol (L^2)

L^2 was synthesized by a procedure similar to that for L^1 except that 2-hydroxy-4-methoxybenzaldehyde was used, and was obtained as yellow powder. Yield: 0.147 g (43 %). IR (ν, cm^{-1}): 3274–2456 (N–H and O–H···N), 1604 (C=N imidazole ring), 1591, 1563, 1544, 1508 (C=C aromatic and C=N phenanthroline ring), 1256 (Ar-O-CH_3); δ_H (300 MHz, DMSO-d_6): 15.81 (1H, s, OH), 12.85 (1H, s, NH), 9.06–8.81 (4H, m, C_{Ar} – H), 7.86–7.71 (3H, m, C_{Ar} – H), 7.11–6.97 (2H, m, C_{Ar} – H) and 3.86 (3H, s, OCH_3); UV-Vis (in DMF, nm): 279, 340, 356, 413, 445 and 550.

2.5. Synthesis of Complexes

CuL^1, CoL^1 and NiL^1

A solution of a metal salt (0.1 mmol) in DMF (2 mL) was added to a hot solution of the L^1 (0.078 g, 0.2 mmol) in DMF (10 mL). The reaction mixture was heated at 80 °C until the reaction was complete. The mixture was then left for two weeks at room temperature, filtered, washed with DMF, water and ethanol and dried at 100 °C in a vacuum oven. The following salts were used for the synthesis; $CuCl_2.H_2O$ (0.017 g, 10 h reaction time), $CoCl_2.6H_2O$ (0.030 g, 24 h reaction time), $NiCl_2.6H_2O$ (0.020 g, 10 h reaction time).

CuL^1: Green compound. Yield: 0.048 g (52 %). IR (ν, cm^{-1}): 3208–2540 (N–H and O–H···N), 1604 (C=N imidazole ring), 1580, 1541, 1511 (C=C aromatic and C=N phenanthroline ring); UV-Vis (in DMF, nm): 453 and 700; (Found: C, 48.96; H, 2.54; N, 11.97 %. Calc. for $C_{38}H_{22}N_8O_2Cl_2Br_2Cu$ (916.89); C, 49.78; H, 2.42; N, 12.22 %); μ_{eff}: 1.86 BM; Λ_M (10^{-3} M, in DMF, Ω^{-1} cm^2 mol^{-1}): 12.43.

CoL^1: Brown compound. Yield: 0.049 g (53 %). IR (ν, cm^{-1}): 3428 (O–H, H_2O), 3190–2406 (N–H and O–H···N), 1607 (C=N imidazole ring), 1583, 1541, 1511 (C=C aromatic and C=N phenanthroline ring); UV-Vis (in DMF, nm): 502; (Found: C, 50.21; H, 3.11; N, 11.50 %. Calc. for $C_{38}H_{24}N_8O_3Cl_2Br_2Co$ (930.30); C, 49.06; H, 2.60; N, 12.04 %); μ_{eff}: 4.83 BM; Λ_M (10^{-3} M, in DMF, Ω^{-1} cm^2 mol^{-1}): 76.84.

NiL^1: Orange compound. Yield: 0.066 g (63 %). IR (ν, cm^{-1}): 3126-2460 (N–H and O–H···N), 1604 (C=N imidazole ring), 1583, 1541, 1511 (C=C aromatic and C=N phenanthroline ring); UV-Vis (in DMF, nm): 452; (Found: C, 43.87; H, 2.88; N, 10.58 %. Calc. for $C_{38}H_{22}N_8O_2Cl_4Br_2Ni_2$ (1041.64); C, 43.82; H, 2.13; N, 10.76 %); μ_{eff}: 1.53 BM; Λ_M (10^{-3} M, in DMF, Ω^{-1} cm^2 mol^{-1}): 10.34.

CuL^2: A ethanolic (20 mL) solution of the (0.025 g, 0.15 mmol) $CuCl_2.H_2O$ was added to a hot ethanolic (40 mL) solution of the L^2 (0.100 g, 0.3 mmol). The mixture was refluxed for 24 h. The mixture was cooled to room temperature, the resulting green solid was filtered, washed with DMF and ethanol then dried at 100 °C in a vacuum oven. Yield: 0.082 g (67 %). IR (ν, cm^{-1}): 3215–2405 (N–H and O–H···N), 1604 (C=N imidazole ring), 1591, 1577, 1544, 1508 (C=C aromatic and C=N phenanthroline ring), 1248 (Ar-O-CH_3); UV-Vis (in DMF, nm): 470; (Found: C, 59.20; H, 4.06; N, 12.93 %. Calc. for $C_{40}H_{28}N_8O_4Cl_2Cu$ (819.15); C, 58.65; H, 3.45; N, 13.68 %); μ_{eff}: 2.13 BM; Λ_M (10^{-3} M, in DMF, Ω^{-1} cm^2 mol^{-1}): 14.82.

CoL^2 and NiL^2

A solution of a metal salt (0.15 mmol) in DMF (2 mL) was added to a hot solution of the L^2 (0.100 g, 0.3 mmol) in DMF (10 mL). The mixture was heated at 80 °C while stirring for 24 h. The mixture was left for two weeks at room temperature, the resulting solid was filtered, washed with DMF, water and ethanol then dried at 100 °C in a vacuum oven. The following salts were used for the synthesis; $CoCl_2.6H_2O$ (0.038 g), $NiCl_2.6H_2O$ (0.036 g).

CoL^2: Brown compound. Yield: 0.057 g (46 %). IR (ν, cm^{-1}): 3423

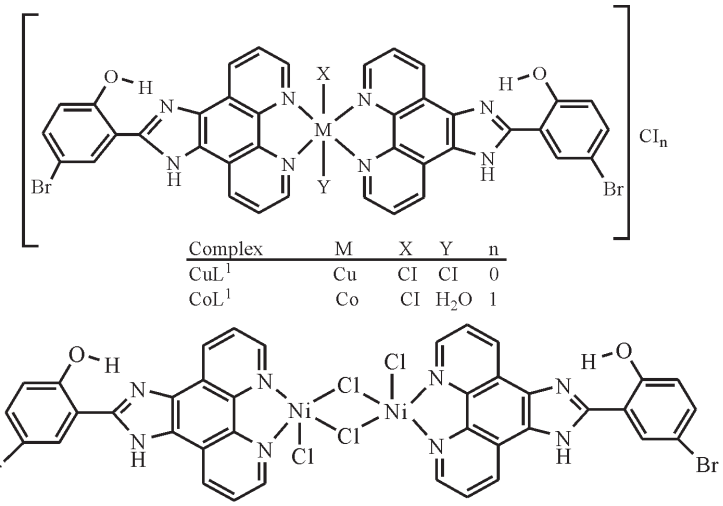

Figure 2 Structure of the CuL^1, CoL^1 and NiL^1 complexes.

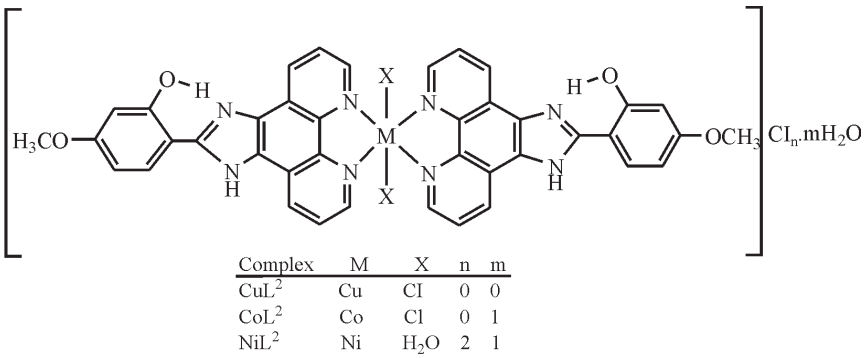

Figure 3 Structure of the CuL^2, CoL^2 and NiL^2 complexes.

(O–H, H_2O), 3115–2400 (N–H and O–H···N), 1604 (C=N imidazole ring), 1591, 1577, 1544, 1508 (C=C aromatic and C=N phenanthroline ring), 1248 (Ar-O-CH_3); UV-Vis (in DMF, nm): 487, 606, 926; (Found: C, 58.56; H, 4.06; N, 13.15 %. Calc. for $C_{40}H_{30}N_8O_5Cl_2Co$ (832.56); C, 57.71; H, 3.63; N, 13.46 %); μ_{eff}: 4.92 BM; Λ_M (10^{-3} M, in DMF, Ω^{-1} cm^2 mol^{-1}): 17.65.

NiL^2: Orange compound. Yield: 0.052 g (40 %). IR (ν, cm^{-1}): 3410 (O–H, H_2O), 3115–2280 (N–H and O–H···N), 1604 (C=N imidazole ring), 1591, 1577, 1544, 1508 (C=C aromatic and C=N phenanthroline ring), 1248 (Ar-O-CH_3); UV-Vis (in DMF, nm): 500, 595, 902; (Found: C, 55.16; H, 3.98; N, 11.63 %. Calc. for $C_{40}H_{34}N_8O_7Cl_2Ni$ (868.35); C, 55.33; H, 3.95; N, 12.90 %); μ_{eff}: 3.26 BM; Λ_M (10^{-3} M, in DMF, Ω^{-1} cm^2 mol^{-1}): 148.42.

3. Results and Discussion

Elemental analyses indicate that the metal:ligand ratio is 1:1 in the case of the NiL^1 complex and 1:2 in the case of the other complexes. In addition, the magnetic moment value of NiL^1 complex indicates a dimeric structure (Figs. 2, 3). The ligands L^1 and L^2 were soluble in EtOH, DMF and DMSO, and the complexes in DMF and DMSO. The melting points of the all compounds were not observed due to decomposition.

3.1. IR Spectra

In IR spectra of CoL^1, CoL^2 and NiL^2, the bands are observed at the 3428, 3423 and 3410 cm^{-1} as broad bands are due to the OH stretching vibrations of H_2O molecules.[23,24,25]

The broadened band between 3274–2420 cm^{-1} in IR spectra of the L^1 and L^2 ligands is due to the stretching vibrations of the both NH of the imidazole ring and intramolecular hydrogen bonding (O–H···N) formed between phenolic OH and nitrogen atom of C=N group of imidazole ring.[26] The same band was observed in IR spectra of metal complexes of these ligands. This observation confirmed that phenolic OH and nitrogen (C=N) of the imidazole ring do not participate in coordination. Moreover, the stretching vibration of the C=N group (imidazole ring) of the ligands L^1 and L^2 were not significantly affected in their complexes, indicating that the nitrogen atom of this group is not involved in coordination for all the complexes. On the other hand, the bands of the C=N (phenanthroline ring) and C=C (Aromatic) groups were shifted to higher frequencies in all the complexes of L^1 and the band at 1563 cm^{-1} in the free L^2 ligand was shifted to higher frequencies (1577 cm^{-1}) in their complexes,[27,28] that indicates the participation of the C=N (phenanthroline ring) groups in coordination of the metal ion.

The bands of the N-H and O–H···N groups in all the complexes of L^1 shifted to negative frequencies after complexations. The N-H, O–H···N and Ar-O-CH_3 groups in all complexes of L^2 are the some as complexes of L^1. The negative frequency shifts of these groups may be attributed to flow of electrons from these groups to the phenanthroline ring due to electron flow from the nitrogen atom of the phenanthroline ring to the metal ion after complexations.

3.2. Electronic Spectra and Magnetic Measurements

In the electronic spectra of L^1 and L^2 ligands, the bands are

observed in the range of 277–552 nm and 279–550 nm, respectively. These bands are attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.[29,30]

The magnetic moment values for the Cu(II) complexes lies in the range 1.86–2.13 BM corressponding to one unpaired electron.[31] The complexes may be considered to possess a tetragonal geometry. The electronic spectra of CuL^1 complex shows two bands at 453 and 700 nm assigned to $^2B_{1g} \rightarrow (^2B_{2g}, ^2E_g)$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ transitions, respectively. The band observed at 470 nm for CuL^2 complex is assigned to $^2E_g(D_{4h}; {}^2B_{1g}, {}^2A_{1g}) \rightarrow {}^2T_{2g}(D_{4h}; {}^2E_g, {}^2B_{2g})$. The band assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ transition cannot be detected for the CuL^2 complex.[32]

The magnetic moment values for the Co(II) complexes in the range 4.83–4.92 BM reported here show that there are three unpaired electrons, indicating a high spin octahedral configuration.[31] The electronic spectra of CoL^2 complex give three bands 487, 606 and 926 nm. These bands may be assigned to the transitions $^4T_{1g}(F)(D_{4h}; {}^4A_{2g}, {}^4E_g) \rightarrow {}^4T_{1g}(P)(D_{4h}; {}^4A_{2g}, {}^4E_g)$, $^4T_{1g}(F)(D_{4h}; {}^4A_{2g}, {}^4E_g) \rightarrow {}^4A_{2g}(F)(D_{4h}; {}^4B_{1g})$ and $^4T_{1g}(F)(D_{4h}; {}^4A_{2g}, {}^4E_g) \rightarrow {}^4T_{2g}(F)(D_{4h}; {}^4B_{2g}, {}^4E_g)$, respectively. The band observed at 502 nm for the CoL^1 complex is assigned to $^4E_g \rightarrow T_{1g}(P)(^4E_g)$. The positions of these bands suggest a tetragonal environment around Co^{2+} ion.[32] The other bands of CoL^1 are not observed because they might be overlap with bands of the L^1 ligand.

The low μ_{eff} (1.53 BM) of NiL^1 complex indicate a dimeric structure.[31,33] The band observed at 452 nm for NiL^1 complex is assigned to $^3B_1 \rightarrow {}^3A_2$, $^3E(P)$ of a distorded square pyramidal structure. The other band assigned to $^3B_1 \rightarrow {}^3B_2$ is not observed because it overlaps with ligand bands of L^1. The magnetic moment value (3.26 BM) for NiL^2 corresponds to two unpaired electron.[31] The electronic spectrum of this complex shows absorption bands at 500, 595 and 902 nm, attributed to $^3A_{2g}(D_{4h}; {}^3B_{1g}) \rightarrow {}^3T_{1g}(P)(D_{4h}; {}^3E_g, {}^3A_{2g})$, $^3A_{2g}(D_{4h}; {}^3B_{1g}) \rightarrow {}^3T_{1g}(F)(D_{4h}; {}^3E_g, {}^3A_{2g})$ and $^3A_{2g}(D_{4h}; {}^3B_{1g}) \rightarrow {}^3T_{2g}(F)(D_{4h}; {}^3B_{2g}, {}^3E_g)$ transitions, respectively, in a tetragonal geometry around the Ni^{2+} ion.[32]

3.3. Thermal Analysis (TGA)

According to the thermogravimetric results CuL^1, NiL^1, and CuL^2 exhibited rather high thermal stability with decomposition temperatures of 320, 280 and 270 °C, respectively. CoL^1, CoL^2 and NiL^2 complexes were stable up to 175, 50 and 50 °C, respectively. In the decomposition process of these complexes, the mass loss corresponded to one coordinated water molecule in the temperature range 175–240 °C for CoL^1 (2.08 % experimental; 1.93 % calculated), one uncoordinated water molecule in the temperature range 50–100 °C for CoL^2 (2.50 % experimental; 2.60 % calculated) and NiL^2 (2.08 % experimental; 2.10 % calculated). In the second stage of the decomposition process of NiL^2 the mass loss corresponded to two coordinated water molecules in the temperature range 160–250 °C (4.16 % experimental; 4.14 % calculated).

3.4. Conductance Measurements

Conductivity measurements of CoL^1 complex resulted in Λ_M 76.84 $\Omega^{-1}cm^2\ mol^{-1}$, which indicates that it is of the 1:1 electrolyte type. NiL^2 had an Λ_M value of 148.42 $\Omega^{-1}\ cm^2\ mol^{-1}$) indicating that it is of the 2:1 electrolyte type. The other complexes were nonelectrolytes.[34]

3.5. Antibacterial Activity

Test results of antibacterial screening are summarized in Tables 1 and 2. According to the results of the antibacterial activity, ligands and all their metal complexes showed antibacterial activity at 30 °C and 37 °C in which there is no distinction between antibacterial activity. The Duncan's multiple range test indicated

Table 1 Antibacterial activity of the ligands and their metal complexes against bacterial strains at 30 °C.

Bacterium	L^1	L^2	CuL^1	CuL^2	CoL^1	CoL^2	NiL^1	NiL^2	DMF	AMP	
A. hydrophila ATCC 7966	17 ± 0.55	17 ± 0.52	17 ± 0.49	16 ± 0.03	18 ± 0.52	18 ± 0.52	13 ± 0.02	13 ± 0.04	8 ± 0.02	0 ± 0.00	13.7 b
S. aureus ATCC 29213	16 ± 0.75	15 ± 0.02	15 ± 0.54	14 ± 1.03	19 ± 0.52	18 ± 0.02	12 ± 0.01	12 ± 0.00	8 ± 0.00	14 ± 0.02	14.3 ab
K. pneumoniae ATCC 21541	18 ± 0.02	18 ± 0.41	14 ± 0.50	15 ± 0.02	17 ± 0.04	17 ± 0.03	13 ± 0.03	13 ± 0.02	8 ± 0.04	14 ± 0.01	14.7 a
P. aeroginosa ATCC 27853	16 ± 0.55	15 ± 0.04	15 ± 0.52	15 ± 0.52	0 ± 0.00	0 ± 0.00	14 ± 0.52	13 ± 0.01	7 ± 0.01	15 ± 0.00	11 c
S. marcescens ATCC 1074	16 ± 0.04	16 ± 0.54	15 ± 0.02	16 ± 0.04	0 ± 0.00	0 ± 0.00	13 ± 0.04	13 ± 0.00	8 ± 0.00	15 ± 0.00	11.2 c
E. aerogenes ATCC 5402	17 ± 0.50	16 ± 0.01	15 ± 0.08	16 ± 0.52	17 ± 0.02	18 ± 0.53	11 ± 0.04	11 ± 0.08	8 ± 0.00	15 ± 0.03	14.4 ab
B. subtilis ATCC 6633	10 ± 0.51	12 ± 0.02	0 ± 0.00	0 ± 0.00	17 ± 0.03	18 ± 0.05	12 ± 0.05	12 ± 0.03	8 ± 0.03	17 ± 0.00	10.6 d
E. coli ATCC 25922	16 ± 0.52	17 ± 0.01	15 ± 0.51	16 ± 0.01	0 ± 0.00	0 ± 0.00	12 ± 0.00	13 ± 0.00	8 ± 0.00	16 ± 0.05	11.3 c
E. faecalis ATCC 29212	17 ± 0.41	17 ± 0.51	16 ± 0.56	17 ± 0.03	17 ± 0.49	17 ± 0.04	13 ± 0.00	13 ± 0.01	7 ± 0.00	15 ± 0.00	14.9 a 12.9 a
	15.9 a	15.9 a	13.6 b	13.9 b	11.7 d	11.8 d	12.6 c	12.6 c	7.8 e	13.4 b	

Mean values on the same column followed by the same letter are not significantly different level according to Duncan's multiple range test ($P > 0.05$). Mean values followed by different letters along vertical column are significantly different by Duncan's multiple range test ($P < 0.05$).

Table 2 Antibacterial activity of the ligands and their metal complexes against bacterial strains at 37 °C.

Bacterium	L^1	L^2	CuL^1	CuL^2	CoL^1	CoL^2	NiL^1	NiL^2	DMF	AMP	
A. hydrophila ATCC 7966	18 ± 0.04	17 ± 0.02	18 ± 0.02	16 ± 0.52	18 ± 0.01	18 ± 0.01	14 ± 0.52	13 ± 0.00	7 ± 0.01	0 ± 0.00	13.9 c
S. aureus ATCC 29213	15 ± 0.51	14 ± 0.53	16 ± 0.04	14 ± 0.52	19 ± 0.02	18 ± 0.49	12 ± 0.00	12 ± 0.06	7 ± 0.02	14 ± 0.00	14.1 bc
*K. pneumoniae*ATCC 21541	18 ± 0.02	18 ± 0.03	14 ± 0.52	15 ± 0.04	18 ± 0.52	17 ± 0.01	13 ± 0.02	13 ± 0.01	7 ± 0.05	14 ± 0.05	14.7 b
P. aeroginosa ATCC 27853	16 ± 0.04	15 ± 0.51	15 ± 0.06	15 ± 0.05	0 ± 0.00	0 ± 0.00	14 ± 0.52	13 ± 0.00	7 ± 0.02	15 ± 0.01	11 de
S. *marcescens* ATCC 1074	16 ± 0.53	16 ± 0.02	15 ± 0.50	16 ± 0.04	0 ± 0.00	0 ± 0.00	13 ± 0.03	13 ± 0.02	7 ± 0.01	15 ± 0.02	11.1 d
E. aerogenes *ATCC 5402*	17 ± 0.04	16 ± 0.03	16 ± 0.04	17 ± 0.03	17 ± 0.02	18 ± 0.02	11 ± 0.05	11 ± 0.05	7 ± 0.00	15 ± 0.00	14.5 b
B. subtilis ATCC 6633	10 ± 0.04	12 ± 0.50	0 ± 0.00	0 ± 0.00	17 ± 0.03	18 ± 0.01	12 ± 0.00	12 ± 0.02	7 ± 0.00	17 ± 0.00	10.5 de
E. coli ATCC 25922	16 ± 0.02	17 ± 0.04	16 ± 0.05	17 ± 0.49	0 ± 0.00	0 ± 0.00	12 ± 0.08	13 ± 0.00	8 ± 0.03	16 ± 0.03	11.5 d
E. faecalis ATCC 29212	17 ± 0.50	17 ± 0.01	17 ± 0.04	18 ± 0.50	16 ± 0.01	16 ± 0.89	14 ± 0.52	14 ± 0.52	8 ± 0.02	15 ± 0.00	15.2 a 12.94 a
	15.9 a	15.8 a	14.1 b	14.2 b	11.7 e	11.7 e	12.8 cd	12.7 d	7.2 f	13.4 c	

Mean values in the same column followed by the same letter are not significantly different level according to Duncan's multiple range test ($P > 0.05$). Mean values followed by different letters along vertical column are significantly different by Duncan's multiple range test ($P < 0.05$).

significant differences of antibacterial activity among ligands and their metal complexes. The ligands displayed weak antibacterial activity against *B. subtilis*. However, good activity was observed against others bacteria. Cu(II) complexes displayed good antibacterial activity against all bacteria except for *B. subtilis*. Co(II) complexes exhibited activity against *S. aureus, B. subtilis, A. hydrophila, K. pneumoniae*, *E. aerogenes and E. coli*. However, no activity was observed against *S. marcescens*, *E. coli* and *P. aeruginosa*. Additionally, Ni(II) complexes exhibited weak effect against to all bacteria tested.

Finally, these results may suggest that the ligands and their metal complexes can be used as antibacterial agents in new drugs for therapy of infectious diseases in humans.

4. Conclusion

In this study, imidazole and phenanthroline containing 4-bromo-2-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenol (L^1), 2-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)-5-methoxyphenol) (L^2) and their complexes were synthesized and characterized. The analytical data and spectroscopic studies suggest that the complexes were of the general formula: $[M(L^1)_2XY]CI_n$ where M is Cu(II) (X = CI, Y = CI, n = 0), Co(II) (X = CI, Y = H_2O, n = 1), $[M_2(L^1)_2CI_4]$ where M = Ni(II) and $[M(L^2)_2X_2]CI_n mH_2O$ where M is Cu(II) (X = CI, n = 0, m=0), Co(II) (X = CI, n = 0, m=1) and Ni(II) (X = H_2O, n = 2, m=1). According to the IR data of the compounds, ligands (L^1, L^2) are coordinated to the metal ions through nitrogen atoms of the C=N (phenanthroline ring) groups.

The results obtained from this research demonstrated that all synthesized compounds have antibacterial activity against the bacterial strains. In this sense, we think that the ligands and their metal complexes might be effective as antibacterial agents against bacteria.

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References

1 S. Bodige and F.M. MacDonnell, *Tetrahedron Lett.*, 1997, **38**, 8159–8160.

2 W. Paw and R. Eisenberg, *Inorg. Chem.*, 1997, **36**, 2287–2293.

3 K. Nobuko, K. Ryuzi, H. Yuichiro, S. Hideki, A. Hironori, and K. Kazuyuki, *J. Chem. Soc., Dalton Trans.*, 2000, **18**, 3053–3054.

4 V. Balzani, A. Juris, M. Venturi, S. Campagna and S. Serroni, *Chem. Rev.*, 1996, **96**, 759–833.

5 E.C. Constable, *Metals and Ligands Reactivity*, VCH, Weinheim, 1996, p. 308.

6 J.P. Sauvage, J.P. Collin, J.C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigeletti, L. De Cola and L. Flamingi, *Chem. Rev.*, 1994, **94**, 993–1019.

7 R.E. Holmlin, P.J. Dandliker and J.K. Barton, *Angew. Chem.*, 1997, **36**, 2714–2730.

8 F. Gao, H. Chao, J.Q. Wang, Y.X. Yuan, B. Sun, Y.F. Wei, B. Peng and L.N. Ji, *J. Biol. Inorg. Chem.*, 2007, **12**, 1015–1027.

9 Q.L. Zhang, J.H. Liu, J.Z. Liu, P.X. Zhang, X.Z. Ren, Y. Liu, Y. Huang and L.N. Ji, *J. Inorg. Biochem.*, 2004, **98**, 1405–12.

10 X.W. Liu, L.C. Xu and H. Li, H. Chao, K.C. Zheng and L.N. Ji, *J. Mol. Struct.*, 2009, **920**, 163–171.

11 D.S. Sigman, *Acc. Chem. Res.*, 1986, **19**, 180–186.

12 Y. Jenkins, A.E. Friedman, N.J. Turro and J.K. Barton, *Biochemistry*, 1992, **31**, 10809–10816.

13 D.L. Carlson, D.H. Huchital, E.J. Mantilla, R.D. Sheardy and W.R. Murphy, *J. Am. Chem. Soc.*, 1993, **115**, 6424–6425.

14 A. Masood and D.J. Hodgson, *Inorg. Chem.*, 1993, **32**, 4839–4844.

15 B. Coyle, K. Kwanagh, M. McCann, M. Devereux and M. Geraghty, *Biometals.*, 2003, **16**, 321–329.

16 H. Qizhuang, Y. Jing, M. Hui and L. Hexing, *Materials Letters*, 2006, **60**, 317–320.

17 J. Bolger, A. Gourdon, E. Ishow and J. P. Launay, *Inorg. Chem.*, 1996, **35**, 2937–2944.

18 H. Xu, K.C. Zheng, Y. Chen, Y.Z. Li, L.J. Lin, H. Li, P.X. Zhang and L.N. Ji, *Dalton Trans.*, 2003, **11**, 2260–2268.

19 C. Hiort, P. Lincoln and B. Norden, *J. Am. Chem. Soc.*, 1993, **115**, 3448–3454.

20 D. Greenwood, R. Snack and J. Peurtherer, *Medical Microbiology: A Guide to Microbial Infections: Pathogenesis, Immunity, Laboratory Diagnosis and Control*, 15th edn., Churchill Livingstone, Edinburgh, United Kingdom, 1997, p. 690.

21 V. Reddy, N. Patil and S.D. Angadi, *E. J. Chem.*, 2008, **5**, 577–583.

22 SAS User's Guide: Statistics, Ver. 8, SAS 2001, SAS Institute, Cary, NC.

23 H. Adams, R. Bastida, A. De Blas, M. Carnota, D.E. Fenton, A. Maci'as, A. Rodriguez and T. Rodriguez-Blas, *Polyhedron*, 1997, **16**, 567–572.

24 W. Radecka-Paryzek and V. Patroniak, *Polyhedron*, 1994, **13**, 2125–2128.

25 S. Liu, L.W. Yang, S.J. Rettig and C. Orvig, *Inorg. Chem.*, 1993, **32**, 2773–2778.

26 J.G. Liu, B.H. Ye, H. Li, Q.X. Zhen, L.N. Ji and Y.H. Fu, *J. Inorg. Biochem.*, 1999, **76**, 265–271.

27 D.H. Busch and J.C. Bailar Jr, *J. Am. Chem. Soc.*, 1956, **78**, 1137–1142.

28 M.M. Mashaly, H.F. El-Shafiy, S.B. El-Maraghy and H.A. Habib, *Spectrochim. Acta A.*, 2005, **61**, 1853–1869.

29 J. Bolger, A. Gourdon, E. Ishow and J.P. Launay, *J. Chem. Soc., Chem. Commun.*, 1995, **17**, 1799–1800.

30 J. Bolger, A. Gourdon, E. Ishow and J.P. Launay, *Inorg. Chem.*, 1996, **35**, 2937–2944.

31 J.E. Huheey, E.A. Keiter and R.L. Keiter, *Inorganic Chemistry, Principle of Structure and Reactivity*, Harper Collins College Publisher, New York, 1993, p. 1052.

32 A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1986, p. 863.

33 F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley-Interscience Publication, New York, 1980, p. 1396.

34 W.J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81–122.