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SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL ACTIVITY OF 2-*p*-TOLYL-1H-IMIDAZO[4,5-f][1,10]PHENANTHROLINE AND ITS Co(II), Ni(II) AND Cu(II) COMPLEXES

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ABSTRACT. In this study, the ligand, 2-*p*-tolyl-1H-imidazo[4,5-f][1,10]phenanthroline (L) was synthesized by the reaction of 1,10-phenanthroline-5,6-dione with 4-methylbenzaldehyde. The complexes of L were prepared with Co(II), Ni(II) and Cu(II) chlorides. The ligand and its complexes were characterized by IR, UV/VIS, ^{1}H NMR, TGA, elemental analyses, molar conductivity and magnetic susceptibility. The complexes were proposed to be distorted octahedral geometry. Antibacterial activity of the ligand and its complexes were tested against selected bacteria. The minimum inhibitory concentration (MIC) was determined for the ligand and its complexes.

KEY WORDS: 1,10-Phenanthroline, Imidazole, Cobalt complex, Nickel complex, Copper complex, Antibacterial activity

INTRODUCTION

Metal complexes containing diimine ligands such as 1,10-phenanthroline and its derivatives have gained importance because of their versatile roles as building blocks for the synthesis of metallo-dendrimers and as molecular scaffolding for supramolecular assemblies, and in analytical chemistry, catalysis, electrochemistry, ring-opening metathesis polymerization and biochemistry [1-10].

1,10-Phenanthroline has a rigid framework and possesses a superb ability to coordinate many metal ions, which show potential for technological applications, due to their strong absorption in the ultraviolet spectral region, bright light-emission and good electro- and photo-active properties [11-14]. The photochemical and redox properties of complexes can be varied systematically through appropriate substitution on the phenanthroline rings [15-17]. 1,10-Phenanthroline, as well as some of its derived complexes, do exhibit antimicrobial properties [18, 19].

We report here the synthesis and characterization of new Co(II), Ni(II) and Cu(II) complexes with 1,10-Phenanthroline imidazole derivative, which is 2-*p*-tolyl-1H-imidazo[4,5-f][1,10] phenanthroline (L). These compounds were screened for antibacterial activity against these bacterial strains; *A. hydrophila*, *S. aureus*, *K. pneumoniae*, *P. aeruginosa*, *S. marcescens*, *E. aerogenes*, *B. subtilis*, *E. coli* and *E. faecalis*.

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EXPERIMENTAL

Materials and physical measurements

1,10-Phenanthroline-5,6-dione was synthesized according to a published method [20]. 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 (Inonu University, Malatya, Turkey). ^{1}H NMR spectra were recorded on a Bruker 300 MHz spectrometer (Inonu University, Malatya, Turkey) in DMSO-d_6. The IR spectra were obtained using KBr discs on a Ati Unicam Mattson 1000 Series FT-IR spectrophotometer (Firat University, Elazig, Turkey). The electronic absorption spectra in the 200-1100 nm range were obtained in DMF on a Shimadzu UV-1700 UV-Visible spectrophotometer (Firat University, Elazig, Turkey). Magnetic susceptibility were measured at room temperature with MK-1 model Gouy balance (Firat University, Elazig, Turkey) 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 ^{o}C using a CMD 750 WPA model conductivity meter (Firat University, Elazig, Turkey). Thermogravimetric analyses (TGA) were carried out by Shimadzu-50 thermal analyzer (Firat University, Elazig, Turkey) in a dynamic nitrogen atmosphere in the 20-600 ^{o}C and a heating rate 20 ^{o}C min^{-1}.

Antibacterial activity

The *in vitro* antibacterial screening effects of the compounds 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).

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, 22, 23]. By using a sterilised cork borer (7 mm diameter), wells were dug in the culture plates. Compounds dissolved in DMF (1000 µg/mL) were added (75 µL) to these wells. The petri dishes were left at 4 ^{o}C for 2 h and then the plates were incubated at 37 ^{o}C for bacteria (18–24 h). At the end of the period, inhibition zones formed on the medium were evaluated is milimeters (mm). DMF was used as a negative control under similar conditions for comparison. Ampicillin (AMP) was used as the reference drug in positive control. All the experiments were repeated three times and the average values are presented.

The minimum inhibitory concentration (MIC) was determined by broth microdilution method [21]. For MIC determination, suspensions of microorganism (0.5 McFarland), Muller-Hinton broth, solutions of the substances to be tested (1000 µg/mL in DMF). An equal volume of bacterial inoculum was added to each well on the microtitre plate. In this manner final concentration of compounds range 1000-3.91 µg/mL in twofold dilution step. The inoculated plates were then incubated at 37 °C for 18-24 h.

Synthesis of ligand (L)

The ligand (L) (Figure 1) was synthesized by a method similar to the one described previously [24, 25]. A mixture of 1,10-phenanthroline-5,6-dione (0.4 g, 2 mmol), ammonium acetate (3.1 g, 40 mmol), 4-methylbenzaldehyde (0.27 g, 2.3 mmol) and glacial acetic acid (30 mL) was refluxed for 2 h, then cooled to room temperature and diluted with water (60 mL). Dropwise

addition of concentrated aqueous ammonia gave 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 ^{o}C. Yield 0.384 g (62%). ^{1}H NMR (300 MHz, DMSO-d_6, δ ppm): 13.69 (s, 1H, NH), 9.05-9.01 (dd, 2H, C_{Ar}-H), 8.95-8.89 (dd, 2H, C_{Ar}-H), 8.21-8.16 (d, 2H, C_{Ar}-H), 7.87-7.80 (m, 2H, C_{Ar}-H), 7.45-7.39 (d, 2H, C_{Ar}-H), 2.41 (s, 3H, CH_3).

Synthesis of complexes

[Co(L)$_2$Cl$_2$].H$_2$O. A ethanolic (10 mL) solution of the $CoCl_2.6H_2O$ (0.075 mmol, 0.019 g) was added a hot solution of the L (0.047 g, 0.15 mmol) in ethanol (10 mL). The reaction mixture was refluxed for 24 h. The mixture was cooled to room temperature, the resulting orange solid was filtered, washed with ethanol and recrystallized in ethanol. The product was dried at 80 ^{o}C in a vacuum oven. Yield: 0.032 g (56 %).

[Ni(L)$_2$Cl$_2$].2H$_2$O. A ethanolic (10 mL) solution of the $NiCl_2.6H_2O$ (0.075 mmol, 0.018 g) was added a hot solution of the L (0.047 g, 0.15 mmol) in ethanol (10 mL). The reaction mixture was refluxed for 26 h. The mixture was cooled to room temperature, the resulting orange solid was filtered, washed with ethanol and recrystallized in ethanol. The product was dried at 80 ^{o}C in a vacuum oven. Yield: 0.038 g (65 %).

[Cu(L)$_2$Cl$_2$].2H$_2$O. A ethanolic (10 mL) solution of the $CuCl_2.H_2O$ (0.075 mmol, 0.013 g) was added a hot solution of the L (0.047 g, 0.15 mmol) in ethanol (10 mL). The reaction mixture was refluxed for 20 h. The mixture was cooled to room temperature, the resulting green solid was filtered, washed with ethanol and recrystallized in ethanol. The product was dried at 80 ^{o}C in a vacuum oven. Yield: 0.028 g (48 %).

RESULTS AND DISCUSSION

Elemental analyses indicate that the metal:ligand ratio are 1:2 in all the complexes (Table 1, Figure 2). The ligand (L) and its complexes are soluble in EtOH, DMF and DMSO.

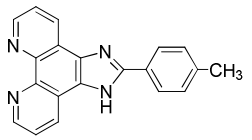

Figure 1. Structure of the ligand (L).

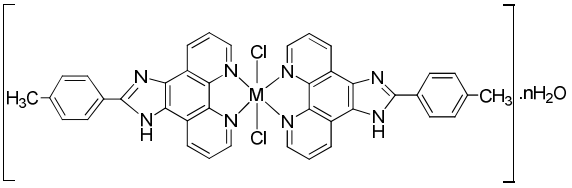

Figure 2. Structure of the $[Co(L)_2Cl_2].H_2O$, $[Ni(L)_2Cl_2].2H_2O$ and $[Cu(L)_2Cl_2].2H_2O$ complexes.

IR spectra

In the IR spectra (Table 2) of $[Co(L)_2Cl_2].H_2O$, $[Ni(L)_2Cl_2].2H_2O$ and $[Cu(L)_2Cl_2].2H_2O$, the bands were observed at the 3420, 3417 and 3428 cm^{-1} as broad bands, respectively, are due to OH stretching vibrations of H_2O molecules [26-28]. The presence of H_2O is also confirmed by TGA analyses.

The presence of broad bands in the IR spectra of the ligand and its complexes in the 3038-3150 cm^{-1} range may be assigned to the N-H stretching vibrations. This is indicating hydrogen-bonding between the molecules [29, 30].

The stretching vibration at 1604 cm^{-1} of the C=N (imidazole ring) group of the ligand not affected in its complexes, indicating that the nitrogen atom of this group is not involved in coordination for all the complexes. On the other hand, the bands observed in the 1503-1561 cm^{-1} range of the C=N (phenanthroline ring) and C=C (Ar) groups were shifted to higher frequencies in the range 1522-1577 cm^{-1} in all the complexes of the ligand, that indicates the participation nitrogen atom of the C=N (phenanthroline ring) groups in coordination of the metal ion [31, 32].

The bands of the N-H and Ar(C-H) groups in all the complexes of the ligand shifted to negative frequencies after complexations. 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.

Table 1. Some analytical data and physical properties of the ligand and its complexes.

Compound	Yield, %	Color	Molecular formula	FW, g/mol	Elemental analyses calculated (found), %			Λ_M (Ω^{-1}. cm^2. mol^{-1})
					C	H	N	
L	62	Yellow	$C_{20}H_{14}N_4$	310.35	-	-	-	-
$[Co(L)_2Cl_2].H_2O$	56	Orange	$C_{40}H_{30}N_8OCl_2Co$	768.56	62.51 (61.96)	3.93 (3.50)	14.58 (15.03)	11.47
$[Ni(L)_2Cl_2].2H_2O$	65	Orange	$C_{40}H_{32}N_8O_2Cl_2Ni$	786.33	61.10 (60.47)	4.10 (4.68)	14.25 (13.77)	9.46
$[Cu(L)_2Cl_2].2H_2O$	48	Green	$C_{40}H_{32}N_8O_2Cl_2Cu$	791.19	60.72 (60.20)	4.08 (4.03)	14.16 (13.58)	10.32

Table 2. Significant bands in the IR spectra (cm^{-1}) of the ligand and its complexes.

Compounds	$(O-H)_{str.}$ H_2O	$(N-H)_{str.}$	Ar $(C-H)_{str.}$	Al $(C-H)_{str.}$	$(C=N)_{str.}$ imidazole ring	Ar $(C=C)_{str.}$ and phen ring $(C=N)_{str.}$
L	-	3150 (br)	3010	2851, 2912	1604	1561, 1519, 1503
$[Co(L)_2Cl_2].H_2O$	3420 (br)	3038 (br)	2978	2851, 2917	1604	1574, 1550, 1522
$[Ni(L)_2Cl_2].2H_2O$	3417 (br)	3038 (br)	2978	2851, 2912	1604	1574, 1550, 1522
$[Cu(L)_2Cl_2].2H_2O$	3428 (br)	3043 (br)	2978	2851, 2912	1604	1577, 1552, 1522

Abbreviations: str = stretching, Ar = aromatic, Al = Aliphatic, phen = phenanthroline, br = broad.

Electronic spectra and magnetic measurements

The electronic spectral data and magnetic moment of the compounds are given in Table 3. In the electronic spectra of the ligand, the bands are observed in the 278-550 nm range. These bands are attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions [33-35].

The magnetic moment value for the Co(II) complex at 4.78 BM reported here indicates a high spin octahedral configuration with three unpaired electrons [36, 37]. The electronic spectrum of the Co(II) complex gives two bands 410 and 500 nm. These bands may be assigned to the transitions $^4T_{1g}(F)(D_{4h}; {}^4E_g) \rightarrow {}^4T_{1g}(P)(D_{4h}; {}^4A_{2g})$ and $^4T_{1g}(F)(D_{4h}; {}^4E_g) \rightarrow {}^4T_{1g}(P)(D_{4h}; {}^4E_g)$, respectively. The positions of these bands suggest a tetragonal environment around Co^{2+} ion [38]. The other bands of complex were not observed because they might be overlapped by the bands of L ligand.

The magnetic moment value (2.93 BM) for the Ni(II) complex corresponds to two unpaired electron [36, 39]. The absorption bands of this complex in the range 405-720 nm suggest a tetragonal environment around Ni^{2+} ion [38].

The magnetic moment value (1.95 BM) for the Cu(II) complex corresponds to one unpaired electron [36, 40]. The complex may be considered to have a tetragonal geometry. The electronic spectrum of the Cu(II) complex shows two bands at 415 and 720 nm assigned to $^2E_g(D_{4h}; {}^2B_{1g}) \rightarrow {}^2T_{2g}(D_{4h}; {}^2B_{2g}, {}^2E_g)$ and $^2E_g(D_{4h}; {}^2B_{1g}) \rightarrow {}^2E_g(D_{4h}; {}^2A_{1g})$ transitions, respectively [38].

Table 3. Magnetic moment and electronic spectral data of the ligand and its complexes.

Compound	μ_{eff} (BM)	λ (nm)	Assigned transitions
L	-	278, 291, 309, 320, 372, 445, 461, 550	$\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$
$[Co(L)_2Cl_2].H_2O$	4.78	410 500	$^4T_{1g}(F)(D_{4h}; {}^4E_g) \rightarrow {}^4T_{1g}(P)(D_{4h}; {}^4A_{2g})$ $^4T_{1g}(F)(D_{4h}; {}^4E_g) \rightarrow {}^4T_{1g}(P)(D_{4h}; {}^4E_g)$
$[Ni(L)_2Cl_2].2H_2O$	2.93	405 418 530 561 720	$^3A_{2g}(D_{4h}; {}^3B_{1g}) \rightarrow {}^3T_{1g}(P)(D_{4h}; {}^3E_g)$ $^3A_{2g}(D_{4h}; {}^3B_{1g}) \rightarrow {}^3T_{1g}(P)(D_{4h}; {}^3A_{2g})$ $^3A_{2g}(D_{4h}; {}^3B_{1g}) \rightarrow {}^3T_{1g}(F)(D_{4h}; {}^3E_g)$ $^3A_{2g}(D_{4h}; {}^3B_{1g}) \rightarrow {}^3T_{1g}(F)(D_{4h}; {}^3A_{2g})$ $^3A_{2g}(D_{4h}; {}^3B_{1g}) \rightarrow {}^3T_{2g}(F)(D_{4h}; {}^3E_g, {}^3B_{2g})$
$[Cu(L)_2Cl_2].2H_2O$	1.95	415 720	$^2E_g(D_{4h}; {}^2B_{1g}) \rightarrow {}^2T_{2g}(D_{4h}; {}^2B_{2g}, {}^2E_g)$ $^2E_g(D_{4h}; {}^2B_{1g}) \rightarrow {}^2E_g(D_{4h}; {}^2A_{1g})$

Thermal analysis (TGA)

According to the thermogravimetric results all the complexes were stable up to 50 °C. In the decomposition process of the complexes, the mass loss corresponded to one uncoordinated water molecule for $[Co(L)_2Cl_2].H_2O$ (2.50% experimental; 2.29% calculated) and two uncoordinated water molecule for $[Ni(L)_2Cl_2].2H_2O$ and $[Cu(L)_2Cl_2].2H_2O$ (4.58% experimental; 4.57% calculated and 4.16 % experimental; 4.55 % calculated) in the temperature range of 50-120 °C.

Conductance measurements

The molar conductivity values (Table 1) of all the complexes indicate that the complexes are non-electrolytes [41].

Antibacterial activity

The results concerning in vitro antibacterial activity of the ligand and its complexes together with the inhibition zone diameter (mm) and MIC values are presented in Tables 4 and 5.

Table 4. Antibacterial activity of the ligand and its complexes (inhibition zone diameter, mm).

Bacteria	Antibacterial activity (IZD in mm)					
	L	$[Co(L)_2Cl_2].H_2O$	$[Ni(L)_2Cl_2].2H_2O$	$[Cu(L)_2Cl_2].2H_2O$	DMF	Ampicillin (AM10)
A. hydrophila ATCC 7966	19	11	–	16	–	–
S. aureus ATCC 29213	21	14	–	15	7	–
K. pneumoni ATCC 21541	18	17	17	17	14	16
P. aeroginose ATCC 27853	14	7	–	8	11	18
S. marcescens ATCC 21074	15	16	7	15	13	18
E. aerogenes ATCC 5402	19	11	–	14	7	16
B. subtilis ATCC 6633	20	15	–	17	7	8
E. coli ATCC 25922	14	11	12	8	14	18
E. faecalis ATCC 29212	22	16	–	20	–	7

IZD = Inhibition zone diameter.

Table 5. Antibacterial activity of the ligand and its complexes (MIC, μg/mL).

Bacteria	MIC (μg/mL)				
	L	$[Co(L)_2Cl_2].H_2O$	$[Ni(L)_2Cl_2].2H_2O$	$[Cu(L)_2Cl_2].2H_2O$	Ampicillin (AM10)
A. hydrophila ATCC 7966	250	125	–	250	_
S. aureus ATCC 29213	250	250	–	125	_
K. pneumoni ATCC 21541	250	250	62.5	125	3.91
P. aeroginose ATCC 27853	250	31.25	–	31.25	7.81
S. marcescens ATCC 21074	31.25	62.5	31.25	62.5	3.91
E. aerogenes ATCC 5402	125	125	–	62.5	7.81
B. subtilis ATCC 6633	125	125	–	125	15.63
E. coli ATCC 25922	125	62.5	31.25	31.25	15.63
E. faecalis ATCC 29212	62.5	250	–	250	7.81

Interestingly, the ligand was found to exhibit significant antibacterial activity against all the bacteria tested. Ni(II) complex showed good antibacterial activity against *E. coli* and *K. pneumoniae*, respectively. Cu(II) complex also displayed good antibacterial activity against the tested bacteria. However, no effect was observed against *P. aeruginosa* and *E. Coli* by both the

ligand and the complexes. Further, antibacterial activity Co(II) complex was found to be significant effect against all bacteria. In contrast no effect was observed against *P. aeruginosa.* The very high antibacterial activities of the ligand, Cu(II) complex and the Co(II) complex could be further studied for the treatment of infections caused by any of the above organisms.

CONCLUSION

In this study, imidazole and phenanthroline containing 2-*p*-tolyl-1H-imidazo[4,5-f][1,10]phenanthroline (L) and its complexes were synthesized and characterized. The analytical data, physical and spectroscopic studies suggest that the complexes were of the general formula $[M(L)_2Cl_2].nH_2O$ where M is Co(II), Ni(II) and Cu(II) and n corresponding to M is 1, 2, 2, respectively. According to the IR data of the compounds, L is coordinated to the metal ions through nitrogen atoms of the C=N (phenanthroline ring) groups. The biological activity test results showed that the ligand and its metal complexes have good antibacterial activity against the bacterial strains except for Ni(II) complex. We think that the ligand and the two metal complexes (Cu(II) and Co(II)) might be effective as antibacterial agents.

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