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# SYNTHESIS, CHARACTERIZATION, AND DFT CALCULATIONS OF NEW FLUORESCENT Cu(II) COMPLEXES OF HETEROCYCLIC LIGANDS*

**S. Rastegarnia, M. Pordel, and S. Allameh**

The synthesis, spectral studies, and quantum chemical investigation of two new copper(II) complexes of fluorescent heterocyclic ligands derived from benzimidazole are reported. The fluorescent heterocyclic ligands are synthesized by the reduction of imidazo[4′,5′:3,4]benzo[1,2-*c*]isoxazole derivatives and characterized by elemental analysis, IR, mass, and NMR spectra. Coordination of the bidentate ligands with the Cu(II) cation produce orange complexes. The structures of the complexes are established by spectral, analytical data and Job′s method. To gain insight into the geometry and spectral properties of the Cu(II) complexes, DFT calculations are performed at the B3LYP/6-311++G(*d*,*p*) level. The DFT-calculated spectral properties are in good agreement with the experimental values, confirming the suitability of the optimized geometries for the copper complexes. The photophysical properties of the ligands and the Cu(II) complexes are characterized by UV-Vis and fluorescence spectroscopy. An efficient charge transfer from the ligand *p* orbital to the Cu(II) *d* orbital may be proposed as the main reason for the color of the complexes.

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**Keywords:** benzimidazole, fluorescent ligands, Cu(II) complex, UV-Vis and fluorescence spectroscopy, DFT.

## INTRODUCTION

Copper is an important bioelement responsible for many catalytic processes in living systems [1]. Copper is present in enzymes of biological systems either alone [2] or in combination with some other metal ions [3] to discharge its function by the redox reactivity. The copper complexes constitute a significant class of molecules from several points of view, *viz.* bioinorganic, catalytic, and magnetic. Copper(II) complexes play an important role in the active sites of a large number of metalloproteins in biological systems and can have the potential application for numerous catalytic processes in living organisms that involve electron transfer reactions or the activation of some antitumor substances [4]. In fact, copper(II) chelates have been found to interact with biological systems and exhibit antineoplastic [5], antibacterial, antifungal [6, 7], and anticancer [8] activities. Some copper(II) N,S,O/N,N-donor chelators are good anticancer agents due to the strong binding ability with a DNA base pair [9]. Also, copper(II) complexes find applications as catalysts for the oxidation of alcohols into

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aldehydes and ketones in organic chemistry with the recognized industrial importance [10].

On the other hand, benzimidazoles are considered as significant heterocyclic compounds due to their presence in a wide range of bioactive compounds such as antiparasitics [11], anticonvulsants [12], analgesics [13], antihistaminics [14], antiulcers [15], antihypertensives [16], antiviral [17], anticancers [18], antifungals [19], anti-inflammatory agents [20], proton pump inhibitors [21], and anticoagulants [22]. The optimization of substituents around the benzimidazole core has resulted in many drugs: albendazole, mebendazole, thiabendazole as antihelmintics; omeprazole, lansoprazole, pantoprazole as proton pump inhibitors; astemizole as antihistaminic; enviradine as antiviral; candesartencilexitil and telmisartan as antihypertensives, and many leading compounds in a wide range of therapeutic areas. Also, benzimidazoles play an important role in determining the function of a number of biologically important metal complexes [23].

Since, copper and benzimidazole play a key role in many disciplines, it is important to study the interactions of benzimidazole ligands with copper. In this work, the synthesis of two new copper (II) complexes of fluorescent heterocyclic ligands derived from benzimidazole is reported. Also, the optical properties of the compounds are investigated by UV-Vis and fluorescence spectroscopy. Moreover, density functional theory (DFT) calculations are performed to provide the optimized geometries, structural parameters, and vibrational frequencies of the investigated compounds.

## EXPERIMENTAL

**Equipment and materials.** Melting points were measured on an Electrothermal type-9100 melting-point apparatus. The FT-IR spectra were recorded for potassium bromide pellets using a Tensor 27 spectrometer and only noteworthy absorptions are listed. The $^{13}$C NMR (75 MHz) and $^{1}$H NMR (300 MHz) spectra were obtained on a Bruker Avance DRX-300 spectrometer. Chemical shifts are reported in ppm downfield from TMS as the internal standard; the coupling constant $J$ is given in Hz. The mass spectrum was recorded on a Varian Mat, CH-7 at 70 eV and the ESI mass spectrum was measured using a Waters Micromass ZQ spectrometer. Elemental analysis was performed on a Thermo Finnigan Flash EA microanalyzer. Absorption and fluorescence spectra were recorded on a Varian 50-bio UV-Visible spectrophotometer and a Varian Cary Eclipse spectrofluorophotometer. UV-Vis and fluorescence scans were recorded from 200 to 1000 nm. The Cu(II) percentage was obtained using a Hitachi 2-2000 atomic absorption spectrophotometer.

All solvents were dried according to the standard procedures. Compounds **1** [24] and **3a,b** [25] were obtained according to the published methods. Other reagents were commercially available.

**Computational methods.** All calculations have been performed using the DFT method with the B3LYP functional [26] as implemented in the Gaussian 03 program package [27]. The 6-311++G($d$,$p$) basis sets were employed, except for Cu(II) where the LANL2DZ basis sets were used with considering its effective core potential. The geometry of the Cu(II) complexes was fully optimized and confirmed to have no imaginary frequency of the Hessian. The geometry optimization and frequency calculation simulate the properties in the gas/solution phases.

The fully-optimized geometries were confirmed to have no imaginary frequency of the Hessian.

The solute-solvent interactions have been investigated using one of the self-consistent reaction field methods, i.e., the sophisticated polarizable continuum model (PCM) [28]. The PCM calculations have been performed in the MeOH solution.

**General procedure for the synthesis of 4a,b ligands from 3a,b.** Iron powder (0.89 g, 16 mmol) was added with stirring to a solution of **3a**,**b** (4 mmol) in EtOH (30 ml) and HCl (2M, 2 ml). Then the mixture was refluxed for 4 h and poured into water. The precipitate was collected by filtration, washed with water, and air-dried to give crude **4a**,**b**.

**(5-Amino-1-propyl-1H-benzo[d]imidazol-4-yl)(phenyl)methanone (4a, L1)** was obtained as shiny yellow needles (EtOH). M.p.: 122-124 °C (Lit. m.p. 121-123 °C)] [ 25 ]; $^{1}$H NMR (CDCl$_3$): δ 0.94 (t, $J$ = 7.5 Hz, 3H, CH$_3$), 1.75-2.10 (m, 2H, CH$_2$), 4.04 (t, $J$ = 7.5 Hz, 2H, NCH$_2$), 4.12 (br s, 2H, NH$_2$), 6.62 (d, $J$ = 8.5 Hz, 1H, Ar H), 7.03 (d, $J$ = 8.5 Hz, 1H, Ar H), 7.11-7.52 (m, 5H, Ar H), 7.75 (s, 1H, Ar H) ppm; $^{13}$C NMR (CDCl$_3$): δ 11.4, 23.2, 46.8, 111.3, 114.1, 114.8, 125.5, 127.1, 127.6, 127.9, 129.0, 132.3, 135.6, 142.2, 195.9(C=O) ppm. IR (KBr): 3315, 3260 cm$^{-1}$ ($NH_2$), 1635 cm$^{-1}$ (C=O). MS (*m*/*z*) 279 ($M^+$). Anal. Calcd. for $C_{17}H_{17}N_3O$ (279.3): C 73.10, H 6.13, N 15.04. Found: C 73.45, H 6.15, N 14.87.

**(5-Amino-1-butyl-1H-benzo[d]imidazol-4-yl)(phenyl)methanone (4b, L2)** was obtained as shiny yellow needles. M.p.: 117-119 °C. Yield: 79%. $^1$H NMR ($CDCl_3$): δ 0.89 (t, *J* = 7.5 Hz, 3H, $CH_3$), 1.21-1.33 (m, 2H, $CH_2$), 1.77-1.88 (m, 2H, $CH_2$), 4.19 (br s, 2H, $NH_2$), 4.31 (t, *J* = 6.9 Hz, 2H, $NCH_2$), 6.67 (d, *J* = 8.5 Hz, 1H, Ar H), 7.01 (d, *J* = 8.5 Hz, 1H, Ar H), 7.09-7.47 (m, 5H, Ar H), 7.73 (s, 1H, Ar H) ppm; $^{13}$C NMR ($CDCl_3$): δ 13.7, 20.01, 33.1, 44.5, 110.8, 114.3, 114.6, 125.3, 127.1, 127.4, 127.8, 128.8, 132.5, 135.9, 142.0, 195.3 (C=O) ppm. IR (KBr): 3320, 3263 cm$^{-1}$ ($NH_2$), 1637 cm$^{-1}$ (C=O). MS (*m*/*z*) 293 ($M^+$). Anal. Calcd. for $C_{18}H_{19}N_3O$ (293.4): C 73.69, H 6.53, N 14.32. Found: C 74.01, H 6.57, N 14.09.

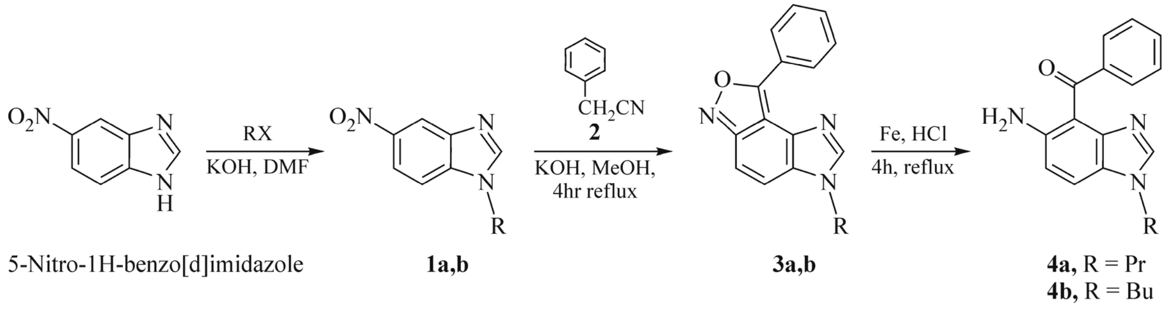
**General procedure for the synthesis of complexes 5a,b from ligands 4a,b.** To the yellow solution of ligands **4a,b** (2 mmol) in a metanolic solution (15 ml, MeOH:$H_2O$ 10:90) copper(II) sulfate pentahydrate (0.25 g, 1 mmol) was added, resulting in a change in the color to shiny green. The reaction was carried out for another 1 h at room temperature. The complex was isolated by evaporation of the solvent and washed with cold MeOH and then $H_2O$.

**Aqua bis (5-amino-1-propyl-1H-benzo[d]imidazol-4-yl)(phenyl)methanone)** copper(II) sulfate $[Cu(L1)_2]SO_4\cdot(H_2O)$ (**5a**) was obtained as an orange powder. M.p. > 300 °C (decomp). IR (KBr): 3378, 3254 cm$^{-1}$ ($NH_2$), 1624 cm$^{-1}$ (C=O). ESI–MS (+) *m*/*z* (%): 622 $[Cu(L1)_2]^{2+}$. Anal. Calcd. for $C_{34}H_{36}CuN_6O_7S$ (736.3): C 55.46, H 4.93, N 11.41, Cu 8.63. Found: C 55.67, H 4.96, N 10.98, Cu 8.69.

**Aqua bis(5-amino-1-butyl-1H-benzo[d]imidazol-4-yl)(phenyl)methanone)** copper(II) sulfate $[Cu(L2)_2]SO_4\times\cdot\times(H_2O)$ (**5b**) was obtained as an orange powder. M.p. > 300 °C (decomp). IR (KBr): 3371, 3260 cm$^{-1}$ ($NH_2$), 1625 cm$^{-1}$ (C=O). ESI–MS (+) *m*/*z* (%): 650 $[Cu(L2)_2]^{2+}$. Anal. Calcd. for $C_{35}H_{38}Cl_7CuN_6O_7S$ (764.4): C 56.57, H 5.27, N 10.99, Cu 8.31. Found: C 57.00, H 5.31, N 10.69, Cu 8.29.

## RESULTS AND DISCUSSION

**Synthesis and structure of new ligands 4a,b and complexes 5a,b.** The reaction of 5-nitro-1H-benzimidazole with propyl and butyl bromide in KOH and DMF leads to the formation of 1-propyl-5-nitro-1H-benzimidazoles (**1a)** and 1-benzyl-5-nitro-1H-benzimidazoles (**1b**) [24]. 3-Propyl-8-phenyl-3H-imidazo[4′,5′:3,4]benzo[1,2-*c*]isoxazole (**3a**) and 3-butyl-8-phenyl-3H-imidazo[4′,5′:3,4]benzo[1,2-*c*]isoxazole (**3b)** are obtained from the reaction of compounds **1a,b** with benzyl cyanide (**2**) in a basic MeOH solution [25]. The reduction of compounds **3a,b** in EtOH with Fe/HCl gives 5-amino-1-propyl-1H-benzo[*d*]imidazol-4-yl)(phenyl)methanone (**4a)** and (5-amino-1-butyl-1H-benzo[*d*]imidazol-4-yl)(4-chlorophenyl) methanone (**4b)** in high yields (Scheme 1).



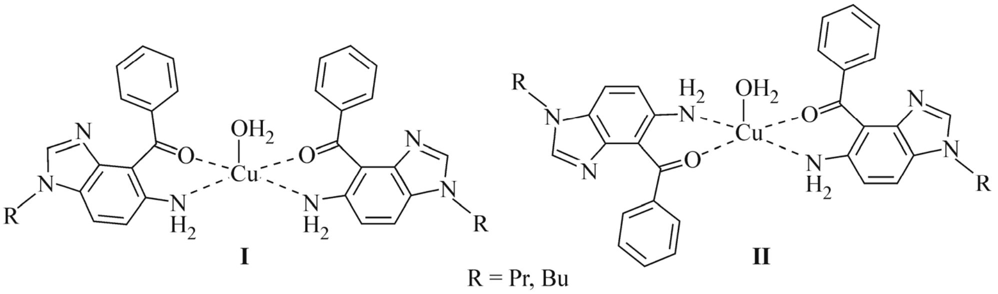
Scheme 1. Synthesis of ligands **4a,b**.

The structural assignments of compounds **4a**,**b** were based on the analytical and spectral data. For example, in the $^1$H NMR spectrum of new compound **4b** there is an exchangeable peak at δ 4.19 ppm attributed to $NH_2$ group protons. Also, there are two doublet signals (δ = 6.67 and 7.01 ppm), a multiplet signal (δ = 7.09–747 ppm), and a singlet signal (δ = 7.73 ppm) assignable to eight aromatic ring protons. In addition, 16 different carbon atom signals are observed in the $^{13}$C NMR spectrum of compound **4b**. Furthermore, the IR spectrum of compound **4b** in KBr showed broad absorption bands at 3320 and 3263 cm$^{-1}$ assignable to $NH_2$ and 1637 cm$^{-1}$ attributed to the C=O groups. The results of mass spectroscopy (*m*/*z* 293 $[M]^+$) and elemental analysis support the structure of the new compound **4b**.

New complexes **5a,b** have been synthesized by treating ligands **4a,b** and $CuSO_4{\cdot}5H_2O$ in the 2:1 molar ratio obtained by Job′s method [29] in an aqueous metanolic solution. Nine aqueous methanolic mixtures of the ligand (0.6 mM) and Cu (II) (0.6 mM) were prepared in an appropriate buffer at 25 °C. Sodium perchlorate was added to give a constant ionic strength of 0.1 M. The volumes of the ligand solution used varied from 9 to 1 ml and those of the Cu(II) solution varied from 1 to 9 ml; the total volume was always 10 ml. The absorption spectra of the complex were achieved immediately after mixing the ligand and Cu(II) solutions. The absorption spectra and Job′s plot of the nine aqueous methanolic mixtures of the ligand and Cu(II) can be found in the Supplementary Data (Figs. S1–S3 of Supplementary Materials).

New complexes were characterized by the elemental and spectroscopic (IR, and mass) analyses. The elemental analysis results for the Cu complexes confirm the proposed $[Cu(L)_2]SO_4{\cdot}(H_2O)$ formulas. In addition, the molecular ion peak at *m*/*z* 622 ($[Cu(L1)_2]^{2+}$) and *m*/*z* 650 ($[Cu(L2)_2]^{2+}$) strongly support the structure of new complexes **5a** and **5b**, respectively.

A square pyramidal geometry was proposed for Cu(II) complexes **5a,b** based on our experimental results and those reported in the literature [30, 31]. Complexes **5a**,**b** can exist as two isomers, differing in coordination of ligands **4a** and **4b** to the Cu atom (Scheme 2).



Scheme 2. Two possible structures of new Cu(II) complexes **5a,b**.

In order to clarify the exact structure of **5a,b**, an effort was taken up to crystallize the complexes in various solvent systems under different experimental conditions. Unfortunately, in all our efforts, only amorphous compounds precipitated, which prevented us from the analysis of the complexes by X-ray crystallization. However, the calculated data can help identify the structure of the Cu complexes, revealing which of the two isomers is energetically more advantageous. Therefore, the geometries of two isomers of the Cu(II) complexes were optimized in both gas phase and MeOH as the solvent (PCM model) by DFT calculations at the B3LYP/6-311++G(*d*,*p*) level. By comparing the sum of the electronic and zero-point energy (*E*) values of isomers I (–2148.306834 kJ/mol) and II (–2160.357074 kJ/mol), it can be concluded that the geometry of isomer II is the most possible structure for complexes **5a,b.** For example, the optimized geometry of complex **5a** is depicted in Fig. 1. Some of the calculated structural parameters of the Cu(II) complex are listed in Table 1. The optimized geometries of ligands **4a,b** are depicted in the Supplementary Data (Figs. S2 and S3 of Supplementary Materials). In the optimized geometry of complex **5a**, ligand **4a** acts as a bidentate ligand and coordinates to Cu(II) *via* the nitrogen atom of the amine functional group and the oxygen atom of the carbonyl group. The ligand aromatic rings are approximately in the same plane. Another position of the complex is filled by a $H_2O$ molecule. The Cu–O and Cu–N bond lengths are collected in Table 1.

The DFT-computed vibrational modes of Cu(II) complex **5a** are listed in Table 2 together with the experimental values for comparison. The atoms are numbered as in Fig. 1. As seen in Table 2, there is good agreement between the experimental and DFT-calculated frequencies of complex **5a**, confirming the validity of the optimized geometry as a proper structure for complex **5a**.

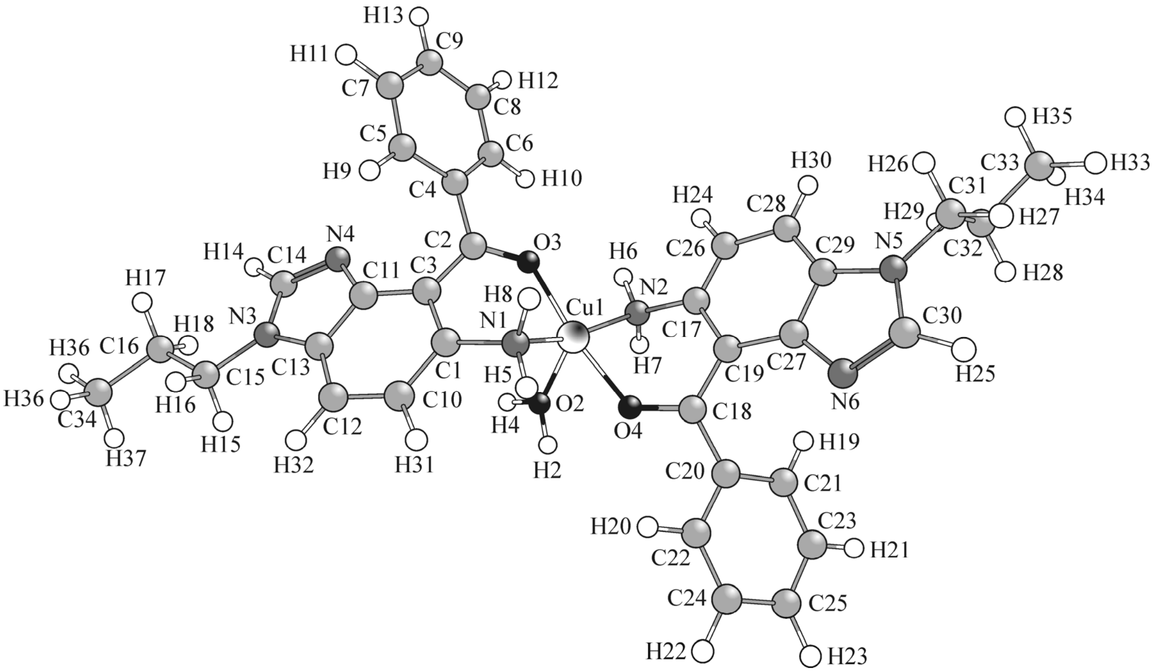


**Fig. 1.** Optimized geometry of complex **5a**.

**TABLE 1.** Selected Structural Parameters of Cu(II) Complex **5a**

| Bond | Bond length (Å) | Angle | (deg.) | Dihedral angle | (deg.) |
|---|---|---|---|---|---|
| Cu–O2 | 2.321 | N1–Cu–N2 | 179.73 | Cu–N2–C17–C19 | 1.076 |
| Cu–O4 | 1.869 | O3–Cu–O4 | 179.23 | Cu–O4–C18–C19 | 22.555 |
| Cu–N1 | 1.961 | O2–Cu–O3 | 119.59 | N1–Cu–N2–C17 | –7.210 |
| Cu–N2 | 1.958 | Cu–O4–C18 | 129.21 | N6–C27–C19–C18 | 38.811 |
| Cu–O3 | 2.277 | Cu–N1–C1 | 119.59 | N4–C11–C13–N3 | 29.512 |
| N1–C1 | 1.459 | Cu–O3–C2 | 113.55 | N5–C30–N6–C27 | –9.110 |
| O4–C18 | 1.304 | C1–C3–C2 | 119.59 | C22–C24–C25–C23 | 0.421 |
| N2–C17 | 1.450 | O3–C2–C4 | 119.124 | O3–C2–C4–C6 | 22.555 |
| C27–C29 | 1.475 | C3–C1–N3 | 129.589 | C1–C10–C12–C13 | 38.717 |
| C27–C19 | 1.422 | N5–C30–N6 | 114.394 | C5–N2–C7–N1 | –0.155 |
| C25–C24 | 1.424 | N3–C29–C28 | 113.900 | O2–Cu–O3–C2 | 25.511 |
| C20–C22 | 1.410 | C19–C18–C20 | 120.231 | N6–C30–N5–C29 | –8.102 |
| C27–N6 | 1.382 | C31–C30–C31 | 119.244 | O4–C18–C20–C22 | 10.285 |
| C14–N3 | 1.373 | C20–C22–C24 | 120.445 | C4–C6–C8–C9 | 7.226 |
| C14–N4 | 1.317 | C10–C12–C13 | 119.811 | N3–C13–C12–C10 | –179.400 |
| C29–N5 | 1.367 | O4–C18–C19 | 119.864 | C34–C16–C13–N3 | –179.095 |
| N3–C15 | 1.474 | C15–C16–C34 | 121.740 | Cu–N1–C2–C3 | 47.602 |
| C15–C16 | 1.515 | C9–C7–C5 | 122.364 | C22–C20–C18–C19 | –179.501 |

**Photophysical properties of the ligands and complexes.** Fluorescent heterocyclic ligands **4a,b** and Cu(II) complexes **5a,b** were characterized by UV-Vis and fluorescence spectroscopy in the wavelength range 200-1000 nm. The absorption and fluorescence emission spectra of **4a,b** and Cu(II) complexes **5a,b** are depicted in Figs. 2 and 3, respectively. Numerical spectral data are also presented in Table 3. Values of extinction coefficient (ε) were calculated as the slope of the plot of absorbance vs. concentration. As seen in Fig. 2, the spectra of complexes **5a,b** have an absorption maximum at

**TABLE 2.** Selected Experimental and Calculated IR Vibrational Frequencies (cm$^{-1}$) of Cu(II) Complex **5a**

| Experimental frequencies | Calculated | | Vibrational assignment |
|---|---|---|---|
| | Frequency | IR Intensity D(10$^{-4}$esu$^2$/cm$^2$) | |
| 673 (w) | 679 | 299 | $\delta\upsilon_{sym}$(Cu–N) |
| 721 (w) | 736 | 49 | $\upsilon_{asym}$(Cu–N) |
| 959 (m) | 976 | 190 | $\delta_{op}$(C–H) aromatic |
| 1278 (m) | 1255 | 140 | υ(C1–N3, C22–N6) |
| 1393 (m) | 1401 | 1734 | $\upsilon_{asym}$(C4–C5–N2) + $\upsilon_{asym}$(C25–C26–N5) |
| 1446 (s) | 1413 | 515 | υ(C=C, C=N) of the aromatic rings |
| | 1452 | 47 | υ(C21–C9) + υ(C42–C30) |
| | 1474 | 256 | υ(C=N) of the aromatic rings + υ(C42–N4, C21–N1) |
| | 1485 | 66 | υ(C=N) of the aromatic rings + υ(C22–N6, C1–N3) |
| 1624 (s) | 1523 | 527 | υ(C=C) of the aromatic rings |
| | 1563 | 4101 | $\delta_{sci}$(H–O–H) of the $H_2O$ ligands |
| | 1638 | 322 | υ(C=C) of the benzene rings |
| | 1657 | 19 | υ(C=C) of 1 moiety |
| 2822 (m) | 3066-3190 | 23-12 | $\upsilon_{sym}$(C–H) aliphatic |
| | 3079-3121 | 24-6 | $\upsilon_{asym}$(C–H) aliphatic |
| | 3185-3224 | 12-5 | υ(C–H) aromatic |
| 3381 (vs,br) | 3549 | 25 | υ(C28–H21) + υ(C7–H2) |
| | 3779 | 11 | $\upsilon_{sym}$(O–H) of the $H_2O$ ligands |
| | 3875 | 43 | $\upsilon_{asym}$(O–H) of the $H_2O$ ligands |

Abbreviations: op is out-of-plane; ip is in-plane; w is weak; m is medium; s is strong; vs is very strong; br is broad; sh is shoulder.

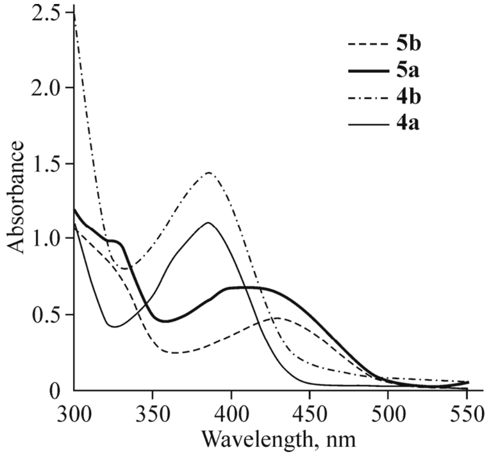


**Fig. 2.** Absorption spectra of **4a,b** and Cu(II) complexes **5a,b** in the MeOH solution (10$^{-4}$ M).

425 nm at which the ligands have no absorbance. Absorption at 425 nm could be attributed to both ligand to-metal charge transfer (LMCT) [32] bands and intraligand transitions.

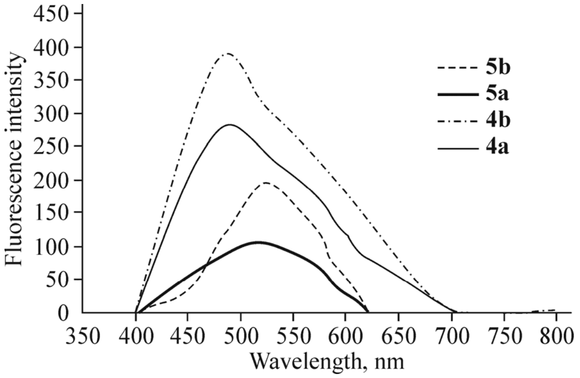


**Fig. 3.** Fluorescence emission spectra of **4a,b** (excitation at 370 nm) and Cu(II) complexes **5a,b** (excitation at 425 nm) in the MeOH solution ($3\times10^{-6}$ M).

**TABLE 3.** Spectroscopic Data for **4a,b** and **5a,b** at 298 K

| Dye | **4a** | **4b** | **5a** | **5b** |
|---|---|---|---|---|
| $\lambda_{abs}$ (nm) [a] | 385 | 365 | 425 | 425 |
| $\varepsilon\times10^{-3}$ $[(mol/L)^{-1}\cdot cm^{-1}]$ [b] | 10.0 | 14.0 | 7.5 | 6.0 |
| $\lambda_{flu}$ (nm)[c] | 485 | 490 | 525 | 525 |
| $\Phi_F$ [d] | 0.66 | 0.73 | 0.49 | 0.55 |

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[a] Maximum absorbance wavelengths ($\lambda_{abs}$).

[b] Extinction coefficient.

[c] Fluorescence emission wavelengths ($\lambda_{flu}$) with excitation at 370 nm for **4a,b** and 425 nm for **5a,b** compounds.

[d] Fluorescence quantum yield.

Furthermore, ligands **4a,b** and copper complexes **5a,b** produced fluorescence in dilute MeOH solution (Fig. 3). The fluorescence quantum yields of the compounds were also determined *via* comparison methods, using fluorescein as the standard sample in a 0.1 M NaOH and MeOH solution [33]. The used value of the fluorescein emission quantum yield is 0.79 and the obtained emission quantum yields of the new compounds are around 0.49-0.73. As can be seen from Table 3, extinction coefficient (ε), fluorescence intensity, and the emission quantum yield of **4b** were the largest values. The excitation spectra of ligands **4a,b** and Cu(II) complexes **5a,b** in the MeOH solution were also presented in Supplementary data (Fig. S6 of Supplementary Materials).

## CONCLUSIONS

Coordination of the ligands derived from benzimidazole with the Cu(II) cation gives new fluorescent Cu(II) complexes. The structures of the complexes have been established by spectral and analytical data and Job′s method, and a square pyramidal geometry was proposed for the complexes. Also, the DFT methods were employed to gain a deeper insight into the geometry and spectral properties of the new complexes. The DFT-calculated vibrational modes of Cu(II) complexes are in good agreement with the experimental values, confirming the suitability of the optimized geometries for the complexes. Fluorescent ligands and copper complexes were spectrally characterized by UV-Vis and fluorescence spectroscopy. The results revealed that the ligands and Cu(II) complexes generated fluorescence in a dilute MeOH solution.

A great attempt to obtain the new complexes from the coordination of the ligands with other cations is in progress and will soon be reported elsewhere.

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