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# Synthesis, characterization and quantum-chemical investigations of new fluorescent heterocyclic Schiff-base ligands and their cobalt(II) complexes

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**Abstract**– Two new fluorescent heterocyclic Schiff base ligands were synthesized and characterized by elemental analyses, IR, mass, and NMR spectra. Results from NOESY experiment confirmed the *E* configuration of Schiff-bases. Coordination of the bidentate ligands with Co(II) cation led to the formation of deep green complexes. The structures of the complexes have been confirmed by spectral, analytical data and Job's method. Schiff-base ligands and cobalt complexes were spectrally characterized by UV-Vis and fluorescence spectroscopy. An efficient charge transfer of electron from p-orbital on ligand to Co(II) d-orbital can be proposed as the main reason for the color of the complexes. In addition, the DFT methods were employed to achieve deeper insight into geometry, spectral properties and energy difference between the HOMO and LUMO frontier orbitals of the synthesized compounds. The DFT-calculated spectral properties are in good agreement with the experimental values, confirming suitability of the optimized geometries for Co(II) complexes.

*Keywords:* Fluorescent Schiff base; Co(II) complex; UV-Vis and fluorescence spectroscopy; Density functional theory.

### 1. Introduction

Cobalt has many strategic and irreplaceable industrial uses but it is as the central component of Vitamin B12 that it is vital. In hence, the cobalt complexes have received considerable attention owing to their effective biological importance such as antibacterial [1–3] antifungal [4,5] antivirus [6] antiproliferative [7,8] and anticancer activity [9–12]. They are also used as catalysts for a diverse range of organic reactions such as electrochemical reactions [13], cross-coupling reactions [14], polymerization [15], hydrogenation [16,17], Lewis acid catalysts in organic synthesis [18], etc.

Benzo[1,2-*c*]isoxazoles are an important class of heterocyclic bioactive and pharmaceuticals compounds prescribed as antipsychotic risperidone [19] and anti-HIV drugs [20] and play a key role in many organic reactions [21]. Isoxazole-metal complexes are often postulated as intermediates in reactions of considerable synthetic utility, for example the reductive ring opening of isoxazoles. Several isoxazole-metal complexes have been reported and well characterized. In a review of the literature of isoxazole-metal complexes [22], the binding characteristics of the isoxazoles in the complexes have been examined, and some tentative conclusions regarding the regularity of isoxazole complexation behavior have been discussed.

On the other hand, Schiff bases are the most versatile studied ligands in coordination chemistry because of their structural varieties and very exclusive characteristics. Schiff bases have number of applications such as preparative use, identification, detection and determination of aldehydes or ketones, purification of carbonyl or amino compounds, or protection of these groups during complex or sensitive reactions. They also form basic units in certain dyes. Transition metal complexes derived from the Schiff base ligands with biological activity have been widely studied

[23–25]. Based on these results, we have synthesized and characterized two new fluorescent heterocyclic Schiff-base bidentate ligands derived from imidazo[4',5':3,4]benzo [1,2-*c*]isoxazole and their Co(II) complexes. The optical properties of the compounds were also investigated by UV-Vis and fluorescence spectroscopy. Furthermore, density functional theory (DFT) calculations are performed to provide the optimized geometries, structural parameters, vibrational frequencies and energy difference between the HOMO and LUMO frontier orbitals of the investigated compounds.

### 2. Experimental

#### Equipment and Materials

Melting points were measured on an Electrothermaltype-9100 melting-point apparatus. The FT-IR spectra were recorded as potassium bromide pellets using a Tensor 27 spectrometer and only noteworthy absorptions are listed. The <sup>13</sup>C NMR (75 MHz), <sup>1</sup>H NMR (300 MHz) and NOESY spectra were obtained on a Bruker Avance DRX-300 spectrometer. Chemical shifts are reported in ppm downfield from TMS as internal standard; coupling constant *J* is given in Hz. The mass spectrum was recorded on a Varian Mat, CH-7 at 70 eV and 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 Varian 50-bio UV-Visible spectrophotometer and Varian Cary Eclipse spectrofluorophotometer. UV–Vis and fluorescence scans were recorded from 200 to 1000 nm. Percentage of the Co(II) was obtained by using a Hitachi 2-2000 atomic absorption spectrophotometer.

All solvents were dried according to standard procedures. Compounds 1[26], 3[27], 4 [28] and **5a,b** [29] were obtained according to the published methods. Other reagents were commercially available.

#### Computational methods

All of the calculations have been performed using the DFT method with the B3LYP functional [30] as implemented in the Gaussian 03 program package [31]. The 6-311+G(d,p) basis sets were employed except for the Co(II) where the LANL2DZ basis sets were used with considering its effective core potential. Geometry of the Co(II) complex was fully optimized, which was confirmed to have no imaginary frequency of the Hessian. Geometry optimization and frequency calculation simulate the properties in the gas/solution phases. Natural Bond Orbitals (NBO) analysis was used for electron population analysis in Gaussian.

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) [32].

### General procedure for the synthesis of 7a,b from 5a,b

To a solution of compound **5a,b** (0.34 g, 1 mmol) in EtOH (15 mL), aldehyde **6a,b** (1 mmol) was added. The reaction mixture was heated under reflux for 5 hours. The solvent was removed under reduced pressure and the yellow product was filtered and washed with cold EtOH to give Schiff base (**7a,b**), which was purified in hot acetone.

((*E*)-*N*-(4-chlorobenzylidene)-8-(4-chlorophenyl)-3-propyl-3H-imidazo[4',5':3,4]benzo[1,2-c] isoxazol-5-amine (**7a, L1, S**cheme 1) was obtained as a yellow powder. m.p.: 178–181 °C; yield: 82%.

(*E*)-4-(((3-butyl-8-(4-chlorophenyl)-3*H*-imidazo[4',5':3,4]benzo[1,2-c]isoxazol-5-yl)imino) methyl) phenol (**7b, L2, S**cheme 1) was obtained as a yellow powder. m.p.: 188-190 °C. yield: 75%.

#### General procedure for the synthesis of the complexes 8a,b from ligands 7a,b

Cobalt(II) nitrate hexahydrate (0.29 gr, 1 mmol) was added to the yellow solution of ligand **7a,b** (2 mmol) in aqueous metanolic solution (15 mL, MeOH, H<sub>2</sub>O, 90:10), resulting in color change to deep green. The reaction was carried out for another 12 h at rt. The complex was isolated by evaporation of the solvent and washed with cold MeOH and then H<sub>2</sub>O.

 $[Co(L1)_2] N_2O_6.2(H_2O)$  (8a, Scheme 1): was obtained as a dark green powder. m.p. > 300 °C (decomp).

 $[Co(L2)_2] N_2O_6.2(H_2O)$  (**8b**, Scheme 1): was obtained as a dark green powder. mp > 300 °C (decomp).

### 3. Results and discussion

#### Synthesis and structure of the new ligands 7*a*,*b* and complexes 8*a*,*b*

Two new heterocyclic Schiff-base ligands were prepared in five steps explained in the following manners. Initial reaction of 5-nitro-1*H*-benzimidazole with 1-bromopropane and 1-bromobutane in KOH and DMF led to the formation of 1-alkyl-5-nitro-1*H*-benzimidazoles (**1a,b**) [27]. The

reaction of 1-alkyl-5-nitro-1*H*-benzimidazoles **1a,b** with (4-chlorophenyl)acetonitrile (**2**) in basic MeOH solution gave 3-alkyl-8-(4-chlorophenyl)-3*H*-imidazo[4',5':3,4]benzo[1,2-*c*]isoxazoles (**3a,b**) [28]. Regioselective nitration of **3a,b** using a mixture of sulfuric acid and potassium nitrate produced 3-alkyl-8-(4-chlorophenyl)-5-nitro-3*H*-imidazo[4',5':3,4]benzo[1,2-*c*]isoxazoles **4a,b** in good yield [29]. Reduction of compounds **4a,b** in EtOH by SnCl<sub>2</sub>, provided the 8-(4chlorophenyl)-3-alkyl-3*H*-imidazo[4',5':3,4]benzo[1,2-*c*]isoxazol-5-amines (**5a,b**) in high yields. The new heterocyclic Schiff-bases **7a,b** were finally obtained by the reaction of amines **5a,b** with *p*-chlorobenzaldehyde **6a** and *p*-hydroxybenzaldehyde **6b** in high yields (Scheme 1).



Scheme 1. Synthesis of the new ligands 7a,b

The unambiguous assignment of Schiff-bases **7a,b** was carried out by elemental analyses, IR, mass, <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy and two-dimensional NMR techniques. For example, in the <sup>1</sup>H NMR spectrum of compound **7b** there is an exchangeable peak at  $\delta$  10.45 ppm attributed to OH group proton. Also, there are four doublet signals ( $\delta$  = 6.95, 7.71, 7.85, 8.93 ppm) and two singlet signals ( $\delta$  = 7.66 and 8.30 ppm) assignable to ten protons of aromatic rings and a singlet

signal ( $\delta = 9.07$ ) attributed to the imine CH proton. Also, 21 different carbon atom signals are observed in the <sup>13</sup>C NMR spectrum of compound **7b**. Furthermore, the IR spectrum of compound **7b** in KBr showed a broad absorption band at 3345 cm<sup>-1</sup> assignable to OH group. The results of mass spectroscopy (m/z 446 [M(<sup>37</sup>Cl)]<sup>+</sup>) and elemental analyses support the structure of Schiffbase **7b**. In addition, the data from NOESY experiment of compound **7b** revealed a cross-peak between the H-4 proton ( $\delta_{\rm H}$  7.71, s, CH-benzene) and the imine CH proton ( $\delta_{\rm H}$  9.07), confirming the *E* configuration of Schiff-base **7b** (Scheme 2).



The coordination of Schiff-bases **7a,b** with Co(II) gave green complexes **8a,b** in aqueous metanolic solution. The stoichiometry of the complexes **8a,b** obtained by Job's method (Figures S1 and S2, Supplementary Data: ML<sub>2</sub>) [33] together with the elemental analysis results

(Experimental section) proposed the formula  $[Co(L)_2]N_2O_6.2(H_2O)$  for the complexes **8a,b** (Scheme 3). Moreover, molecular ion peak at m/z 955 ( $[Co(L1)_2]^{2+}$ ) and m/z 947 ( $[Co(L2)_2]^{2+}$ ) strongly support the structure of the new complexes **8a** and **8b**, respectively.



Scheme 3. The structure of the Co(II) complexes 8a,b.

#### 3.1.Photophysical properties of the new ligands and complexes.

New fluorescent heterocyclic Schiff base ligands **7a,b**, and Cobalt(II) complexes **8a,b** were characterized by UV-Vis and fluorescence spectroscopy in the wavelength range of 200–1000 nm. The absorption and fluorescence emission spectra of Schiff base **7a,b** and Cobalt(II) complexes **8a,b** are depicted in Figures 1 and 2, respectively. Numerical spectral data are also presented in Table 1. Values of extinction coefficient ( $\varepsilon$ ) were calculated as the slope of the plot of absorbance *vs* concentration. As seen in Figure 1, the spectra of the complexes **8a,b** have an absorption maximum at 690 nm at which the ligands have no absorbance. An efficient charge transfer of electron from p-orbital on ligand to Co(II) d-orbital can be considered as the main reason for the color of the complexes described as Ligand to-Metal charge transfer (LMCT) [34]. Moreover Schiff-base ligands **7a,b**, and Cobalt complexes **8a,b** produced fluorescence in dilute

solution of MeOH (Figure 2). Also, using fluorescein as a standard sample in 0.1 M NaOH and MeOH solution, the fluorescence quantum yields of the compounds were determined *via* comparison methods [35]. The used value of the fluorescein emission quantum yield is 0.79 and the obtained emission quantum yields of the new compounds are around 0.21 - 0.61. As can be seen from Table 1, extinction coefficient ( $\varepsilon$ ) in Schiff-base **7a**, fluorescence intensity and the emission quantum yield in Schiff-base **7b** were the biggest values.



Figure 1. The absorption spectra of Schiff-base 7a,b and Co(II) complexes 8a,b in MeOH

solution  $(1 \times 10^{-4} \text{ M})$ 



Figure 2. The fluorescence emission spectra of 7a,b and Co(II) complexes 8a,b in MeOH

solution (1  $\times$  10<sup>-5</sup> M)

Table 1. Spectroscopic data for **7a,b** and **8a,b** at 298 K.

Dye	7a	7b	8a	8b
$\lambda_{abs} (nm)^{a}$	370	435	690	690
$\epsilon \times 10^{-3}  [(mol  L^{-1} )^{-1} cm^{-1}]^{b}$	10.3	9.9	5.9	7.9
$\lambda_{\rm flu} (\rm nm)^{c}$	550	550	555	555
$\Phi_{F}{}^{d}$	0.36	0.61	0.21	0.27

<sup>a</sup> Wavelengths of maximum absorbance ( $\lambda_{abs}$ )

<sup>b</sup> Extinction coefficient

 $^{c}$  Wavelengths of fluorescence emission ( $\lambda_{flu})$  with excitation at 370 nm

<sup>d</sup> Fluorescence quantum yield

#### 3.2.DFT Calculations

Based on our experimental results and reported literatures [36, 37], an octahedral geometry was proposed for Co(II) complexes **8a,b**. To get a deeper insight into the geometries, structural parameters and role of HOMO and LUMO frontier orbitals in the UV-visible absorption spectra of ligands **7a,b** and Cobalt complexes **8a,b**, DFT calculations at the B3LYP/6-311+G(d,p) level were performed and the optimized geometries and HOMO and LUMO frontier orbitals of fluorescent ligands **7a,b** and Co(II) complex **8b** were obtained. Geometry of Co(II) complex **8b** was optimized in both of the gas phase and MeOH as the solvent (PCM model). Figure 3 shows the optimized geometry of the ligands **7a,b**. The optimized geometry of the complex **8b** in two different views with labeling of its atoms is also shown in Figure 4. Some of the calculated structural parameters of the Co(II) complex are listed in Table 2. Selected structural parameters of the ligands **7a,b** can be found in Supplementary Data (Tables S1 and S2)



Figure 3. The optimized geometry of the fluorescent ligands 7a (left) and 7b (right).

In the optimized geometry of the complex **8b**, the ligand **7b** coordinates to the Co(II) *via* nitrogen atom of the imine group (–N=CH) and nitrogen atom of the isoxazole ring and acts as a bidentate ligand.





The aromatic rings of the ligand are approximately in a same plane. Two other positions of the complex are filled by two  $H_2O$  molecules, which are *Trans* to each other. The  $H_2O$  ligands are perpendicular to the square plane of the complex. The Co-O and Co-N Lengths bonds are collected in Table 2.

Bond	Bond length (A <sup>0</sup> )	Angle	(°)	Dihedral angle	(°)
Co-N1	2.059	N1-Co-N5	161.26	N1-N4-N5-N8	-18.504
Co-N4	2.495	N1-Co-N4	74.228	N1-N4-N5-Co	-13.405
Co-N5	2.095	N5-Co-N8	77.596	01-N1-Co-O6	-110.484
Co-N8	2.297	N1-Co-N8	97.249	O3-N5-Co-O6	-101.793
Co-O6	2.143	N4-Co-N5	113.342	O1-N1-Co-N8	-15.932
Co-O5	2.252	N1-Co-O5	83.004	C27-N5-Co-O6	116.874
N5-O3	1.396	N5-Co-O3	17.282	C27-N5-Co-O5	-76.825
O3-C31	1.357	N1-Co-O6	104.171	C27-C28-N8-O6	-20.405
C31-C26	1.400	N5-Co-O5	80.140	C28-N8-Co-N5	-25.540
C26-C27	1.423	O5-Co-O6	165.245	C28-N8-N1-Co	-60.302
C27-C28	1.429	Co-N5-C27	109.901	01-C7-C2-C3	-0.589
C31-C36	1.447	N5-C27-C28	123.210	01-C7-C12-C13	2.936
C36-C38	1.410	C3-N1-Co	117.662	C7-C2-C1-N2	-1.463
C28 – N8	1.420	Co- N1-O1	133.125	C6-C1-N2-C8	-0.010
N8-C42	1.307	C3-C4-N4	115.388	N2-C8- N3-C6	-0.538
C27-N5	1.337	Co-O5-N1	45.598	C2-C7-C12-C14	2.941
C25-N6	1.365	C3- C2-C1	116.723	N5-C27-C26-C31	-0.590
N6-C32	1.321	N1-O1-C7	110.464	C1-C6-N3-C8	0.477
C32-N7	1.366	C1-C6-N3	104.816	C3-C4-C5-C6	1.430
N7-C33	1.469	C1-N2-C8	104.669	N3-C9-C10-C11	-179.894

Table 2. Selected calculated structural parameters of Co(II) complex 8b.

The DFT computed vibrational modes of Co(II) complex **8b** are listed in Table 3 together with the experimental values for comparison. The atoms are numbered as in Figure 4. As seen in Table 3, there is good agreement between the experimental and DFT-calculated frequencies of the complex **8b**, confirming validity of the optimized geometry as a proper structure for the complex **8b**.

### Table 4. Selected experimental and calculated IR vibrational frequencies (cm<sup>-1</sup>) of Co(II)

complex 8b.

	Calculated		
Experimental		IR	
frequencies	Frequency	Intensity	Vibrational assignment
		$(km.mol^{-1})$	
476 (w)	497	63	v <sub>sym</sub> (Co-N)
699 (w)	627	191	v <sub>asym</sub> (Co-N)
1024 (m)	1027	67	$\delta_{op}(C-H)$ aromatic
1095 (vs)	1105	294	v(C-Cl)
1262 (vs)	1237	82	υ(C1-N2, C9-N3, C25-N6, C33-N7)
1459 (m)	1427	105	$v_{asym}$ (C1-C6-N3) + $v_{asym}$ (C25-C30-N7)
	1457	279	v(C=C, C=N) of the aromatic rings
	1482	1256	υ(C7-C12)+ υ(C31-C36)
1549 (s)	1485	119	v(C=N) of the aromatic rings + $v(C9-N3, C33-N7)$
	1506	178	v(C=N) of the aromatic rings + $v(C4-N4, C28-N8)$
1626 (s)	1588, 1620	85, 67	v(C=C) + v(C=N) of the aromatic rings
	1647	157	$\delta_{sci}$ (H-O-H) of the H <sub>2</sub> O ligands
	1656	954	$\upsilon$ (C18-N4)+ $\upsilon$ (C42-N8) of the azomethine C=N groups
	1666	779	v(C=C) of the benzene rings
	1696	38	v(C=C) of 1 moiety
2964 (m)	3059-3081	9-38	v <sub>sym</sub> (C-H) aliphatic
	3152	33	υ(C18-H13)+ υ(C42-H30)
	3151-3139	13-67	v <sub>asym</sub> (C-H) aliphatic
	3197-3213	5-76	υ(C-H) aromatic
	3240	8	v(C8-H2) + v(C32-H19)
	3736	49	$v_{sym}$ (O-H) of the H <sub>2</sub> O ligands
3430 (vs,br)	3782	127	v <sub>asym</sub> (O-H) of the H <sub>2</sub> O ligands
	3865	52	v <sub>sym</sub> (O-H) of the aromatic rings
	3910	93	$v_{sym}$ (O-H) of the aromatic rings

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

The 3D-distribution map for the highest-occupied-molecular orbital (HOMO) and the lowestunoccupied-molecular orbital (LUMO) of the ligands **7a,b** and the complex **8b** are illustrated in Figure 5. As seen, the HOMO orbital of the ligands is localized on the benzimidazole and isoxazole rings. On the other hand, the LUMO orbital is mainly localized on the benzene ring and its substitutions. Since, electron transition from the HOMO orbital to the LUMO orbital is  $\pi \rightarrow \pi^*$  transition in the ligands **7a,b**. In contrast, the HOMO and LUMO frontier orbitals of the complex **8b** species are mainly localized on the isoxazole ring and Co atom, respectively. It implies that electron transition from the HOMO orbital to the LUMO orbital is Ligand to-Metal charge transfer (LMCT) [34].

The energy difference between the HOMO and LUMO frontier orbitals is one of the important characteristics of molecules, which has a determining role in such cases as electric properties, electronic spectra and photochemical reactions. Energy separation between the HOMO and LUMO ( $\Delta \varepsilon = \varepsilon_{LUMO} - \varepsilon_{HOMO}$ ) of **7a**, **7b** and **8b** is 3.28 eV (378 nm), 3.21 eV (386 nm) and 1.91 eV (649 nm), compared with the experimental values of 370, 435 and 690 nm respectively.

Also, a quantitative molecular orbital diagram along with a table containing the energies and the composition of all calculated orbitals can be found in Supporting Information, Table S3 and Figure S3.

The quenching fluorescence properties of Co (II) complex in comparison to the ligands can also be deduced from the 3D-distribution maps for HOMO and LUMO of the ligands **7a,b** and the complex **8b.** An efficient intramolecular charge transfer (ICT) states from the donor sites (endocyclic N and O of benzimidazole and isoxazole rings) to the acceptor moiety (imine group) can be considered as the main reason for the fluorescence intensity in ligands **7a,b**. As shown in

Figure 5, intramolecular charge transfer can be influenced by coordinating Co (II) to the ligands and leads to the quenching fluorescence intensity of cobalt(II) complex compared to the ligands (see also Figure 2 and Table 1).



Figure 5. The HOMO (down) and LUMO (up) frontier orbitals of 7a,b and Co(II) complex 8b.

### Conclusion

Two new fluorescent heterocyclic Schiff base ligands were synthesized from the reaction of 8-(4-chlorophenyl)-3-alkyl-3*H*-imidazo[4',5':3,4]benzo[1,2-*c*]isoxazol-5-amines with aldehydes. NOESY experiment of the ligands confirmed the *E* configuration of Schiff-bases. Coordination of the ligands with Co(II) cation produce deep green complexes. The structures of the complexes have been confirmed by spectral, analytical data and Job's method and an octahedral geometry was proposed for the complexes. Fluorescent Schiff-base ligands and cobalt complexes were

spectrally characterized by UV-Vis and fluorescence spectroscopy. Results revealed that Schiffbase ligands and Co(II) complexes generate fluorescence in dilute solution of MeOH. The DFT methods were also employed to gain a deeper insight into geometry and spectral properties of the synthesized compounds. The DFT-calculated vibrational modes of Co(II) complex are in good agreement with the experimental values, confirming suitability of the optimized geometries for Co(II) complexes. Moreover, Energy separation between the HOMO and LUMO of ligands and Co(II) complexes is comparable with the experimental values.

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### **Highlights**

- New Co(II) complexes were synthesized by reaction of Co(II) with Schiff base ligands. •
- The structures of the ligands and complexes were characterized by spectral data. •
- Their optical properties and quantum chemical calculations were studied. •
- L S WS Their energy gap between the HOMO and LUMO frontier orbitals was obtained. •

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## **Graphical abstract**

