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Synthesis, Structure, and Characterization of a Fluorescent Cobalt(II) Complex for the Recognition of Cations and Small Molecules[1]

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Abstract—A fluorescent cobalt(II) complex for the recognition of cations and small molecules constructed with 5-nitroisophthalic acid (5-H_2Nipa) and 2,2'-bibenzimidazole (H_2Bibim), namely, [Co(H_2Bibim)$_3$](5-Nipa) · H_2O (**I**) has been synthesized and structurally characterized by elemental analysis, IR spectroscopy, PL and single-crystal X-ray diffraction. Complex **I** possesses distorted CoN_6 octahedral linked by the H_2Bibim ligands in a bidentate chelating mode and the 5-H_2Nipa groups act as counterions. 2D supramolecular network is formed by intermolecular O–H···O and N–H···O hydrogen-bonding interactions. Complex **I** exhibits fluorescence and thus has detection capabilities for different cations and small solvents molecules in the solution state at room temperature.

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INTRODUCTION

Much attention has recently been paid to the supramolecular architectures that possess versatile chemical and physical properties and potential applications in catalysis, molecular adsorption, magnetism, nonlinear optics, and heterogeneous catalysis [1–5]. Extensive efforts have especially been made on the recognition and sensing of cations and small molecules which have an important function in biological and environmental systems [6–10]. As the functional groups of the active sites of a number of enzymes, benzimidazoles can participate in many important biochemical reactions. In the polyphenol oxidase, orgotein (superoxide dismutase, SOD) and carbonic anhydrase (CA), benzimidazole units can coordinate to transition metal ions and play very important roles for their biologic functions. These ligands can be used for imitating the active sites of the natural orgotein to investigate their biological activities [11]. The bidentate chelating ligand 2,2'-bibenzimidazole (H_2Bibim) with four nitrogen donor sites can coordinate to a transition metal ion in non-deprotonated (neutral, H_2Bibim), mono-deprotonated (monoanion, $HBibim^-$) and di-deprotonated (dianion, $Bibim^{2-}$) forms to form supramolecular assemblies through intermolecular hydrogen bonds [12–16] and π–π stacking interactions [17–20]. We have reported some complexes [21–23] in the last several years. Considering all the aspects above, we chose 5-nitroisophthalic (5-Nipa) acid and 2,2'-bibenzimidazole to synthesize a fluorescent cobalt(II) complex, [Co(H_2Bibim)$_3$](5-Nipa) · H_2O (**I**), and studied their potential for the recognition and sensing of different cations and small molecules.

EXPERIMENTAL

Equipment and measurements. All reagents were obtained from commercial sources and used without further purification. The elemental analyses were carried out on a PE 1700 CHN auto elemental analyzer. The infrared spectra (IR) (KBr pellets) were recorded in the 400–4000 cm^{-1} range using a Bruker IFS66V vacuum-type FT-IR spectrophotometer. Fluorescence measurements were performed on a Model FL3-P-TCSPC spectrofluorimeter. The crystal structures were determined by a Bruker APEX area-detector diffractometer employing the Shelxtl crystallographic software.

Synthesis of the ligand H_2Bibm. The ligand H_2Bibm was prepared according to the method described by Lane [24].

Synthesis of complex I. A mixture of $CoCl_2 \cdot 6H_2O$ (0.154 g, 0.2 mmol), 5-Nipa (0.018 g, 0.1 mmol) and H_2Bibim (0.0211 g, 0.1 mmol) was added to H_2O (15.0 mL). The pH value was adjusted to 7.0 with NaOH solution. After being refluxed for 4 h, the resulting solution was filtered and left to stand at room temperature and pressure. After approximately one

[1] The article is published in the original.

Table 1. Crystal data and refinement details for complex **I**

Parameter	Value
	I
Empirical formula	$C_{50}H_{35}N_{13}O_7Co$
Formula weight	988.84
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	13.138(4)
b, Å	16.807(5)
c, Å	24.658(6)
α, deg	90.00
β, deg	113.465(13)
γ, deg	90.00
V, Å^3	4995(2)
Z	4
ρ_{calcd}, g m^{-3}	1.315
μ, mm^{-1}	0.408
F(000)	2036
θ Range, deg	2.27–23.71
Limiting indices h, k, l	$-15 \le h \le 15$, $-19 \le k \le 17$, $-29 \le l \le 21$
Reflections collected/unique, R_{int}	26682/8793 (0.0878)
Observed data, $I > 2\sigma(I)$	4475
Number of parameters	646
R, wR_2; S	0.0618, 0.1581; 0.934
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	−0.549/0.318

Table 2. Selected bond lengths (Å) and angles (deg) for complex **I**

Bond	d, Å	Bond	d, Å
Co–N(2)	2.125(3)	Co–N(8)	2.133(3)
Co–N(4)	2.154(3)	Co–N(10)	2.156(3)
Co–N(6)	2.164(3)	Co–N(12)	2.158(3)
Angle	ω, deg	Angle	ω, deg
N(2)CoN(4)	78.70(13)	N(8)CoN(4)	96.35(13)
N(2)CoN(6)	91.75(11)	N(8)CoN(6)	78.64(11)
N(2)CoN(8)	169.03(11)	N(8)CoN(10)	90.13(12)
N(2)CoN(10)	96.26(13)	N(8)CoN(12)	94.49(11)
N(2)CoN(12)	95.53(11)	N(10)CoN(6)	96.44(12)
N(4)CoN(6)	92.92(12)	N(10)CoN(12)	78.27(12)
N(4)CoN(10)	169.52(11)	N(12)CoN(6)	171.41(12)
N(4)CoN(12)	92.97(12)		

week, red block-shaped crystals of **I** were obtained with yield 43.3% (based on Co).

For $[Co(H_2Bibim)_3](5\text{-Nipa}) \cdot H_2O$

anal. calcd., %:	C, 60.73;	H, 3.57;	N, 18.42.
Found, %:	C, 60.74;	H, 3.55;	N, 18.40.

IR (ν, cm^{-1}): 3277 s, 3181 m, 1733 s, 1671 s, 1539 m, 1466 s, 1382 m, 1354 w, 1297 s, 1215 m, 1164 w, 1083 s, 877 m, 812 m, 758 s, 661 w, 578 w, and 513 m.

X-ray structure determinations. The diffraction data were collected on a Bruker Smart Apex CZN diffractometer with graphite-monochromated MoK_α radiation (λ = 0.71073 Å) at 296(2) K. Absorption correction was applied by SADABS [25]. The structure was solved by direct methods and refined with full-matrix least-squares technique using SHELXTL [26]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters. Experimental details for X-ray data collection of complex **I** are presented in Table 1, while selected bond lengths and angles are listed in Table 2.

Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (no. 827561; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Single-crystal X-ray diffraction analysis has shown that the asymmetric unit of complex **I** consists of mononuclear cations, $[Co(H_2Bibim)_3]^{2+}$, separated by 5-Nipa anions and water molecules. The Co(II) atom is coordinated by six nitrogen atoms from three H_2Bibim ligands in a chelating μ_1-(η_2-N_1, N_2) mode (Co–N 2.125(3)–2.164(3) Å) in a distorted octahedral geometry, as shown in Fig. 1. The equatorial positions are occupied by N(2), N(6), N(8), and N(12), and the axial positions are occupied by N(4) and N(10). The Co–N bond lengths are 2.125(3) and 2.164(3) Å (Table 2), which are comparable to those detected in $[Co(Phen)(Oba)]_n \cdot 0.5nH_2O$ (Phen = 1,10-phenanthroline, Oba = 4,4'-oxybis(benzoate)] [27] and slightly shorter than the apical distances (2.141(2)–2.176(2) Å) in $[Co_2(H_2O)(TATP)_2(Oba)_2]_n \cdot 2nH_2O$ (TATP = 1,4,8,9-tetranitrogen-trisphene) [27]. The NCoN angles range between 78.64(11)° and 169.52(11) (Table 2).

In complex **I**, there exist interesting intermolecular hydrogen bonding interactions. The O–H···O hydrogen bonds are between carboxyl oxygen atoms (O(2) and O(4)) from two different 5-Nipa anions and the water molecule (O(7)) with O···O separations of 2.620(4) and 2.649(4) Å (Fig. 1, Table 3). The N–H groups of each bibenimidazole molecule are involved in hydrogen bonds with carboxyl oxygen atoms and water molecules (O(3), O(7)). The N(7)···O(3) distance of 2.720(4) Å and the N(11)···O(7) distance of 2.812(5) Å correspond to strong interactions (Fig. 1,

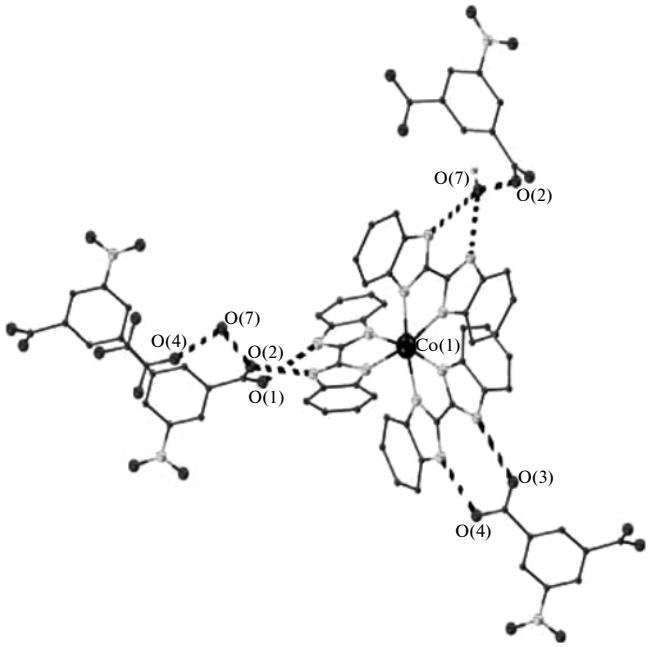

Fig. 1. Perspective view of the Co(II) coordination environment in complex **I**.

Table 3. Geometric parameters of hydrogen bonds for complex **I**

Contact D–H···A	Distance, Å			Angle D–H···A	Symmetry codes of A atom
	D–H	H···A	D···A		
O(7)–H(7B)···O(2)^{ii}	0.85	1.84	2.620(4)	153	$-x+1, y+1/2, -z+3/2$
O(7)–H(7C)···O(4)^{i}	0.85	1.80	2.649(4)	177	$x, -y+3/2, z-1/2$
N(1)–H(1)···O(1)^{iii}	0.86	1.84	2.660(5)	159	$x, y+1, z$
N(3)–H(3A)···O(2)^{iii}	0.86	1.86	2.714(5)	174	$x, y+1, z$
N(5)–H(5A)···O(4)	0.86	1.80	2.658(4)	174	
N(7)–H(7A)···O(3)	0.86	1.87	2.720(4)	170	
N(9)–H(9A)···O(7)	0.86	1.89	2.706(4)	157	
N(11)–H(11A)···O(7)	0.86	2.02	2.812(5)	152	

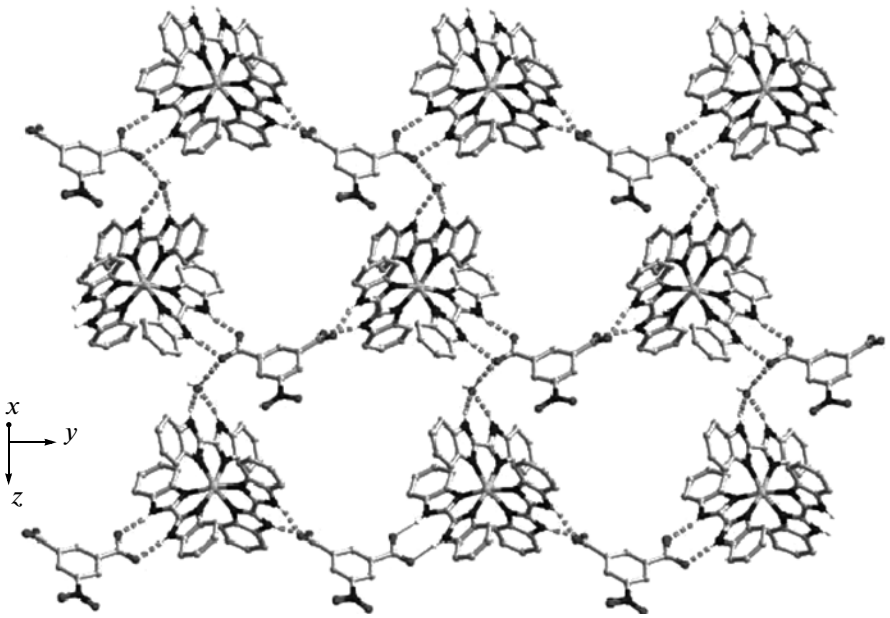

Fig. 2. The two-dimensional frameworks formed in complex of **I**.

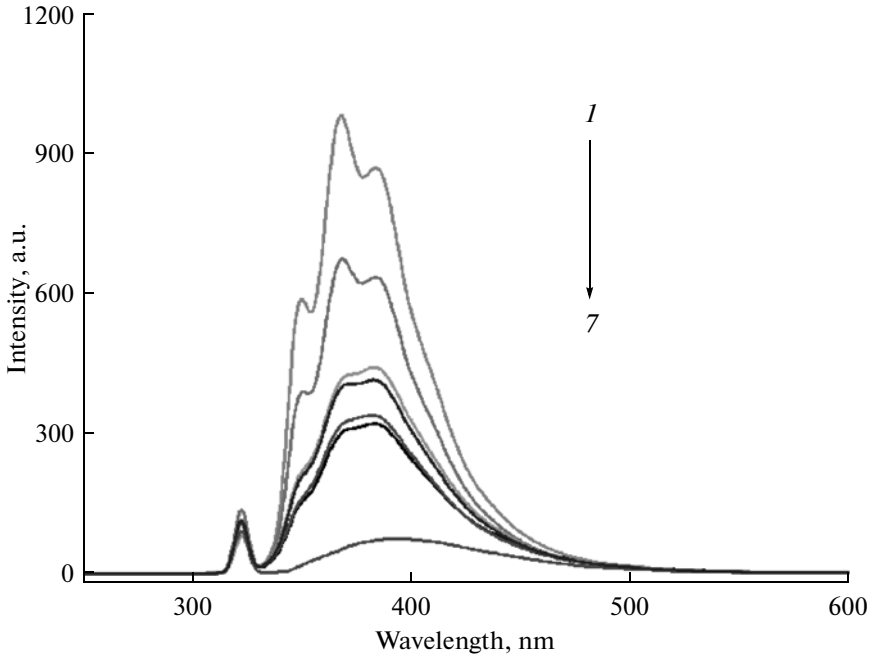

Fig. 3. Fluorescence spectra of complex **I** at different pH, [complex **I**]/[DMSO] = 1.0×10^{-6} mol/L, *1* → *7*; pH 5.7, 3.9, 7.6, 8.6, 9.5, 11.2, 13.4.

Table 3). As a consequence, the interchain hydrogen-bonding interactions all help stabilizing the two-dimensional framework along the [011] direction with Co–Co separations at 9.779(2) Å (Fig. 2).

As shown in Fig. 3, the fluorescence emission spectra of complex **I** were measured in the solution state at room temperature with a bandwidth of 5 nm. Upon excitation at 315 nm, complex **I** displays a strong emis-

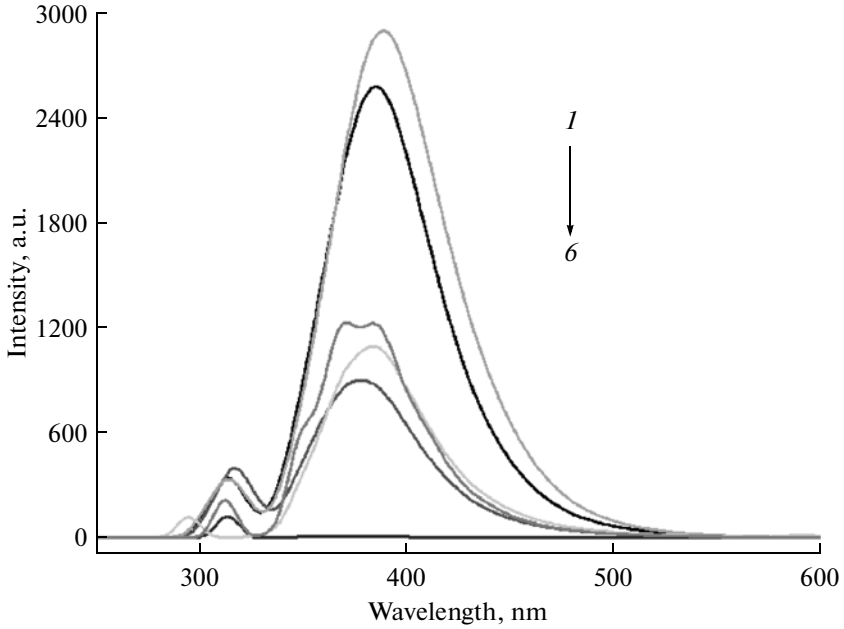

Fig. 4. Fluorescence spectra of complex **I** with different metal ions [complex **I**]/[DMSO] = 5.0×10^{-6} mol/L, *1* → *6*: Zn^{2+}, Na^{+}, Mn^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, [metal ions concentration] = 1.0×10^{-6} mol/L; pH 7.6, v : v = 1 : 1.

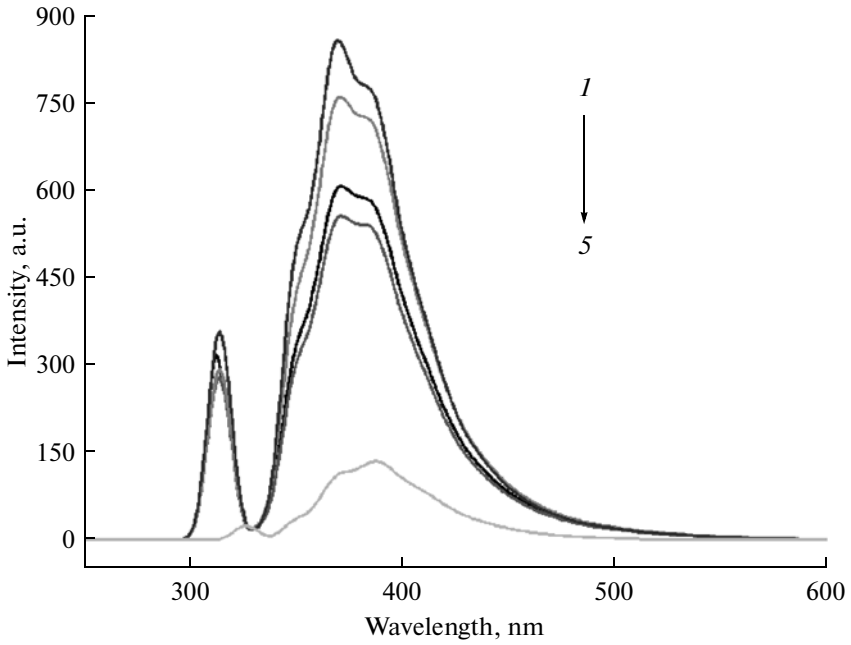

Fig. 5. Fluorescence spectra of complex **I** in different organic solvents. [complex **I**] = 1.0×10^{-6} mol/L; *1* → *5*: C_2H_5OH, H_2O, CH_3OH, acetone, benzene, v : v = 1 : 2.

sion band at 384 nm. It can be observed that the fluorescence intensities of complex **I** decrease gradually with the increase of the pH values, probably due to the strong acidity of the complex. In strong acidic media (pH 3.9), the stronger acidity can destroy the ability of electron transfer of hydrogen bond, which results in weak fluorescence. In pH 5.7, H_2Bibim ligand is protonated and its newtralization may reinforce the hydrogen bonds, thereby decreasing the loss of energy as a result of a non-radiative decay of the intraligand excited state and electron transfer, which results in having the strongest fluorescence. In pH above 7.6, the Co^{2+} ion can integrate with OH negative ion and form precipitate, the fluorescence is quenched almost com-

pletely for complex **I**, which may dissipate of the excitation energy through other pathways and result in weaker fluorescence.

Figure 4 shows the fluorescence emission spectra of complex **I** in the solution state at room temperature with a bandwidth of 5 nm. Complex **I** has a strong absorption band at 368 nm when excited at 315 nm. Upon the addition of different metal ions to dimethyl sulfoxide solutions of complex **I**, their fluorescence emission intensities are affected. The Zn^{2+} ion exhibits the strongest emission band (Fig. 4), which can be accounted for by a different overlap of the emission peak of the ligands (as an energy donor) with the absorption of Zn^{2+} ions leading to a different degree of energy transfer.

On Fig. 3 upon exitation at 315 nm the emission band appears at 384 nm because of [complex **I**]/[DMSO] = 1.0×10^{-6} mol/L, but on Fig. 4 the emission band appears at 368 nm due to [complex **I**]/[DMSO] = 5.0×10^{-6} mol/L.

The emission spectra of complex **I** in the solution state at room temperature are shown in Fig. 5. The emission of complex **I** may be assigned to intraligand π–π^* charge-transfer. It is should be noted that the fluorescence spectra intensity of complex **I** are influenced by different organic solvents with alcohol showing the strongest emission.

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