

КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURAL AND FLUORESCENCE PROPERTIES OF A TWO-DIMENSIONAL COBALTOUS COORDINATION POLYMER CONTAINING BIS(BENZIMIDAZOLE) LIGAND

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A new 2D coordination polymer $\{[\text{Co}(\text{IPA})(\text{L})] \cdot 0.25\text{H}_2\text{O}\}_n$ ($\text{L} = 1,4\text{-bis}(5,6\text{-dimethyl-benzimidazolyl})\text{-2-butene}$, $\text{H}_2\text{IPA} = 5\text{-hydroxyisophthalic acid}$) is hydrothermally synthesized and characterized by elemental analysis, IR, and single crystal X-ray diffraction. The structure analysis indicates that the compound belongs to the orthorhombic system, space group $Pnma$, $a = 17.5256(2) \text{ \AA}$, $b = 15.2074(2) \text{ \AA}$, $c = 9.7633(1) \text{ \AA}$ and $Z = 4$. The complex possesses a 2D (4, 4) network structure and the adjacent layers are further assembled into a 3D supramolecular framework *via* intermolecular $\text{O} \cdots \text{H} \cdots \text{O}$ hydrogen bond interactions. The luminescent properties of the compound and free ligand L are investigated in the solid state.

Keywords: 1,4-bis(5,6-dimethyl-benzimidazolyl)-2-butene, Co(II) complex, crystal structure.

Recently, benzimidazole derivatives have proved to be useful ligands for metal ions due to their reactivity and adaptability in the stabilization of diverse structures. The metal coordination polymers bearing various benzimidazole-base functional groups have received much attention of researchers in supramolecular chemistry and crystal engineering, which stems from not only their intriguing variety of architectures and topologies, but also their potential applications in chemical separation, ion exchange, microelectronics, conductivity, luminescence magnetism, sensors, and nonlinear optics [1–8]. Among the series of benzimidazole derivatives, flexible bis(benzimidazole)-based ones have become an area of intense interests [9–15] owing to the following features: (i) the nitrogen atoms of bis(benzimidazole) ligands have a strong coordination ability; (ii) these ligands contain both imidazole ring and larger conjugated π -system, capable of acting as hydrogen bond donors and for π – π stacking interactions; (iii) the flexible nature of spacers allows the ligands to bend and rotate when coordinated to metal centers, and this often causes the structural diversity. In addition, 5,6-dimethylbenzimidazole serves as an axial ligand for cobalt in vitamin B_{12} [16]. However, the ternary metal coordination polymers based on flexible bis(5,6-dimethylbenzimidazole) ligands and aromatic carboxylic acid have only scarcely been reported [17–23]. For continuing our works [24–26], herein we reported the synthesis, crystal structure, and luminescent properties of a new 2D Co(II) coordination polymer $\{[\text{Co}(\text{IPA})(\text{L})] \cdot 0.25\text{H}_2\text{O}\}_n$ ($\text{L} = 1,4\text{-bis}(5,6\text{-dimethyl-benzimidazolyl})\text{-2-butene}$, $\text{H}_2\text{IPA} = 5\text{-hydroxyisophthalic acid}$), which is further extended to a 3D supramolecular framework by hydrogen bond interactions.

Experimental. Materials and physical measurements. All solvents and reagents for the synthesis were purchased from Sigma-Aldrich unless otherwise specified and used as received. The L ligand was prepared according to the literature procedures [20]. Elemental analyses (C, H, and N) were taken on a Perkin-Elmer 240C analyzer. IR spectra were recorded on a Nicolet FT-IR Avatar 360

spectrophotometer in the range 4000—400 cm^{-1} using KBr pellets. The fluorescence spectra were measured with a Hitachi F-7000 fluorescence spectrophotometer at room temperature.

Synthesis of $\{[\text{Co}(\text{IPA})(\text{L})] \cdot 0.25\text{H}_2\text{O}\}_n$. Hydrothermal reactions have recently been demonstrated to be a versatile technique for the construction of coordination polymers, and a few of flexible bis(5,6-dimethylbenzimidazole) complexes have been synthesized by this method [12, 24].

The mixture of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (24 mg, 0.1 mmol), **L** ligand (29 mg, 0.1 mmol), H_2IPA (18 mg, 0.1 mmol), and H_2O (16 ml) was sealed in a Teflon-lined stainless vessel, which was heated at 140 °C for 72 h under autogenous pressure. The purple crystals were obtained on standing at room temperature, washed with water and ethanol, and dried in air to give the complex. The complex is air-stable and does not dissolve in general organic solvent such as CHCl_3 , CH_3CN , $\text{C}_2\text{H}_5\text{OH}$, H_2O , and DMF. Yield: 56 % (based on $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$). Anal. Calcd. for $\text{C}_{30}\text{H}_{28.50}\text{CoN}_4\text{O}_{5.25}$ (%): C, 61.28; H, 4.90; N, 9.53. Found (%): C, 61.40; H, 4.72; N, 9.70. IR (solid KBr pellet, cm^{-1}): 3449w, 3122w, 2983w, 2935m, 2370w, 1658m, 1567m, 1509w, 1443w, 1398m, 1350m, 1320m, 1210s, 973m, 838m, 716w, 623w, 523w.

X-ray crystallography. X-ray single-crystal diffraction data of the complex were collected on a Bruker Smart 1000 CCD diffractometer equipped with graphite crystal monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) and the ω -2 θ scan mode at 293(2) K. Intensities of reflections were measured using graphite-monochromated radiation with scanning; unit cell dimensions were obtained with least-squares refinements, and semi-empirical absorption corrections were applied using the SADABS program [28]. Cobalt atoms in the complex were located from the E-map and other non-hydrogen atoms were obtained in successive difference Fourier syntheses. The structures were solved by direct methods and final refinements were performed by full-matrix least-squares methods on F^2 by the SHELXL-97 program package [29]. Hydrogen atoms of the hydroxyl group and the water molecule in the complex were found in Fourier difference syntheses, while other hydrogen atoms were included in the calculated positions and refined with isotropic thermal parameters riding on the corresponding parent atoms. The summary of the crystallographic data and structure analysis are given in Table 1.

Table 1

Crystal data and structure refinements for the complex

Empirical formula	$\text{C}_{30}\text{H}_{28.50}\text{CoN}_4\text{O}_{5.25}$
M , g/mol	588.00
T , K	293(2)
Wavelength, \AA	0.71073
Crystal system	Orthorhombic
a , b , c , \AA	17.5256(2), 15.2074(2), 9.7633(1)
Space group	$Pnma$
Volume, \AA^3	2602.1(5)
Z	4
Calculated density, $\text{mg} \cdot \text{m}^{-3}$	1.501
Absorption coefficient, mm^{-1}	0.710
$F(000)$	1222
Crystal size, mm	0.22×0.19×0.08
θ_{\min} — θ_{\max} , deg.	2.32—25.01
Limiting indices	$-19 \leq h \leq 19$, $-12 \leq k \leq 18$, $-11 \leq l \leq 11$
Reflections collected / unique [R_{int}]	12479 / 2363 [0.0949]
Data / restraints / parameters	2363 / 7 / 218
Goodness-of-fit on F^2	1.088
Final R indices [$I > 2\sigma(I)$] ^[a]	$R1 = 0.0563$, $wR2 = 0.1189$
R indices(all data)	$R1 = 0.1021$, $wR2 = 0.1398$

Table 2

Selected bond lengths (Å) and angles (deg.) for the complex

Co1—N1	1.891(4)	N1A—Co1—O2	110.41(13)	N1A—Co1—O3B	106.07(14)
Co1—N1A	1.892(4)	N1—Co1—N1A	112.8(2)	N1—Co1—O2	110.40(13)
Co1—O3B	2.013(5)	N1—Co1—O3B	106.06(14)	O3B—Co1—O2	111.0(2)
Co1—O2	2.080(4)				

Symmetry transformations used to generate equivalent atoms: A = x, -y+1/2, z; B = x, y, z+1.

The selected bond lengths and bond angles are listed in Table 2. CCDC 940641 contains the supplementary crystallographic data for the complex. These data can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk.

Results and discussion. Crystal structure of $\{[\text{Co}(\text{IPA})(\text{L})] \cdot 0.25\text{H}_2\text{O}\}_n$. The single crystal X-ray diffraction analysis reveals that the complex crystallizes in the orthorhombic space group $Pnma$. The asymmetric unit consists of half of the Co(II) ion, one half of the L ligand, half of IPA^{2-} , and a quarter of the lattice water molecule. Both IPA^{2-} and L are situated on the inversion centre. The cobalt center is four-coordinated by two nitrogen atoms from two different L ligands and two oxygen atoms from two carboxylate groups of distinct IPA^{2-} anions in an almost perfect tetrahedral coordination geometry ($\tau_4 = 0.97$). The τ_4 values range from 1.00 for a perfect tetrahedral geometry to zero for a perfect square planar geometry [30]), as shown in Fig. 1. The Co—O distances are 2.013(5) Å for Co1—O3B and 2.080(4) Å for Co1—O2, and the Co—N/N1A bond length is almost similar with 1.891 Å (symmetry code: A = x, -y+1/2, z; B = x, y, z+1).

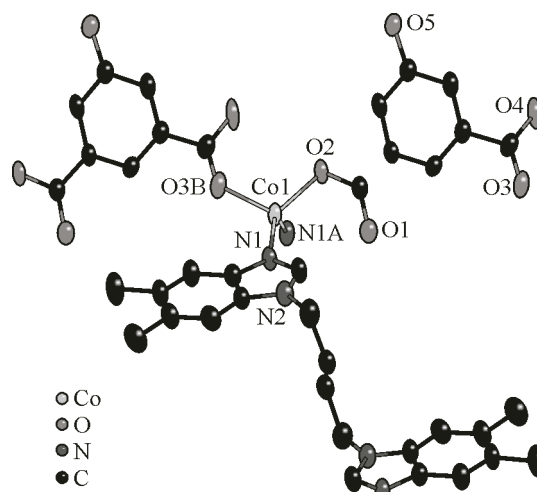


Fig. 1. Coordination environment around the cobalt center in the complex (symmetry code: A = x, -y+1/2, z; B = x, y, z+1)

In the complex, the L ligand acts as a bis(monodentate) coordination mode, adopting a *trans*-conformation fashion; the two benzimidazole rings of one L ligand are parallel to each other. Each L

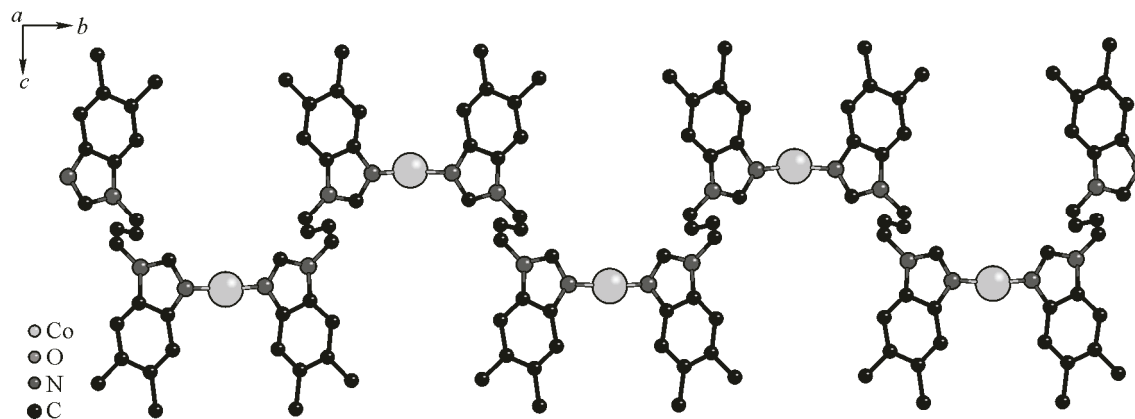


Fig. 2. 1D zigzag chain connected by L in the complex

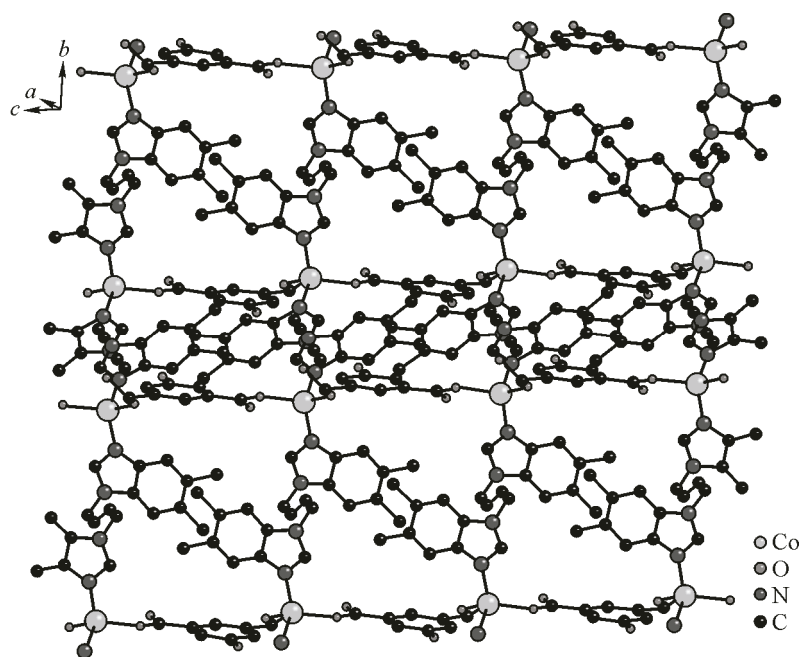


Fig. 3. 2D (4, 4) network of the complex

ligand bridges the adjacent two Co(II) cations into an infinite 1D $[\text{Co}(\text{L})]_n$ zigzag chain (Fig. 2). The IPA^{2-} ligand displays a $\mu_2\text{-}\eta^1:\eta^1$ linker to connect two Co^{2+} ions. Two adjacent parallel 1D chains are further bridged by IPA^{2-} anions to generate a 2D (4, 4) grid that contains a 38-member ring oblong shape windows with Co^{2+} at each corner and L or IPA^{2-} ligands at each edge. The bonding of L or IPA^{2-} ligands with a through-ligand Co—Co distance are 12.170 Å and 9.763 Å, respectively (Fig. 3). In addition, the 2D layers are further extended into a 3D supramolecular framework *via* strong O—H \cdots O hydrogen bonding interactions between the hydroxyl group and carboxylate oxygen atoms of IPA^{2-} (O5 \cdots O1 = 2.822 Å and O5—H5 \cdots O1 = 163°).

IR spectrum. The main features of the IR spectrum of the title complex concern the carboxylate groups, water molecules, and N-containing ligands. As shown in Fig. 4, the broad band at 3449 cm^{-1} in the spectrum of complex can be attributed to the stretching vibrations (ν_{OH}) of water molecules and the intermolecular hydrogen bonding, and the broad shape of this band suggests the existence of H bonds [31]. The weak absorption peaks of —CH₂— and —CH₃ groups in the complex appear at around 2983 cm^{-1} and 2935 cm^{-1} . The characteristic peaks of the carboxyl groups appear at 1658 cm^{-1}

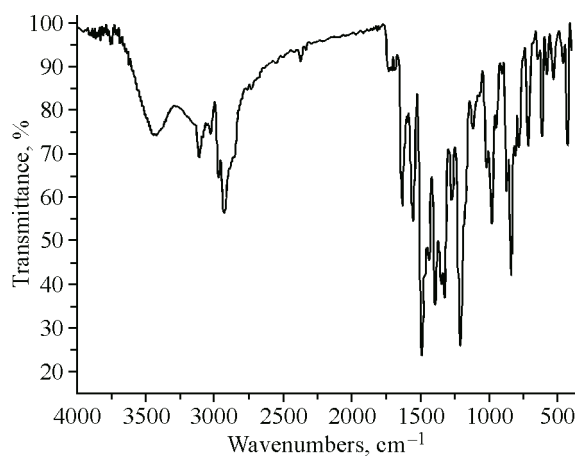


Fig. 4. FT-IR spectra of the complex

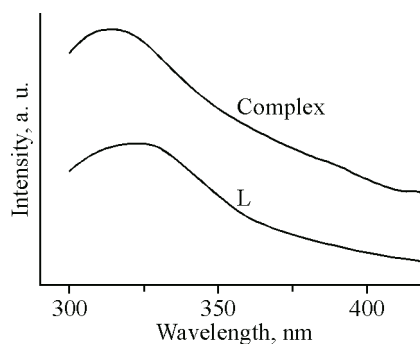


Fig. 5. Solid-state fluorescence spectra of L and the complex

for asymmetric vibrations and at 1398 cm^{-1} for symmetric vibrations in the complex. $\Delta\nu[\nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})]$ is 245 cm^{-1} , indicating the monodentate coordination of the carboxylate group to the metal center [32]. The absorption band at 1509 cm^{-1} may be assigned to the $\nu_{(\text{C}=\text{N})}$ absorption of the benzimidazole rings.

Luminescent properties. The luminescence spectra of **L** and the cobalt (II) complex in the solid state were measured at room temperature. In Fig. 5 the free **L** ligand shows an emission peak at 323 nm on excitation at 280 nm, which may arise from $n \rightarrow \pi$ or $\pi \rightarrow \pi^*$ transitions of the **L** ligand. In addition, the complex displays a broad emission band around 315 nm upon excitation at 270 nm. It is obvious that the emission band of the complex could still be assigned to $n \rightarrow \pi$ or $\pi \rightarrow \pi^*$ transitions of the **L** ligand. Due to quite similar band profiles of the ligand and the complex, the emission bands are tentatively assigned to the intraligand luminescence.

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