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Structural modulation of Co(II) coordination polymers with flexible bis(benzimidazole) and different dicarboxylate ligands

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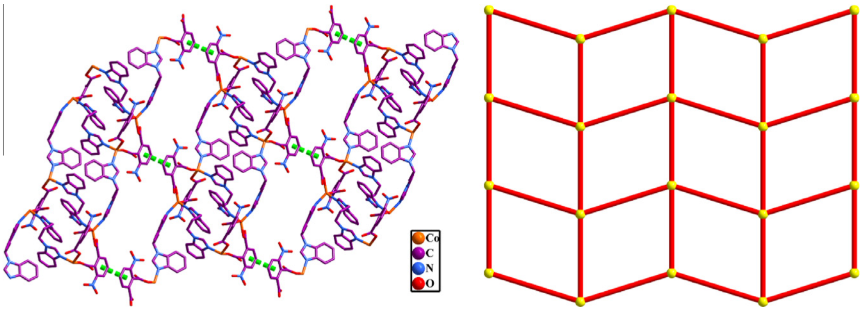
HIGHLIGHTS

- Two Co coordination polymers constructed by mixed-ligands have been characterized.
- Effect of aromatic carboxylates on the structures of compounds was discussed.
- Luminescence properties of complexes have been investigated.
- Complexes show high catalytic activity for degradation of methyl orange.

GRAPHICAL ABSTRACT



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ABSTRACT

Two complexes $[Co_2(L)_2(npht)_2{\cdot}H_2O]_n$ (**1**) and $[Co(L)(mip){\cdot}0.5H_2O]_n$ (**2**) (H_2npht = 3-nitrophthalic acid, L = 1,3-bis(5,6-dimethylbenzimidazol)propane, H_2mip = 5-methylisophthalic acid) were obtained under hydrothermal conditions. In compound **1**, two $npht^{2-}$ ligands connect two crystallographically independent Co atoms to form a binuclear $[Co_2(npht)]_2$ subunit, further linked by L ligands to generate a 1D ladder-like chain, which is arranged into a 2D supramolecular layer through face-to-face π–π stacking interactions. Compound **2** exhibits a 2D 4-connected coordination network. The fluorescence properties of **1** and **2** have been investigated in the solid-state. Both complexes show higher catalytic behaviors for degradation of methyl orange dye.

1. Introduction

The rational design and synthesis of novel metal–organic frameworks (MOFs) is currently attracting considerable attention because of their fascinating topological structures and potential applications as functional materials in porosity, catalysis, luminescence, conductivity, magnetism, and so on [1–6]. From a synthetic point of view, the judicious selection of appropriate organic ligands is proved to be one of the most effective ways to manipulate the diverse structures of MOFs. Among multitudinous organic ligands, benzimidazole-containing ligands, in particular, have proven to be good candidates for the construction of novel MOFs due to their remarkable coordination ability and versatile conformations [7–10]. To date, some bis(benzimidazole) derivatives such as 1,1-(1,4-butanediyl)bis-1H-benzimidazole, 1,1-(1,4-butanediyl) bis(2-methyl-benzimidazole have been reported in the assembly of preparing such crystalline materials [11–15]. However, MOFs constructed from a flexible 1,3-bis(5,6-dimethylbenzimidazol)propane (L) ligand are relatively scarce, in which 5,6-dimethylbenzimidazole serves as an axial ligand for cobalt in vitamin B_{12} [16–19]. In addition, dicarboxylates have been witnessed to be excellent structural contributors for their various coordination modes. The employment of mixed ligands of N-donor ligands and dicarboxylates can compensate charge balance, coordination deficiency, repulsive vacuum, and weakly interaction all at once, which enrich further the versatility of coordination complexes [20–23].

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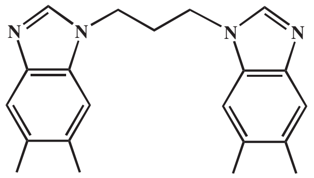
Wastewater from the textile industry contains significant concentrations of organic matter that contribute to the toxicity of the effluents. It is well known that the stability and high degree of aromaticity in azo dyes prevent mineralization of these compounds by conventional aerobic biological treatment processes. Thus, there is currently considerable interest in developing alternative techniques that can degrade organic pollutants and be more cost effective and environmentally benign [24,25]. In recent years, using MOFs as catalysts has becoming an interesting field [26–28], which mainly stems from many inherent advantages, such as the controlled oxidation state of the cation, the possibility to tune the electron density on the metal as a contribution of different ligands, as well as multiactive central metal atoms available within the molecule. The activated persulfate oxidation is an emerging approach for the removal of organic compounds in water and soil, and can produce the highly oxidative species—sulfate free radicals, which further react with a variety of organic pollutants [29,30]. Moreover, the MOFs are a candidate to catalyze the degradation of these organic pollutants. Persulfate can be activated to generate sulfate free radicals by metal–organic complexes for chemical oxidation of the azo dyes such as methyl orange in a simulated wastewater by Fenton-like process.

On the basis of the above considerations, by introducing two aromatic carboxylate coligands into the Co(II)-bis(benzimidazole) system, two coordination polymers with different structures, namely $[Co_2(L)_2(npht)_2 \cdot H_2O]_n$ (**1**) and $[Co(L)(mip) \cdot 0.5H_2O]_n$ (**2**) (H_2npht = 3-nitrophthalic acid, L = 1,3-bis(5,6-dimethylbenzimidazol)propane, H_2mip = 5-methylisophthalic acid) have been obtained. The crystal structures of these compounds, along with a systematic investigation of the effect of different aromatic carboxylates on the ultimate frameworks, will be represented and discussed. In addition, the photoluminescence properties and catalytic behaviors of **1** and **2** have also been discussed in detail below.

2. Experimental

2.1. Materials and measurements

All reagents and solvents were commercially available except for L ligand (Chart 1), which was synthesized according to the literature [31]. FT-IR spectra were recorded in the range of 4000–400 cm^{-1} on an Avatar 360 (Nicolet) spectrophotometer using KBr pellets with a resolution of 2 cm^{-1}. Elemental analyses (C, H, and N) were carried out on a Perkin–Elmer 240C elemental analyzer. Thermal analyses were performed on a Netzsch TG 209 thermal analyzer from room temperature at a heating rate of 10 °C/min. The luminescence spectra for the powdered solid samples were measured on a Hitachi F-7000 fluorescence spectrophotometer at room temperature. The X-ray powder diffraction (XRPD) patterns were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator.



L

Chart 1. The ligand L.

2.2. Preparation of the complexes **1** and **2**

2.2.1. $[Co_2(L)_2(npht)_2 \cdot H_2O]_n$ (**1**)

A mixture of $CoCl_2 \cdot 6H_2O$ (0.1 mmol, 23.8 mg), L (0.1 mmol, 33.2 mg), H_2npht (0.1 mmol, 21.1 mg), NaOH (0.2 mmol, 8.0 mg), and H_2O (14 mL) was placed in a 25 mL Teflon-lined stainless steel vessel. The mixture was sealed and heated at 140 °C for three days. After the mixture was cooled to room temperature at a rate of 5 °C/h, purple block-shaped crystals of **1** were obtained with a yield of 25% (based on Co). Anal. Calcd. for $C_{58}H_{56}Co_2N_{10}O_{13}$ (Mr = 1218.99): C 57.15, H 4.63, N 11.49%. Found: C 57.01, H 4.45, N 11.67%. IR (KBr, cm^{-1}): ν = 3450(vs), 2918(w), 2366(w), 1629(s), 1579(w), 1465(w), 1378(w), 1213(w), 1076(m), 850(w), 789(w), 477(w).

2.2.2. $[Co(L)(mip) \cdot 0.5H_2O]_n$ (**2**)

The same synthetic method as that for **1** was used except that H_2npht was replaced by H_2mip (0.1 mmol, 17.8 mg). The purple block-shaped crystals of **2** (yield: 40%) were obtained. Anal. Calcd. for $C_{30}H_{31}CoN_4O_{4.50}$ (Mr = 578.52): C 62.28, H 5.40, N 9.68%. Found: C 62.07, H 5.22, N 9.87%. IR (KBr, cm^{-1}): ν = 3450(vs), 2929(w), 2372(w), 1629(m), 1577(w), 1433(w), 1370(w), 1213(w), 1083(m), 786(w), 730(w), 468(m).

2.3. X-ray crystallography

The data for **1** and **2** were collected on a Bruker Smart 1000 CCD diffractometer (Mo Kα, λ = 0.71073 Å) at a temperature of 20 °C. Absorption corrections were applied by using a multiscan program. The structures were solved by direct methods and refined with a full-matrix least-squares technique based on F^2 with the SHELXL-97 crystallographic software package [32]. Hydrogen atoms of water molecules were located on a difference Fourier map, while other hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on the parent atoms. Crystallographic crystal data and structure processing parameters for **1** and **2** are summarized in Table 1. Selected bond lengths and bond angles of **1** and **2** are listed in Table S1 (Supporting Information).

Table 1
Crystal and refinement data for complexes **1** and **2**.

	1	**2**
Empirical formula	$C_{58}H_{56}Co_2N_{10}O_{13}$	$C_{30}H_{31}CoN_4O_{4.50}$
Formula weight	1218.99	578.52
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a, Å	12.2034(13)	13.2595(16)
b, Å	15.8289(13)	10.1405(13)
c, Å	16.2361(13)	21.134(3)
α, deg	105.9470(10)	
β, deg	94.6610(10)	92.917(2)
γ, deg	107.0880(10)	
V, $Å^3$	2837.3(4)	2838.0(6)
Z	2	4
D_{calc}, g/m^3	1.427	1.354
μ, mm^{-1}	0.658	0.648
$F(000)$	1264	1208
Crystal size, mm	0.16 × 0.16 × 0.15	0.19 × 0.18 × 0.16
Total reflections	14543	13947
Unique reflections	9871	4996
R_{int}	0.0355	0.0518
GOF	0.978	1.029
R_1 ($I > 2\sigma(I)$)	0.0536	0.0515
wR_2 ($I > 2\sigma(I)$)	0.1711	0.1488
$\Delta\rho$max, $eÅ^{-3}$	0.728	1.105
$\Delta\rho$min, $eÅ^{-3}$	−0.417	−0.439

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2 = \Sigma\ [w\ F_o^2 - F_c^2\ ^2]/\Sigma\ [w\ F_o^2\ ^2]^{1/2}$.