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Coordination polymers of the bis(imidazole) ligand modulated by dicarboxylate ligands: From 2D layer to 3D framework

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ABSTRACT

Three new coordination polymers, $[Zn(H_2biim)(pzdc)]_n$ (**1**), $[Cd(H_2biim)(pzdc)]_n$ (**2**) and $[Cd(H_2biim)_{0.5}(ip\text{-}OH)]_n$ (**3**) (H_2biim = 2,2′-biimidazolate, H_2pzdc = 2,3-pyrazinedicarboxylic acid, H_2ip-OH = 5-hydroxylisophthalic acid), have been hydrothermally synthesized and characterized by elemental analysis, infrared spectra and X-ray single-crystal diffraction. Complexes **1** and **2** are isostructural and display two-dimensional (2D) undulated layers with 3-connected (4.8^2) topologies, which are further extended into three-dimensional (3D) supramolecular structures through hydrogen-bonding and C–H···π interactions. Complex **3** is a relatively rare 3D compound, featuring a binodal (4,5)-connected ($4^4.6^2$)($4^4.6^6$) topology. A comparison of all the complexes demonstrates that the structural characteristics of the dicarboxylate ligands play a great role in the modulation of the coordination structures. Moreover, their luminescent properties and thermal stabilities were also investigated.

1. Introduction

Generally speaking, coordination polymers (CPs) are constructed from inorganic nodes (single metal ions, polynuclear metal cluster, SBUs) and organic linkers (polycarboxylate, N-donors, phosphonate and so on) through coordination interactions. They have received considerable attention, not only because of their topological diversities but also for their potential applications in the following fields: catalysis, luminescence, gas adsorption, magnetism [1–10]. Up until now, a variety of remarkable CPs have been documented, which include 1D chains or ladders, 2D grids and 3D porous motifs. However, the modulation of the coordination structure, which is closely related to the chemical environment, is still a significant challenge in the area of crystal engineering. So far, mixed-ligand coordination polymers involving rigid N-donor ligands have been widely constructed [11–15]. Among these rigid N-donor ligands, the 2,2′-biimidazole (H_2biim) ligand arouses our interest [16–19]. Firstly, as a neutral ligand, the two nitrogen atoms of the imino moieties have a high affinity for coordinating to metals in the chelating or bridging coordination modes. Secondly, the H_2biim ligand can be partly ($Hbiim^-$) or fully ($biim^{2-}$) deprotonated. Therefore, it can act as a bridging ligand and form up to four bonds. Thirdly, under the existence of different torsional angles between the imidazole rings, H_2biim may display different conformations, which provide rich structural diversities. Additionally, due to the existence of imidazole rings, the H_2biim ligand can form weak interactions such as hydrogen-bonding, π···π and C–H···π interactions. To our best knowledge, the use of H_2biim as a μ_2-bridging ligand to construct 3D frameworks is comparatively rare. Only two examples have been reported for polyoxometallates (POMs) [20–21]. On the other hand, multidentate organic carboxylate ligands have been extensively employed in the construction of CPs with diverse structures and excellent properties, not only because of their many types of bridging coordination modes, but also because of their potential function as hydrogen-bonding acceptors and donors [22–25].

In order to explore the influence of dicarboxylate ligands on the tuning of coordination structures, two kinds of dicarboxylate ligands, namely H_2pzdc (2,3-pyrazinedicarboxylic acid) and H_2ip-OH (5-hydroxylisophthalic acid), were introduced into the Cd/Zn-H_2biim system. Three interesting coordination polymers, $[Zn(H_2biim)(pzdc)]_n$ (**1**), $[Cd(H_2biim)(pzdc)]_n$ (**2**) and $[Cd(H_2biim)_{0.5}(ip\text{-}OH)]_n$ (**3**) (H_2biim = 2,2′-biimidazolate), have been successfully synthesized under hydrothermal conditions. Although the three complexes were prepared in a similar way, we found that the different dicarboxylate ligands greatly influence the final structures produced. The structures display a 2D layer to 3D framework transition. In this paper, we report the syntheses,

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crystal structures, fluorescence properties and thermal stabilities of the three compounds.

2. Experimental

2.1. Materials and physical measurements

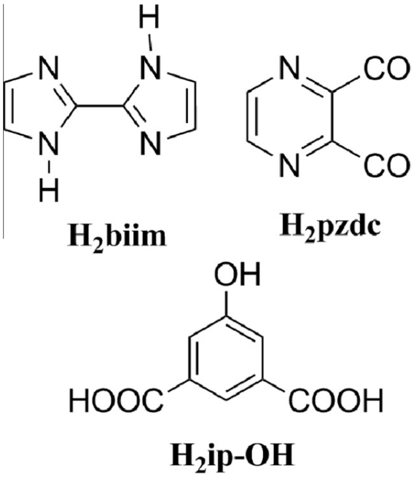
The reagents were purchased commercially and were used without further purification. The ligand H_2biim was prepared according to the literature procedures [26]. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku Dmax 2000 X-ray diffractometer with graphite monochromatized Cu Kα radiation ($\lambda = 0.15418$ nm), 2θ ranging from 5° to 50° with an increment of 0.02° and a scanning rate of 5° min^{-1}. IR (KBr pellets) spectra were obtained from 4000 to 400 cm^{-1} using a Perkin–Elmer Spectrum One FT-IR spectrometer. Elemental analyses for C, H and N were performed on a Perkin–Elmer 2400 Elemental Analyzer. Thermogravimetric (TG) analyses were recorded on a Perkin–Elmer Thermal Analyzer at a heating rate of 10 °C min^{-1} and a flow rate of 100 $cm^3\ min^{-1}$ (N_2). Luminescent spectra were performed on a Cary Eclipse spectrofluorometer (Varian) equipped with a xenon lamp and quartz carrier in the solid state at room temperature (Scheme 1).

2.2. Synthesis of [Zn(H_2biim)(pzdc)]$_n$ (**1**)

A mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (0.1 mmol, 30 mg), H_2biim (0.1 mmol, 13 mg), H_2pzdc (0.1 mmol, 20 mg) and H_2O (8 mL) was adjusted to pH 5.0 with 0.05 mol L^{-1} NaOH solution. It was then sealed in a 25 mL Teflon reactor and heated at 150 °C for 72 h. Finally the mixture was cooled to room temperature at a cooling rate of 3 °C h^{-1} and block colorless crystals of **1** were obtained by filtration. **1** was washed with distilled water and dried in air. Yield: 47% based on the Zn(II) salt. Anal. Calc. for $C_{12}H_8N_6O_4Zn$: C, 39.42; H, 2.21; N, 22.99. Found: C, 39.40; H, 2.20; N, 22.91%. IR (KBr, cm^{-1}): 3088 (w), 2993 (w), 2897 (w), 2777 (s), 1608 (s), 1564 (s), 1536 (s), 1457 (s), 1442 (s), 1359 (m), 1322 (m), 1231 (m), 1204 (s), 1170 (s), 1121 (m), 1107 (m), 1064 (s), 993 (s), 946 (m), 859 (s), 833 (m), 772 (m), 740 (s), 693 (s), 665 (s).

2.3. Synthesis of [Cd(H_2biim)(pzdc)]$_n$ (**2**)

The preparation of **2** was similar to that of **1** except that $CdCl_2{\cdot}2.5H_2O$ (0.1 mmol, 30 mg) was used instead of $Zn(NO_3)_2{\cdot}6H_2O$. Block colorless crystals of **2** were obtained. Yield: 57% based on the Cd(II) salt. Anal. Calc. for $C_{12}H_8N_6O4Cd$: C, 34.93; H, 1.95; N, 20.37. Found: C, 34.91; H, 1.96; N, 20.38%. IR (KBr, cm^{-1}): 3082 (w), 2986 (w), 2909 (w), 2799 (w), 1588 (s), 1561 (s), 1530 (s), 1454 (s), 1437 (s), 1390 (s), 1358 (m), 1317 (m), 1231 (m), 1196 (s), 1166 (s), 1118 (s), 1105 (m), 1063 (s), 989 (s), 920 (m), 889 (s), 833 (m), 770 (m), 742 (s), 691 (s), 661 (s).



Scheme 1. Schematic representation of the organic ligands.

2.4. Synthesis of [Cd(H_2biim)$_{0.5}$(ip-OH)]$_n$ (**3**)

A mixture of $CdCl_2{\cdot}2.5H_2O$ (0.1 mmol, 30 mg), H_2biim (0.1 mmol, 10 mg) and H_2ip-OH (0.1 mmol, 20 mg) and H_2O (8 mL) was adjusted to pH 5.0 with 0.05 mol L^{-1} NaOH solution. It was then sealed in a 25 mL Teflon reactor and heated at 150 °C for 72 h. The mixture was cooled to room temperature after 40 h. Slightly purple crystals were obtained. Yield: 42% based on the Cd(II) salt. Anal. Calc. for $C_{11}H_7N_2O_5Cd$: C, 36.70; H, 1.95; N, 7.79. Found: C, 36.76; H, 1.95; N, 7.80%. IR (KBr, cm^{-1}): 3461 (m), 3058 (w), 2930 (w), 2866 (w), 1630 (s), 1583 (s), 1508 (m), 1397 (s), 1333 (s), 1291 (s), 1208 (m), 1165 (w), 1098 (w), 1014 (w), 859 (s), 750 (s), 661 (m), 428 (w).

2.5. X-ray crystallography

Single-crystal X-ray diffraction data for complexes **1**–**3** were recorded on a Bruker Apex CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Empirical absorption corrections were applied using the multiscan technique. The structures were solved by direct methods and refined by full-matrix least-squares based on F^2 using SHELXL-97. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms of organic ligands were located geometrically. The crystal data and structure refinements of **1**–**3** are summarized in Table 1. Selected bond lengths and angles are listed in Table S1, while hydrogen-bonding, C–H···π and π···π interactions in **1**–**3** are listed in Tables S2–S4, respectively.

Table 1
Crystal data and structure refinements for compounds **1**–**3**.

Compound	1	2	3
Empirical formula	$C_{12}H_8N_6O_4Zn$	$C_{12}H_8N_6O_4Cd$	$C_{11}H_7N_2O_5Cd$
Formula weight	365.63	412.65	359.60
T (K)	293(2)	293(2)	293(2)
Wavelength λ (Å)	0.71073	0.71073	0.71073
Crystal system	*Pbca*	*Pbca*	$P\bar{1}$
Space group	orthorhombic	orthorhombic	triclinic
a (Å)	10.5585(2)	10.7029(4)	8.2763(8)
b (Å)	14.3946(3)	14.6422(6)	8.3342(8)
c (Å)	17.4888(3)	17.8357(8)	8.8041(14)
α (°)	90	90	107.567(2)
β (°)	90	90	107.865(2)
γ (°)	90	90	102.6640(10)
V (Å^3)	2658.04(9)	2795.1(2)	517.48(11)
Z	8	8	2
D_{calc} (g cm^{-3})	1.827	1.961	2.308
F(000)	1472	1616	350
R_{int}	0.0219	0.0400	0.0176
Goodness-of-fit (GOF) on F^2	1.027	1.013	1.094
R_1[a], wR_2[b] [$I > 2\sigma(I)$]	0.0233, 0.0616	0.0278, 0.0538	0.0297, 0.0778
R_1[a], wR_2[b] (all data)	0.0279, 0.0639	0.0459, 0.0595	0.0347, 0.0932

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2 = \sum\{w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)]^2\}^{1/2}$.