Syntheses, Structures and Characterizations of Two New Zinc(II) Coordination Polymers Constructed from 3-(1H-Pyrazol-4-yl)-5-(pyridin-2-yl)-1,2,4-triazole and Different Carboxylate Ligand (Postprint)

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Abstract

Two new zinc(II) coordination polymers, [Zn(ph)(H2L) · H2O]2n (1) and [Zn(ip)(H2L)(H2O)]n (2) (H2ph = phthalic acid, H2ip = isophthalic acid, H2L = 3-(1H-pyrazol-4-yl)-5-(pyridin-2-yl)-1,2,4-triazole), have been successfully synthesized via hydrothermal reaction. It has been structurally characterized by X-ray single-crystal analysis, IR spectra, fluorescence spectroscopy and thermogravimetry analysis. The single-crystal X-ray diffraction studies reveal that compounds 1 and 2 both exhibit 1D chain structures, and assemble into 2D and 3D supermolecules through hydrogen bonds or - interactions. Moreover, the thermal stability and luminescent properties of compounds 1 and 2 were also studied.

Full Text

Preamble

Syntheses, Structures and Characterizations of Two New Zinc(II) Coordination Polymers Constructed from 3-(1H-Pyrazol-4-yl)-5-(pyridin-2-yl)-1,2,4-triazole and Different Carboxylate Ligands

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ABSTRACT

Two new zinc(II) coordination polymers, [Zn(ph)(H L) · H O] n (1) and [Zn(ip)(H L)(H O)]n (2) (H ph = phthalic acid, H ip = isophthalic acid, H L = 3-(1H-pyrazol-4-yl)-5-(pyridin-2-yl)-1,2,4-triazole), have been successfully synthesized via hydrothermal reaction. They have been structurally characterized by X-ray single-crystal analysis, IR spectroscopy, fluorescence spectroscopy, and thermogravimetric analysis. Single-crystal X-ray diffraction studies reveal that compounds 1 and 2 both exhibit 1D chain structures, which assemble into 2D and 3D supramolecular architectures through hydrogen bonds or – interactions. Moreover, the thermal stability and luminescent properties of compounds 1 and 2 were also investigated.

Keywords: zinc(II); coordination polymer; crystal structure; luminescent property

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1. INTRODUCTION

In recent years, coordination polymers have attracted considerable attention due to their fascinating structures and potential applications in gas absorption and separation, luminescence, catalysis, molecular magnetism, sensors, and other areas [1-6]. Although many metal-organic frameworks (MOFs) with diverse structures and properties have been synthesized through various methods and strategies over the past few decades, obtaining desirable frameworks with specific structures and functions remains challenging because several key factors —including metal centers, organic ligands, reaction temperature, solvents, templates, and pH—can affect the self-assembly of coordination polymers [7]. Therefore, the most effective strategy for obtaining various functional coordination polymers involves the self-assembly of metal ions with multidentate organic ligands containing two or more coordination atoms such as N and O [8]. Significantly, mixed-ligand systems incorporating N-donor ligands and multicarboxylates have proven effective for constructing intriguing coordination polymers. In this work, we selected 3-(1H-pyrazol-4-yl)-5-(pyridin-2-yl)-1,2,4-triazole, phthalic acid, and isophthalic acid as ligands (see Table 1), which yielded two new complexes: [Zn(ph)(H L) · H O] n (1) and [Zn(ip)(H L)(H O)]n (2). Their luminescent properties in the solid state were explored at room temperature, revealing that compounds 1 and 2 exhibit different emission wavelengths compared with previously reported Zn(II)-L polymers.

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2. EXPERIMENTAL

2.1 Materials and Characterization

All chemicals were commercially available and used without further purification. X-ray single-crystal diffraction data were collected on a Rigaku Oxford Diffraction system equipped with a graphite-monochromated MoK radiation source (= 0.71073 Å) using the -scan technique. IR spectra were recorded in the 3500–500 cm ^{1} region on an IRAffinity-1S (SHIMADZU) FT-IR spectrometer. Fluorescence measurements were performed on an F-7000 (HITACHI) fluorescence spectrophotometer (220–240 V). Thermogravimetric analyses (TGA) were carried out under nitrogen at a heating rate of 10 °C · min ^{1} using a TG/DTA 6300 integrated thermal analyzer. Powder X-ray diffraction (PXRD) patterns for compounds 1 and 2 were recorded at 293 K on a Bruker D8 Advance diffractometer (CuK , = 1.54056 Å) operated at 40 kV and 30 mA using a Cu-target tube and graphite monochromator.

2.2 Preparation of Compounds 1 and 2

Compound 1: A mixture of H L (21.2 mg, 0.10 mmol), H ph (33.2 mg, 0.20 mmol), and Zn(OAc) · 2H O (21.9 mg, 0.10 mmol) was dissolved in water and transferred to a 10 mL glass vial. After stirring, the vial was sealed in a 25 mL Teflon-lined stainless-steel autoclave and heated at 135 °C for 96 h, followed by cooling to room temperature at a rate of 5 °C · h ^{1}. Light yellow block crystals were isolated and washed with distilled water to afford [Zn(ph)(H L) · H O] n (1). IR (cm ^{1}): 3398(w), 2980(w), 2881(w), 2355(m), 1570(m), 1384(m), 1145(m), 1040(m), 930(m), 830(m), 740(m).

Compound 2: A mixture of H L (21.2 mg, 0.10 mmol), H ip (33.2 mg, 0.20 mmol), and Zn(NO) · 6H O (89.1 mg, 0.30 mmol) was dissolved in CH CN/H O (v:v = 1:4, 4 mL total) and transferred to a 10 mL glass vial. After stirring, the vial was sealed in a 25 mL Teflon-lined stainless-steel autoclave and heated at 135 °C for 72 h, then cooled to room temperature at a rate of 5 °C · h ^{1}. Colorless block crystals were isolated and washed with distilled water to afford [Zn(ip)(H L)(H O)]n (2). IR (cm ^{1}): 3271(w), 3127(w), 2974(w), 2365(m), 1630(m), 1546(m), 1457(m), 1357(m), 1150(m), 1052(m), 927(m), 720(m).

2.3 X-ray Crystallography

Single crystals of 1 and 2 were mounted on a Rigaku Oxford Diffraction system equipped with a graphite-monochromated MoK radiation source (= 0.71073 Å) using the -scan technique. Empirical absorption corrections were applied using the SADABS program [9]. Structures were solved by direct methods using SHELXS-97 [10] and refined on F^2 by full-matrix least-squares using SHELXL-97 [11]. All non-hydrogen atoms were refined anisotropically, while hydrogen

atoms were assigned common isotropic displacement parameters and included in the final refinement using geometric restraints. Crystallographic data for 1 and 2 are listed in Table 2 , with selected bond lengths and angles provided in Tables 3 and 4 , and hydrogen bond parameters in Table 5 .

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3. RESULTS AND DISCUSSION

3.1 IR Spectroscopy

The IR spectra of compounds 1 and 2 show weak broad characteristic peaks for N–H of the H L ligand and O–H or C–H stretching vibrations of the aromatic rings in the ranges of 2281–3398 and 2974–3271 cm ^{1}, respectively. Medium-intensity bands at 2355 and 2365 cm ^{1} are attributed to Zn–O and Zn–N stretching vibrations. Characteristic bands for coordinated carboxylate groups appear at 1570–1384 and 1630–1357 cm ^{1}, while out-of-plane bending vibrations of aromatic rings are observed at 1145–740 and 1150–720 cm ^{1}. These IR spectroscopic results are in good agreement with the single-crystal X-ray structures and previous reports [5, 12-15].

3.2 Crystal Structure Description of 1 and 2

Compound 1: X-ray single-crystal diffraction analysis reveals that 1 crystallizes in the orthorhombic space group P2 2 2 and exhibits a 1D chain structure. The coordination environment of Zn(II) in 1 is shown in Fig. 1a [Figure 1: see original paper]. The asymmetric unit contains two crystallographically independent Zn(II) ions, two H L ligands, two ph^{2} ligands, and two lattice water molecules. Both Zn(II) ions are five-coordinated: the Zn1 ion is bound by three nitrogen atoms (N(1), N(2), N(5)#1) from two different H L ligands and two oxygen atoms (O(1) and O(4)#1) from two different H ph ligands, while the Zn2 ion is coordinated by three nitrogen atoms (N(7)#3, N(10)#3, N(12)) from two H L ligands and two oxygen atoms (O(5) and O(8)#2) from two H ph ligands. The Zn–O and Zn–N bond distances range from 1.970(6) to 2.033(6) Å and 2.128(8) to 2.197(7) Å, respectively, which are consistent with values reported for similar complexes [16-18]. As shown in Fig. 1b [Figure 1: see original paper], the H L ligand acts as a bridge connecting two Zn(II) ions through its imidazole N atom, adjacent pyridine N atom, and pyrazole N atom. Simultaneously, two adjacent Zn(II) ions are bridged by one carboxylate oxygen atom from the H ph ligand, generating a one-dimensional helical double-chain along the xy plane [19]. Complex 1 features abundant intramolecular and intermolecular hydrogen bonds, including intermolecular hydrogen bonds between carboxylate oxygen atoms of H ph and pyrazole N atoms of H L (N(5)–H(5) $\cdots$ O(4), N(5)–H(5) $\cdots$ O(1)), intramolecular hydrogen bonds between carboxylate oxygen atoms of H ph and imidazole N atoms of H L (N(4)–H(4) $\cdots$ O(7)), between lattice water and imidazole N atoms of H L (N(9)–H(9) $\cdots$ O(9)), and between lattice water and carboxylate oxygen atoms of H ph (O(9)–H(9A) $\cdots$ O(3), O(9)–H(9B) $\cdots$

O(4), O(10)–H(10A)···O(8)). These hydrogen bonds extend complex 1 into a two-dimensional supramolecular architecture that enhances its structural stability [20] (Fig. 1c [Figure 1: see original paper]).

Compound 2: X-ray single-crystal structural analysis reveals that 2 crystallizes in the monoclinic space group P2 /n and features a 1D chain structure. The coordination environment of Zn(II) in 2 is shown in Fig. 2a [Figure 2: see original paper]. The asymmetric unit contains one Zn(II) ion, one H L ligand, one ip² ligand, and one coordinated water molecule. The Zn(II) ion is five-coordinated by two oxygen atoms (O(2) and O(5)#1) from two different H ip ligands, one oxygen atom (O(1)) from a coordinated water molecule, and two nitrogen atoms (N(1) and N(2)) from one H L ligand. All bond angles and distances fall within normal ranges [16-18], with Zn–O distances of 2.006(2)–2.189(2) Å and Zn–N distances of 2.091(2)–2.172(2) Å. As depicted in Fig. 2b [Figure 2: see original paper], two Zn(II) ions are bridged by the imidazole N atom and adjacent pyridine N atoms of one H L ligand acting as a terminal ligand to form planar units, which are further connected by a carboxylic oxygen atom from an isophthalic acid ligand acting as a bridge, ultimately producing a chain structure along the yz plane. The presence of coordinated water molecules in complex 2 gives rise to both intramolecular and intermolecular hydrogen bonds, including intermolecular hydrogen bonds between coordinated water and carboxylate oxygen atoms of H ip (O(1)–H(1B)···O(3), O(1)–H(1B)···O(5)), and intermolecular hydrogen bonds between carboxylate oxygen atoms of H ip and imidazole/pyrazole N atoms of H L (N(4)–H(4)···O(4), N(5)–H(5)···O(3)). Notably, complex 2 exhibits – stacking interactions with a distance of 3.699 Å. These hydrogen bonds and – stacking interactions contribute to the structural stability and generate a 3D supramolecular architecture (Fig. 2c [Figure 2: see original paper]).

Structural analysis clearly demonstrates that different dicarboxylates exert synergistic effects on the diverse structures of the title complexes. The carboxylate groups adopt a bis(monodentate) bridging mode (- ¹:) to link two Zn(II) ions, which are five-coordinated and display slightly distorted square-pyramidal geometry in both compounds. However, in complex 1, the H L ligand adopts -bridging and chelating modes to bind two Zn(II) atoms, forming abundant hydrogen bonds that create a 2D layered structure. In contrast, the H L ligand in compound 2 adopts a -chelating mode to coordinate one Zn(II) atom (Table 1), generating not only hydrogen bonds but also – stacking interactions that produce a 3D network structure.

3.3 XRD Analyses

To verify that the crystal structures are representative of the bulk materials, powder X-ray diffraction (PXRD) experiments were performed for 1 and 2 at room temperature. As shown in Fig. 3 [Figure 3: see original paper], the peak positions of the simulated and experimental PXRD patterns are in good agreement, confirming that the bulk synthesized materials and measured single

crystals are identical.

3.4 Thermogravimetric Analyses

The thermal stabilities of complexes 1 and 2 were examined from 20 to 800 °C under nitrogen atmosphere at a heating rate of 10 °C · min ^{1} using a TG/DTA 6300 integrated thermal analyzer. The TGA curves are shown in Fig. 4 [Figure 4: see original paper]. Complex 1 undergoes two main weight loss steps: the first below 165 °C corresponds to the loss of two uncoordinated water molecules per unit cell (observed 3.11%, calculated 3.93%), after which the desolvated sample remains stable up to 285 °C. Subsequent rapid weight loss occurs due to framework decomposition, though the polymeric framework begins slow decomposition at approximately 310 °C. For complex 2, gradual weight loss occurs before 310 °C, attributed to the loss of one coordinated water molecule per unit cell (observed 4.97%, calculated 3.92%); the small discrepancy may result from adsorbed solvent on the crystal surface. Faster weight loss follows due to framework decomposition. The final residues for both compounds are likely ZnO (observed 20.05%, calculated 17.78% for 1; observed 18.91%, calculated 17.70% for 2) along with unburned carbon. These results indicate that the framework of 2 is more thermally robust than that of 1, resisting decomposition up to 310 °C.

3.5 Photoluminescent Properties

The solid-state luminescent properties of as-synthesized samples 1 and 2 and the free ligands were measured at room temperature under identical conditions (slit width = 2.5 nm, lamp voltage = 700 V). As shown in Fig. 5 [Figure 5: see original paper], the free ligands H L, H ph, and H ip exhibit photoluminescence with emission maxima at 380 nm (= 325 nm), 343 nm (= 312 nm), and 392 nm (= 350 nm), respectively, likely arising from → * or n → * transitions [21]. Complexes 1 and 2 show emission peaks at 408 nm (= 325 nm) and 418 nm (= 330 nm), respectively, representing red shifts of 28 and 38 nm relative to the free H L ligand. These red-shifted emissions are best attributed to metal-to-ligand charge transfer [22, 23], which may result from different coordination modes of the organic ligands, varied architectures, and distinct components [24].

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Figure Captions

Fig. 1a. Coordination environment of Zn(II) in 1
Fig. 1b. A one-dimensional helical double-chain of 1
Fig. 1c. A 2D structure (c-axis) connected by hydrogen bonds in 1
Fig. 2a. Coordination environment of Zn(II) in 2
Fig. 2b. A one-dimensional chain structure of 2
Fig. 2c. A 3D structure (c-axis) connected by hydrogen bonds and ··· interactions in 2
Fig. 3. PXRD patterns of compounds 1 and 2
Fig. 4. TGA curves of compounds 1 and 2
Fig. 5. Solid-state fluorescence of H L, H ph, H ip, 1, and 2

Table Captions

Table 1. Coordination modes of Zn(II) and the ligand in compounds
Table 2. Crystallographic data for compounds 1 and 2
Table 3. Selected bond lengths (Å) and bond angles (°) for compound 1
Table 4. Selected bond lengths (Å) and bond angles (°) for compound 2
Table 5. Hydrogen bond lengths (Å) and bond angles (°) for compounds 1 and 2

Note: Figure translations are in progress. See original paper for figures.