Synthesis and Crystal Structure of a New Zinc(II) Coordination Polymer Assembled by 4-Nitrophthalic Acid and Bis(imidazol) Ligands (Postprint)

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Date: 2017-11-05T00:00:00+00:00

Abstract

A new complex [Zn(4-nph)(bib)]2n · nH2O (1) has been obtained by the reaction of metal (Zn(II)), 1,4-bis(imidazol-1-yl)-butane (bib) with 4-nitrophthalic acid (4-H2nph). The crystal structure of 1 has been determined by single-crystal X-ray diffraction analysis. Compound 1 is of triclinic system, space group P with a = 10.3251, b = 12.4503, c = 16.6497 Å, = 88.487(3), = 72.529(3), = 79.991(3)°, V = 2009.8(5) Å3 and Mr = 945.47. Complex 1 shows a three-dimensional (3D) framework. Moreover, through intermolecular hydrogen bonds, compound 1 is assembled into a supramolecular structure. The thermal stability and luminescent properties of 1 are also investigated.

Full Text

Preamble

Synthesis and Crystal Structure of a New Zinc(II) Coordination Polymer Assembled by 4-Nitrophthalic Acid and Bis(imidazol) Ligands

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ABSTRACT

A new complex, [Zn(4-nph)(bib)] n · nH O (1), has been synthesized by reacting

Zn(II) acetate with 1,4-bis(imidazol-1-yl)-butane (bib) and 4-nitrophthalic acid (4-H nph). The crystal structure of 1 was determined by single-crystal X-ray diffraction analysis. Compound 1 crystallizes in the triclinic system, space group P, with unit cell parameters a = 10.3251, b = 12.4503, c = 16.6497 Å, = 88.487(3), = 72.529(3), = 79.991(3)°, V = 2009.8(5) Å^3, and M = 945.47. Complex 1 exhibits a three-dimensional (3D) framework structure and assembles into a supramolecular architecture through intermolecular hydrogen bonds. The thermal stability and luminescent properties of 1 were also investigated.

Keywords: Zn(II) coordination polymer; bis(imidazole) ligand; luminescent property; synthesis
DOI: 10.14102/j.cnki.0254-5861.2011-1669

1. INTRODUCTION

Current interest in coordination polymers (CPs) stems not only from their potential applications in gas storage [**?**], luminescence [**?**], and magnetism [**?**], but also from their intriguing variety of topologies and entanglement motifs [**?**]. The exploitation of diverse organic ligands is vital for increasing the structural diversity of coordination polymers and provides new insights into structure-function relationships. Among organic ligands, imidazole-containing ligands have proven to be excellent candidates for constructing novel CPs due to their versatile coordination modes [**?**].

Carboxylate ligands have also received considerable attention in the designed synthesis of CPs because of their many coordination modes—monodentate, chelating, and/or bridging—which enable a wide variety of structures [**?**]. In this paper, we employ a dicarboxylate ligand together with 1,4-bis(imidazol-1-yl)-butane to construct a new Zn(II) coordination polymer, [Zn(4-nph)(bib)] n · nH O (1). Complex 1 features a 3D framework with a (4,4) topological net, and its luminescent properties and thermogravimetric behavior were investigated in the solid state at room temperature.

2. EXPERIMENTAL

2.1 Materials and Instruments

All chemicals were commercially purchased and used without further purification. Elemental analyses for C, H, and N were performed on an Elementar Vario III Elemental Analyzer. The IR spectrum was recorded in the range of 4000–400 cm ^{1} on a Nicolet 6700 spectrometer using a KBr pellet. Thermogravimetric analyses (TGA) were carried out on a Perkin-Elmer thermal analyzer under nitrogen at a heating rate of 10 °C · min ^{1}. Powder X-ray diffraction (PXRD) patterns were collected in the 2 range of 5–50° with a scan speed of 0.1° · s ^{1} on a Bruker D8 Advance instrument using CuK radiation (= 0.154056 nm) at room temperature. Fluorescence studies were performed on a computer-controlled JY Fluoro-Max-3 spectrometer at room temperature.

2.2 Synthesis of [Zn(4-nph)(bib)] n · nH O

A mixture of Zn(OAc) · 2H O (0.2 mmol, 0.044 g), 4-H nph (0.04 g, 0.2 mmol), and bib (0.038 g, 0.2 mmol) was dissolved in 15 mL H O. The final mixture was placed in a Parr Teflon-lined stainless-steel vessel (25 mL) under autogenous pressure and heated at 130 °C for five days, yielding parallelogram-shaped crystals. The reaction yield was approximately 28% based on Zn. Anal. Calcd. for C H N O Zn : C, 45.73; H, 3.62; N, 14.81%. Found: C, 45.21; H, 3.08; N, 14.32%. IR (KBr, cm ^{1}): 3462(w), 3139(w), 1630(s), 1521(m), 1342(m), 1099(w), 1060(w), 838(w), 722(w), 650(w).

2.3 X-ray Crystallographic Study

A single crystal of the title compound with dimensions of 0.28 mm × 0.10 mm × 0.06 mm was mounted on a Bruker Smart APEX II CCD diffractometer equipped with a graphite-monochromated MoK radiation source (= 0.71073 Å). Data were collected using an scan mode at 293(2) K. In the range of 2.56 < 2 < 52.16°, a total of 11046 reflections were collected, of which 7829 were independent (R = 0.0597), with 3521 observed reflections having I > 2 (I). Corrections for Lorentz and polarization factors were applied. The structure was solved by direct methods, and all non-hydrogen atoms were refined anisotropically on F^2 using the full-matrix least-squares technique with the SHELXL-97 crystallographic software package [?]. Hydrogen atoms of coordinated water molecules were located from difference Fourier syntheses, while those of organic ligands were generated geometrically and refined isotropically. The final refinement converged at R = 0.0710 and wR = 0.1524 (w = 1/[^{2}(F ^{2}) + (0.0840P)^2 + 0.0000P], where P = (F ^{2} + 2F_c^2)/3), with S = 0.962, (Δ) = 0.712, (Δ) = -0.590 e/Å^3, and (Δ/) = 0.000. Selected bond lengths and angles are listed in Table 1 .

3. RESULTS AND DISCUSSION

3.1 Crystal Structure Description of [Zn(4-nph)(bib)] n · nH O (1)

Compound 1 crystallizes in the triclinic crystal system with space group P and features a three-dimensional (3D) network. The coordination environment of Zn(II) in 1 is shown in Fig. 1 [Figure 1: see original paper]. The asymmetric unit contains two crystallographically unique Zn(II) centers, two 4-nph ligands, two bib ligands, and one lattice water molecule.

Both Zn(1) and Zn(2) adopt a four-coordinated tetrahedral geometry, each coordinated by two carboxylate oxygen atoms from two different 4-nph^2 ligands and two nitrogen atoms from two different bib ligands, differing only in bond lengths and angles. The Zn–O bond distances range from 1.942(5) to 1.981(5) Å, while the Zn–N bond distances vary from 1.987(6) to 2.021(6) Å, which are comparable to those reported for other Zn(II) complexes [?]. Both the 4-nph and bib ligands exhibit a monodentate coordination mode. Each 4-nph^2 ligand bridges adjacent Zn(II) cations to form binuclear subunits, which are further linked by bib ligands to generate a zigzag double chain with Zn(II) ··· Zn(II) distances of 12.544 and 13.987 Å (Fig. 2 [Figure 2: see original paper]). These one-dimensional double chains are then interconnected by 4-nph^{2} and bib ligands to form a 3D network. From a topological perspective, the Zn(II) cations can be considered as (4,4) nodes (Fig. 3 [Figure 3: see original paper]). Furthermore, a 3D supramolecular framework is constructed through C-H ··· O and C-H ··· N hydrogen bonds (Table 2).

3.2 IR Analysis of Complex 1

The IR spectrum of 1 shows a broad absorption band at 3462 cm ^{1}, corresponding to the O-H stretching of crystal water molecules in the complex. Asymmetric and symmetric COO stretching modes of the lattice 4-nph^{2} anion are evidenced by very strong, slightly broadened bands at 1630 and 1342 cm ^{1} [?], consistent with the X-ray analysis results.

3.3 Thermal Stability and Powder X-ray Diffraction (PXRD)

To confirm the phase purity of complex 1, powder X-ray diffraction patterns were recorded and found to be comparable to the simulated patterns calculated from single-crystal diffraction data (Fig. 4 [Figure 4: see original paper]), indicating a pure bulk phase. To better understand the thermal stability of complex 1, its thermal decomposition behavior was investigated from 50 to 800 °C under nitrogen atmosphere (Fig. 5 [Figure 5: see original paper]). The TG curve shows no obvious weight loss from 25 to 171 °C, followed by a weight loss of 1.79% from 171 to 299 °C corresponding to the removal of one crystal water molecule (calcd. 1.91%). The TG curve then exhibits a plateau before the framework begins to decompose at 304 °C.

3.4 Photoluminescent Properties

Luminescence properties are highly important in photochemistry and photophysics [?, ?]. In this study, the solid-state photoluminescence spectra of 1 (Fig. 6 [Figure 6: see original paper]) and the free 4-H nph and bib ligands were investigated at room temperature. Upon excitation at 355 nm, 1 exhibits broad green emission with a maximum peak at 531 nm and a shoulder peak at 452 nm. In contrast, the emission spectra of 4-H nph and bib ligands show no luminescence in the 400–800 nm range. The significant fluorescence emission of 1 can be tentatively assigned to ligand-to-metal charge transfer (LMCT) [?]. Given its strong fluorescent intensity, 1 appears to be a promising candidate for novel hybrid inorganic-organic photoactive materials.

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Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for 1

Dist.		Dist.	
Zn(1)-O(3)	1.946(5)	Zn(1)-N(5)	2.009(6)
Zn(1)-O(8)	1.942(5)	Zn(1)-N(3)	2.021(6)
Zn(2)-O(2)	1.972(5)	Zn(2)-O(11A)	1.981(5)
Zn(2)-N(2)	1.987(6)	Zn(2)-N(9)	2.015(6)

Angle		Angle		Angle	
O(8)-Zn(1)-O(3)	126.4(2)	O(3)-Zn(1)-N(3)	107.3(3)	O(11A)-Zn(2)-N(7)	106.5(2)
O(8)-Zn(1)-N(5)	109.8(2)	N(5)-Zn(1)-N(3)	114.5(3)	O(2)-Zn(2)-N(9)	95.7(2)
O(3)-Zn(1)-N(5)	101.2(2)	O(2)-Zn(2)-O(11A)	103.4(2)	O(11A)-Zn(2)-N(9)	117.5(2)
O(8)-Zn(1)-N(3)	98.2(3)	O(2)-Zn(2)-N(7)	124.6(3)	N(5)-Zn(1)-N(9)	109.6(3)

Symmetry code: A: x+1, y, z

Table 2. Hydrogen Bonds for Complex 1

D-H ⋯ A	d(D-H)	d(H ⋯ A)	d(D ⋯ A)	(DHA)	Symmetry codes
C(3)-H(3) ⋯ O(5)			3.412(13)		x, 1+y, z
C(17)-H(17) ⋯ O(11)			3.1676(10)		1+x, y, z
C(19)-H(19) ⋯ O(1)			3.181(11)		1-x, 1-y, -z
C(24)-H(24) ⋯ O(4)			3.406(12)		-x, 1-y, 1-z
C(27)-H(27) ⋯ O(7)			3.267(10)		1-x, 1-y, -z
C(27)-H(27) ⋯ O(12)			3.100(10)		1-x, 1-y, -z
C(32)-H(32) ⋯ O(4)			3.354(11)		1+x, y, z
C(32)-H(32) ⋯ O(12)			2.998(9)		1+x, y, z
C(35)-H(35A) ⋯ O(10)			3.499(13)		-x, 1-y, 1-z
C(35)-H(35A) ⋯ N(1)			3.534(13)		-x, 1-y, 1-z
C(36)-H(36B) ⋯ O(1W)			3.45(2)		1-x, -y, 1-z

Fig. 1. View of the asymmetric unit of complex 1. All hydrogen atoms are omitted for clarity.

Fig. 2. View of the one-dimensional double chain of complex 1.

Fig. 3. Schematic view of the topology of complex 1.

Fig. 4. PXRD analysis of the title complex: bottom—simulated, top—experimental.

Fig. 5. TG curve of complex 1.

Fig. 6. Solid-state emission spectrum of 1 at room temperature.

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