Syntheses, Crystal Structures, and Fluorescence Properties of Three Coordination Polymers Based on Benzoic Acid and Its Derivatives Postprint

Authors: LIU Guang-Zeng, CHEN Hong-Tai, ZHANG Xiu-Tang[1]

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Abstract

Three new different dimensional coordination polymers, namely, [Zn(BA-)2(4,4 -bib)1.5]n (1), [Zn(4-BrBA-)2(1,4-bmb)]n (2) and [Mn(4-BrBA-)2(4,4 -bib)]n (3) have been assembled through the mixed-ligand synthetic strategy (4-HBrBA = 4-bromobenzoic acid, HBA = benzoic acid, 1,4-bmb = 1,4-bis(1H-imidazol-4-yl)benzene, 4,4 -bib = 4,4 -bis(imidazolyl)biphenyl). Their structures have been determined by single-crystal X-ray diffraction analyses and further characterized by elemental analyses (EA), powder X-ray diffraction (PXRD), and thermogravimetric (TG) analyses. Single-crystal X-ray diffraction analysis reveals that the crystals of complexes 1∼3 are all in triclinic systems, space group P. Complexes 1 and 2 are 0D binuclear structures, and 3 is a 1D chain. Moreover, the solid state fluorescence properties of 1 and 2 have been investigated

Full Text

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Guang-Zeng Liu, Hong-Tai Chen, Xiu-Tang Zhang

Advanced Material Institute of Research, College of Chemistry and Chemical Engineering, Qilu Normal University, Jinan 250013, China

ABSTRACT

Three new coordination polymers (CPs) of different dimensions, namely [Zn(BA) (4,4 -bib) .] (1), [Zn(4-BrBA) (1,4-bmb)] (2), and [Mn(4-

BrBA) (4,4 -bib)] (3), have been assembled through a mixed-ligand synthetic strategy (4-HBrBA = 4-bromobenzoic acid, HBA = benzoic acid, 1,4-bmb = 1,4-bis(1H-imidazol-4-yl)benzene, 4,4 -bib = 4,4 -bis(imidazolyl)biphenyl). Their structures were determined by single-crystal X-ray diffraction analyses and further characterized by elemental analysis (EA), powder X-ray diffraction (PXRD), and thermogravimetric (TG) analyses. Single-crystal X-ray diffraction reveals that complexes 1–3 all crystallize in the triclinic system, space group P. Complexes 1 and 2 exhibit 0D binuclear structures, while 3 forms a 1D chain. Moreover, the solid-state fluorescence properties of 1 and 2 have been investigated.

Keywords: 4-bromobenzoic acid; benzoic acid; 1,4-bis[(1H-imidazol-1-yl)methyl]benzene; 4,4 -bis(imidazolyl)biphenyl

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1. INTRODUCTION

Over the past few decades, coordination polymers (CPs) have attracted extensive experimental and theoretical interest due to their regulated and intriguing structural topologies, as well as their potential applications in luminescence, magnetism, catalysis, gas storage, conductivity, ion exchange, nonlinear optics, and spin-transition behavior [1, 2]. Such materials are typically constructed from metal ions as connected centers and multifunctional organic ligands as linkers. In principle, the targeted assembly of materials with desired structural features and physicochemical properties depends greatly on the nature of the organic ligands and metal ions, among which the appropriate choice of well-designed organic building blocks represents one of the most effective strategies [3, 4].

Among the numerous organic ligands available, carboxylic acid ligands and N-donor linkers are particularly favored for their strong coordinating ability, which can stabilize the packing architecture. Benzoic acid and its derivatives possess certain rigidity and stability in their structures, and the introduction of different substituents on the aromatic ring can lead to varied crystal structures of the resulting complexes. For example, bipyridine linkers as N-donor ligands are beneficial for synthesizing extended CPs and can generate high-dimensional structures owing to their simple bridging mode and strong coordination ability [5-7]. Additionally, the cis- or trans-configurations of bis(imidazole) linkers often cause structural diversity when they coordinate to metal centers [8-11].

These considerations motivated us to explore new coordination networks assembled from benzoic acid and its derivatives with transition metal salts under solvothermal conditions in the presence of bis(imidazole) linkers. Herein, we report the syntheses and characterizations of three CPs, along with a systematic comparison of their properties. Furthermore, the fluorescence properties of

complexes 1 and 2 have been investigated.

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2. EXPERIMENTAL

2.1 General Procedures

All chemical reagents were purchased from Jinan Henghua Sci. & Tec. Co. Ltd. and used without further purification. Elemental analyses were carried out on a CE Instruments EA 1110 elemental analyzer. Thermogravimetric analysis (TGA) was performed from 0 to 800 °C on a SDT Q600 instrument at a heating rate of 10 °C/min under N atmosphere (100 mL/min). Powder X-ray diffraction patterns were measured on a Panalytical X-Pert pro diffractometer with CuK radiation. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

2.2 Syntheses

2.2.1 Synthesis of [Zn(BA) (4,4 -bib) .] (1) A mixture of HBA (0.20 mmol, 0.024 g), 4,4 -bib (0.30 mmol, 0.085 g), Zn(OAc) (0.30 mmol, 0.066 g), 12 mL H O, and NaOH (0.40 mm, 0.016 g) was sealed in a 25 mL Teflon-lined stainless-steel vessel and heated to 170 °C for 3 days, followed by slow cooling to room temperature at a rate of 10 °C/h. The yield was 47% (based on HBA). Anal. Calcd. (%) for C H N O Zn : C, 66.81; H, 4.21; N, 11.40. Found (%): C, 65.62; H, 4.72; N, 11.30.

2.2.2 Synthesis of [Zn(4-BrBA) (1,4-bmb)] (2) A mixture of 4-HBrBA (0.20 mm, 0.040 g), 1,4-bmb (0.20 mm, 0.047 g), ZnSO (0.40 mm, 0.115 g), 12 mL H O, and NaOH (0.30 mm, 0.012 g) was sealed in a 25 mL Teflon-lined stainless-steel vessel and heated to 170 °C for 3 days, followed by slow cooling to room temperature at a rate of 10 °C/h. Colorless block crystals of 2 were obtained. Yield: 39% (based on HBrBA). Anal. Calcd. (%) for C H Br N O Zn : C, 47.79; H, 3.12; N, 8.67. Found (%): C, 48.23; H, 3.54; N, 8.92.

2.2.3 Synthesis of [Mn(4-BrBA) (4,4 -bib)] (3) The synthetic method was similar to that for complex 2, except that 1,4-bmb and ZnSO were replaced by 4,4 -bib and MnSO . Colorless block crystals of 3 were obtained in 33% yield (based on HBrBA). Anal. Calcd. (%) for C H Br MnN O : C, 55.34; H, 2.98; N, 3.80. Found (%): C, 54.28; H, 3.09; N, 3.96.

2.3 Structure Determination

Suitable single crystals of complexes 1-3 were carefully selected under an optical microscope and mounted on thin glass fibers. Single-crystal X-ray diffraction

analyses were performed on a Siemens SMART diffractometer using Mo-K radiation (= 0.71073 Å) at 296(2) K. Absorption corrections were applied based on multiple and symmetry-equivalent reflections in the data set using the SADABS program based on the method of Blessing. The structures were solved by direct methods and refined by full-matrix least-squares techniques using the SHELXS-97 package, and further refined by the SHELXL-97 procedure. All non-hydrogen atoms were refined anisotropically [12]. All hydrogen atoms except those for water molecules were generated geometrically with fixed isotropic thermal parameters and included in the structure factor calculations. Hydrogen atoms attached to oxygen were refined with O–H = 0.85 Å and Uiso(H) = 1.2Ueq(O). The crystallographic data and details for complexes 1–3 are listed in Table 1 , and selected bond lengths and bond angles are shown in Table 2 .

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3. RESULTS AND DISCUSSION

3.1 Structure Description of [Zn(BA) (4,4 -bib) .] (1)

X-ray crystallography reveals that complex 1 is a zero-dimensional structure crystallizing in the triclinic system, space group P. As shown in Fig. 1 [Figure 1: see original paper], the asymmetric unit consists of one Zn(II) ion, two completely deprotonated BA ligands, and one and a half 4,4 -bib ligands. The Zn(II) center adopts a distorted {ZnN O } trigonal bipyramidal geometry, completed by two carboxylate groups from two distinct BA ligands and two N atoms from two 4,4 -bib ligands, with = 0.441 (= | - |/60°, where and are the two largest bond angles in the five-coordinate complex: = N(5)Zn(1)O(2) = 118.87°, = O(1)Zn(1)O(3) = 145.34°) [13]. The Zn–O bond lengths fall in the normal range of 1.9310(19)–2.8128(26) Å, and the Zn–N bond lengths are 2.0003(26) and 2.0167(28) Å, respectively.

Two Zn(II) ions are linked by one 4,4 -bib ligand to form a 0D binuclear structure. Each Zn(II) ion coordinates with two BA ligands that adopt - ^{1} and - ^{2} coordination modes, respectively, and two monodentate 4,4 -bib ligands. The complex exhibits a centrosymmetric character, with Zn · · · Zn distances of 17.9276(10) Å, as shown in Fig. 2a [Figure 2: see original paper]. Adjacent molecules are linked through C–H · · · O and C–H · · · N hydrogen bonding interactions (H · · · A distances between 2.35 and 2.57 Å) to form a 3D supramolecular structure (Fig. 2b). The hydrogen bonding data for complex 1 are summarized in Table 3 .

3.2 Structure Description of [Zn(4-BrBA) (1,4-bmb)] (2)

X-ray crystallography reveals that complex 2 is a zero-dimensional structure crystallizing in the triclinic system, space group P. As shown in Fig. 4 [Figure 4: see original paper], the asymmetric unit consists of one Zn(II) ion, two 4-BrBA ligands, and one 1,4-bmb ligand (Fig. 3 [Figure 3: see original paper]).

The Zn(II) center is located in a slightly distorted {ZnN O } trigonal bipyramidal coordination environment, completed by two carboxylate groups from two distinct 4-BrBA ligands and two N atoms from two 1,4-bmb ligands, with = 0.856 (= | - |/60°, where and are the two largest bond angles in the five-coordinate complex: = O(1)Zn(1)O(3) = 165.88°, = N(1)Zn(1)N(3) = 114.54°). The Zn–O bond lengths vary from 1.9352(37) to 2.7170(33) Å, and the Zn–N bond distances are in the normal range of 1.9994(35)–2.0220(48) Å.

The 4-HBrBA ligand is completely deprotonated and exhibits - ^{1} and - ^{1}: ^{1} coordination modes. Two Zn(II) ions are linked by two flexible 1,4-bmb ligands to form a binuclear structure, with dihedral angles between the central phenyl ring and the two imidazole rings of 88.02° and 75.54°, respectively. The complex exhibits a centrosymmetric character, with a Zn · · · Zn distance of 10.79(7) Å. Adjacent molecules are further joined by hydrogen bonds to form 3D supramolecular structures (Fig. 4a), with hydrogen bond lengths (H · · · A) between 2.43 and 2.61 Å. Complexes 1 and 2 have similar hydrogen bonding connections; the hydrogen bonding data for 2 are summarized in Table 3. We also identified partial · · · packing interactions, with a center-to-center distance of 3.979 Å between two parallel imidazole ring planes and a lateral displacement of 1.938 Å between the two centers (Fig. 4b).

3.3 Structure Description of [Mn(4-BrBA) (4,4 -bib)] (3)

X-ray crystallography reveals that complex 3 is a one-dimensional structure crystallizing in the triclinic system, space group P. As shown in Fig. 7 [Figure 7: see original paper], the asymmetric unit consists of one Mn(II) ion, two 4-BrBA ligands, and one 4,4 -bib ligand (Fig. 5 [Figure 5: see original paper]). The Mn(II) ion is located in a distorted {MnN O } octahedral coordination environment, completed by three carboxylate groups from three 4-BrBA ligands that adopt - ^{2} and - ^{1}: ^{1} coordination modes, and two N atoms from two different 4,4 -bib ligands. The Mn–O/N bond lengths fall in the normal range of 2.1091(22)–2.2533(35) Å.

Each 4,4 -bib ligand connects two Mn(II) ions and further extends into two parallel chains, with dihedral angles between the two phenyl rings of 0° or 7.35°, and 0° or 5.14° for the two terminal imidazole rings. The 4-BrBA ligand (- ^{1}: ^{1}) bridges two adjacent Mn(II) ions, causing the two parallel chains to form a binuclear chain with a distance of 4.099 Å between two adjacent Mn(II) ions (Fig. 6a [Figure 6: see original paper]). Owing to the presence of C–H · · · Br and C–H · · · O hydrogen bonds, complex 3 is linked from a 1D binuclear chain into a 3D supramolecular structure (Fig. 6b). The hydrogen bonding data for complex 3 are summarized in Table 3.

Three coordination polymers of different dimensions have been constructed from mixed ligands of benzoic acid and its derivatives with two bis(imidazole) linkers (4,4 -bib, 1,4-bmb). The diverse coordination modes of the carboxylate groups and the differential flexibility of the ancillary ligands lead to the formation of

complexes with distinct structures in different dimensions. These three structures demonstrate that benzoic acid and its derivatives are effective ligands with rich coordination modes, which provides useful insights for better understanding synthon selectivity in multifunctional crystal structures.

3.4 Powder X-ray Diffraction

To verify the phase purity of these complexes, the PXRD patterns of the title complexes were recorded at room temperature. As shown in Fig. 7 [Figure 7: see original paper], the peak positions of the simulated and experimental PXRD patterns are in good agreement, demonstrating the high phase purity of the complexes. The differences in intensity may be attributed to preferred orientation of the crystalline powder samples.

3.5 Thermogravimetric Analysis

To investigate the thermal stability of these polymers, thermogravimetric analyses (TGA) of complexes 1–3 were performed (Fig. 8 [Figure 8: see original paper]). The TGA curves indicate that the framework of complex 1 begins to collapse at 285 °C, while complexes 2 and 3 are stable up to 330 °C, where framework decomposition initiates. The final residues of compounds 1 and 2 correspond to ZnO (calcd.: 9.1%, found: 11.8% for 1; calcd.: 11.3%, found: 13.6% for 2) after complete decomposition of the organic ligands. For compound 3, decomposition is complete at approximately 710 °C, with the remaining residue presumed to be Mn O (calcd.: 11.1%; found: 13.3%).

3.6 Photoluminescent Investigation

The emission spectra of complexes 1 and 2 and the free ligands were investigated in the solid state at room temperature under identical conditions. As depicted in Fig. 9 [Figure 9: see original paper], the emission spectra of 4,4 -bib and complex 1 show main peaks at 359 nm (= 307 nm) and 373 nm (= 332 nm), respectively. Meanwhile, 1,4-bmb and complex 2 exhibit main peaks at 524 nm (= 489 nm) and 509 nm (= 496 nm), respectively. Comparison of the two groups reveals that both ligands and complexes have similar emission peaks, with differences reflected in the variation of relative intensity. These emissions can be assigned to intraligand ($\rightarrow n$ *or* $\rightarrow$) transitions, as they are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature, given that Zn(II) ions are difficult to oxidize or reduce due to their d^1 configuration [14]. The differences in emission behavior between complexes 1 and 2 likely derive from the different conformations of the organic ligands as well as variations in the rigidity of the solid-state crystal packing structures. Because of their favorable photoluminescence properties, complexes 1 and 2 may serve as potential photosensitive materials.

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Table 1. Crystallographic Data and Details of Diffraction Experiments for Complexes 1, 2 and 3

Complex	Empirical formula	Formula weight	Crystal system	Space group	a (Å)	b (Å)	c (Å)	α (º)	β (º)	γ (º)	V (Å³)	Dc (g·cm⁻³)	μ (Mo-Kα) / mm⁻¹	F(000)	Reflections collected	θ range for data collection (°)	Refinement method	Data / restraints / parameters	Goodness-of-fit on F²	R1, wR2 (I > 2σ(I))	R1, wR2 (all data)	Largest diff. peak and hole (e·Å⁻³)
1	C H N O Zn	[illegible]	Triclinic	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible] – 25.00	Full-matrix least-squares on F²	[illegible]	[illegible]	[illegible]	[illegible]	[illegible] and –0.285
2	C H B F N O Zn	[illegible]	Triclinic	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible] – 25.00	Full-matrix least-squares on F²	[illegible] / 0 / 352	[illegible]	[illegible]	[illegible]	[illegible] and –1.478
3	C H B F Mn N O	[illegible]	Triclinic	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible] – 25.00	Full-matrix least-squares on F²	[illegible] / 0 / 388	[illegible]	[illegible]	[illegible]	[illegible] and –1.439

Table 2. Selected Bond Lengths (Å) and Bond Angles (°) for 1–3

Complex 1 - N(1)–Zn(1): 2.001(2) - N(5)–Zn(1): 2.017(2) - O(2)–Zn(1): 1.934(2) - O(3)–Zn(1): 1.931(2) - C(1)–N(1)–Zn(1): 124.4(2) - C(2)–N(1)–Zn(1): 129.2(2) - C(33)–N(5)–Zn(1): 131.3(2) - C(34)–N(5)–Zn(1): 122.9(2) - C(26)–O(2)–Zn(1): 112.9(2) - C(19)–O(3)–Zn(1): 127.34(19) - O(3)–Zn(1)–

N(1): 118.04(10) - O(2)-Zn(1)-N(1): 109.41(10) - O(3)-Zn(1)-N(5): 95.59(9) - O(2)-Zn(1)-N(5): 118.88(10) - N(1)-Zn(1)-N(5): 110.32(10)

Symmetry transformations used to generate equivalent atoms: #1: -x+3, -y+1, -z+1

Complex 2 - Zn(1)-O(2): 1.943(3) - Zn(1)-O(3): 1.973(3) - Zn(1)-N(3): 2.002(3) - Zn(1)-N(1): 2.017(4) - O(2)-Zn(1)-O(3): 112.44(14) - O(2)-Zn(1)-N(3): 97.18(13) - O(3)-Zn(1)-N(3): 110.32(13) - O(2)-Zn(1)-N(1): 106.51(14) - O(3)-Zn(1)-N(1): 114.49(13) - N(3)-Zn(1)-N(1): 114.57(15) - C(10)-N(3)-Zn(1): 130.3(3) - C(21)-N(1)-Zn(1): 129.3(3) - C(19)-N(1)-Zn(1): 125.4(3)

Symmetry transformations used to generate equivalent atoms: #1: -x+2, -y+2, -z+1

Complex 3 - Mn(1)-O(8): 2.157(3) - Mn(1)-O(1): 2.108(3) - Mn(1)-O(9): 2.227(3) - Mn(1)-N(8): 2.251(3) - Mn(1)-N(6): 2.248(3) - Mn(1)-O(2): 2.394(3) - O(8)-Mn(1)-O(1): 147.32(11) - O(8)-Mn(1)-O(9): 117.85(11) - O(1)-Mn(1)-O(9): 94.38(11) - O(8)-Mn(1)-N(6): 86.60(12) - O(9)-Mn(1)-N(6): 91.33(12) - O(1)-Mn(1)-N(6): 84.86(11) - O(8)-Mn(1)-N(8): 90.01(12) - O(1)-Mn(1)-N(8): 96.52(11) - O(9)-Mn(1)-N(8): 91.67(12) - N(6)-Mn(1)-N(8): 176.60(12) - O(8)-Mn(1)-O(2): 150.77(11) - O(1)-Mn(1)-O(2): 56.55(10) - O(9)-Mn(1)-O(2): 92.22(11) - N(6)-Mn(1)-O(2): 88.08(11) - N(8)-Mn(1)-O(2): 86.7(2) - C(16)#2-O(8)-Mn(1): 149.1(3) - C(16)-O(1)-Mn(1): 118.3(2) - C(19)-O(2)-Mn(1): 124.5(3) - C(19)-O(9)-Mn(1): 128.3(3) - C(10)-N(6)-Mn(1): 94.1(2) - C(5)-N(6)-Mn(1): 129.4(2) - C(22)-N(8)-Mn(1): 126.9(3)

Symmetry transformations used to generate equivalent atoms: #1: x+1, y, z+1; #2: -x+1, -y+2, -z+1; #3: x-1, y, z-1

Table 3. Hydrogen Bonds for Complexes 1-3

D-H ⋯ A	d(H ⋯ A) (Å)	d(D ⋯ A) (Å)	(D-H ⋯ A) (º)	Symmetry code
Complex 1				
C(2)-H(2) ⋯ O(4)	2-x, 2-y, -z			
C(16)-H(16) ⋯ O(4)	1-x, 1-y, -z			
C(3)-H(3) ⋯ O(4)	3-x, 2-y, -z			

D–H ··· A	d(H ··· A) (Å)	d(D ··· A) (Å)	(D–H ··· A) (º)	Symmetry code
C(37)–H(37) ··· N(4)	2–x, 1–y, 1–z			
Complex 2				
C(7)–H(7) ··· O(2)	3–x, 1–y, 1–z			
C(16)–H(16) ··· N(2)				
C(8)–H(8) ··· O(3)				
C(9)–H(9) ··· O(4)				
C(21)–H(21) ··· O(4)				
Complex 3				
C(24)–H(24) ··· Br(1)	–x, 3–y, 1–z			
C(21)–H(21) ··· O(1)	–x, 2–y, 1–z			
C(17)–H(17) ··· O(4)				
C(10)–H(10) ··· O(2)				

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