Crystal Structures and Luminescent Properties of Three Coordination Polymers Based on 2,5-Furandicarboxylic Acid Ligand and 1,10-Phenanthroline Postprint

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Abstract

Three new coordination polymers, namely [Zn(FDA)(phen)(H2O) · H2O]n (1), [Cd(HFDA)(phen)2(NO3)] (2) and [Cd(FDA)(phen)]n (3) (H2FDA = 2,5-furandicarboxylic acid, phen = 1,10-phenanthroline) have been synthesized by the solvothermal method and characterized by elemental analysis, IR, powder X-ray diffraction, thermogravimetric analysis and X-ray single-crystal diffraction analysis. For 1, the neighboring Zn2+ ions are bridged by FDA2- as linkers to form one-dimensional (1D) chains, and phen ligands are as the terminal ligands. Furthermore, the 1D chains are packed into a three-dimensional (3D) supramolecular structure through hydrogen bonds and - interactions. For 2, the H2FDA ligand is partial deprotonation, which is a rare phenomenon among other coordination polymers based on H2FDA. Under the synergetic effect of phen ligands and the partial deprotonation of H2FDA, the structure of 2 is discrete. For 3, the Cd2+ ions are linked by two carboxylates of FDA2- ligand to give rise to 1D zig-zag chains, and phen ligands chelate the Cd2+ ions like 1. In addition, solid-state luminescent spectra of three coordination polymers were also studied at room temperature.

Full Text

Preamble

Crystal Structures and Luminescent Properties of Three Coordination Polymers Based on 2,5-Furandicarboxylic Acid Ligand and 1,10-Phenanthroline

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ABSTRACT

Three new coordination polymers, namely [Zn(FDA)(phen)(H O) · H O] (1), [Cd(HFDA)(phen) (NO)] (2), and [Cd(FDA)(phen)] (3) (H FDA = 2,5-furandicarboxylic acid, phen = 1,10-phenanthroline), have been synthesized via solvothermal methods and characterized by elemental analysis, IR spectroscopy, powder X-ray diffraction, thermogravimetric analysis, and single-crystal X-ray diffraction. In complex 1, neighboring Zn^{2} ions are bridged by FDA^{2} linkers to form one-dimensional (1D) chains, with phen ligands serving as terminal ligands. These 1D chains further pack into a three-dimensional (3D) supramolecular structure through hydrogen bonds and – interactions. In complex 2, the H FDA ligand undergoes partial deprotonation—a rare phenomenon among H FDA-based coordination polymers. Under the synergistic effect of phen ligands and this partial deprotonation, complex 2 adopts a discrete structure. In complex 3, Cd^{2} ions are linked by two carboxylates of the FDA^{2} ligand to generate 1D zigzag chains, with phen ligands chelating the Cd^{2} ions as in complex 1. Additionally, the solid-state luminescence spectra of all three coordination polymers were investigated at room temperature.

Keywords: 2,5-furandicarboxylic acid; 1,10-phenanthroline; crystal structure; luminescence

1 INTRODUCTION

Coordination polymers (CPs) have attracted considerable attention due to their fascinating topological structures assembled from metal ions and organic ligands, as well as their potential applications in selective adsorption and separation, catalysis, molecular magnetism, fluorescence, and other fields. It is well established that organic ligands play a crucial role in the structural assembly of CPs because their length, angle, rigidity, coordination mode, coordination capacity, functional groups, and substituents all significantly influence the self-assembly process. Therefore, selecting appropriate organic ligands enables the construction of desired frameworks.

To date, multidentate carboxylic acid ligands have been widely employed in CP synthesis. Among these, 2,5-furandicarboxylic acid (H FDA) is a typical multidentate carboxylate ligand that has generated numerous H FDA-based CPs due to its strong coordination ability as a multifunctional "V-shaped" dicarboxylic acid. To further enrich the coordination chemistry of H FDA and develop new functional CPs, we introduced 1,10-phenanthroline (phen) as a typical chelating

N,N -based secondary ligand, leveraging its excellent coordination ability and large conjugated system. In this work, we used H FDA as the primary organic building block and phen as the auxiliary ligand to construct three new CPs, and we investigated their luminescent properties.

2 EXPERIMENTAL

2.1 General Procedures

All solvents and reagents for synthesis were commercially available and used as received. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C analyzer. IR spectra were measured on a Tensor 27 OPUS (Bruker) FT-IR spectrometer using KBr pellets. Thermogravimetric (TG) analyses were carried out on a Rigaku standard TG-DTA analyzer at a heating rate of 10 °C · min ^{1} from ambient temperature to 700 °C, using an empty Al O crucible as reference. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV and 100 mA with a Cu-target tube and graphite monochromator. PXRD pattern simulations were performed using the single-crystal data and diffraction-crystal module of the Mercury (Hg) program version 1.4.2, available free of charge via the Internet at http://www.iucr.org. Luminescence spectra were investigated on an Edinburgh FS5 spectrophotometer.

2.2 Synthesis

[Zn(FDA)(phen)(H O) · H O] (1). Zn(NO) · 6H O (0.0297 g, 0.1 mmol), H FDA (0.0156 g, 0.1 mmol), and phen (0.0180 g, 0.1 mmol) were mixed with DMAC:H O (V:V = 1:1, 5 mL) in a 25 mL Teflon liner under hydrothermal conditions at 120 °C for three days, then cooled to room temperature at a rate of 4 °C · h ^{1}. Colorless crystals were obtained (yield: 20% based on Zn). FT-IR (KBr pellets, cm ^{1}): 3261 m, 1629 s, 1608 s, 1576 s, 1517 m, 1495 w, 1428 m, 1358 s, 1336 s, 1222 w, 1161 w, 1031 w, 965 w, 869 w, 855 m, 815 w, 785 m, 727 m, 644 w, 552 w, 491 w. Anal. Calcd. for C H ZnN O : C, 49.62; H, 3.24; N, 6.43%. Found: C, 49.55; H, 3.26; N, 6.39%.

[Cd(HFDA)(phen) (NO)] (2). Cd(NO) · 4H O (0.0308 g, 0.1 mmol), H FDA (0.0156 g, 0.1 mmol), and phen (0.0180 g, 0.1 mmol) were mixed with water (10 mL) in a 25 mL Teflon liner under hydrothermal conditions at 120 °C for three days, then cooled to room temperature at a rate of 4 °C · h ^{1}. Colorless crystals were obtained (yield: 35% based on Cd). FT-IR (KBr pellets, cm ^{1}): 3435 s, 1724 m, 1651 w, 1594 s, 1574 m, 1557 w, 1515 m, 1427 m, 1384 s, 1368 s, 1346 s, 1266 m, 1214 w, 1145 w, 1101 w, 844 m, 815 w, 790 w, 728 s, 637 w. Anal. Calcd. for C H CdN O : C, 52.23; H, 2.77; N, 10.15%. Found: C, 52.38; H, 2.60; N, 10.13%.

[Cd(FDA)(phen)] (3). This complex was synthesized by a procedure similar to that for complex 2, except that water was used instead of ethanol. Colorless

crystals were obtained (yield: 35% based on Cd). FT-IR (KBr pellets, cm ^{1}): 3431 m, 3115 m, 1568 s, 1517 s, 1434 m, 1418 m, 1376 s, 1222 w, 1140 w, 1102 w, 1039 w, 964 m, 857 w, 821 s, 795 m, 728 s, 642 w, 574 w, 507 w. Calcd. for C H CdN O : C, 48.40; H, 2.26; N, 6.27%. Found: C, 48.36; H, 2.23; N, 6.23%.

2.3 Crystal Structure Determination and Refinement

Single-crystal X-ray diffraction data were collected on a Bruker-AXS SMART APEX2 CCD diffractometer at 296(2) K using Mo-K radiation (= 0.71073 Å). The program SAINTPLUS was used for integration of the diffraction profiles. All structures were solved by direct methods using SHELXS and refined by full-matrix least-squares methods with SHELXL; semi-empirical absorption corrections were applied using the SADABS program. Metal atoms in each complex were located from E-maps, and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^{2}. Hydrogen atoms of ligands were generated theoretically onto specific atoms and refined isotropically with fixed thermal factors. Crystallographic data are listed in Table 1 . Selected bond lengths and angles for 1–3 are given in Table 2 . Hydrogen bonds for 1–3 are listed in Table 3 .

3 RESULTS AND DISCUSSION

3.1 Crystal Structure of [Zn(FDA)(phen)(H O) · H O] (1)

Single-crystal X-ray diffraction analysis reveals that complex 1 crystallizes in the triclinic space group *P*1. The asymmetric unit of 1 consists of one Zn^{2} ion, one FDA^{2} ligand, one phen ligand, one coordinated water molecule, and one lattice water molecule. The Zn^{2} center is five-coordinated by two carboxylate oxygen atoms from two distinct FDA^{2} ligands, one oxygen atom from a coordinated water molecule, and two nitrogen atoms from a phen ligand, forming a trigonal bipyramidal geometry (Fig. 1a [Figure 1: see original paper]). The Zn(II)–O and Zn(II)–N distances range from 2.012(5) to 2.099(6) Å and from 2.107(6) to 2.135(6) Å, respectively.

The FDA^{2} ligand adopts a -(^{1})-(^{1}) coordination mode to connect two Zn^{2} ions. Neighboring Zn^{2} ions are bridged by FDA^{2} linkers to form one-dimensional (1D) chains, with phen ligands acting as terminal ligands (Fig. 1b). The neighboring phen ligands are stacked with centroid–centroid distances of approximately 3.643(5) and 3.569(6) Å, indicating significant - interactions. Additionally, intermolecular - interactions between the furan rings of H FDA ligands (centroid-centroid distance = 3.650(3) Å) link adjacent 1D chains. Consequently, the 1D chains pack into a three-dimensional (3D) supramolecular structure through hydrogen bonds (O–H ··· O) and - interactions (Fig. 1c).

3.2 Crystal Structure of [Cd(HFDA)(phen) (NO)] (2)

Single-crystal X-ray diffraction analysis reveals that complex 2 crystallizes in the monoclinic space group *Cc* with an asymmetric unit containing one Cd² ion, one HFDA ligand, two phen ligands, and one NO anion. As shown in Fig. 2a [Figure 2: see original paper], the Cd(II) center is seven-coordinated by two carboxylate oxygen atoms from a single FDA² ligand, one oxygen atom from an NO anion, and four nitrogen atoms from two phen ligands, forming a pentagonal bipyramidal geometry. The Cd(II)–O and Cd(II)–N distances range from 2.371(8) to 2.547(6) Å and from 2.362(7) to 2.464(9) Å, respectively.

In complex 2, the H FDA ligand is partially deprotonated—a rare phenomenon among H FDA-based coordination polymers. Under the synergistic effect of phen ligands and this partial deprotonation, complex 2 adopts a discrete structure. The hydrogen atom from the COOH group forms a hydrogen bond with an oxygen atom from NO , connecting adjacent discrete units to construct 1D zigzag chains (Fig. 2b). Additionally, intermolecular - interactions between the furan ring of the H FDA ligand and the benzene ring of a phen ligand (centroid–centroid distance = 3.767(7) Å) link adjacent discrete units. Moreover, these 1D chains pack into a 3D supramolecular structure through hydrogen bonds (O–H ··· O) and - interactions (Fig. 2c).

3.3 Crystal Structure of [Cd(FDA)(phen)] (3)

Single-crystal X-ray diffraction analysis shows that complex 3 crystallizes in the monoclinic space group *P*2 /*n* with an asymmetric unit consisting of one Cd² ion, one FDA² ligand, and one phen ligand. The Cd² ion is coordinated by four oxygen atoms from two carboxyl groups of two different FDA² ligands and two nitrogen atoms from one phen ligand, exhibiting distorted octahedral coordination geometry (Fig. 3a [Figure 3: see original paper]). The Cd(II)–O and Cd(II)–N distances range from 2.338(16) to 2.387(11) Å and from 2.314(17) to 2.32(2) Å, respectively.

The FDA² ligand adopts a -(¹, ¹)-(¹, ¹) coordination mode to connect two Cd² ions. The Cd² ions are linked by two carboxylates of the FDA² ligand to generate infinite zigzag chains, while phen ligands chelate the Cd² ions and prevent further extension of the 1D chain (Fig. 3b). However, the phen ligands provide abundant hydrogen bond donors (C–H ··· O) that facilitate construction of a supramolecular structure (Fig. 3c).

3.4 Powder X-ray Diffraction of 1–3

The experimental PXRD patterns of 1–3 match well with their simulated counterparts, demonstrating that the samples are phase-pure (Fig. 4 [Figure 4: see original paper]). Differences in reflection intensities between simulated and experimental patterns may be attributed to preferred orientation of the crystalline powder samples.

3.5 Thermal Analysis

Thermogravimetric analyses of complexes 1–3 were performed to investigate their thermal degradation behavior from 30 to 700 °C at a heating rate of 10 °C • min ^{1} under nitrogen atmosphere (Fig. 5 [Figure 5: see original paper]). For complex 1, the first weight loss of 8.21% (calcd: 8.26%) between 60 and 106 °C corresponds to removal of one lattice and one coordinated water molecule per formula unit. The weight then remains stable until 310 °C, after which the organic framework collapses dramatically due to decomposition of organic ligands, leaving ZnO as the final residue (obs.: 18.60%, calcd.: 18.69%). Complexes 2 and 3 exhibit thermal stability up to 210 and 310 °C, respectively. The final residues are CdO (obs.: 18.58%, calcd.: 18.64% for 2, and obs.: 28.81%, calcd.: 28.75% for 3).

3.6 Photoluminescent Properties

As a series of d^{1} metal-organic coordination polymers, the emission spectra of complexes 1–3 and their corresponding organic ligands were recorded in the solid state at room temperature. As shown in Fig. 6 [Figure 6: see original paper], the emission bands appear at 377 nm (= 312 nm) for H FDA and at 416, 439, and 465 nm (= 380 nm) for phen. Complexes 1, 2, and 3 exhibit maximum emission peaks at 390 nm (= 359 nm), 386 nm (= 346 nm), and 393 nm (= 353 nm), respectively. Compared with the free ligands, the photoluminescence intensity of complex 1 is enhanced, while those of complexes 2 and 3 are reduced. The enhanced photoluminescence intensity in complex 1 likely originates from its unique structure, which increases rigidity and reduces energy loss through non-radiative vibrational decay. Additionally, complex 1 contains abundant hydrogen bonds compared with the other complexes, which may contribute to the photoluminescence enhancement. Thus, complex 1 shows potential for application in photoluminescent materials.

4 CONCLUSION

In summary, three new coordination polymers with diverse structures have been synthesized under solvothermal conditions by reacting H FDA with the N-containing auxiliary ligand phen and different metal ions. Due to chelation by phen, all three coordination polymers exhibit low dimensionality: 1D for complex 1, 0D for complex 2, and 1D for complex 3. Notably, H FDA undergoes partial deprotonation in complex 2, which is a rare phenomenon among H FDA-based coordination polymers. Furthermore, the luminescent properties of all three complexes have been investigated.

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