A Dinuclear Cd(II) Cluster-based Coordination Polymer: Synthesis, Structure and Luminescence Property postprint

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Abstract

One two-dimensional coordination polymer with a formula of {Cd(L)(imidazole)(H2O)}n (1) was obtained by the synthetic reactions in aqueous solution using a newly synthesized H2L (H2L = methyl-3-hydroxy-5-carboxy-2-thiophenecarboxylate) ligand. Compound 1 crystallizes in monoclinic system, space group C2/c with a = 18.3176(11), b = 8.5366(9), c = 8.4152(5) Å, = 101.789(6)º, V = 2797.1(3) Å3, Dc = 1.979 g/cm3, C10H12N2O7SCd, Mr = 416.68, F(000) = 1648, = 1.745 mm-1, F(000) = 1648, the final R = 0.0323 and wR = 0.0604 for 2604 observed reflections with I > 2s(I). Structure analyses reveal that the compound is constructed by dinuclear Cd(II) clusters bridged by two hydroxyl oxygens of L2- anions, which features a two-dimensional network with 4-connected sql topology. Furthermore, the compound exhibits high thermal stability and intense fluorescent emission, and could be explored for potential luminescent materials.

Full Text

Preamble

A Dinuclear Cd(II) Cluster-based Coordination Polymer: Synthesis, Structure and Luminescence Property

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Abstract

A two-dimensional coordination polymer with the formula {Cd(L)(imidazole)(H O)} (1) was synthesized via aqueous solution reactions using a newly prepared H L

ligand (H L = methyl-3-hydroxy-5-carboxy-2-thiophenecarboxylate). Compound 1 crystallizes in the monoclinic system, space group C2/c, with unit cell parameters a = 18.3176(11), b = 8.5366(9), c = 8.4152(5) Å, = 101.789(6)°, V = 2797.1(3) Å³, Dc = 1.979 g/cm³, C H N O SCd, M = 416.68, F(000) = 1648, = 1.745 mm ¹. The final refinement converged at R = 0.0323 and wR = 0.0604 for 2604 observed reflections with I > 2 (I).

Structural analysis reveals that the compound is constructed from dinuclear Cd(II) clusters bridged by two hydroxyl oxygens of L² anions, featuring a two-dimensional network with 4-connected sql topology. Furthermore, the compound exhibits high thermal stability and intense fluorescent emission, suggesting its potential as a luminescent material.

Keywords: methyl-3-hydroxy-5-carboxy-2-thiophenecarboxylate; topology; luminescence property
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1. Introduction

Recently, considerable attention has been devoted to the assembly of coordination polymers (CPs) due to their intriguing structural diversity and potential applications as functional materials [1-6]. Rational design and assembly of metal ions or metal clusters with diverse multifunctional bridging linkers represent sensible and effective strategies for synthesizing novel CPs [7-10]. Among these, organic bridging linkers containing multidentate carboxylic acids have been extensively employed as building blocks in crystal engineering. However, building blocks based on thiophenedicarboxylic acids remain relatively rare. In recent years, our group and others have been engaged in synthesizing CPs constructed from various thiophenedicarboxylic acids, including 2,5-thiophenedicarboxylic acid, 3,4-thiophenedicarboxylic acid, 2,3-thiophenedicarboxylic acid, and 3-nitro-2,5-thiophenedicarboxylic acid, yielding many interesting CPs [11-15].

In this context, methyl-3-hydroxy-5-carboxy-2-thiophenecarboxylate (H L) was selected as a precursor for constructing CPs because this novel thiophene-2,5-dicarboxylic acid derivative possesses multiple potential coordination sites, including carboxyl, hydroxyl, and carbomethoxyl groups. Additionally, the Cd(II) ion, with its larger ionic radius, can accommodate various coordination numbers and geometries in crystal engineering. Encouraged by these considerations, we employed H L and imidazole as mixed linkers to investigate their assembly with Cd(II) ions, successfully obtaining a two-dimensional CP constructed from dinuclear Cd(II) clusters. The compound, which features 4-connected sql topology, was characterized by infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA), and its luminescent properties were investigated.

2. Experimental

All reagents and solvents were purchased commercially and used without further purification. IR spectra were recorded as KBr pellets on a Nicolet Avatar-360 spectrometer in the range of 4000–400 cm ^{1}. Elemental analyses for C, H, and N were performed on a Flash 2000 elemental analyzer. TGA was conducted on a SDTQ600 thermogravimetric analyzer using a platinum pan at a heating rate of 10 °C/min under air atmosphere. Fluorescence measurements were recorded with a Hitachi F4500 fluorescence spectrophotometer.

2.1 Synthesis of {Cd(L)(imidazole)(H O)} (1)

A mixture of H L (20.2 mg, 0.1 mmol), Cd(OAc) · 2H O (26.7 mg, 0.1 mmol), imidazole (13.62 mg, 0.2 mmol), NaOH (2.00 mg, 0.05 mmol), and 4 mL deionized water was sealed in a 20 mL Pyrex glass tube and heated at 80 °C for 72 h, followed by cooling to room temperature at a rate of 5 °C · h ^{1}. Block yellow crystals were collected (yield: 62% based on Cd). Elemental analysis calcd. (%) for C H CdN O S: C, 28.79; H, 2.88; N, 6.72. Found (%): C, 28.81; H, 2.89; N, 6.69. Selected IR peaks (KBr, cm ^{1}): 3517 (s), 3357 (m), 3296 (m), 2639 (m), 1593 (s), 1536 (s), 1464 (s), 1433 (s), 1375 (s), 1342 (s), 1166 (m), 920 (m), 836 (m), 755 (m), 734 (m), 715 (m), 686 (m).

2.2 X-ray Structure Determination

A suitable crystal of compound 1 was mounted on a glass fiber using viscous hydrocarbon oil as a coating. Diffraction data were collected on an Oxford Diffraction SuperNova Eos2 diffractometer equipped with graphite-monochromated MoK radiation at 293(2) K. Data collection and processing were performed using CrysAlisPro software. The structure was solved and refined using the Olex2 program as an interface to SHELXS and SHELXL [16–18]. Heavy atoms were refined anisotropically. Hydrogen atoms of water molecules were located from difference Fourier maps and fixed at O–H distances of 0.85 Å, while other hydrogen atoms were added using the riding model without refinement. Selected bond distances and angles are summarized in Table 1 . The final refinement converged at R = 0.0323 and wR = 0.0604 for 2604 observed reflections with I > 2 (I), and R = 0.0418 and wR = 0.0634 for all data. ( ) = 0.641, ( ) = -0.496 e/Å^{3}, and S = 1.061.

3. Results and Discussion

3.1 Crystal Structure

Complex 1 was obtained as block yellow crystals by reacting H L with cadmium acetate and imidazole in aqueous medium. Notably, weakly basic pH values in the initial reaction solution were essential for successful synthesis; attempts under acidic or neutral conditions failed. This likely reflects that weakly basic

environments facilitate H L deprotonation, enabling coordination with Cd^{2} ions, consistent with the single-crystal X-ray analysis.

Complex 1 crystallizes in the monoclinic space group C2/c, with one Cd^{2} ion, one L^{2} anion, one imidazole ligand, one coordinated water molecule, and one lattice water molecule in the asymmetric unit (Fig. 1 [Figure 1: see original paper]). The Cd^{2} ion adopts a distorted octahedral geometry, coordinated by four oxygen atoms from three L^{2} anions, one nitrogen atom from a terminal imidazole ligand, and one coordinated water molecule.

Fig. 1. Coordination environment of the Cd(II) center. Hydrogen atoms are omitted for clarity. Symmetry codes: #1: 1.5 − x, 0.5 -y, 2 -z; #2: 1.5 − x, y -0.5, 1.5 -z.

The Cd-N bond length is 2.263(3) Å, while Cd-O bond lengths range from 2.265(2) to 2.379(2) Å, which are within normal ranges [19,20]. O—Cd—O angles vary between 77.34(9) and 171.31(9)°, and O—Cd—N angles fall in the range of 86.16(11)-161.94(11)° (Table 2).

In compound 1, each L^{2} anion adopts a tridentate -(^{2})-(^{1})-(^{1}) bridging mode to link adjacent Cd^{2} ions, generating a 2D layer structure parallel to the bc plane that is further decorated by terminal imidazole ligands (Fig. 2a [Figure 2: see original paper] and Fig. 2b). A pair of Cd^{2} ions is bridged by two hydroxyl oxygen atoms to form a dinuclear Cd O cluster with a Cd · · · Cd separation of 3.5500 Å. Topologically, each Cd O cluster can be considered a 4-connected node linking four equivalent nodes through four L^{2} anions, forming a 4-connected sql-type network with 4 · 6^{2} topology (Fig. 2c). These 2D layers are further extended into an overall three-dimensional (3D) network via intermolecular O-H · · · O interactions between lattice water (O(7)) and oxygen atoms of L^{2} anions or coordinated water molecules (O(7)-H(3W) · · · O(5), O(7)-H(3W) · · · O(6), and O(7)-H(4W) · · · O(5); detailed hydrogen-bonding geometry is listed in Table 2), as shown in Fig. 2d.

Fig. 2. (a) 2D layer structure in 1. (b) 2D layer decorated by imidazole ligand. (c) Schematic representation of the 4-connected sql topology. (d) View of the 3D hydrogen-bonded network.

Additionally, the structure contains intramolecular hydrogen bonding involving carbonyl and terminal imidazole moieties (N(2)-H(2) · · · O(4) and O(6)-H(2W) · · · O(5); see Table 2 for detailed geometry), which further enhances the stability and integrity of the 3D supramolecular network.

3.2 IR Spectrum and Thermal Study

The IR spectrum of compound 1 shows strong absorption bands centered at 3517-2639 cm ^{1}, corresponding to N-H/O-H stretching vibrations of the imidazole ligand and water molecules. Characteristic carboxylate stretching vibrations appear at 1593-1536 cm ^{1} (asymmetric) and 1342-1464 cm ^{1} (symmetric).

The absence of absorption peaks in the 1690–1730 cm ^{1} region indicates complete deprotonation of carboxylate groups in the H L ligand.

Thermal stability was investigated on a crystalline sample at a heating rate of 10 °C · min ^{1} under air atmosphere. As shown in Fig. 3 [Figure 3: see original paper], a two-step weight loss was observed. The first step (observed: 7.62%) between 57 and 117 °C corresponds to the loss of two water molecules (expected: 7.68%). A stable plateau appears in the temperature range of 117–234 °C. Further heating leads to continuous weight loss due to decomposition of organic moieties.

3.3 Luminescent Property

Fig. 3. TGA curve for 1.

Fig. 4. Solid-state emission spectra of 1 and the free H L ligand measured at room temperature.

Since compound 1 is air-stable and insoluble in water and most organic solvents, the luminescent properties of crystalline samples of 1 and the H L ligand were investigated in the solid state at room temperature. As shown in Fig. 4 [Figure 4: see original paper], complex 1 exhibits fluorescent emission with a maximum at 430 nm (= 272 nm). This fluorescence likely originates from intraligand transitions of coordinated L^{2} anions, as the free H L ligand shows similar emission at 452 nm (= 276 nm). The blue-shifted emission of 1 results from coordination of L^{2} anions to metal centers [21].

4. Conclusion

In this study, a Cd(II) coordination polymer containing dinuclear Cd(II) clusters was successfully synthesized and characterized. Single-crystal X-ray diffraction reveals that the L^{2} anion adopts a bidentate -(^{1}, ^{1})-(^{1}) bridging mode to link adjacent Cd(II) ions, forming a 2D layer structure with 4-connected sql topology. These layers are further connected by O–H ··· O hydrogen bonding interactions to generate a 3D supramolecular framework. The compound exhibits high thermal stability and intense fluorescent emission, making it a promising candidate for luminescent materials.

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

Bond/Angle	Value
Cd(1)−N(1)	2.263(3)
Cd(1)−O(6)	2.290(3)
Cd(1)−O(2)	2.379(3)
Cd(1)−O(3)	2.282(2)
Cd(1)−O(3)#1	2.265(2)
Cd(1)−O(4)#2	2.328(2)
N(1)−Cd(1)−O(6)	99.44(12)

Bond/Angle	Value
O(3)−Cd(1)−O(2)	77.45(9)
O(3)#1−Cd(1)−O(2)	93.26(9)
O(3)−Cd(1)−O(3)#1	77.34(9)
O(3)#1−Cd(1)−O(4)#2	83.73(9)
O(3)−Cd(1)−O(4)#2	157.11(10)
O(3)−Cd(1)−O(6)	95.65(10)
O(4)#2−Cd(1)−O(2)	81.29(10)
O(6)−Cd(1)−O(2)	90.88(11)
N(1)−Cd(1)−O(2)	98.76(11)
N(1)−Cd(1)−O(3)	92.11(11)
N(1)−Cd(1)−O(3)#1	161.94(11)
N(1)−Cd(1)−O(4)#2	109.68(9)
O(3)−Cd(1)−O(6)	171.31(9)
O(3)#1−Cd(1)−O(6)	86.16(11)

Symmetry transformations: #1: 1.5 − x, 0.5 -y, 2 -z; #2: 1.5 − x, y -0.5, 1.5 -z

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