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A New 3D Metal-organic Framework with Tetranuclear Cadmium(II) Clusters: Synthesis, Structure, and Luminescent Property

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ABSTRACT A unique metal-organic framework \([\text{Cd}_2(L)_{1.5}(\mu_3\text{-OH})(\text{H}_2\text{O})_2]\cdot2\text{H}_2\text{O}\) (1, \(\text{H}_2\text{L} = \text{2,5-dibenzoylterephthalic acid}\)) has been synthesized under hydrothermal conditions, and characterized by single-crystal X-ray diffractions, elemental analyses, IR spectra and fluorescence spectrum. The compound is of triclinic system, space group \(\text{P1}\), \(\text{C}_{33}\text{H}_{27}\text{CdO}_{14}\), \(\text{Mr} = 870.33\), \(a = 12.2939(17)\), \(b = 12.5135(9)\), \(c = 13.2046(10)\) Å, \(\alpha = 115.3190(10)\), \(\beta = 96.9140(10)\), \(\gamma = 109.7950(10)\)°, \(V = 1641.6(3)\) Å³, \(Z = 2\), \(D_c = 1.761\) g/cm³, \(F(000) = 862\), \(\mu(\text{MoK}\alpha) = 1.366\) mm⁻¹, \(R_{\text{int}} = 0.0148\), \(R = 0.0240\) and \(wR = 0.0639\) for 5995 observed reflections with \(I > 2\sigma(I)\). X-ray analysis shows that the title complex exhibits a 3D framework with \((4\text{I}^2)\cdot6^3\) topology, in which the tetra-nuclear \([\text{Cd}_4(\mu_3\text{-OH})_2]\) clusters act as 6-connected nodes, and the \(L\) ligands can be simplified to be linear connectors. Moreover, the thermal stability and fluorescence have been studied in detail.

Keywords: hydrothermal, tetranuclear cluster, 2,5-dibenzoylterephthalic acid, luminescence, crystal structure

1 INTRODUCTION

The design and synthesis of new coordination polymers have been of great interest as their promising potential applications in fluorescence, host-guest chemistry, ferroelectricity, magnetic properties, and catalysis[1-6]. In general, the construction of charming structure immensely depends on the organic ligands and the coordination geometry of central metal ions. Therefore, the selection of suitable organic ligands is crucial for self-assembly of special architectures. 1,4-benzenedicarboxylic acid (\(\text{H}_2\text{BDC}\)) with different coordination modes has been successfully employed to the synthesis of intriguing coordination polymers. The research groups of Yaghi and Férey have reported a series of metal organic frameworks (MOFs) based on \(\text{H}_2\text{BDC}\), such as MOF-5, MOF-71, MIL-47, etc.[7-9]. In recent

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years, the organic spacers with suitable functional groups and molecular skeletons have been illustrated to be most critical to fine-tune the coordination motifs. Among the organic ligands, the versatile dicarboxyl complexes, especially the R-terephthalic acid (R = -NO2, -CH3, -C(CH3)3, -Br, -I, -Cl, -NH2), have been widely used in the preparation of fascinating coordination polymers[10-12]. In our previous work[13-17], we have obtained a series of intriguing architectures by using 4,6-dibenzoylisophthalic acid, which was utilized as excellent bridges in the self-assembly of coordination polymers. Polynuclear metal clusters always have intriguing chemical and/or physical properties, such as magnetism, heterogeneous catalysis and fluorescence, and are always employed as secondary building units (SBUs) to build coordination polymers. Especially, polynuclear d10 metal complexes have attracted extensive interest in recent years because of their high transparency in the UV region and photoluminescent properties[18-19].

In order to further investigate the influence of steric bulk of isophthalic acid on the structure and properties, we choose 2,5-dibenzoylterephthalic acid (H2L) as a bridging carboxylate ligand. In this paper, we report the synthesis and structural characterization of a new fluorescent coordination polymer [Cd2(L)1.5(μ3-OH)(H2O)2]·2H2O (1), which exhibits a 3-D open framework with the default pcu net (412·63). The fluorescent property and thermal stability of complex 1 have been investigated in detail.

2 EXPERIMENTAL

2.1 Materials and physical measurements

All the chemicals were purchased commercially and used as received without further purification. H2L was synthesized according to the literature[20]. The FT-IR spectra were recorded using KBr pellets in the range of 4000~400 cm⁻¹ on a Mattson Alpha-Centauri spectrometer. Elemental analyses for C, H and N were performed on a Perkin-Elmer 2400 Elemental Analyzer. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku Dmax 2000 X-ray diffractometer equipped with a graphite-monochromatized Cu-Kα radiation (λ = 0.15406 nm) and 2θ range from 5 to 50° with a step size of 0.02°. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer Thermal Analyzer under N2 atmosphere at a heating rate of 5 °C·min⁻¹. The luminescent properties and lifetime were measured on a FLS920 Edinburgh Luminescence Spectrometer.

2.2 Synthesis of [Cd2(L)1.5(μ3-OH)(H2O)2]·2H2O (1)

A mixture of CdCl2·2.5H2O (22.8 mg, 0.1 mmol), H2L (56.10 mg, 0.15 mmol) and H2O (10 mL) was stirred in a 50 mL beaker for 30 min. The pH was adjusted to 5.0 with 0.1 M NaOH solution. Then it was sealed in a 25 mL Teflon-lined autoclave and heated at 160 °C for 72 h. After cooling to room temperature at the rate of 3 °C·h⁻¹, colorless block crystals were obtained with a ~63% yield based on Cd(II). Anal. Calcd. (%) for C33H27Cd2O14 (870.33): C, 45.54; H, 3.13. Found (%): C, 45.40; H, 3.03. IR (KBr, cm⁻¹): 3453 (m), 3070 (w), 1675 (s), 1618 (s), 1539 (m), 1483 (m), 1391 (s), 1353 (s), 1176 (w), 1145 (w), 1044 (w), 923 (w), 807 (w), 720 (m), 690 (w), 554(w), 477 (w).

2.3 Structure determination

Single crystals were glued to a fiberglass for X-ray diffraction data collection. Data sets of 1 with approximate dimensions of 0.22mm × 0.19mm × 0.18mm were collected on a Bruker Smart Apex CCD diffractometer, using a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293 K. Absorption correction of 1 was applied by using the SADABS. The structure was solved by direct methods followed by difference Fourier method and refined by full-matrix least-squares on F² using the SHELXS-97 package[21]. A total of 8538 reflections were collected in the range of 1.80≤θ≤25.50°, of which 5995 were unique (Rint = 0.0148) and 5619 were observed with I > 2σ(I). The O(2W) atom is split over two sites (O(2WA), O(2WB)) with equal site occupation factors of 0.3 and 0.7, respectively.
All non-hydrogen atoms were refined anisotropically. The thermal factors of Cd(1) and O(5) were refined with DELU restraints. Hydrogen atoms were added according to the theoretical models except for O(10), O(2WA) and O(2WB). H(10) was added by Fourier map while hydrogen atoms on O(2WA) and O(2WB) were not located. The position of hydrogen atom of μ3-OH was refined using DFIX restraints (d_{O-H} = 0.82 Å). The final R = 0.024, wR = 0.0639 (w = 1/[σ²(Fo²) + (0.0691P)² + 0.1088P]), where P = (Fo² + 2Fσ²)/3), S = 1.099, (Δρ)_{max} = 0.499, (Δρ)_{min} = −0.857 e/Å³ and (Δ/σ)_{max} = 0.002. The selected bond lengths and bond angles are listed in Table 2.

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

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Symmetry transformation: #1: x, −y + 1, z + 1

### 3 RESULTS AND DISCUSSION

#### 3.1 Structure description of [Cd4(L)1.5(μ3-OH)(H2O)2]·2H2O (1)

Single-crystal X-ray diffraction analysis reveals that complex 1 crystallizes in triclinic space group P1, which features a 3D coordination framework. The asymmetric unit of 1 comprises two crystallographically independent Cd(II) ions, one and a half L ligands, one hydroxide ion, two coordinated water molecules, and two solvent water molecules. As shown in Fig. 1b, there are two kinds of different Cd(II) atoms in the asymmetric unit of 1. Each Cd(1) atom with distorted octahedral coordination geometry is six-coordinated by four carboxylate oxygen atoms (O(1), O(4), O(5), O(8)) from three different L ligands and two μ3-OH groups (O(10), O(10A)), while Cd(2) assumes the same distorted octahedral coordination geometry, but different donor set is coordinated by three carboxylate oxygen atoms (O(2), O(5), O(7A)) from different L ligands, one μ3-OH group (O(10)) and two coordinated water molecules (O(3W), O(4W)). The Cd–O bond lengths are in the range of 2.1698(19)−2.5720(18) Å (Table 1). In the polymeric structure of 1, all carboxylic groups are deprotonated and L ligands display two types of bridging modes: μ2-(η¹1:η²2)-(η¹1:η²1)-bridging and μ4-(η¹1:η¹1)-(η¹1:η¹1), as shown in Scheme 1a–1b. As illustrated in Fig. 1b, two Cd(1) and two Cd(2) construct a rhombic tetranuclear [Cd4(μ3-OH)2] cluster through the bonding of two bridging μ3-OH groups and six carboxylate groups of L ligands. The adjacent tetranuclear [Cd4(μ3-OH)2] clusters are bridged by L ligands from three different directions to form a 3D architecture. From a topological perspective, the tetranuclear cadmium-oxygen clusters can be seemed as 6-connected nodes, and the L ligands can be simplified as linear connectors, as shown in Fig 2a. Thereafter, the structure of 1 can be described as a six-connected 3D network with the
default $\text{pcu}$ net ($4^{12}6^3$) (Fig 2b).

Scheme 1. Two coordination modes (a–b) of L ligand

Fig. 1. (a) Coordination environment of the tetranuclear Cd(II) cluster in 1. (b) Coordination environment of the tetranuclear [Cd$_4$(μ$_3$-OH)$_2$] cluster (Symmetry codes: A: $-x+1, -y+1, -z+1$). H atoms and lattice water molecules are omitted for clarity.
3.2 XRD patterns and thermal analysis

The synthesized product of complex 1 has been characterized by powder X-ray diffraction (PXRD), as shown in Fig. 3. The experimental PXRD pattern is in accordance with the result simulated from the single-crystal data, indicating the high purity of the synthesized sample.

The thermal stability of complex 1 was carried out from room temperature to 900 °C under a nitrogen atmosphere with a heating rate of 5 °C min⁻¹. As shown in Fig. 4, the TGA curve suggests a weight loss of 8.12% occurring from 70 to 170 °C, corresponding to the removal of lattice and coordinated water molecules (calcd. 8.27%). The residual framework started to decompose gradually at 390 °C and collapsed at 580 °C. The remaining weight indicated that the final product was CdO (found: 14.69%, Calcd.: 14.75%).

3.3 Photoluminescence properties

The solid-state photoluminescent spectra of 1 and free H₂L ligand at room temperature are depicted in Fig. 5. The photoluminescent spectra of H₂L ligand displays emission peak at 473 nm upon excitation at 373 nm. The emission can be ascribed to the π* → π or π* → n transitions as previously reported[22-23]. The emission spectra of complex 1 exhibit emission maxima at 454 nm (λex = 380 nm). The emission peak of complex 1 is similar to that of the free H₂L ligand. Since the Cd(II) ions are difficult to oxidize or reduce due to their d⁰ configuration, the emission...
shift is neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature\textsuperscript{[24-25]}. Compared with the emission spectrum of H\textsubscript{2}L, the blue shift of emission bands for 1 is probably due to the deprotonated effect and the coordination interactions of H\textsubscript{2}L ligand to Cd(II) ions\textsuperscript{[24, 26]}.

Fig. 5. Solid-state fluorescent emission spectra of free H\textsubscript{2}L and complex 1

4 CONCLUSION

In summary, a luminescent Cd\textsuperscript{II} coordination polymer [Cd\textsubscript{2}(L)\textsubscript{1.5}(\mu\textsubscript{3}-OH)(H\textsubscript{2}O)\textsubscript{2}]	extsubscript{2}H\textsubscript{2}O with a 3D metal-organic framework has been obtained through hydrothermal reactions, which exhibits 6-connected pcu topology with a point symbol of (4\textsuperscript{12}, 6\textsuperscript{3}). The \mu\textsubscript{3}-OH group in the crystal structure gives rise to the formation of a tetranuclear [Cd\textsubscript{4}(\mu\textsubscript{3}-OH)\textsubscript{2}] cluster, which is further extended into a 3D net through the bridging carboxylate ligand 2,5-dibenzoylterephthalic acid. The self-assembly of this compound extended the application of hydrothermal technique in luminescent coordination polymer synthesis.

REFERENCES


