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A novel 1D Cd^{II} coordination polymer with 4-sulfobenzoate and 2,2′-bipyridine containing an approximate rectangular molecular box unit with blue fluorescent emission

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Abstract

The hydrothermal reaction of cadmium hydroxide with 4-sulfobenzoic acid and 2,2′-bipyridine yields 1D coordination polymer $[Cd_2(L)_2(2,2'\text{-bipy})_2(H_2O)_2]_n$ **1** (where L = 4-sulfobenzoic acid), with blue fluorescent emission in which each $[Cd_2(L)_2(2,2'\text{-bipy})_2(H_2O)_2]$ unit (an approximate rectangular molecular box) is linked together by μ_3 carboxylate to result in the formation of 1D chain coordination polymer. Crystal data for **1**: triclinic, space group P-1(No.2), $a = 8.8350(16)$, $b = 9.4770(16)$, $c = 11.8019(15)$ Å; $\alpha = 99.174(11)$, $\beta = 105.776(13)$, $\gamma = 113.718(15)°$; $V = 829.1(2)$ Å^3; $Z = 2$; $R_1 = 0.0206$, $wR_2 = 0.0526$ for 2925 independent reflections with $I > 2\sigma(I)$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cadmium; One-dimensional coordination polymer; 4-Sulfobenzoate; Hydrothermal synthesis

1. Introduction

The construction of supramolecular architectures are currently of great interest owing to their intriguing network topologies and potential function as new classes of materials which function in the solid state as candidate host species for selective guest binding [1–7] such as sensors for volatile organic compounds (VOCs) or as molecular sieves. On the other hand, luminescent organic and coordination compounds have been an active research area for decades because of their various potential applications in materials sciences. The most notable recent interest in luminescent compounds concerns their application in electroluminescent display [8–10]. Electroluminescent devices using various compounds involve organic polymers, small organic molecules, and coordination compounds. To achieve full-color electroluminescent displays, three color components, i.e., green, blue, and red, must be available. Stable blue luminescent compounds that are useful in electroluminescent devices are still rare and vary challenging to prepare. To the best of our knowledge, the 4-sulfobenzoic acid transition metal coordination polymer or its compound with strong blue fluorescent still remains unknown although some other ligands complexes have been found to exhibit intriguing structural and photoluminescent properties [11–16]. To our surprise, by employing the correct combination of bridging and terminal ligands, the condensed neutral rectangular coordination polymer, $[Cd_2(4\text{-sulfobenzoate})_2(2,2'\text{-bipy})_2(H_2O)_2]_n$ (**1**) can be formed, which represents first example of the 4-sulfobenzoic acid coordination polymer with blue-luminescent emission. Herein, we report its synthesis, crystal structure and fluorescent property.

2. Experiment

Chemicals and solvents in this work were purchased from Aldrich and used as received, except that $Cd(OH)_2$ was prepared by the reaction of $Cd(NO_3)_2 \cdot 4H_2O$ and NaOH in aqueous solution. The FT-IR spectra were recorded as solid in KBr matrix in the range

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PII: S 1 3 8 7 - 7 0 0 3 (0 1) 0 0 2 2 1 - 0

4000–400 cm^{-1} on a Nicolet Inpact 170SX FT-IR spectrometer. Elemental analyses were performed on Perkin-Elmer 240C elemental analyzer.

2.1. Preparation of the complex **1**

Samples of 0.044 g (0.3 mmol) $\mathrm{Cd(OH)_2}$, 0.121 g (0.6 mmol) 4-sulfobenzoic acid and 0.016 g (0.1 mmol) 2,2′-bipy were placed in a thick Pyrex tube (ca. 20 cm long). After addition of 2 ml water, the tube was frozen with liquid N_2, evacuated under vaccum and sealed with a torch. The tube was then heated at 130°C for 10 h to give pure colorless plate crystals of **1** in 58% yield based on 4-sulfobenzoic acid. Anal. Calc. For $\mathrm{C_{17}H_{14}CdN_2O_6S}$: C, 41.94; H, 2.88; N,5.76; Found: C, 42.06; H, 3.02; N, 5.84. IR spectrum (cm^{-1}): 3450 (s), 3100 (w), 1600 (s), 1560 (s), 1480 (s), 1440 (s), 1385 (s), 1320 (m), 1200 (s), 1170 (m), 1120 (m), 1040 (s), 1000 (s), 840 (m), 790 (m), 780 (s), 740 (s), 700 (s), 650 (s), 570 (s), 460 (s).

2.2. X-ray structure determination for **1**

A single crystal of **1** was prepared as described above. A colorless block crystal with dimensions $0.40 \times 0.20 \times 0.10\ \mathrm{mm}^3$ was employed for structural analysis at 293(2) K on an Enraf-Nonius CAD4 diffractometer using Mo-Kα radiation ($\lambda = 0.71073$). Crystal data for **1**: triclinic, space group P-1(No.2), $a = 8.8350(16)$, $b = 9.4770(16)$, $c = 11.8019(15)$; $\alpha = 99.174(11)$, $\beta = 105.776(13)$, $\gamma = 113.718(15)°$; $V = 829.1(2)\ \mathrm{\AA}^3$; $Z = 2$; $R_1 = 0.0206$, $wR_2 = 0.0526$ for 2925 independent reflections with $I > 2\sigma(I)$. The structure was solved by direct methods and refined by the full-matrix least-squares method on F^2 using the SHELX-97 program set, $R_1 = 0.0206, wR_2 = 0.0526$.

3. Results and discussion

The results of elemental analysis and IR spectra for **1** indicate that the reaction of $\mathrm{Cd(OH)_2}$ with 4-sulfobenzoic acid and 2,2′-bipy yielded the titled complex. The IR spectra show a strong peak at 1600 cm^{-1}, indicating that the carboxylic acid of the ligand is deprotonated because of the absence of a strong peak at 1720 cm^{-1}. Compared to the free 4-sulfobenzoic acid, the band at 3000 cm^{-1} (s), corresponding to ν (O–H) in the ligand is changed into 3100 cm^{-1} (w), the medium peak at 1250 cm^{-1} related to ν ($\mathrm{SO_2}$) is shifted to 1200 cm^{-1} (s). The strong peaks at 1480, 1440, and 1385 cm^{-1} indicate that the 2,2′-bipy is coordinated to the cadmium atom.

X-ray single crystal structure determination reveals that **1** has 1D chain motif with each unit containing a novel neutral approximate rectangular molecular box, as shown in Fig. 1. In the asymmetric unit there are two Cd ions composed of $\mathrm{M_2L_2}$ type molecular box in which the local coordination geometry around each cadmium ion in **1** can be best described as approximately pentagonal bipyramidal with one bidentate chelating carboxylate and 2,2′-bipy as well as one of oxygen of another carboxylate group in the equatorial plane and with two oxygen atoms from sulfonate and water in the apical positions. Thus, each rectangular molecular box (defined by Cd(1B)O(1AA)Cd(1C)O(1B), dotted line, with a dimension of $9.150 \times 3.1966\ \mathrm{\AA}^2$) is linked together by two μ_3 oxygen atoms of two carboxylate groups to form 1D chain coordination polymer while two μ_3 oxygen atoms and Cd ions consist of four-membered ring [Cd(1B)O(4)Cd(1A)O(4AA)]. Thus, each 4-sulfobenzoate group acts as a tetradentate ligand to connect between two Cd ions. The two phenyl rings in each box displays some π–π stacking interaction (3.1966 Å) to stabilize this polymer. To take into the van der Waals contact consideration, there is no space available for guest inclusion. For further investigation, Fig. 2 shows how sulfonate polyhedron locates in the polymer. From its crystal packing view, as shown in Fig. 3, there exist a

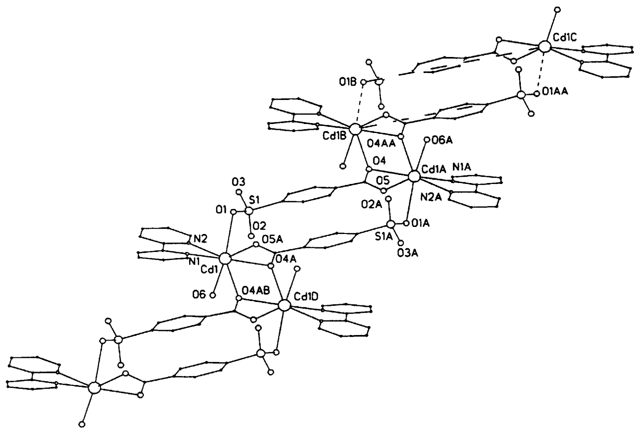

Fig. 1. 1D Cd coordination polymer **1** shows how each rectangular box unit is linked together by two μ_3 carboxylate groups. The dotted line stands for a rhomb with a dimension of $9.150 \times 3.1966\ \mathrm{\AA}^2$. The open circles with increasing size represent C, O, N, S and Cd atom, respectively. The selected bond lengths (Å) and bond angles (°): Cd(1)–N(1) 2.318(2), Cd(2)–N(2) 2.348(2), Cd(1)–O(4A) 2.2632(18), Cd(1)–O(5A) 2.536(2), Cd(1)–O(1) 2.546(2), Cd(1)–O(4AB) 2.586(2); N(1)–Cd(1)–N(2) 70.73(7), O(5A)–Cd(1)–O(4A) 54.01(6), O(1)–Cd(1)–O(6) 160.85(8), O(6)–Cd(1)–O(4AB) 72.59(8), O(4AB)–Cd(1)–O(4A) 69.62(7), O(1)–Cd(1)–N(1) 83.07(7), O(1)–Cd(1)–N(2) 85.10(7), O(6)–Cd(1)–N(1) 100.72(8), O(6)–Cd(1)–N(2) 78.61(8), O(1)–Cd(1)–O(4AB) 126.49(7), O(1)–Cd(1)–O(4A) 91.40(7), O(1)–Cd(1)–O(5A) 78.83(7).

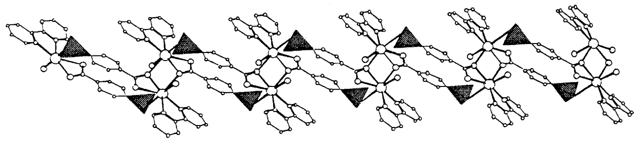

Fig. 2. The S atom is highlighted by tetra-polyhedral representation.

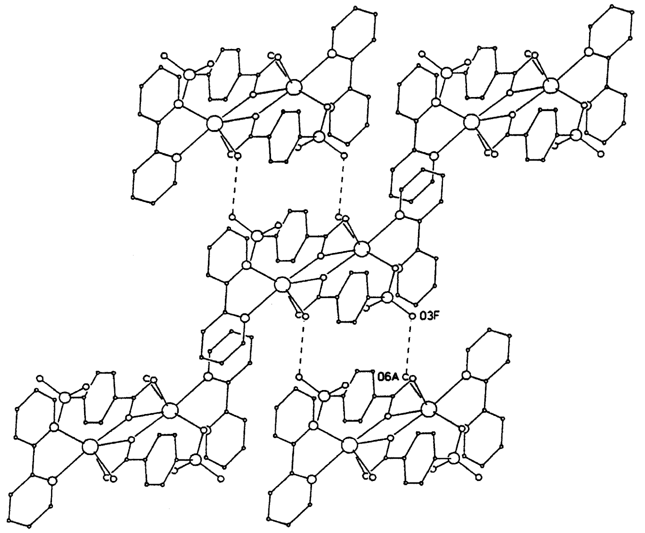

Fig. 3. A crystal packing perspective view of **1** along *c*-axis.

lot of hydrogen bondings (between water (O6) and one (O3) of three oxygen atoms of sulfonate group of the another polymer chain, 2.809 Å) in **1** to resulting in the formation of 3D network. To the best of our knowledge, the coordination mode of 4-sulfobenzoate in **1** is unprecedented in the known complexes containing sulfobenzoate derivatives.

The Cd–O distances (2.2632(18)–2.536(2) Å), corresponding to the carboxylate are quite similar to normal Cd–OCO distances (2.251–2.879 Å) [17]. The Cd(1)–O(5A) bond (2.536(2) Å) is much longer than Cd(1)–O(4A) bond (2.2632(18) Å), suggesting that carboxylate group coordination mode is quite asymmetric and common in μ_3 carboxylate metal coordination chemistry [18]. In addition, Cd(1)–O(1) (sulfonic group) bond is 2.546(2) Å, indicating that it shows some pendant oxygen characteristics. The Cd(1)–N(1) bond distance (2.318 (2) Å) is slightly shorter than the Cd(1)–N(2) bond (2.348 (2) Å) in the same ligand, suggesting that there is some twist in the 2,2′-bipy ring [dihedral angle (9.2°) between the two pyridyl rings].

A salient feature is that strong blue emissions of **1** at 365, 380 and 418 nm, as shown in Fig. 4 in the solid state at room temperature may suggest that these fluorescent emissions come from the two ligands, 2,2′-bipy and 4-sulfobenzoate since a similar emission may be observed for free 2,2′-bipy (365 and 380 nm) and 4-sulfobenzoate (417 nm). However, it is worth noting that the fluorescent intensity of the coordination polymer **1** is significantly stronger than that of free ligands, probably due to the conformational rigidity enhancement of the coordinated ligands, thereby reducing the non-radiative decay of the intraligand $1(\pi\text{–}\pi^*)$ excited state [19]. Thus, **1** may be used as an advanced material for blue-light emitting diode devices and may be an excellent candidate for highly thermally stable and solvent-resistant blue fluorescent material because it is almost insoluble in most common solvents such as ethanol, chloroform, ethyl acetate, acetone, acetonitrile, benzene, and water.

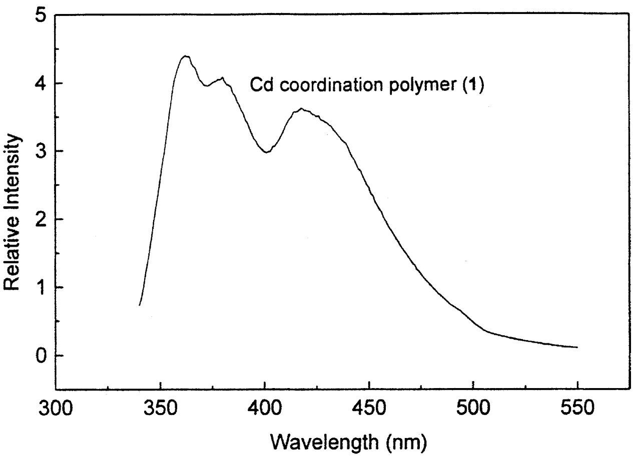

Fig. 4. Fluorescent emission spectrum of **1** at the solid state ($\lambda_{ex} = 250$ nm).

In conclusion, we have synthesized an unprecedented 1D Cd coordination polymer in which each unit contains an M_2L_2 type rectangular molecular box as building block with blue fluorescent emission using 4-sulfobenzoic acid under hydrothermal conditions. At present, we are trying to use other chiral ligands instead of 4-sulfobenzoic acid in order to obtain some chiral molecular boxes.

Supplementary material

X-ray crystallographic files in CIF format for compound **1** is available from Prof. S.-M. Peng and Dr. Ren-Gen Xiong.

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