Synthesis and Characterization of a Novel Coordination Complex Based on Fluorescein: Postprint

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Abstract

A novel coordination complex, {[Cd2(C20H10O5)2(H2O)4]·10H2O}n, has been synthesized based on fluorescein (2-(6-hydroxy-3-oxo-3H-xanthen-9-yl) benzoic acid) and systematically characterized by elemental analysis, infrared (IR) spectrum, thermo gravimetric analysis (TGA), powder X-ray diffraction (PXRD) and single-crystal X-ray diffraction. Compound 1 crystallizes in monoclinic, space group P2/n with a = 20.428(5), b = 8.084(2), c = 21.689(5) Å,   = 96.360(5)º, Mr = 993.46, V = 3559.7(15) Å3, Z = 4, Dx = 1.845 g/cm3,   = 1.276 mm-1, F(000) = 1974.0, GOOF = 1.044, (MoK) = 0.71073 Å, the final R = 0.0553 and wR = 0.1720 for 7245 observed reflections with I > 2 (I).

Full Text

Preamble

Synthesis and Characterization of a Novel Coordination Complex Based on Fluorescein

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ABSTRACT

A novel coordination complex, {[Cd (C H O) (H O)] · 10H O} , has been synthesized based on fluorescein (2-(6-hydroxy-3-oxo-3H-xanthen-9-yl)benzoic acid) and systematically characterized by elemental analysis, infrared (IR) spectroscopy, thermogravimetric analysis (TGA), powder X-ray diffraction (PXRD), and single-crystal X-ray diffraction. Compound 1 crystallizes in the monoclinic space group P2 /n with unit cell parameters a = 20.428(5), b = 8.084(2), c = 21.689(5) Å, = 96.360(5)°, M = 993.46, V = 3559.7(15) Å^3, Z = 4, D = 1.845 g/cm^3, = 1.276 mm ^{1}, F(000) = 1974.0, GOOF = 1.044, (MoK) = 0.71073 Å. The final R = 0.0553 and wR = 0.1720 for 7245 observed reflections with I > 2 (I).

Keywords: crystal structure; coordination complex; fluorescein

1 INTRODUCTION

The design and synthesis of coordination complexes have attracted considerable attention in the field of coordination polymers due to their structural diversity and versatile applications in photochemistry, catalysis, gas absorption and separation, energy storage and conversion, and other areas. Employing functional ligands has become a widespread strategy for the purposeful construction of coordination polymers with specific structures and properties. Fluorescein, a classic dye first synthesized in the 19th century, has recently garnered particular interest because it is widely used as a colorant and biochemical probe in daily life, owing to its broad emission spectrum, high fluorescence quantum yield, and non-toxic properties. However, among all reported metal coordination complexes containing fluorescein, few have been accompanied by crystal structure determination.

Herein, we report the synthesis and structure of a six-coordinated cadmium complex based on fluorescein, {[Cd (C H O) (H O)] · 10H O} (1), which possesses a unique Cd O cluster.

2 EXPERIMENTAL

2.1 Materials and Instruments

All solvents and reagents were purchased from commercial sources of analytical reagent grade and used without further purification. Infrared spectra were measured on a Vertex 70 instrument using KBr pellets. Elemental analysis of compound 1 was performed using a Vario EL-Cube elemental analyzer. Thermogravimetric analysis was conducted on a TGA/DSC 1 STARe system at a heating rate of 10 °C/min under a nitrogen atmosphere. Powder X-ray diffraction was performed at room temperature on a Rigaku MiniFlex II diffractometer using CuK radiation (= 0.154 nm).

2.2 Synthesis Procedures

Fluorescein (16.7 mg, 0.05 mmol) was dissolved in 1.8 mL DMF, after which 2.2 mL of an aqueous solution of Cd(NO) (14.9 mg, 0.05 mmol) was added. Following ten minutes of ultrasonic processing in open air, the mixture was sealed in a 10 mL glass vessel, heated to 383 K, and maintained at this temperature for two days before being slowly cooled to room temperature over another two days. Red block-shaped single crystals were filtered, washed with pure water, and dried in air. Yield: 27% (based on fluorescein). Calculated (%): C, 49.71; H, 2.90; O, 23.18. Found (%): C, 49.16; H, 2.72; O, 23.85.

2.3 X-ray Crystallographic Study

A suitable red prism single crystal of 1 was selected and mounted on a glass fiber for single-crystal X-ray diffraction analysis. The SCXRD measurement was performed on a Saturn 724+ CCD diffractometer with MoK radiation (= 0.71073 Å) at T = 293 K. Data reduction was processed using CrystalClear software, and cell parameters were reduced and refined using the same program. The structure was solved and refined using Olex2-1.2.8 with the ShelXS program (Direct Methods) for structure solution and ShelXL (least-squares method) for refinement. All non-hydrogen atoms were refined anisotropically. One of the oxygen atoms of the carboxylate group on fluorescein was disordered and modeled over two sites. Hydrogen atoms for fluorescein ligands were placed in calculated positions and treated as riding on their parent atoms before the final cycle of refinement, whereas hydrogen atoms of unbound water molecules were not included due to large thermal vibrations that made them difficult to locate. A total of 8161 reflections for 1 were collected in the range 2.52 27.49° using an -scan mode (-26 h 25, -10 k 10, -28 l 28), of which 7245 were independent with R = 0.0377. The final R = 0.0552 and wR = 0.1716 for 8161 observed reflections with I > 2 (I), with (Δ/) = 0.001. Selected bond lengths and bond angles related to Cd1 and Cd2 for 1 are listed in Table 1 .

3 RESULTS AND DISCUSSION

3.1 Structural Description

Single-crystal X-ray diffraction study reveals that compound 1 crystallizes in the monoclinic system with space group P2 /n, forming a two-dimensional layer that packs to afford a three-dimensional structure. In one asymmetric unit, there exist two cadmium atoms, two fluorescein ligands, and four coordinating water molecules. Four Cd atoms are bonded to a single fluorescein ligand (Fig. 1a [Figure 1: see original paper]), while each Cd(II) ion is hexa-coordinated by four oxygen atoms from four different fluorescein ligands and two water molecules in an octahedral coordination geometry (Fig. 1b). The disordered oxygen atoms have been simplified for clarity.

Notably, two adjacent Cd atoms are bridged by two -O atoms from two independent fluorescein ligands (Fig. 1c), with each Cd further connected to two additional fluorescein ligands and two water molecules, forming a unique Cd O cluster. The Cd-O bond lengths range from 2.218(4) to 2.361(5) Å, while the Cd-O-Cd bond angles are 104.076(1)° and 104.388(1)°, and the O-Cd-O bond angles vary from 75.711(1)° to 172.234(1)°. Of the six coordinating fluorescein ligands associated with this cluster, two contribute the bridging -O atoms O(5) and O(10), two provide the other coordinating O atoms O(3) and O(8), and the remaining two ligands supply the coordinating O atoms from their carboxylate groups, O(1) and O(6). The other four coordination sites are occupied by water molecules.

Two types of weak - interactions are observed between two sets of parallel fluorescein ligands, with centroid-to-centroid distances of 4.312/4.317 Å and perpendicular distances of 3.326/3.387 Å, respectively. The Cd O clusters are linked through fluorescein ligands via these weak - interactions and seven distinct hydrogen bonding interactions (Table 2), affording an intricate two-dimensional layer structure (Fig. 2 [Figure 2: see original paper]). This layer further packs through weak - interactions and a C(23)-H(23)···O(14) hydrogen bond to form the complete three-dimensional structure containing two types of nanochannels (Fig. 3 [Figure 3: see original paper]).

3.2 Characterizations

3.2.1 Powder X-ray Diffraction The crystalline phase purity of compound 1 was confirmed by powder X-ray diffraction. The experimental pattern agreed well with the simulated pattern (Fig. 4a [Figure 4: see original paper]). The sample was kept in open air for two days with no significant loss of crystallinity, indicating that 1 is quite stable toward water and oxygen.

3.2.2 IR Spectroscopy Infrared spectroscopy provided characteristic absorption bands for compound 1. IR data (KBr, cm ^{1}): (Ar-O) 1290 (s), 1328 (s); (COO) 1513 (m), 1207 (m); (COO) 1577 (s), 1452 (s).

3.2.3 Thermogravimetric Analysis Thermogravimetric analysis was conducted to determine the solvent content and thermal stability of compound 1. The TGA curve (Fig. 4b [Figure 4: see original paper]) shows several weight loss processes across the full measurement range (30-900 °C). The first stage occurs from 30 to 120 °C, corresponding to the loss of ten water molecules of crystallization. The second stage from 120 to 158 °C is attributed to the release of four coordinated water molecules. A plateau from 158 to 475 °C follows, indicating that the framework possesses excellent thermal stability in this temperature range. The sudden weight drop after 475 °C can be attributed to collapse of the framework.

4 CONCLUSION

In summary, a novel cadmium-fluorescein coordination complex has been synthesized via hydrothermal reaction and systematically characterized. Single-crystal X-ray diffraction analysis reveals that compound 1 possesses a unique Cd O core, which is linked by fluorescein ligands to afford a two-dimensional layer that packs into a three-dimensional supramolecular structure, with two different types of one-dimensional channels observed.

REFERENCES

(1) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B. L.; Reineke, T. M.; O' Keeffe, M.; Yaghi, O. M. Modular chemistry: secondary building units as a basis for the design of highly porous and robust metal-organic carboxylate frameworks. *Acc. Chem. Res.* **2001**, *34*, 319-330.

(2) Janiak, C. Engineering coordination polymers towards applications. *Dalton Trans.* **2003**, *14*, 2781-2804.

(3) Kitagawa, S.; Kitaura, R.; Noro, S. Functional porous coordination polymers. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334-2375.

(4) Furukawa, K.; Cordova, K. E.; Keeffe, M. O.; Yaghi, O. M. The chemistry and applications of metal-organic frameworks. *Science* **2013**, *341*.

(5) Wang, C. H.; Liu, X. L.; Demir, N. K.; J. Paul Chen, J. P.; Li, K. Applications of water stable metal-organic frameworks. *Chem. Soc. Rev.* **2016**, *45*.

(6) Hu, Z. C.; Deibert, B. J.; Li, J. Luminescent metal-organic frameworks for chemical sensing and explosive detection. *Chem. Soc. Rev.* **2014**, *43*.

(7) Lee, J. Y.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyena S. B. T.; Hupp J. T. Metal-organic framework materials as catalysts. *Chem. Soc. Rev.* **2009**, *38*, 1450-1459.

(8) Li, J. R.; Kupplera, R. J.; Zhou, H. C. Selective gas adsorption and separation in metal-organic frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1477-1504.

(9) Li, J. R.; Sculley, J. L.; Zhou, H. C. Metal-organic frameworks for separations. *Chem. Rev.* **2012**, *112*, 869-932.

(10) Xia, W.; Mahmood, A.; Zou, R.; Xu, Q. Metal-organic frameworks and their derived nanostructures for electrochemical energy storage and conversion. *Energy Environ. Sci.* **2015**, *8*, 1837-1866.

(11) Wang, L.; Han, Y. Z.; Feng, X.; Zhou, J. W.; Qi, P. F.; Wang, B. Metal-organic frameworks for energy storage: batteries and supercapacitors. *Coord. Chem. Rev.* **2016**, *307*, 361-381.

(12) Robin, A. Y.; Fromm, K. M. Coordination polymer networks with O- and N-donors: what they are, why and how they are made. *Coord. Chem. Rev.* **2006**, *250*, 2127-2157.

(13) Tranchemontagne, D. J.; Mendoza-Cortés, J. L.; Keeffea, M. O.; Yaghi, O. M. Secondary building units, nets and bonding in the chemistry of metal-organic frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1257-1283.

(14) Stock, N.; Biswas, S. Synthesis of metal-organic frameworks (MOFs): routes to various MOF topologies, morphologies, and composites. *Chem. Rev.* **2012**, *112*, 933-969.

(15) Li, S. Z.; Huo, F. W. Metal-organic framework composites: from fundamentals to applications. *Nanoscale* **2015**, *7*, 7482-7501.

(16) Baeyer, A. Ueber eine neue Klasse von Farbstoffen. *Ber. Dtsch. Chem. Ges.* **1871**, *4*, 555-558.

(17) Xiong, X. Q.; Song, F. L.; Wang, J. Y.; Zhang, Y. K.; Xue, Y. Y.; Sun, L. L.; Jiang, N.; Gao, P.; Tian, L.; Peng, X. J. Thermally activated delayed fluorescence of fluorescein derivative for time-resolved and confocal fluorescence imaging. *J. Am. Chem. Soc.* **2014**, *136*, 9590-9597.

(18) Ge, J. C.; Jia, Q. Y.; Liu, W. M.; Guo, L.; Liu, Q. Y.; Lan, M. H.; Zhang, H. Y.; Meng, X. M.; Wang, P. F. Red-emissive carbon dots for fluorescent, photoacoustic, and thermal theranostics in living mice. *Adv. Mater.* **2015**, *27*, 4169-4177.

(19) Walkup, G. K.; Burdette, S. C.; Lippard, S. J.; Tsien R. Y. A new cell-permeable fluorescent probe for Zn^2 . *J. Am. Chem. Soc.* **2001**, *122*, 5644-5645.

(20) McCormick, T. M.; Han, Z. J.; Weinberg, D. J.; Brennessel, W. W.; Holland, P. L.; Eisenberg R. Impact of ligand exchange in hydrogen production from cobaloxime-containing photocatalytic systems. *Inorg. Chem.* **2011**, *50*, 10660-10666.

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