Syntheses, Crystal Structures, and Photoluminescent Properties for One New Cd(II) CP Based on 3,5-Bis(4 -carboxy-phenyl)-1,2,4-triazole and 1,4-Bis(imidazol-1-ylmethyl)benzene (Postprint)

Authors: HOU Xiang-Yang, Xiao Wang, REN Yi-Xia, WANG Ji-Jiang, JIN Wei, KANG Wei-Wei, MA Xin, HAN Xing-Xing

Date: 2017-11-05T00:00:00+00:00

Abstract

One new coordination polymer (CP) [Cd(bct)(bib)]·2(H2O) (1), based on 3,5-bis(4 -carboxy- phenyl)-1,2,4-triazole (H2bct) and 1,4-bis(imidazol-1-ylmethyl)benzene(bib), has been synthesized by hydrothermal method, and its structure was determined and characterized by single-crystal X-ray diffraction analysis, elemental analysis, IR spectroscopy, and thermogravimetric analysis. The crystal structure of CP 1 is a three-dimensional framework with (3,5)-connected topology, where the bct ligands adopt a µ3-kO,kO,kO coordination mode connecting with three Cd centers and the bib ligands adopt a µ2-kN,kN coordination mode bridging two Cd ions. It crystallizes in monoclinic system, space group C2/c, with a = 2.6838(4), b = 1.24221(17), c = 1.8011(2) nm, = 102.939(2)º, V = 5.8522(13) nm3, Z = 8, C30H27CdN7O6, Mr = 694.00, Dc = 1.566 g/cm3, F(000) = 2784, S = 1.055, R = 0.0294 and wR = 0.0731. Furthermore, solid-state photoluminescence measurements show that CP 1 produces strong emissions at room temperature.

Full Text

Syntheses, Crystal Structures, and Photoluminescent Properties for One New Cd(II) CP Based on 3,5-Bis(4 -carboxy-phenyl)-1,2,4-triazole and 1,4-Bis(imidazol-1-ylmethyl)benzene

HOU Xiang-Yang; WANG Xiao; REN Yi-Xia; WANG Ji-Jiang; JIN Wei; KANG Wei-Wei; MA Xin; HAN Xing-Xing

Department of Chemistry and Chemical Engineering, Yan’ an University Laboratory of New Energy & New Function Materials, Yan’ an University, Yan’ an, Shaanxi 716000, China

ABSTRACT

One new coordination polymer (CP) [Cd(bct)(bib)]·2(H O) (1), based on 3,5-bis(4 -carboxy-phenyl)-1,2,4-triazole (H bct) and 1,4-bis(imidazol-1-ylmethyl)benzene (bib), has been synthesized by hydrothermal method, and its structure was determined and characterized by single-crystal X-ray diffraction analysis, elemental analysis, IR spectroscopy, and thermogravimetric analysis. The crystal structure of CP 1 is a three-dimensional framework with (3,5)-connected topology, where the bct ligands adopt a μ -kO,kO,kO coordination mode connecting with three Cd centers and the bib ligands adopt a μ -kN,kN coordination mode bridging two Cd ions. It crystallizes in monoclinic system, space group C2/c, with a = 2.6838(4), b = 1.24221(17), c = 1.8011(2) nm, = 102.939(2)º, V = 5.8522(13) nm^3, Z = 8, C H CdN O , M = 694.00, Dc = 1.566 g/cm^3, F(000) = 2784, S = 1.055, R = 0.0294 and wR = 0.0731. Furthermore, solid-state photoluminescence measurements show that CP 1 produces strong emissions at room temperature.

Keywords: cadmium CPs; synthetic, crystal structure; fluorescence
DOI: 10.14102/j.cnki.0254-5861.2011-1628

1. INTRODUCTION

In recent years, functional CPs have received considerable attention owing to their intriguing structures[1-3] and promising applications in catalysts, adsorption, magnetism, and so on[4-7]. Especially, luminescent coordination compounds have attracted intensive research interest for their potential applications as chemical sensors, light-emitting devices, etc. It is well established that many factors, such as pH values, molar ratios between metal ions and ligands, reaction temperature, in particular, the coordination ability of metal centers and the coordination sites in organic ligands, have significant influence on the assembly process of MOFs[8-11].

Therefore, systematic researches of the effect of these factors on the assembly process are a key challenge to construct desirable coordination polymers by using proper ligands. In the reported studies, organic aromatic polycarboxylate ligands are good candidates for the construction of metal organic frameworks due to their various coordination modes to metal ions.

Recently, we have been interested in the use of semirigid multicarboxylate linkers, such as pyridine-3,5-bis(phenyl-4-carboxylic acid), 3,5-bis(3-carboxyphenyl)-1,2,4-triazole, 1,4-bis(1,2,4-triazol-1-yl)butane, 1,4-bis(2-methyl-imidazol-1-yl)-butane, 1,3-bis(5,6-dime-thylbenzimidazole)butane, 1,4-bis(N-imidazolyl)butane, etc. to construct coordination polymers and to promote the investigation of structure-property relationship. Many interesting frameworks have been observed[12-15].

In continuation of this theme, we choose semirigid ligand H bct and bib as the neutral ligands to attempt to build coordination polymers and to investigate their structure-related properties. This has two obvious characteristics. Firstly, H bct adopts various coordination modes when it coordinates to metals and thus may produce various structures; secondly, the introduction of a second bridging ligand to extend the metal carboxylate systems is one of the common ways to obtain higher dimensional networks. Using hydrothermal method, compound 1 formulated as [Cd(bct)(bib)]·2(H O) has been synthesized. In this contribution, we present the syntheses and detailed structure descriptions of CP 1, thermal stability analyses, as well as the photoluminescent investigations.

2. EXPERIMENTAL

2.1 Materials and Methods

All chemicals of analytical grade were commercially available and used without further purification. The elemental analyses were performed on an Elementar Vario EL III microanalyzer. The FT-IR spectra were obtained on a Perkin-Elmer Spectrum using KBr disks in the range of 4000–400 cm^{1}. Thermogravimetric analysis (TGA) experiments were done on a NETZSCH STA449C Jupiter thermogravimetric analyzer in the nitrogen atmosphere at a heating rate of 10 K min^{1}. Photoluminescence analyses of the solid samples were performed on an Edinburgh Instrument F920 fluorescence spectrometer at ambient temperature.

2.2 Synthesis of [Cd(bct)(bib)]·2(H O) (1)

A mixture of H bct (0.5 mmol), bib (0.5 mmol), Cd(CH COO) ·2H O (0.5 mmol), and NaOH (1.0 mmol) in aqueous solution (15 mL) was sealed into a 25 mL poly(tetrafluoroethylene)-lined stainless-steel container under autogenous pressure and then heated at 130 °C for 4 days and cooled to 30 °C at a rate of 5 °C·h^{1}. Colorless block crystals suitable for X-ray analyses were obtained, washed with distilled water and dried in air. Yield: 46% (based on Cd) for 1. Anal. Calcd. for C H N O Cd: C, 51.92; H, 3.92; N, 14.13%. Found: C, 51.86; H, 3.81; N, 14.33%.

2.3 Crystal Structure Determination

The single-crystal X-ray diffraction measurement was performed on a Bruker Smart-1000CCD for 1, which is equipped with a graphite-monochromated MoK radiation source (= 0.71073 Å) by a - scan mode (1.81 26.37°). A total of 16127 reflections were collected and 5986 were independent (R_int = 0.0367), of which 4710 were observed with I > 2 (I). The structure was solved by direct methods using the SHELXS-97[16]. The subsequent successive difference Fourier syntheses yielded other non-hydrogen atoms. The final structure was refined using a full-matrix least-squares refinement on F^2 by SHELXL-97[17]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to oxygen were located from difference Fourier maps. The remaining hydrogen atoms were calculated in idealized positions and allowed to ride on their parent atoms. The final R = 0.0271 and wR = 0.0593 (w = 1/[^{2}(F_o^2) + (0.030P)^2 + 4.5526P], where P = (F_o^2)/3) for 4710 observed reflections. (Δ/)_max = 0.001, (Δ)_max = 1.005 and (Δ)_min = -1.296 e/Å^3. The selected interatomic distances are given in Table 1 .

3. RESULTS AND DISCUSSION

3.1 Crystal Structure of [Cd(bct)(bib)]·2(H O) (1)

X-ray single-crystal diffraction analysis reveals that 1 is a 3D framework incorporating two 1D double-strand chains. It crystallizes in the monoclinic crystal system with space group C2/c. The asymmetric unit contains one Cd^2 ion, one H bct ligand, one bib, and two guest water molecules. As shown in Fig. 1a [Figure 1: see original paper], the Cd(1) is five-coordinated by three oxygen atoms (O(1), O(2#1), O(4#2), #1: 0.5 -x, 0.5 -y, -z; #2: -0.5 + x, 0.5 -y, 0.5 + z) from three H bct ligands and two nitrogen atoms (N(4), N(7#3), #3: 0.5 + x, -0.5 + y, z) from two bib ligands, displaying a distorted triangular bipyramidal geometry. The Cd–O and Cd–N bond lengths fall in the range of 0.2259(2)–0.2385(2) nm, which are well-matched with those observed in similar complexes[18].

Two carboxylate groups of the bct ligands show two coordination modes that coordinate to Cd^2 respectively in CPs 1. One carboxylate group (O(3), O(4)) of bct anions forms bonds to one Cd^2 ion through a μ -kO mode, while another (O(1), O(2)) to two Cd^2 ions through the μ -kO,kO mode. Thus, each bct ligand shares the same coordination environment by coordinating to three cadmium ions with its two carboxylate groups in all (Fig. 1b). The nearest Cd atoms are bridged via carboxyl oxygen atoms to form a dimer unit [CdCO] with the Cd···Cd separation of 3.9306 Å. In turn, each deprotonated dianionic bct^2 ligand links two [CdCO] via two carboxylate groups, resulting in a 1D double-strand chain along the a axis. The shortest Cd···Cd separation in the 1D chain is 17.7635 Å. The bib ligand provides nitrogen atom (N(4), N(7)) as binding sites to interval link the basic units [CdCO] of adjacent 1D double chains, giving rise to a 2D layered undulating framework in the ac plane (Fig. 1c). Further, the bib ligands in accordance with identical chain method link the remaining basic units [CdCO] of adjacent 1D double chains along the b axis, which changes the framework from 2D to 3D (Fig. 1d). To analyze the net, we can define the bct ligands and Cd(II) as three- and five-connected nodes, and the bib ligands are regarded as lines. These two nonequivalent nodes lead to a (3,5)-connected topology network of CP 1, as shown in Fig. 1e. The strong intermolecular hydrogen bonding interactions formed between two lattice water molecules (O(5), O(6)), the oxygen atoms (O(3), O(4)) and the nitrogen atoms (N(2), N(3)) of bct ligands. The geometrical parameters of all hydrogen bonds are listed in Table 2 . It is worth nothing that hydrogen bonding interactions play a critical role in stabilizing the structure.

3.2 IR Spectra

The IR spectra display characteristic absorption bands for water molecules, carboxylate, and phenyl units (Fig. 2 [Figure 2: see original paper]). CP 1 shows broad absorption bands in the range of 3100–3700 cm ^{1}, which indicates the presence of O–H stretching frequencies of coordinated water molecules. CP 1 also exhibits strong characteristic absorption around the frequency range of 1500–1700 cm ^{1} _asCOO . The characteristic IR band of the phenyl ring at 840–870 cm ^{1} due to the =C–H vibrations for 1.

3.3 Thermogravimetric Analyses

The thermal analysis curve of complex 1 was investigated. The first weight loss of 5.31% observed from 80 to 270 °C of complex 1 corresponds to the departure of one coordinated water molecule (calculated 5.19%). It keeps losing weight from 290 to 430 °C (observed 34.57%, calculated 34.34%), which can be attributed to the removal of the remaining bib ligand. Above 650 °C, a plateau region is observed, implying that the bct decomposes. The framework further decomposes from 320 to 460 °C, which is attributed to the decomposition of the framework.

3.4 UV-Visible Spectra

The UV-vis absorption spectra of the free ligand H bct and CP 1 measured in solid state are shown in Fig. 3 [Figure 3: see original paper]. The absorption maxima are 267 and 343 nm for H bct, which can be attributable to the singlet-singlet n- * and - * absorptions of the aromatic and triazine rings. Nevertheless, compared with the H bct ligand, a slight blue shift is discernible in the absorption maximum of CP 1, which could be assigned to the perturbation induced by the metal ion coordination.

3.5 Luminescent Property

Considering coordination complexes with d^{1} metal ions usually indicate relatively strong luminescence, the solid-state photoluminescence properties of complex 1, the corresponding free H bct and bib ligands have been investigated at room temperature (Fig. 4 [Figure 4: see original paper]). The pure H bct and bib ligands show emission of 420 and 440 nm under 350 and 360 nm excitation. Complex 1 excited at 420 nm produces an intense emission band with a maximum at 360 nm, compared with the emission spectra of H bct and bib ligands, a certain degree of red shift in complex 1 was observed. Since the Cd(II) ion is difficult to oxidize or reduce due to its electronic configuration, the emission bands of the related complexes are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature[19].

4. CONCLUSION

One new CPs [Cd(bct)(bib)]·2(H O) (1) has been synthesized by hydrothermal methods, and the structure was determined and characterized by single-crystal X-ray diffraction analysis, elemental analysis, IR spectroscopy, and thermogravimetric analysis. The crystal structure of complex 1 is a three-dimensional framework, where the bct ligands adopt a μ -kO,kO,kO coordination mode connecting with three Cd^{2} centers and the bib ligands adopt a μ -kN,kN coordination mode bridging two Cd^{2} ions. Furthermore, solid-state photoluminescence measurements show that complex 1 produces strong emission at room temperature. Most interestingly, the reported complex [Cd(bct)(H O)]·3(H O)[20] (H bct = 3,5-bis(4 -carboxyphenyl)-1,2,4-triazole) is a one-dimensional framework, where the bct ligands adopt a μ -kO,kO,kO coordination mode connecting with three Cd centers. And compared with complex 1, the bib ligands dominantly affect the formation of the 3D structure and luminescent properties for CP 1.

REFERENCES

(1) Gao, R.; Zhou, S. X.; Li, W.; Chen, M.; Wu, L. M. Facile synthesis of uniform and well-defined single-crystal sodium tantalate cubes and their assembly into oriented two-dimensional nanofilm. CrystEngComm. 2013, 14, 7031–7035.

(2) Li, X. J.; Yu, Z. J.; Guan, T.; Li, X. X.; Ma, G. C.; Guo, X. F. Substituent effects of isophthalate derivatives on the construction of zinc(II) coordination polymers incorporating flexible bis(imidazolyl) ligands. Cryst. Growth Des. 2015, 15, 278–290.

(3) Borjigin, T.; Sun, F.; Zhang, J.; Cai, K.; Ren, H.; Zhu, G. A. Microporous metal-organic framework with high stability for GC separation of alcohols from water. ChemCommun. 2012, 48, 7613–7615.

(4) Yang, J.; Ma, J. F.; Batten, S. R. Polyrotaxane metal-organic frameworks (MOFs). ChemCommun. 2012, 48, 7899–7912.

(5) Lu, J. F.; Liu, J.; Jiang, M.; Ge, H. G. Synthesis, structure and luminescent property of a 2D Cd(II) coordination polymer based on mixed-ligands of 1,3-bis(imidazol)propane and pyridine-3,5-dicarboxylic acid. Chin. J. Struct. Chem. 2015, 2, 248–252.

(6) Hen, S. Y.; Yang, E.; Xie, C. L.; Xiao, X. F. Synthesis, structure and luminescent property of a new Zn( ) coordination polymer based on 1,3,5-benzenetricarboxylate and 4,4 -bipyridine ligands. Chin. J. Struct. Chem. 2015, 2, 235–240.

(7) Zhang, J. P.; Zhang, Y. B.; Lin, J. B.; Chen, X. M. Metal azolate

frameworks: from crystal engineering to functional materials. Chem. Rev. 2012, 112,

(8) Chen, W. X.; Wu, S. T.; Long, L. S.; Huang, R. B.; Zheng, L. S. Construction of a three-fold parallel interpenet-ration network and bilayer structure based on copper(II) and trimesic acid. Cryst. Growth Des. 2007, 7, 1171–1175.

(9) Fang, R. Q.; Zhang, X. M. Diversity of coordination architecture of metal 4,5-dicarboxyimidazole. Inorg.Chem. 2006, 45, 4801–4810.

(10) Hunger, J.; Krautscheid, H.; Sieler, J. Hydrothermal synthesis and structure of coordination polymers by combination of bipyrazole and aromatic dicarboxylate ligands. Cryst. Growth Des. 2009, 9, 4613–4625.

(11) Zhai, Q. G.; Lin, Q. P.; Wu, T.; Zheng, S. T.; Bu, X. H.; Feng, P. Y. Induction of trimeric [Mg (OH)(CO)] in a porous framework by a desymmetrized tritopic ligand. Dalton Trans. 2012, 41, 2866–2868.

(12) Jia, J. H.; Lin, X.; Wilson, C.; Blake, A. J.; Champness, N. R.; Walker, G.; Cussen, E. J.; Schroder, M. Twelve-connected porous meta-organic frameworks with high H adsorption. Chem. Commun. 2007, 8, 840–842.

(13) Han, M. L.; Wang, J. G.; Ma, L. F.; Guo, H.; Wang, L. Y. Construction of Cd(II) coordination polymers based on R-isophthalate (R = -CH or -OCH) and flexible N-donor co-ligands: syntheses, structures and photoluminescence. CrystEngComm. 2012, 14, 2691–2701.

(14) Jiao, C. H.; He, C. H.; Geng, J. C.; Cui, G. H. Syntheses, structures, and photoluminescence of three cadmium(II) coordination polymers with flexible bis(benzimidazole) ligands. J. Coord. Chem. 2012, 65, 2852–2861.

(15) SAINT, Version 6.02A.; Bruker AXS Inc.: Madison W12002.

(16) Sheldrick, G. M. SHELXS-97, Program for the Solution of Crystal Structures. University of Gottingen, Germany 1997.

(17) Sheldrick, G. M. SHELXL-97, Program for the Refinement of Crystal Structures. University of Gottingen, Germany 1997.

(18) Agarwal, R. A. Structural diversity luminescence properties novel {[Zn(TBIB)(HBTC)] · 3H O} {[Cd (TBIB) (BTC)] · 2C H OH · 11H O} coordination polymers. Polyhedron 2015, 85, 740–747.

(19) Huang, X. Y.; Yue, K. F.; Jin, J. C.; Liu, J. Q.; Wang, C. J.; Wang, Y. Y.; Shi, Q. Z. Three-dimensional fivefold interpenetrating microporous

metal-organic framework based on mixed flexible ligands. Inorg. Chem. Commun. 2010, 13, 338-341.

(20) Yu, M. H.; Hu, M.; Wu, Z. T. Synthesis, crystal structures and properties of transition metal coordination polymers based on a rigid triazole dicarboxylic acid. RSC. Adv. 2013, 3, 25175-25183.

Fig. 1a. Coordination environment of Cd(1) in 1. Symmetry codes: #1: 0.5 -x, 0.5 -y, -z; #2: -0.5 + x, 0.5 -y, 0.5 + z; #3: 0.5 + x, -0.5 + y, z

Fig. 1b. Coordination environment of bct in CPs 1 and 2

Fig. 1c. 2D structure of [Cd(bct)(bib)] · 2(H O) (1)

Fig. 1d. 3D structure of [Cd(bct)(bib)] · 2(H O) (1)

Fig. 1e. Topology structure of [Cd(bct)(bib)] · 2(H O) (1)

Fig. 2. Infrared spectroscopy of [Cd(bct)(bib)] · 2(H O) (1)

Fig. 3. UV-vis absorption of H bct and complex 1

Fig. 4. Emission spectra of complex 1, H bct and bib in the solid state at room temperature

Table 1. Selected Bond Lengths (nm) and Bond Angles (°) in CP 1

Bond/Angle	Value
Cd(1)-O(1)	0.2376(2)
Cd(1)-O(4)#2	0.2385(2)
Cd(1)-O(2)#1	0.2347(2)
Cd(1)-N(7)#3	0.2266(2)
Cd(1)-N(4)	0.2259(2)
N(7)#3-Cd(1)-O(2)#1	87.27(9)
N(7)#3-Cd(1)-O(1)	84.54(8)
N(7)#3-Cd(1)-O(4)	88.70(5)
O(2)-Cd(1)-O(2)#1	74.62(8)
O(4)-Cd(1)-N(7)	88.93(2)
O(2)#1-Cd(1)-O(4)#2	95.48(5)
O(1)-Cd(1)-O(2)#1	126.37(9)

Symmetry codes: #1: 0.5 -x, 0.5 -y, -z; #2: -0.5 + x, 0.5 -y, 0.5 + z; #3: 0.5 + x, -0.5 + y, z

Table 2. Hydrogen Bond Lengths (Å) and Bond Angles (°) for CP 1

D-H ⋯ A	d(D-H)/Å	d(H ⋯ A)/Å	d(D ⋯ A)/Å	DHA/°
N(2)-H(2A)#4 ⋯ O(6)	-	-	2.695(3)	-
O(5)-H(5A) ⋯ N(3)#1	-	-	2.883(4)	-
O(5)-H(5B) ⋯ O(1)	-	-	2.873(3)	-
O(6)-H(6A) ⋯ O(3)#2	-	-	2.824(3)	-
O(6)-H(6B) ⋯ O(4)#3	-	-	2.990(3)	-

Symmetry codes: (a) -x, -y+1, -z; (b) -x+1/2, -y+3/2, -z; (c) x, y, z-1

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

Source: ChinaXiv —Machine translation. Verify with original.