



Unique entangling Cd^{II}-framework featuring 2D → 3D inclined polycatenate motif and (4,6)-connected self-catenated H-bonding topology

Xi-Jun Ke^a, Dong-Sheng Li^{a,b,*}, Jun Zhao^a, Liang Bai^a, Jing-Jing Yang^a, Ya-Ping Duan^a

^a College of Mechanical & Material Engineering, Research Institute of Materials, China Three Gorges University, Yichang 443002, PR China

^b State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, PR China

ARTICLE INFO

Article history:

Received 6 March 2012

Accepted 18 April 2012

Available online 25 April 2012

Keywords:

Cadmium compound

Squaric acid

Topology

Luminescent property

ABSTRACT

A novel Cd^{II}-coordination framework [Cd(C₄O₄)(btb)(H₂O)₂]_n (**1**) constructed by squaric acid (H₂C₄O₄) and secondary N-donor spacer 1,4-bis(1,2,4-triazol-4-yl)butane (btb) is presented, which displays 2D → 3D inclined polycatenate framework consisting of two of sets of equivalent 2D 4⁴-**sql** layers and (4,6)-connected self-catenated H-bonding topology. In addition, the thermal stability and photo-luminescence property of **1** were also investigated.

Crown Copyright © 2012 Published by Elsevier B.V. All rights reserved.

One of the traits of coordination networks is their topologically diverse and exceptionally beautiful structures, many of which are derived from minerals in nature. More importantly, these materials have unquestionably enormous potential for many practical applications, as detailed in several distinguished reviews [1,2]. Fundamentally, to reverse-engineer the pleasing structures from nature, the first step is to understand the underlying topological structures. For this goal, the network topological approach can serve as an effective tool to understand and further manipulate the complicated coordination networks in such practice [3,4]. Therefore, new or unusual network topologies are of considerable focus [5], particularly those deliberately constructed from the nodes with connectivity commonly displayed by typical metal ions and organic ligands used in coordination network synthesis. In this respect, they contain the required geometrical information and the directional binding modes that will facilitate the crystallization of coordination networks with pre-designed topologies. Meanwhile, particular attention has also been devoted to entangled systems for their undisputed beauty and potential applications as above-mentioned materials. As a result, a variety of novel entangled systems, such as interpenetrating, polycatenating, polythreading, polyknotting and molecular braids, have been discovered thus far [6]. Despite the meaningful progress in this hotspot, there is an unfavorable lack of systematic and characteristic researches on more sophisticated entangled architectures, especially cases for the relatively unusual polycatenation and self-catenated structures [7,8].

On the other hand, nodes of 3-, 4-, and 6-connectivity are of most relevance, and numerous such network topologies have been known [3,4,9]. However, examples for single-connected (3-4- and 6-c) and mixed connected ((3,6)-, (3,4)- and (4,6)-c) complicated entangled nets are quite rare [8], implying a challenging issue because it is difficult to predict such target materials prior to synthesis.

With this background information, our groups have been focusing our attention on utilizing polycarboxylate ligands with specific configuration and N-donor ancillary ligands and different metal ions for constructing novel topological networks [5b,8a,10]. As an extension of our work, a rigid square-planar tecton, squaric acid (H₂C₄O₄) was used to assemble with Cd^{II} in this work, incorporating secondary N-donor spacer 1,4-bis(1,2,4-triazol-4-yl)butane (btb). As expected, the entangled coordination polymer, [Cd(C₄O₄)(btb)(H₂O)₂]_n (**1**), was obtained, which displays 2D → 3D inclined polycatenation framework consisting of two of sets of equivalent 2D 4⁴-**sql** layers and (4,6)-connected self-catenated H-bonding topological structure.

Yellow block crystals of **1** were prepared by hydrothermal reaction of Cd^{II} acetate, squaric acid, btb, and NaOH [11], which were characterized by IR spectra, elemental analysis, PXRD, and TGA techniques. In the experimental process, we have also gained one isomorphous sample [Zn(C₄O₄)(btb)(H₂O)₂]_n (**2**) in same condition [12] (see the archived CIF file for detailed crystallographic data (CCDC-870040)). Therefore, only the structure and properties of **1** will be discussed as a representative in this communication. The asymmetric unit of **1** contains an independent Cd^{II} atom with 0.5 position occupation, which is located in crystallographic inversion center, half a C₄O₄²⁻ anion, half a btb linker, and one coordinated water molecule. Each Cd^{II} center takes a [CdO₄N₂] octahedral geometry (Fig. 1), being surrounded by four oxygen atoms from two C₄O₄²⁻ anions and two water molecules,

* Corresponding author at: College of Mechanical & Material Engineering, Research Institute of Materials, China Three Gorges University, Yichang, PR China. Tel./fax: +86 717 6397516.

E-mail address: lidongsheng1@126.com (D.-S. Li).

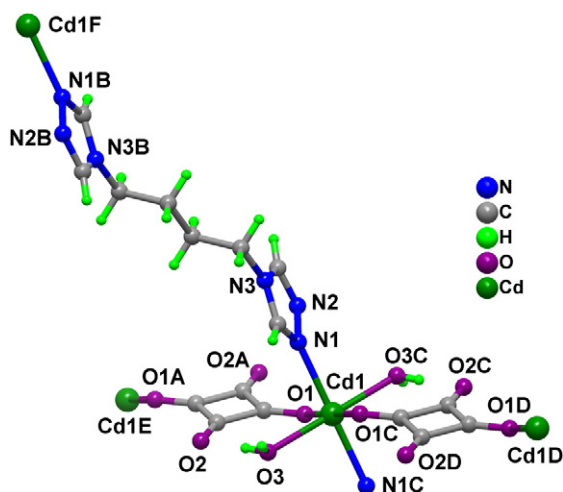


Fig. 1. Coordination environment of the Cd^{II} center in compound **1**. Symmetry codes: A $-x + 1, -y, -z$; B $-x + 2, -y + 1, -z + 1$; C $-x + 1, -y, -z + 1$; D $x, y, 1 + z$; E $x, y, -z + 1$; F $x + 1, y + 1, z$.

and two N-donors from two btb ligands. The Cd–N and Cd–O bond lengths vary from 2.292(2) to 2.307(2) Å, and the O/N–Cd–O/N are in the range of 86.2(3)–180.0° (Table S1), thus being in the normal range observed in other C₄O₄²⁻-based compounds [13,14].

Notably, in **1**, μ_2 -C₄O₄²⁻ and btb both serve as 2-connected spacer to bridge Cd^{II}, resulting in an extended unevenly 4⁴-**sql** net, as shown in Fig. 2a. The rectangular window has a dimension of 14.37 Å × 8.14 Å with angles of 76.3° and 103.7° (defined by Cd···Cd distances and Cd···Cd···Cd angles). Interestingly, packing of the layers generates two sets of layers oriented toward the [1, 1, 0] and [−1, 1, 0] direction (Fig. 2b), respectively, in which the angle between these two sets of layers is 75.6°. These two sets of layers catenate to each other in a parallel–parallel (p–p) arrangement to form a 2D → 3D inclined polycatenate framework (Fig. 2b and c). Further insight into one window of a layer shows that each window is catenated with other four windows from two adjacent layers in the other set via Hopf links (DOC = 4, Fig. 2d). The parallel/parallel inclined polycatenation is somewhat exceptional, although the 4⁴-**sql** net is rather common [15].

Since S. Neeraj et al. first synthesizing sodalite networks (M^{II}-suarate, M^{II} = Co^{II}, Mn^{II} and Zn^{II}) by making use of squaric acid as the 4-membered square unit [16], the squaric acid, H₂C₄O₄²⁻, has been widely used as a polyfunctional ligand, such as hydrogen bonding or π – π interactions, for the construction of extended supramolecular architectures and also used as a bridging ligand with various coordination modes to build up many coordination polymers with novel extended networks [13,14,17]. As expected, in this work, μ_2 -C₄O₄²⁻ is hydrogen bonded to two water ligands in same layer and other sets of layer, respectively (same layer: O3–H3A···O2, H···O/O···O distances: 1.904/2.715 Å; angle: 170.6°; other sets of layer: O3–H3B···O2G (symmetry code: $x, -y + 1/2, z + 1/2$), H···O/O···O distances: 1.850/2.697 Å; angle: 178.0°) (Fig. 3a), thus creating a zigzag hydrogen-bonded chain [···3HG–O3G–H3AG···O2G···H3B–O3–H3A···O2···]_n (Fig. 3a and b). Undoubtedly, these weak interactions may contribute to the additional stability of the whole structure.

From a topological point of view, if the strong H-bonding is considered, then C₄O₄²⁻ anions are 4-connecting and the Cd(H₂O)₂ moieties act as the 6-connected nodes. Thus a new (4,6)-connected H-bonding network is formed, which has dinoal topology with the point of (4⁴.6²)(4⁴.6¹⁰.8) (Fig. 3c). Significantly, this H-bonding network can be viewed as the cross-linking of 2D → 3D inclined polycatenation framework, in which the 6-membered circuits in **1** mutually interweave into a self-catenated architecture (Fig. 3d). In fact, only limited (4,6)-connected self-catenated networks have been known [18], and compound **1** represents the first example for such an architecture based on the cross-linking of 2D → 3D inclined polycatenate motifs.

To confirm the phase purity of the bulk materials, X-ray power diffraction (XRPD) experiments have been carried out. The XRPD experimental and computer-simulated patterns are in good agreement with each other, indicating phase purity of the as-synthesized products (Fig. S1). Compound **1** is air stable and can keep its crystalline integrity at ambient conditions. Thermogravimetric analysis of **1** (Fig. S2) demonstrates that the first weight loss in the temperature range of 130–190 °C, which can be ascribed to the removal of lattice water molecules (obsd: 8.08% and calcd: 7.95%), and the expulsion of organic components occurs at ca. 306 °C. Solid-state luminescence properties of **1** were investigated at room temperature. Upon excitation at ca. 310 nm, compound **1** exhibits the fluorescence emission band at ca. 410 and 457 nm. In comparison to that of the free squaric

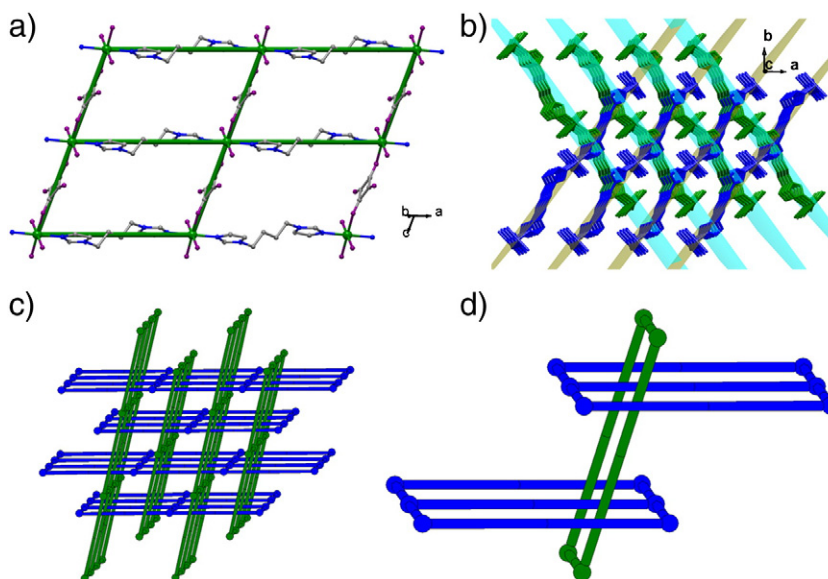


Fig. 2. (a) the unevenly 4⁴-**sql** layer constructed from Cd^{II} centers linked by C₄O₄²⁻ and btb ligands; (b) two sets of layers oriented in different directions with the dihedral angle of 75.6°; (c) schematic illustration of 2D → 3D inclined polycatenate framework; and (d) the topological links of the four-membered windows.

Download English Version:

<https://daneshyari.com/en/article/7750145>

Download Persian Version:

<https://daneshyari.com/article/7750145>

[Daneshyari.com](https://daneshyari.com)