

A new supramolecular net constructed with 2D (4,4) layer subunits displaying unique 4-connected msw/P42/nm topology: Structure, fluorescence and catalytic properties



Li Qin, Jing Zheng, Shu-Lin Xiao, Xiao-Hua Zheng, Guang-Hua Cui *

College of Chemical Engineering, Hebei United University, 46 West Xinhua Road, Tangshan, 063009, Hebei, PR China

ARTICLE INFO

Article history:

Received 28 March 2013

Accepted 9 May 2013

Available online 15 May 2013

Keywords:

Bis(benzimidazolyl)butane

Hydrogen bonds

Degradation

Supramolecular framework

ABSTRACT

A new three-dimensional supramolecular framework based on 1,4-bis(5,6-dimethylbenzimidazole)butane (L) with 5-hydroxyisophthalic acid (H₂hip) has been synthesized by hydrothermal reaction, namely, [Co(L)_{0.5}(hip)]_n, exhibiting an unprecedented topology architecture through hydrogen bonds, viz. supramolecular net 4-connected uninodal 3D net with (6⁵·8) msw/P42/nm topology. The fluorescence and remarkable catalytic performances of the complex for the degradation of methyl orange by sodium persulfate have been investigated.

© 2013 Elsevier B.V. All rights reserved.

Metal–organic frameworks (MOFs) and supramolecular framework have recently attracted much attention due to their potential applications, such as guest exchange, gas storage, catalysis, drug delivery, luminescence, and magnetic materials, but also for their intriguing variety of topologies [1]. From both zeolite chemistry and crystal engineering points of view, the nets built from four-connected (4-c) centers capture much attention both for their inherent interest (all zeolites are 4-c nets) and from a theoretical point of view, and many 4-c nets have been deduced and summarized firstly by Wells followed by several comprehensive discussions [2]. However, it is still an enormous challenge to accurately predicate molecular structures for 4-connected nets such as diamond, NbO, quartz, sodalite, lonsdaleite, CdSO₄, CrB₄, SrAl₂, moganite, and PtS [3], owing to the process of architecture influenced by many factors, for instance different ligands, coordinated metals ion, reaction conditions, template, molar ratio, etc [4].

The rational design of organic building blocks plays the key role in adjusting the coordination frameworks, and the nature of the coordinating donors may lead to the formation of unique networks with desired properties and functions [5]. Substituted benzimidazoles attract much attention and have been used as a classic N-containing ligand, which can satisfy the coordination needs of the metal centers and consequently generate more robust and intricate networks. The most prominent compound of benzimidazole derivatives is 5,6-dimethylbenzimidazole, which serves as an axial ligand for cobalt in vitamin B₁₂ [6]. Herein we employ a long and flexible bis(5,6-dimethylbenzimidazole)butane ligand L, and

have successfully prepared an unprecedented 4-connected msw/P42/nm net with a point symbol of {6⁵·8}.

The free L ligand was prepared according to literature procedures [7]. The complex was obtained by the hydrothermal method (140 °C) for 72 h [8], and further characterized by X-ray crystallographic analysis [9]. The complex crystallizes in the orthorhombic space group *Pnma*. The asymmetric unit consists of one Co^{II} ion, half of one L ligand, and one hip²⁻ anion. As shown in Fig. 1a, each Co displays a distorted tetrahedral coordination environment, surrounded by two oxygen atoms from two different nip²⁻ anions (Co–O = 1.958(4) and 1.965(3) Å) and two nitrogen atoms from two distinct L ligands (Co–N = 2.032(3) Å), where the bond angles range from 101.74(10)° to 124.72(16)°.

Each hip²⁻ ligand adopts a bis-monodentate mode to link adjacent Co atoms to form 1D parallel chains, and these chains are further connected by L ligands to form a undulated 2D (4,4) networks (Fig. 1b), which each 38-member rhombic grid consists of four Co^{II} atoms at the corners connected by two L ligands and two hip²⁻ ligands, generating a [Co₄(L)₂(hip)₂] unit with the Co···Co distances 12.339(16) and 9.854(21) Å for L and hip²⁻ bridgings (Fig. 1c).

The 2D layers are further assembled by intermolecular hydrogen bonds with a H(5)···O(1) distance of 1.85 Å and the angle of 169° [O(5)—H(5)···O(1)], leading to formation of a 3D supramolecular framework (Fig. S1). To simplify the structure of the complex, in light of both coordinative and hydrogen-bonding interactions, topological analysis by reducing multidimensional structures to simple node-and-linker nets was performed. Since each Co²⁺ ion linking four other Co²⁺ ions can be defined as four-connecting node, the hip²⁻ anion is linked by two Co²⁺ ions and two others hip²⁻ ligands act as a 4-connected node and Each L ligand is considered as linker. Thus the resulting structure of the complex is a 4-connected uninodal 3D net with (6⁵·8) topology

* Corresponding author.

E-mail address: tscghua@126.com (G.-H. Cui).

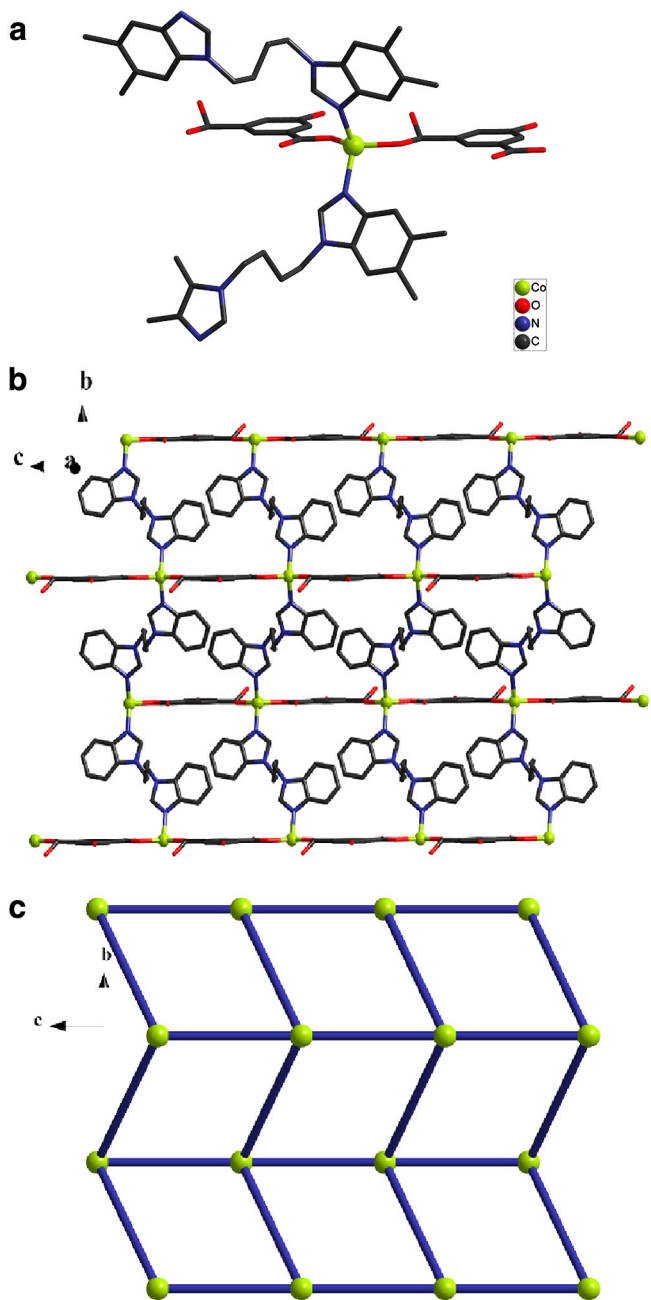


Fig. 1. (a) The tetrahedral coordination environment of Co^{II} ; (b) the 2D layer connected by L and hip^{2-} ligands (The methyl groups are omitted for clarity); (c) the undulated (4,4) layer (for interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

(Fig. 2a), calculated by TOPOS 4.0 program [10]. According to the nomenclature of derived uninodal nets, the notation of this net is *msw-P42/nmm*. The long (Schäfli) notation of the topology can be described as 6.6.6.6.6(2).8(2), indicative of two different kinds of six hexagons forming the 3D net sustained by the interplay of the coordinative and hydrogen-bonding interactions (Fig. 2b). It is notable that Sun et al. [11] reported the zinc compound has a self-interpenetrating 3D *msw-4-C2/c* net with $(6^5\cdot 8)$ topology, unlike this 4-connected *msw-P42/nmm* topology, to the best of our knowledge, this 3D supra-molecular topology represents the first example of a metal-organic replica of the *msw-P42/nmm*.

The emission spectra of the complex and ligand L in the solid state at room temperature are shown in Fig. 3. The luminescence property

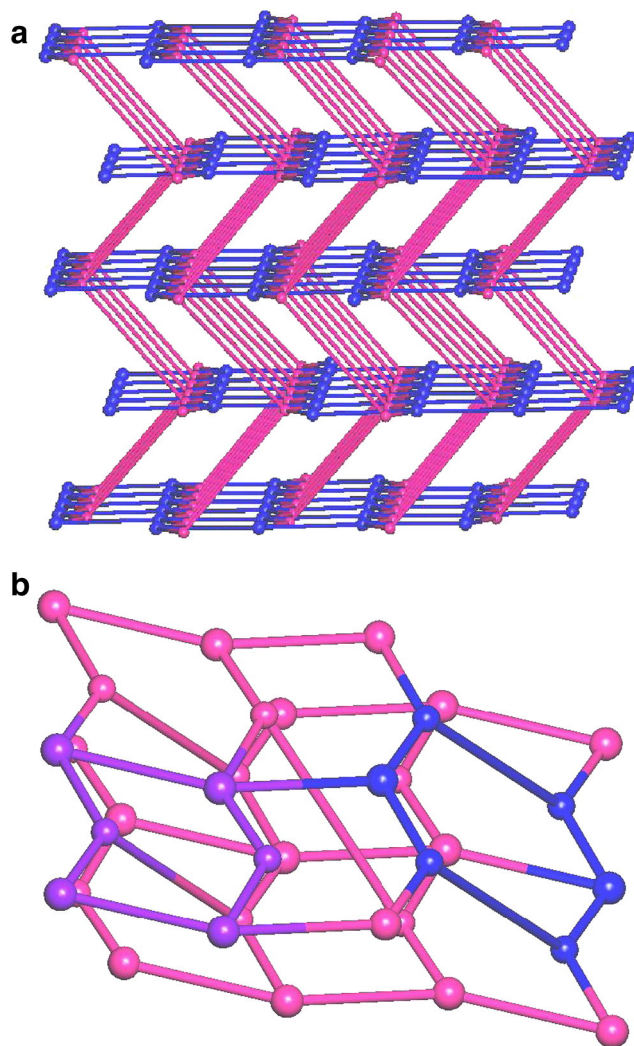


Fig. 2. (a) The 4-connected uninodal 3D net with $(6^5\cdot 8)$ topology network; (b) node-and-connector representation showing two different kinds of six hexagons.

of the metal-organic compound indicates that it may be candidates for potential photoactive materials. The free ligand L has the similar emission bands as the complex, showing a strong emission band at

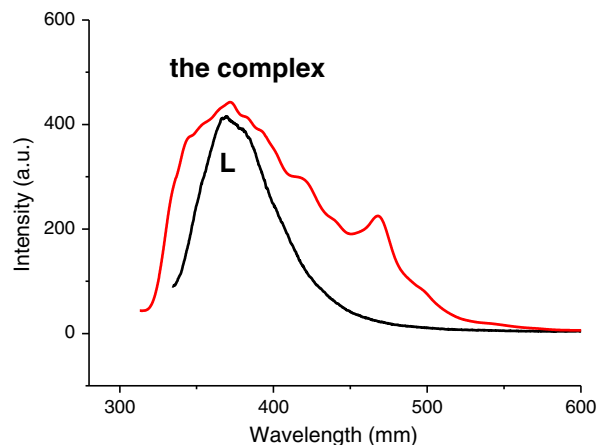


Fig. 3. Emission spectra of the complex and ligand L in the solid state at room temperature.

Download English Version:

<https://daneshyari.com/en/article/7749731>

Download Persian Version:

<https://daneshyari.com/article/7749731>

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