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An unusual four-connected (6^5,8) topology in a coordination polymer

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Abstract

A new 3-fold interpenetrating three-dimensional zinc(II) coordination polymer $\{[Zn(bime)(O_2N–BDC)]\cdot H_2O\}_n$ (**1**) has been solvothermally synthesized from the reaction of 1,2-bis(imidazol-1′-yl)ethane (bime), 5-nitroisophthalic acid ($O_2N–H_2BDC$), KOH and $Zn(NO_3)_2\cdot 6H_2O$. Single-crystal X-ray diffraction analysis reveals that **1** exhibits a rare tetrahedrally four-connected (6^5,8) topological network, in which all of the zinc(II) centers are in tetrahedral coordination.

Keywords: Bridging ligands; Topology; X-ray diffraction; Zinc(II)

The observation and exploration of infinite high-dimensional coordination polymers with various topological networks is a compelling area of research in supramolecular chemistry and crystal engineering and has undergone an explosive growth in recent years [1]. In addition to the useful properties and applications directly arising from those networks, another motivation stimulated by the activity is to prepare and investigate the particularly diversified topologies of the structures [2]. A useful, powerful and simplifying method to analyze the extended frameworks, especially for the complicated interpenetrating three-dimensional networks, is based on a valuable conceptual catalogue of nets where Wells has described a fundamental class of networks called uniform nets and illustrated many networks using a general symbol [3]. The classic monograph is extremely helpful for synthetic chemists to prepare and understand the various topological networks. Some intriguing topological networks, such as three-connected (6,3) [4], (8,3) [5], (10,3) [6], (12,3) [7], nets, four-connected diamond [8], NbO [9], PtS [10], $CdSO_4$ [11] nets, and six-connected α-Polonium-like net [12] have been successfully generated. However, O'Keeffe et al. [13] discovered that there were only a handful of nets actually observed in the real crystal structures through analyzing the underlying topology of extended metal-organic frameworks reported in the Cambridge Structure Database. Therefore, seeking various architectures with different topological networks plays an important role in constructing a comprehensive theory of the topology of nets.

As is well-known, it still remains a challenging task to accurately design or predicate the target results with given connectivity of nets owing to coordination diversity of the metal ions and various structural configurations of the organic ligands in self-assembly process [1,13]. In particular, the application of mixed ligands with different lengths between coordination sites can further increase the difficulty of predication about the resultant structures because of the incorporation of more components. However, it is also reasonably convincing that taking advantage of the mixed ligands can generate some special topological structures, because the combination of different configurational ligands not only can afford added opportunities for inducing more structural diversity into coordination polymers, but also can result in greater tunability of growing the crystals with desirable networks [14]. In our previous research, three diamondoid frameworks with different

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interpenetrating degrees have been synthesized through the mixed bridging ligands with zinc(II) centers [15], in which all of metal ions can be considered as tetrahedral nodes, characteristic of diamondoid nets. Continuing our research, using tetrahedral zinc(II) ions, 1,2-bis(imidazol-1′-yl)ethane (bime) and 5-nitroisophthalic acid (O_2N–H_2BDC) as starting materials under solvothermal condition, a new 3-fold interpenetrating three-dimensional architecture $\{[Zn(bime)(O_2N–BDC)]\cdot H_2O\}_n$ (**1**) was generated, interestingly, in which a rare tetrahedrally four-connected uniform (6^5,8) net, related but different from diamondoid and $CdSO_4$ topological networks, is presented.

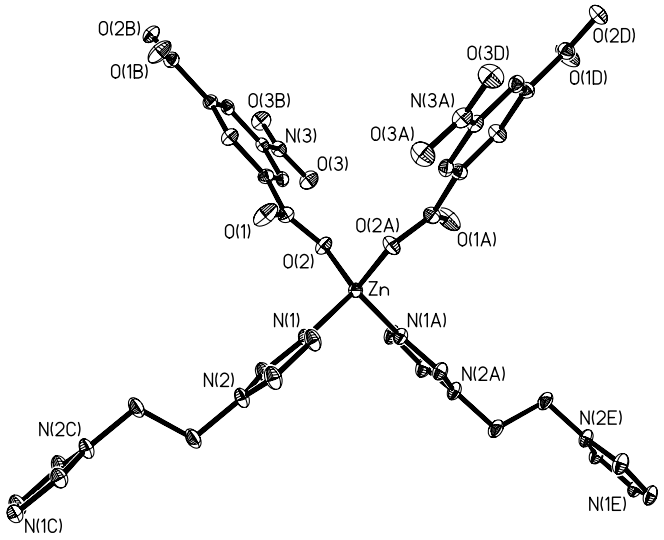

Fig. 1. ORTEP drawing of the asymmetric unit in **1** with atom labeling scheme showing 30% thermal ellipsoids. Free water and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn–O(2) 1.980(3), Zn–N(1) 2.021(4); O(2A)–Zn–O(2) 113.43(2), O(2)–Zn–N(1) 120.35(1), O(2)–Zn–N(1A) 96.37(1), N(1A)–Zn–N(1) 111.7(2). Symmetry codes: A x, $-y+1/2$, $-z+1/2$; B $x-1/2$, $-y+1$, z; C $-x+1$, $-y+1$, $-z$; D $x-1/2$, $y-1/2$, $-z+1/2$; E $-x+1$, $y-1/2$, $z+1/2$.

Colorless needle crystals of **1** [16] were obtained in high yield (75%, based on Zn) by the mild solvothermal reaction of $Zn(NO_3)_2\cdot 6H_2O$, bime, O_2N–H_2BDC and KOH (1:1:1:2) in the mixture solvent of CH_3OH and H_2O (v:v = 4:5) at 160 °C for four days. Single-crystal X-ray diffraction analysis shows that compound **1** possesses a complicated 3-fold interpenetrating three-dimensional structure, in which only one unique Zn^{2+} atom is observed. As shown in Fig. 1, each zinc(II) center is coordinated by two nitrogen atoms from different bime and two carboxylate oxygen atoms from different O_2N–BDC in a distorted tetrahedral geometry with the bond angles ranging from 96.37(1)° to 120.35(1)°. The bond distances of Zn–O (1.980(3) Å) and Zn–N (2.021(4) Å) are in the normal range of those observed in other zinc(II) complexes [17]. O_2N–BDC ligand adopts a bis-monodentate coordination mode, in accordance with the result of IR spectrum: 1634 and 1348 cm^{-1} for asymmetric and symmetric stretching vibrations of the carboxylate group with Δ value of ca. 286 cm^{-1}, the nitro group does not take part in coordination. The bime ligand behaves in an *anti*-conformation to link zinc(II) centers. Two kinds of closed circuits are formed through the two different organic bridges connecting zinc(II) atoms (Fig. 2), one is a small six-membered closed circuit built through two O_2N–BDC and one bime ligands alternatively linking zinc(II) atoms, and the other is a large eight-membered closed circuit constructed through two

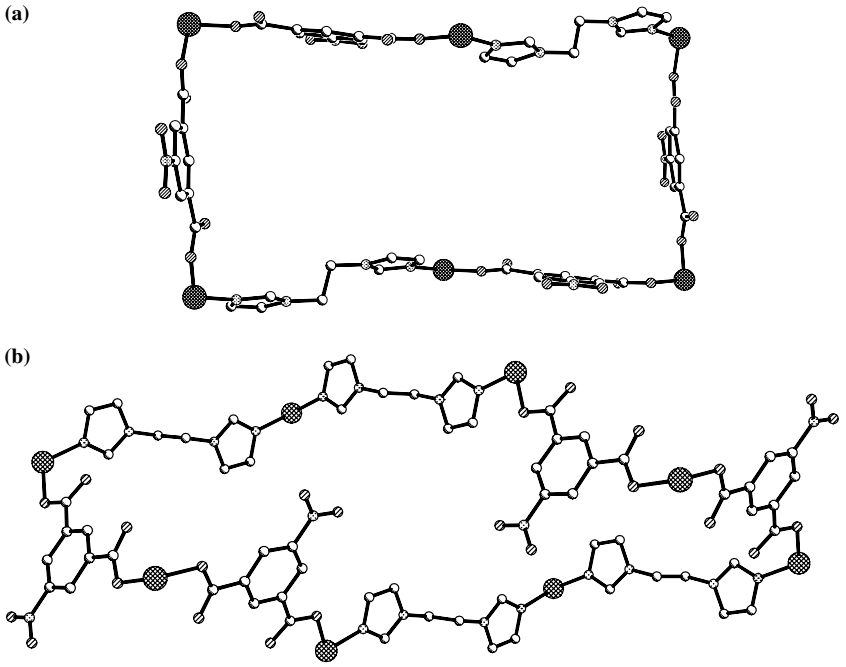

Fig. 2. Two kinds of closed circuits in **1**: the smallest six-membered circuit (a) and the larger eight-membered circuit (b).