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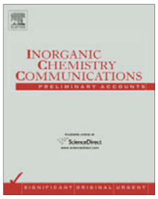

An unusual 2-fold interpenetrated 3D PtS framework containing circular and rhombic tubular building blocks and hydrogen-bonded –O–metal–O–chain

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ABSTRACT

Circular and rhombic tubular building blocks interweave mutually into a novel 2-fold interpenetrated 3D PtS framework $[Zn(ADB)(H_2O)]_n$ (**1**) (H_2ADB = azobenzen-4,4′-dicarboxylic acid), with hydrogen-bonded–O–metal–O–chain. In additional, solid-state properties such as photoluminescence and thermal stability of the complex **1** have also been studied.

Due to the intriguing structural topologies and potential applications as functional solid materials, the investigation of metal-organic frameworks (MOFs), built from metal clusters and multifunctional carboxylates, have been a field of rapid growth [1–5]. Among them, zinc coordination polymers have attracted much attention owing to their thermal stability and photoluminescent properties [6,7]. In where, the multinuclear zinc clusters, which act as building blocks, can be used to build up extended frameworks [8–10], and to date, the zinc coordination polymers with discrete multinuclear zinc clusters have been successfully isolated [11–14]. However, the coordination polymers based on the assembly of infinite multinuclear zinc clusters are scarce [12,15–18]. It has been demonstrated that the presence of hydroxy or oxo groups facilitates the formation of discrete clusters by M–OH–M or M–O–M linkage [8,14], and this is also true for the case of infinite building blocks. To best of our knowledge, there are few examples in which the Zn–OH–Zn or $Zn–(O–C–O)_2–Zn$ connectivity participates in the formation of one-dimensional (1D) rod-shaped building blocks [15–18], and there is a recent report of a 3D Zn coordination network with carboxylate-bridged Zn3 units and Zn chains [19], but such building blocks interweave mutually into a 3D PtS framework contain hydrogen-bonded –O–M–O– chain have not been reported so far.

In this context, along with our recent work on coordination chemistry of a versatile organic ligand biphenylethene-4,4′-dicarboxylic acid have presented distinct Zn^{II} and Cd^{II} coordination polymers, which exhibit intriguing 3D polycatenated array featuring an uneven "density of catenation" and ninefold interlocked homochiral helices [20,21], respectively, and thus triggered our further activity on this topic, we chose a comparable multidentate building block azobenzen-4,4′-dicarboxylic acid (H_2ADB) as bridging ligand, to prepare novel materials with intriguing architectures and good physical properties, Fortunately, we have recently isolated a new complex based on H_2ADB, $[Zn(ADB)(H_2O)]_n$ (**1**). The structure of complex **1** exhibits unusual features: (i) the circular and rhombic tubular building blocks interweave to form a 2-fold interpenetrated network with PtS topology; (ii) the unique hydrogen-bonded –O–metal–O– chains enchase between the interpenetrated frameworks.

Complex **1** was prepared by hydrothermal method in 66% yield [22] and the structure was determined by X-ray single crystal diffraction [23]. Structural analysis shows that the structure of **1** is a 3D neutral coordination polymer featuring two distinct tubular structures constructed from zinc atom and ADB linkers, in which the asymmetric unit contains one zinc atom, one ADB ligand, and one coordinated water molecule. Each ligand possesses a 4-connected geometry to connect the Zn atoms (Fig. S1) by bridging bis-bidentate coordination modes, and each Zn atom adopts a distorted trigonal bipyramid coordination mode to link one water molecular and four separate ADB ligands (Fig. S2). The Zn–O bonds

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fall in the range of 1.962(5)–2.218(6) Å (Table S1). The shortest Zn$\cdots$Zn separation connected by the same carboxylate group is 4.372 Å, while the shortest one connected by the space unit of the ADB ligand is 15.950 Å.

The most striking feature of complex **1** is the alternately arranged two distinct tubular structures (Fig. 1). In order to interpret the whole network clearly, the structure of **1** could be described as two kinds of building blocks, circular (block **A**) and rhombic (block **B**) tubes. Firstly, the bridge of the carboxyl pattern of the ADB ligands leads to form infinite Zn–(O–C–O)$_2$–Zn rod-shaped building blocks running along the *b* axes, namely circular tube (block **A**). Secondly, the rods of block **A** are linked by the ADB arms (as the spacer), which connect each rod to four neighboring rods along the *c*-axis, giving rise to rhombic tube building blocks (block **B**). Notably, such tubular building blocks are not isolated but interweaved with each other across Zn atom, and decorated with coordinated water molecules alternately at two sides. Moreover, when viewed along the *c*-axis, it can be found that blocks **A** and **B** are alternately arranged, leading to a complicated 3D network.

Not surprisingly, from the topological point of view, when each ligand acts as a square-planar node, and each central atom can be looked as a 4-connecting tetrahedral/square-planar node, the whole structure can be represented to a PtS/lvt net [24,25], in our work, each ligand and five-coordinated Zn atom can be described as a square-planar and tetrahedral node, respectively, thus interweaving of tubular building blocks leads to a 3D network with a PtS topology, as displayed in Fig. 2a. Furthermore, owing to no bulky solvent molecules occupied in the crystal, two such nets interpenetrate with catenation of just the large rhombic channels of 25.55 × 10.90 Å along the *c*-axis (Figs. 2b and S3), and there are some examples of the interpenetrated PtS nets [24,26–31]. This is in accord with the fact that tetrahedral, trigonal, and octahedral metal templates have a high tendency to form interpenetrated or self-inclusion compounds, if the cavity generated in this way is more than 50% of the crystal by volume [32].

Another remarkable character of the complex **1** is the formation of hydrogen-bonded –O–metal–O– chains that is made up of (–O–H$\cdots$O–Zn–O$\cdots$H–O–)$_n$ repeat units and Zn–O bridging group (Fig. S4). In **1**, the arrangement of the 2-fold interpenetration provides an opportunity to form the hydrogen-bonded chains, which, in turn, play an important role in the stability of interpenetrated structure. The coordinated water molecule (O3) of one framework acts as the hydrogen-bond donor and the carboxylic oxygen (O1) of the other framework as hydrogen-bond acceptor (O3–H$\cdots$O1 2.687 Å 164.32°), additionally, the coordinated water molecules (H–O3–H: 107.97°), which decorated alternately at two sides of circular tube, play a orienting action at an angle, leading to the formation of chains. More wonderfully, Zn–O3 group represent as a bridge by linking the adjacent chains, giving rise to the arrangement of hydrogen-bonded chains. Recently, a rare –metal–O–metal– helix has been reported [33], in which, the arrangement of the triple-helical chains provided an opportunity to form the single-helical chain. As far as we know, **1** represents the first example of metal-organic framework containing hydrogen-bonded –O–metal–O– chain.

To examine the thermal stability of the whole frameworks, thermal gravimetric analysis (TGA) and X-ray powder diffraction (XRPD) measurements were carried out (Figs. S5 and S6). For complex **1**, the TGA trace exhibits two weight losses: one (5.66%) from 145 to 190 °C is attributed to the loss of two coordinated water molecules (calcd 5.12%); the other from 400 to 600 °C corresponds to the removal of the ADB ligand. The final product is assumed to

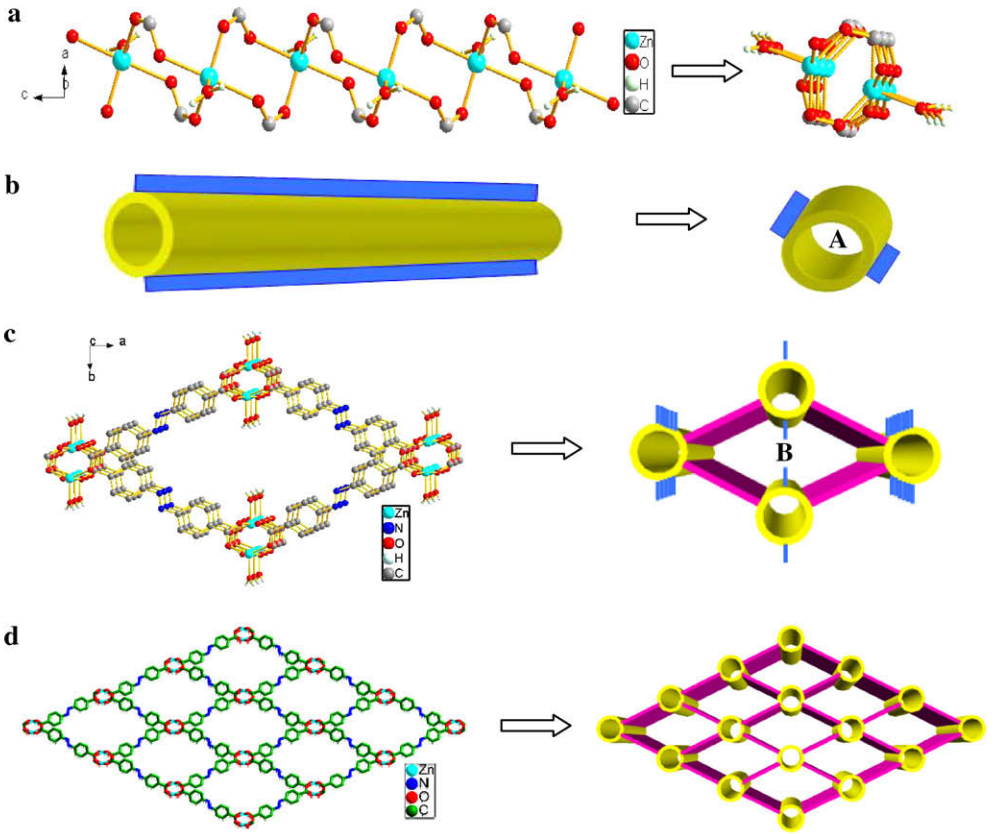

Fig. 1. (a) Infinite Zn–O–C–O rod-shaped building block running along the *b*-axis. (b) Schematic view of infinite rod-shaped building block (block **A**). (c) Left: the perspective view of block A are linked by the ADB arms (block **B**), right: schematic view of block B. (d) Left: the framework of **1** viewed along the c-axis (coordinated water molecules are omitted for clarity), right: schematic view of the two types of tubes arranged alternately along the c-axis.

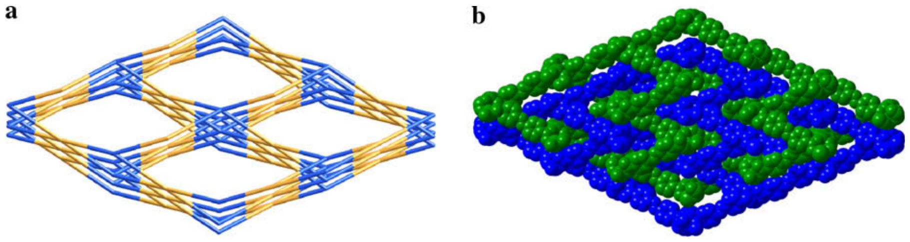

Fig. 2. (a) 3D coordination framework of **1** with PtS topology (color codes: blue for 4-connected tetrahedral nodes, yellow for 4-connected square-planar nodes); (b) Space-filling view of the 2-fold interpenetration in **1**. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

be ZnO (found weight 23.02), which is supported by the expected value of 23.14% and also confirmed by the powder X-ray diffraction (PXRD) patterns (Fig. S6, beyond 400 °C, the diffraction peaks of ZnO appear). Notably, the XRPD measurement is in accordance with the TGA analyses. In addition, photoluminescence property of powder samples of **1** has also been examined at room temperature (Fig. S7). Up on the excitation at 300 nm, complex **1** exhibits an intense emission at 413 nm, while the free H_2ADB ligand displays weak luminescence at 422 nm. The luminescent behavior of **1** is such that its high-dimensional condensed polymeric structure leads to significant enhancement of fluorescence intensity compared to the free ligand. The blue-shift (about 9 nm) of this emission bands with respect to the free H_2ADB ligand is probably due to the (π^*–π) transitions changing into the (π^*–n) transitions after forming the coordination polymer. The enhanced luminescence efficiency is therefore attributed to ADB coordinated to Zn^{II} ions resulting in a decrease in the nonradiative decay of intraligand excited states [24,34,35].

In summary, we have prepared and characterized an unusual 2-fold interpenetration 3D PtS framework assembled from circular and rhombic tubular building blocks. Meanwhile, the first hydrogen-bonded –O–metal–O– chains were formed between the interpenetrated frameworks. In addition, complex **1** shows strong fluorescent emission. Further studies for the construction of novel coordination polymers with unusual topologies and interesting physical properties, by reacting long spacer ligand and different metal ions, are progress.

Acknowledgements

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2009.05.015.

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[22] Synthesis of $[Zn(ADB)(H_2O)]_n$ (**1**): A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.5 mmol, 0.149 g), H_2ADB (0.5 mmol, 0.123 g), triethylamine (0.15 mL), and deionized water (9 mL) was stirred for 20 min in air, then transferred and sealed in a 23 mL Parr Teflon-lined stainless steel vessel, which was heated at 120 °C for 6 days, and then cooled to room temperature. Orange yellow crystals were obtained (yield 66%). Elemental analysis calc. for $C_{14}H_{10}N_2O_5Zn$ (%): C, 47.82; H, 2.87; N, 7.97. Found: C, 47.78; H, 2.89; N, 7.94. Selected IR(KBr) spectra for **1**: ν (cm^{-1}) 3152 (s), 1598 (m), 1542 (m), 1419 (m), 1397 (m), 1073(w), 1010(w),772(m),724 (w), 679 (w), 642(w).
[23] Crystal diffraction intensities for **1** were collected at 293(2) K with a Siemens SMART system equipped with a CCD detector with Mo Kα radiation at 0.71073 Å. Absorption corrections were applied using SADABS program. The structure was solved with direct methods and refined with the full-matrix least-squares technique based on F^2 using the SHELXTL program package. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were placed in constrained positions with isotropic temperature factors. Crystal data: formula $C_{14}H_{10}N_2O_5Zn$, $M = 351.62$, Monoclinic, space group $P2/c$, with $a = 14.6000(2)$ Å, $b = 6.4230(15)$ Å, $c = 7.3600(16)$ Å, $\alpha = 90^\circ$, $\beta = 91.040(2)^\circ$, $\gamma = 90^\circ$, $V = 690.08(24)$ Å^3, $T = 293(2)$ K, $Z = 2$, $F(0\,0\,0) = 356$, $D_c = 1.692$ g cm^{-3}, $\mu = 1.805$ mm^{-1}, the final $R_1 = 0.0730$, $wR_2 = 0.2253$ (all data), and GOF = 1.019.
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