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Communication

Synthesis and Characterization of a Tetrazolate-Bridged Coordination Framework Encapsulating D_{2h}-Symmetric Cyclic $(H_2O)_4$ Cluster Arrays

Jun Tao,* Zhi-Jie Ma, Rong-Bin Huang, and Lan-Sun Zheng

Department of Chemistry and State Key Laboratory for Physical Chemistry of Solid Surface, Xiamen University, Xiamen 361005, P. R. China

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Reaction of 5,5′-(1,4-phenylene)bis(1H-tetrazole), which was prepared in two steps, with cadmium nitrate in DMF produced a three-dimensional framework with one-dimensional channels (35% void volume), in which unprecedented hydrogen-bond-supported D_{2h} tetrameric cyclic water clusters ranked.

Coordination frameworks containing channels or pores have attracted much attention for the past decade because of their advantageous applications in catalysis,[1] separation,[2] ion exchange,[3] and gas sorption and storage.[4] To this end, a strategy for the assembly into open frameworks of functionalized organic ligands containing N and/or O donors with metal or metal clusters is essential.[5] In addition, the frameworks must remain intact upon guest removal or reversible gas sorption. Although the shapes and properties of channels and pores are mainly determined by the host frameworks, guest molecules also play important roles through their interactions among themselves or with host frameworks.[6] For the purpose of expanding the contemporary strategy of synthesizing novel coordination frameworks and elucidating the controlling factors in influencing their shapes, properties, and stabilities, we have now begun to systematically synthesize 5-substituted tetrazolate-bridged coordination frameworks.

The 5-substituted tetrazolate group, isosteric with the carboxylate group and having good coordination capacities, however, has scarcely been explored in building coordination frameworks, because no effective method for synthesizing 5-substituted tetrazoles in high yields was known before Sharpless and Demko's work.[7] In the past several years, they have developed a convenient route to synthesize 5-substituted tetrazoles by addition of azide to organic nitriles catalyzed by zinc salts in water, and since then, studies on 5-substituted tetrazolate-bridged coordination frameworks have been slowly emerging.[8] Recently, Metzger and Fürmeier[9] reported that 5-substituted tetrazolates can also be synthesized from nitriles in toluene, and Pizzo and Amantini[10] reported the conversion of nitriles into 5-substituted tetrazolates by using anionic activation of silicon−nitrogen bond[11] in the presence of tetrabutylammonium fluoride as the catalyst under solventless conditions. In this communication, we report the syntheses and characterization of 5,5′-(1,4-phenylene)bis(1H-tetrazole) (2H-pbtz, **1**) and the pbtz-bridged coordination framework $[Cd_3(pbtz)_3(DMF)_4(H_2O)_2]\cdot(DMF)_4(H_2O)_4$ (**2**).

The reaction of terephthalonitrile with NaN_3 and $Et_3N\cdot HCl$ in toluene under reflux yields a crude powder of **1**, which is further heated to 180 °C in water for 60 h to give the crystalline product **1**·$2H_2O$. **2** is obtained by treatment

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* To whom correspondence should be addressed. E-mail: taojun@jingxian.xmu.edu.cn. Fax: (+86) 592 2183047.

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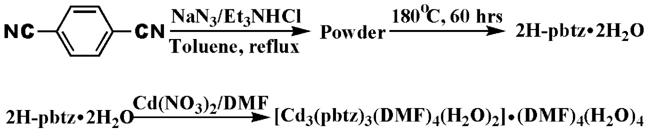
Scheme 1



of **1**·$2H_2O$ and $Cd(NO_3)_2$·$4H_2O$ in DMF at ambient temperature (Scheme 1).[12] The IR spectrum of **1**·$2H_2O$ shows peaks consistent with the formation of 2H-pbtz and the absence of a cyano peak in the 2100 cm^{-1} region. In the spectrum of **2**, strong peaks at 1652 and 1434 cm^{-1} represent the presence of deprotonated tetrazolate groups, and the broad band above 3000 cm^{-1} suggests that coordinated and guest water are present.

As indicated in Figure 1,[13] each molecule of **1** affords two hydrogen-bond donors (N−H) and four hydrogen-bond acceptors (N), and each water molecule has one hydrogen-bond acceptor and two hydrogen-bond donors. Thus, each molecule of **1** is involved in six hydrogen-bond rings, which fall into two types, A and B. The N−H···O1W bond distance [2.67(1) Å] is somewhat shorter than that of O1W−H···N [2.88(1) Å], consistent with the statistical distances for these two kinds of hydrogen bonds.[14] It should be noted that, in ring A, the $R_4^4(10)$-hydrogen-bond moiety is composed of four O−H donors and four N acceptors, whereas in the larger ring B, the four hydrogen bonds are built from two N−H and two O−H donors and two O and two N acceptors.

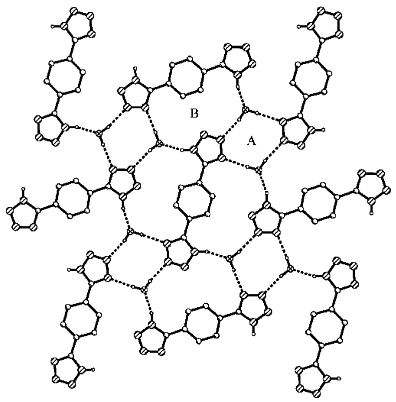


Figure 1. Hydrogen-bond 2D network structure of **1**·$2H_2O$ showing two kinds of hydrogen-bond rings. Hydrogen atoms on carbons are omitted for clarity.

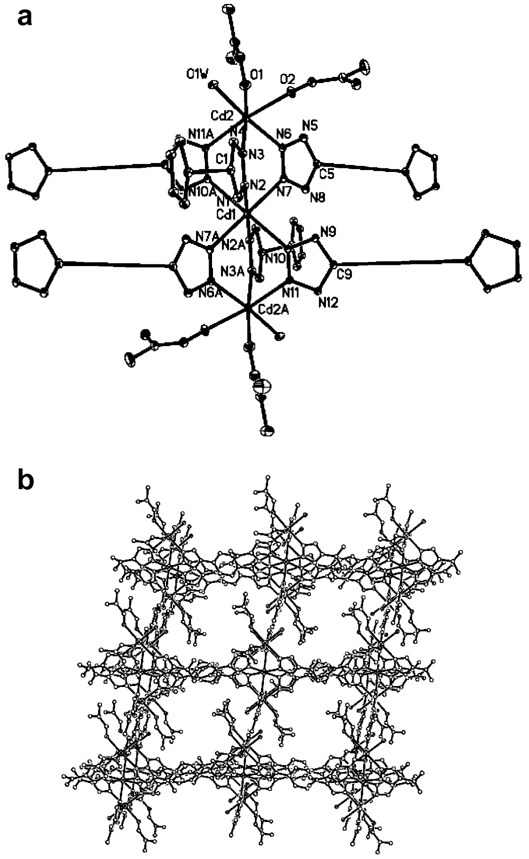


Figure 2. (a) Tetrazolate-bridged trinuclear unit of **2** showing the local coordination geometry around the Cd centers (50% displacement ellipsoid probability). Guest DMF and water molecules are omitted and phenylene groups are simplified for clarity by linking tetrazolates directly. (b) Three-dimensional structure of **2** showing rhombic channels viewed down *a* axis. Guest DMF and water molecules as well as hydrogen atoms are omitted for clarity.

The structure of **2**[13] is the first tetrazolate-bridged three-dimensional framework, to our knowledge, whose building unit is a trinuclear cadmium cluster (Figure 2a). The Cd1 atom is located at an inversion center and in a slightly distorted octahedral coordination geometry formed by the coordination of six bridging pbtz ligands. Four nitrogen atoms (N7, N7A, N10, and N10A) form a planar parallelogram arrangement around the Cd1 center, and the other two nitrogen atoms (N2 and N2A) occupy the apical positions. The two symmetry-related cadmium atoms (Cd2 and Cd2A) are bridged through the six pbtz ligands bound to Cd1, and then a trinuclear cluster is generated with solvent DMF and water molecules capped on both sides. It is obvious that the existence of capped solvent molecules restricts the formation of a tetrazolate-bridged cadmium chain. The

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(12) Preparation of **1**·$2H_2O$: A mixture of terephthalonitrile (10 mmol), sodium azide (60 mmol), and triethylamine hydrochloride (60 mmol) in dry toluene (70 mL) was heated under reflux for 3 days. The reaction mixture was dissolved in NaOH solution (1 M, 100 mL) and filtered; the filtrate was acidified (pH = 1) with concentrated HCl and filtered to give the crude powder of **1**, which was further purified by alternate treatment with 1 M NaOH and 1 M HCl solutions. A mixture of the purified powder of **1** (0.500 g) and water (8 mL) was placed in a Parr Teflon-lined stainless vessel and heated at 180 °C for 60 h to give **1**·$2H_2O$ as colorless parallelpiped crystalline product with only one phase. The overall yield of **1**·$2H_2O$ (1.25 g) was about 50% based on terephthalonitrile. Anal. Calcd for $C_8H_{10}N_8O_2$ (%): C, 38.40; H, 4.03; N, 44.78. Found (%): C, 38.30; H, 4.15; N, 44.65. IR (KBr, cm^{-1}): 3387 (br, s), 1590 (m), 1507 (w), 1452 (m), 1126 (m), 1086 (m), 993 (m), 911 (m), 735 (m), 709 (m), 527 (m), 481 (m). Preparation of **2**: **1**·$2H_2O$ (0.125 g, 0.50 mmol) and $Cd(NO_3)_2$·$4H_2O$ (0.154 g, 0.50 mmol) was dissolved in DMF (10 mL) with stirring at ambient temperature. After several days, a colorless irregularly shaped crystalline product with only one phase was filtered and dried in air. The yield of **2** (0.22 g) was about 80% based on **1**·$2H_2O$. Anal. Calcd. for $C_{48}H_{80}Cd_3N_{32}O_{14}$ (%): C, 34.59; H, 4.84; N, 26.89. Found (%): C, 34.70; H, 4.67; N, 26.69. IR (KBr, cm^{-1}): 3407 (br, m), 1653 (s), 1434 (s), 1385 (m), 1108 (m), 1010 (m), 855 (m), 750 (m), 666 (m), 485 (m).

(13) Crystal data for **1**·$2H_2O$: $C_8H_{10}N_8O_2$, $M = 250.24$, monoclinic, $P2_1/c$, $a = 3.6982(3)$ Å, $b = 12.4327(10)$ Å, $c = 11.6718(9)$ Å, $\beta = 92.97(1)°$, $V = 535.93(7)$ Å^3, $Z = 4$, $D_c = 1.551$ Mg m^{-3}, $R_1 = 0.0402$, $wR_2 = 0.1159$, $T = 173(2)$ K, $\mu = 0.119$ mm^{-1}, $S = 1.080$. Crystal data for **2**: $C_{48}H_{80}Cd_3N_{32}O_{14}$, $M = 1666.64$, triclinic, $P\bar{1}$, $a = 11.8400(6)$ Å, $b = 12.3247(6)$ Å, $c = 13.7362(6)$ Å, $\alpha = 92.62(1)°$, $\beta = 112.68(1)°$, $\gamma = 109.04(1)°$, $V = 1714.25(14)$ Å^3, $Z = 1$, $D_c = 1.614$ Mg m^{-3}, $R_1 = 0.0317$, $wR_2 = 0.0823$, $T = 173(2)$ K, $\mu = 1.005$ mm^{-1}, $S = 1.061$.

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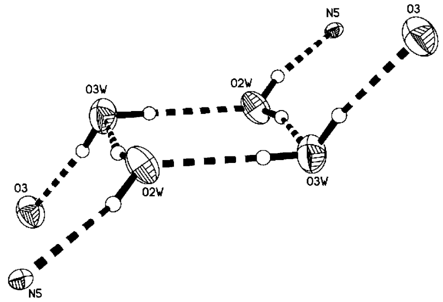

Figure 3. ORTEP plot showing that the water tetramer is supported by the framework tetrazolate rings (N5) and guest DMF molecules (O3) via hydrogen bonds. Covalent bonds are shown as solid lines, and hydrogen bonds are shown as dashed lines. The four water oxygen atoms are completely coplanar and $(H_2O)_4$ cluster is D_{2h}-symmetric.

equatorial plane of the octahedrally coordinated Cd2 atom is filled by two nitrogen atoms from two different pbtz ligands (N3 and N6), one oxygen atom (O1) from a DMF molecule, and one water (O1W) molecule, and the coordination sphere is completed by one nitrogen atom (N11A) from a pbtz ligand and one oxygen atom (O2) from the terminal DMF molecule in the axial positions.

Each pbtz ligand in **2** is coordinated to four cadmium atoms in a μ_4-bridging mode, which is similar to the bridging bis-bidentate coordination mode of terephthalate anion.[15] The six pbtz ligands in the trinuclear building unit are oriented in six different directions and link six adjacent trinuclear units to form a three-dimensional framework with one-dimensional channels (Figure 2b).

Although each trinuclear unit is capped by four DMF molecules and two water molecules, which occupy part of the space of the one-dimensional channels, there exists a largish void (35% per unit cell as calculated by Platon[16] software) that encapsulates solvent DMF and water molecules. It is noteworthy that, in each grid, four guest water molecules form a D_{2h}-symmetric cyclic $(H_2O)_4$ cluster (Figure 3). Three kinds of cyclic $(H_2O)_4$ clusters, namely, C_4, S_4, and C_s tetramers, have been studied both theoretically and experimentally,[17] but no D_{2h}-symmetric cyclic $(H_2O)_4$ cluster has ever been reported.

Within the D_{2h}-symmetric cyclic $(H_2O)_4$ cluster, each water monomer acts as both a single hydrogen-bond donor and a single hydrogen-bond acceptor and has another hydrogen atom oriented above or below the ring. The four water molecules are completely coplanar without regard to connectivity of the hydrogen atoms, and the hydrogen-bond distances are O2W−H···O3W = 2.807(5) Å and O3W−H···O2W = 2.812(4) Å, which are slightly longer than the average hydrogen-bond distance of liquid water tetramer (2.78 Å).[18] At the same time, the water tetramer also forms hydrogen bonds with guest DMF molecules and framework tetrazolate rings. Because of the rigidity of the framework, the water tetramer can be regarded as being stabilized by the framework through the hydrogen bond between O2W and N5 [3.033(4) Å], and consequently, the water tetramer stabilizes the guest DMF molecules [O3W−H···O3 = 2.848(4) Å], with other guest DMF molecules (O4) being stabilized by coordinated water [O1W−H···O4 = 2.844(3) Å]. In the solid state, **2** exhibits a strong emission peak at 326 nm, whereas a broad emission peak at 473 nm is observed for the free ligand **1**, which means that the emission peak of **2** corresponds not to ligand donation but to the formation of tetrazolate-bridged trinuclear cadmium clusters and/or the occurrence of ligand-to-metal charge transfer (LMCT).[19]

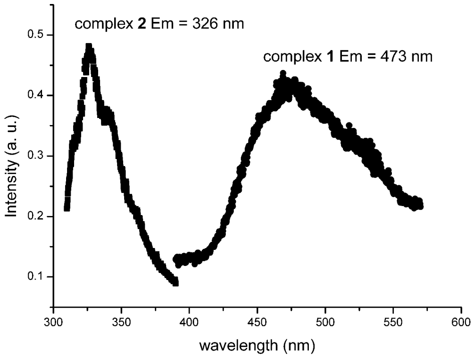

Figure 4. Solid-state photoluminescent spectra of **1** and **2** at room temperature.

The TG curve of **2** indicates that the release of guest water and DMF molecules occurs up to 150 °C and the framework begins to decompose above 150 °C along with the release of the coordinated water and DMF molecules.

In conclusion, we have synthesized a new tetrazolate-bridged framework that encapsulates unprecedented D_{2h}-symmetric cyclic water tetramers. This host framework contains a large void volume (35%) and might exhibit interesting gas sorption and guest inclusion properties. The investigation of these properties and synthesis of other metal−pbtz frameworks are in progress.

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Supporting Information Available: Experimental procedures, IR data, figures depicting the ORTEP plot of **1**·$2H_2O$ with labeling atoms and stacking mode as well as asymmetric unit and three-dimensional structure of **2**, photoluminescent spectra, X-ray thermodiffractogram and TGA of **2**, and X-ray data in CIF format are available free of charge via the Internet at http://pubs.acs.org.

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