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Communication

An Infinite Water Chain Passes through an Array of Zn(II) Metallocycles Built with a Podand Bearing Terminal Carboxylates

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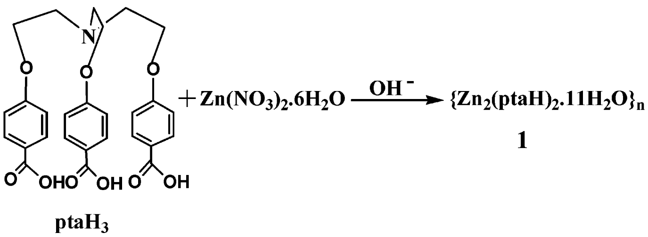
A podand bearing three carboxylic acid groups was synthesized by condensation of tris(2-chloroethyl)amine with 4-hydroxyethylbenzoate followed by hydrolysis of the ester group. An aqueous solution of $Zn(NO_3)_2 \cdot 6H_2O$ reacts with the tetraethylammonium salt of the podand at room temperature, to form a porous coordination polymeric structure with infinite interlinked chains of Zn(II) metallocycles. An infinite water chain passes through the metallocycles like a thread. The compound was characterized by X-ray crystallography, X-ray powder diffraction, TGA, IR spectroscopy, and elemental analysis.

Studies of water clusters of different nuclearities and structures continue[1−8] to be of considerable interest, as they facilitate understanding of hydrogen-bonding interactions and rearrangement dynamics among a collection of water molecules with the ultimate aim of achieving an accurate description of liquid water and its anomalous properties. Infinite chains of hydrogen-bonded water molecules[9] constitute a potentially important form of water that is poorly understood.[10] Water chains appear to be important[11−16] in the control of proton fluxes in a variety of biomolecules and also to facilitate the selective permeation[17] of water across membranes. However, the existence of hydrogen-bonded chains of water molecules in abiological molecules is rare.[9] Therefore, the knowledge of structural constraints required in the stabilization of water chains and the influence of the chain structure on the host remains incomplete.

Scheme 1. Synthetic Scheme for **1**



Crystal engineering of metal−organic frameworks (MOFs) has attracted much interest because of the potential applications and unusual topologies of these materials. Our research efforts are directed toward constructing MOFs with high porosity and thermal stability. To this end, we designed[18] and synthesized the podand ligand $ptaH_3$ (see Scheme 1), bearing one aromatic carboxylate group at each terminal and a long linker from the bridgehead nitrogen. In this communication, we describe the synthesis and characterization of the porous coordination polymer $\{Zn_2(ptaH)_2 \cdot 11H_2O\}_n$ (**1**), which forms an infinite array of metallocycles. However, the macrocyclic pores are not empty but contain hydrogen-bonded water molecules that form a wavelike infinite chain passing through these pores.

Compound **1** was synthesized[19] as colorless crystals by slow evaporation of an aqueous solution of $ptaH_3$ and $Zn(NO_3)_2 \cdot 6H_2O$ at pH 9 and characterized by X-ray crystallography, X-ray powder diffraction, TGA, IR spectroscopy, and elemental analysis.

The structure[20] of **1** consists of Zn(II) ions, partially deprotonated $ptaH^{2-}$ and water molecules. The asymmetric

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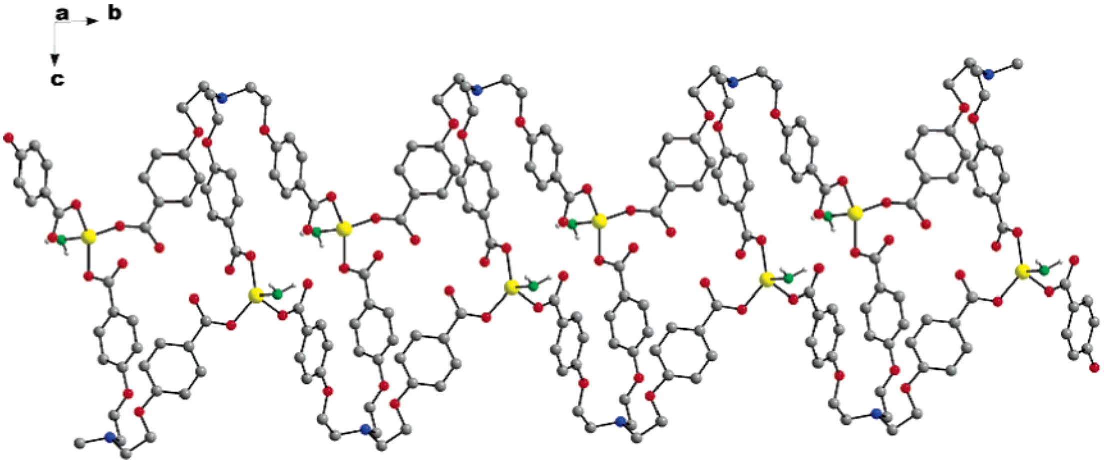

Figure 1. View of the interlinked metallomacrocycles extending along the crystallographic *b* axis. For clarity, only the H atoms belonging to metal-bound water are shown. Color code: C, gray; H, light gray; N, blue; O, red; Ow, green; Zn, yellow.

unit contains two Zn(II) ions, two ptaH^{2-} ligands, and 11 H_2O molecules. The metal ion is bonded to three carboxylates from three different ligand units, each donating a single O atom, and the fourth coordination site is occupied by a water molecule, forming a slightly distorted tetrahedral coordination geometry. The H atom attached to one of the carboxylates of the ligand could not be located in the difference map. The resulting coordination polymer looks like an array of metallomacrocycles (Figure 1). The Zn−O(carboxylate) bond distances in **1** span the range 1.922(3)−1.978(3) Å, which compares well with the distance found in other zinc(II) carboxylate structures.[21] The Zn−O(H_2O) bond distances at the two Zn(II) centers are 2.020(3) and 2.027(3) Å, which are also similar to other Zn−OH_2 bond distances reported[22] in the literature. The bond distances and bond angles in the ligand moiety are found to be within normal[21] statistical errors. The large voids created in the structure are not empty; rather, an infinite chain of hydrogen-bonded water molecules weaves through them in an unprecedented fashion (Figure 2). The geometrical parameters pertaining to the water cluster are collected in Table 1. Of the remaining nine water molecules in the asymmetric unit, Ow1−Ow6 constitute part of the infinite chain. The dimer Ow9···Ow8 is hydrogen-bonded to Ow3 through Ow8, and Ow7 is hydrogen-bonded to Ow6 of this chain sideways to fill the voids in the MOF. Each water molecule in the chain forms two hydrogen bonds, one as a donor and the other as an acceptor. Only Ow3 and Ow6 act as double donors and single acceptors because of the sideways hydrogen bonding (Figure 3). The free hydrogen available with each water molecule act as a donor to the available carboxylate O atoms (Table 1), further stabilizing the chain structure. Thus, none of the O atoms in the cluster exhibits four-coordination. Although each O atom in an assembly of water molecules tends to achieve four-coordination, hydrogen-bond-deficient water molecules are found[23] at the surface of ice, and recent X-ray absorption spectroscopy and Raman scattering studies of liquid water also suggest that significant numbers of O atoms show less than tetracoordination in liquid water.[24] The oxygen atoms of the water molecules in the chain are not coplanar but rather form an unprecedented wave pattern extending along the

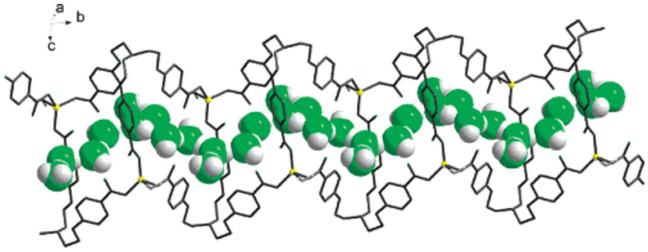

Figure 2. Perspective view of the water chain inside the metallocycles. For clarity, only H atoms belonging to water are shown.

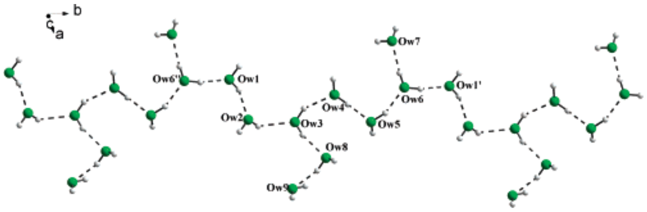

Figure 3. Close view of the water cluster showing the atom numbering scheme.

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(19) Synthesis of **1**: The tripodal ligand ptaH_3 (0.13 g, 0.25 mmol) was dissolved in THF (10 mL) solution containing tetraethylamonium hydroxide (2 mL), and the mixture was then stirred continuously. To this aqueous solution was added $Zn(NO_3)_2 \cdot 6H_2O$ (0.15 g, 1.5 × 0.25 mmol), and the reaction mixture was stirred for 2 h at room temperature. Colorless crystals of **1** were collected from the filtrate after **7** days in ~50% yield. Anal. Calcd for $C_{54}H_{72}N_2O_{29}Zn_2$:C, 48.26; H, 5.40; N, 2.08%. Found:C, 48.43; H, 5.29; N, 2.14%.

(20) Crystal data for **1**: $C_{54}H_{72}N_2O_{29}Zn_2$, $M = 1343.88$, rectangular, colorless, 0.12 × 0.10 × 0.08 mm, triclinic, space group $P\bar{1}$, $a = 11.003(5)$ Å, $b = 12.974(5)$ Å, $c = 22.041(5)$ Å, $\alpha = 89.721(5)°$, $\beta = 81.283(5)°$, $\gamma = 70.265(5)°$, $U = 2923.8(2)$ Å^3, $T = 100$ K, $Z = 2$. μ(Mo K_α) = 0.914 mm^{-1}, 19866 reflections were measured, 9382 [$I \geq 2\sigma(I)$] unique reflections were used in all calculations. The final values were R1= 0.0653, wR2 = 0.1376, $S = 0.985$.

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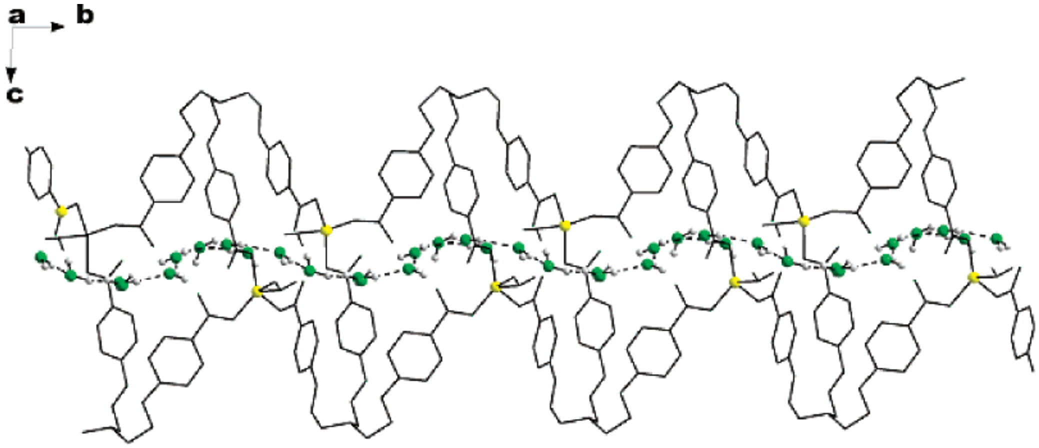

Figure 4. View illustrating the wavelike water chain inside the metallomacrocycles.

Table 1. Geometrical Parameters of Hydrogen Bonds (Å, deg) for the Water Chain[a]

Ow1···Ow2	2.770	Ow1···Ow2···Ow3	121.27
Ow2···Ow3	2.855	Ow2···Ow3···Ow4	136.23
Ow3···Ow4	2.852	Ow3···Ow4···Ow5	110.39
Ow4···Ow5	2.795	Ow4···Ow5···Ow6	99.55
Ow5···Ow6	2.828	Ow5···Ow6···Ow7	121.09
Ow6···Ow7	2.833	Ow5···Ow6···Ow1′	132.40
Ow3···Ow8	2.802	Ow2···Ow3···Ow8	129.85
Ow8···Ow9	2.697	Ow3···Ow8···Ow9	90.81
Ow6···Ow1′	2.704		
Ow1···O5	2.827	Ow1−H···O5	148.84
Ow2···O3	2.771	Ow2−H···O3	135.22
Ow4···O9	2.835	Ow4−H···O9	156.65
Ow5···O17	2.858	Ow5−H···O17	163.58
Ow7···O9	2.969	Ow7−H···O9	146.67
Ow7···O12	2.905	Ow7−H···O12	167.27
Ow8···Ow11	2.808	Ow8−H···Ow11	163.28
Ow9···O5	2.675	Ow9−H···O5	167.60
Ow1−H···Ow2	151.52	Ow6−H···Ow7	161.50
Ow2−H···Ow3	140.72	Ow3−H···Ow8	160.79
Ow3−H···Ow4	147.04	Ow8−H···Ow9	159.35
Ow4−H···Ow5	175.72	Ow6′−H···Ow1	166.39
Ow5−H···Ow6	156.43		

[a] Please refer to Figure 3 for atom designations pertaining to the water cluster.

crystallographic *b* axis (Figure 4). Bulk water exhibits short-range O···O order in the X-ray diffraction radial distribution curve at 2.85 Å, whereas for the gas phase, this value is ~0.1 Å longer.[25] The 1D helical chains of water molecules anchored onto a helical supramolecular host exhibit[9b] long O···O distances (2.9−3.0 Å), whereas in the water chain stabilized by imidazole channels, these distances are found[9a] to be in the range of 2.763(2)−2.783(2) Å. In **1**, a wide variation in the hydrogen-bonding interactions is observed (range of O···O distances, 2.697−2.855 Å; range of O···H−O angles, 140.72−175.72°), attributable to the fact that the water molecules in the chain are sufficiently flexible to respond to changes in the chain's environment. Here, both water−MOF and water−water interactions are important for the stability of the overall structure.

The interaction between the MOF and the water cluster is moderately strong, as thermal gravimetric analysis with a 12.20-mg sample in air shows that weight loss occurs in stages beginning at 80° C and the loss of 14.57% corresponding to all of the water (calculated 14.74%) takes place above 270° C. Complete decomposition is achieved at ~280° C. The FTIR spectrum of **1** shows a broad band centered around 3500 cm^{-1} due to water molecules that vanishes when the compound is heated under vacuum (0.1 mm) at 180° C for 2 h. The IR spectrum of ice[26] shows the O−H stretching at 3220 cm^{-1}, whereas this stretching vibration in liquid water[26] appears at 3490 and 3280 cm^{-1}. Hence, the water chain in **1** shows O−H stretching vibrations similar to those of liquid water. Water clusters identified in other MOFs show[6−8] O−H stretching vibrations in the range 3400−3500 cm^{-1}. Powder X-ray diffraction patterns of **1** show changes in peak positions as well as intensities before and after water expulsion, although sharp peaks remain, indicating that the degree of crystallinity is relatively unchanged.

In conclusion, we have identified an infinite chain of water molecules passing through an array of metallocycles like a thread. The stability of the water chain is derived from strong hydrogen-bonding interactions between neighboring water molecules along the chain as well as strong H-bonding interactions with the available carboxylate O atoms and metal-bound water molecules.

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Supporting Information Available: X-ray crystallographic files in CIF format, TGA curve, infraredspectra, and X-ray powder diffraction patterns for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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