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Metal–Organic Framework H-Bonded Like a Polycatenane: Coexistence of Acyclic Water Trimer and Nonamer

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Pyridine-2,6-dicarboxylic acid and 1,2-di-4-pyridylethylene react hydrothermally with nickel(II) nitrate, forming a metal–organic framework that forms a polycatenane-like structure through H-bonding interactions between water molecules and carboxylate O atoms with void spaces. Discrete acyclic trimeric and nonameric water clusters occupy the voids in the structures. X-ray powder diffraction and X-ray structure analysis have been used to characterize this compound. Crystal data for **1** $\{(3dpeH_2)[Ni(pdc)_2]_3 \cdot 15H_2O\}$: monoclinic space group $P2_1/c$, $a = 24.730(5)$ Å, $b = 19.895(2)$ Å, $c = 17.257(4)$ Å, $\beta = 104.832(5)°$, $V = 8208(4)$ Å^3, $Z = 4$, R1 = 0.0429, wR2 = 0.1072, and $S = 1.051$.

Structural studies of small water clusters in different surroundings are important because they help to correctly describe the many-body interactions[1] required for obtaining an accurate description of bulk water over an extended range. Structural diversity of the water clusters is crucial for several biomolecules to function[2] besides their important role(s) in their stabilization.[3] For chemical systems, the degree of structuring of a water cluster that can be imposed by its environment and vice versa can be of importance[4] in the design as well as stabilization of new structures. In the past several years, considerable attention has been paid to theoretical[5−8] and experimental[9−15] studies of small water clusters. It is quite interesting to note that clusters with even numbers of water molecules are larger in number than the odd-numbered ones.[16] Only trimers and pentamers are common in crystal hydrates, and higher nuclearity, odd-numbered clusters are much less known. We report here the structures of acyclic nonameric and trimeric water clusters present in the cavity of a metal−organic framework (MOF) built from Ni(II), pyridine-2,6-dicarboxylic acid (pdcH$_2$), and 1,2-di-4-pyridylethylene (dpe). pdcH$_2$ has been in constant use as a ligand to form discrete as well as coordination polymeric structures with a variety of metal ions including Ni(II).[17] We show here that changing the reaction conditions can lead to a very different structure with the Ni(II) ion.

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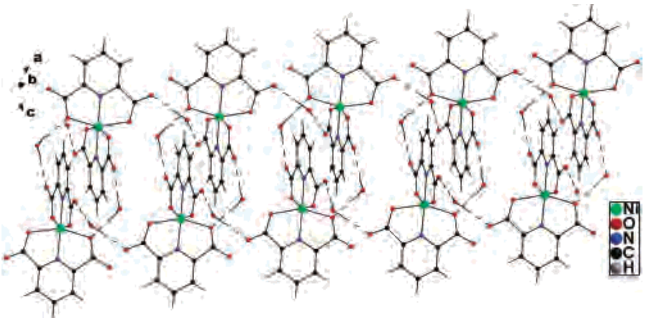

Figure 1. Hydrogen-bonded catenane-like structure.

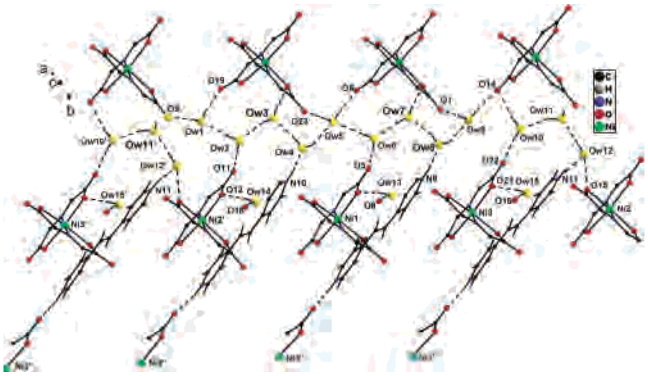

Figure 2. View showing the interactions of the water clusters with the MOF.

Compound **1** is prepared[18] hydrothermally by reacting $Ni(NO_3)_2{\cdot}6H_2O$, $pdcH_2$, and dpe in equimolar amounts as green crystals in 56% yield and characterized by X-ray crystallography,[19] elemental analysis, vibrational spectroscopy, and X-ray powder diffraction.

The asymmetric unit of **1** contains 3 $\{(pdc)_2Ni\}^{2-}$ dimers, 3 $dpeH_2^{2+}$, and 15 water molecules. A total of 2 out of the 15 water molecules connect the dimers through hydrogen bonding, and another water molecule is involved in connecting these dimers of dimers sideways, forming a catenane-like structure (hereafter only catenane) (Figure 1). These catenane units are connected by the $dpeH_2^{2+}$ molecules that are H-bonded on one end to a water molecule and at the other to a carboxylate O atom belonging to different catenane units (Figure 2).

The remaining 12 water molecules occupy the voids between two catenane units, where they are hydrogen-bonded to the carboxylate O atoms (Figure 3). These 12 water molecules form two types of discrete water clusters: one is a bent trimer and the other is a zigzag nonamer (Figure 4). The structural landscape associated with the nonamer is extensive, and theoretical calculations[20] carried out at the HF as well as the DFT levels predict a number of cyclic structural isomers for this cluster (Figure 5). The minimum-energy structure is the one as a D_{2d} octamer with an extra two-coordinated water molecule inserted into one of the edges (Figure 5b), which was also suggested by infrared depletion spectroscopy of size-selective clusters.[21] The lattice of a crystal host, on the other hand, may offer an environment for stabilizing a higher energy isomer. To date, a discrete nonamer having a quasi-planar cyclic structure[16] has been reported. The cyclic structure is possibly more stable than a linear one owing to the possibility of formation of a maximum number of hydrogen bonds within the cluster. In **1**, the shape and size of the void space in this structure prevent cyclic arrangement of the water molecules. Here, the nonamer adopts an acyclic zigzag conformation and its stability is derived from strong hydrogen-bonding interactions

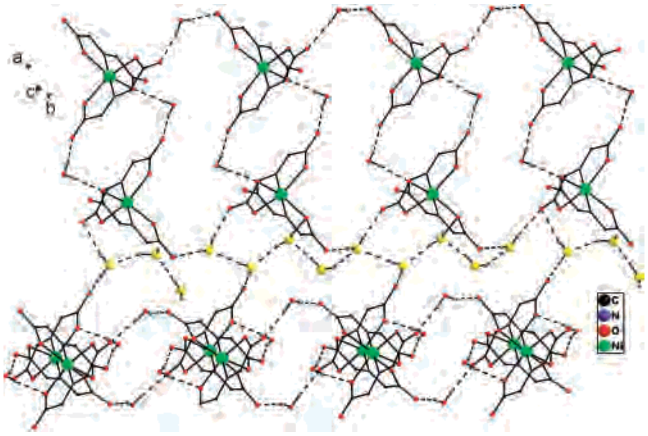

Figure 3. View illustrating how the water clusters connect two catenane-like units. The O atoms of the water clusters are colored yellow.

Figure 4. Close view of the water clusters.

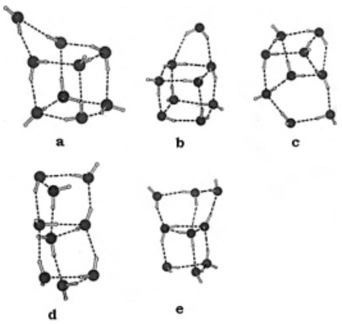

Figure 5. Theoretically predicted structures for the nonamer.

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[18] This compound was synthesized solvothermally by reacting $Ni(NO_3)_2{\cdot}6H_2O$, $pdcH_2$, and dpe in the molar ratio of 1:1:1 in the presence of 8 mL of water for 3 days at 200 °C and then cooling for 7 h. The desired product was isolated as green flakes in ~56% yield. Anal. Calcd for $C_{78}H_{84}N_{12}O_{39}Ni_3$: C, 47.08; H, 4.25; N, 8.45. Found: C, 47.25; H, 4.33; N, 8.26.

[19] Crystal data of **1**: $M = 1989.70$ g mol^{-1}, monoclinic, space group $P2_1c$, $a = 24.730(5)$ Å, $b = 19.895(2)$ Å, $c = 17.257(4)$ Å, $\beta = 104.832(5)°$, $V = 8208(4)$ Å^3, $Z = 4$, $R1 = 0.0429$, $wR2 = 0.1072$, $S = 1.051$, $T = 100$ K, $D_c = 1.610$ g cm^{-3}, $\mu = 0.788$ mm^{-1}, $F(000) = 4128$, and crystal size $= 0.15 \times 0.12 \times 0.11$ mm^3. A total of 20256 reflections up to $\theta = 28.30$ were collected, of which 15698 unique reflections were used. The structure was solved using SHELXS-97 and refined using SHELXL-97 to $R1 = 0.0429$, $wR2 = 0.1072$, and GOF = 1.051. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in successive difference Fourier maps, and they were treated as riding atoms using SHELXL default parameters.

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Table 1. Geometrical Parameters of Hydrogen Bonds (Å and deg) for the Water Nonamer and Trimer

Ow1···Ow2	2.763(6)	Ow2···Ow3	2.671(4)
Ow3···Ow4	2.686(4)	Ow4···Ow5	2.881(4)
Ow5···Ow6	2.873(4)	Ow6···Ow7	2.683(4)
Ow7···Ow8	2.698(4)	Ow8···Ow9	2.824(4)
Ow10···Ow11	2.725(4)	Ow11···Ow12	2.721(4)
Ow1···H1−Ow2	173.92	Ow···H1−Ow3	162.53
Ow3···H1−Ow4	169.66	Ow5···H2−Ow4	151.56
Ow5···H1−Ow6	175.46	Ow6···H2−Ow7	169.54
Ow7···H2−Ow8	164.55	Ow9···H1−Ow8	151.97
Ow10···H2−Ow11	158.58	Ow11···H1−Ow12	175.15
Ow1···O9	2.808(6)	Ow1···O19	2.725(6)
Ow2···O11	2.731(6)	Ow3···O23	2.864(6)
Ow4···N10	2.687(6)	Ow5···O6	2.733(6)
Ow5···O24	2.750(6)	Ow6···O3	2.699(6)
Ow7···O2	2.837(6)	Ow8···N8	2.662(6)
Ow9···O1	2.735(6)	Ow9···O14	2.874(6)
Ow10···O14	2.931(6)	Ow10···O22	2.735(6)
Ow11···O10	3.132(6)	Ow11···O9	3.143(6)
Ow12···O15	2.934(6)	Ow12···N11	2.671(6)
Ow1−H2···O9	173.68	Ow1−H1···O19	164.33
Ow2−H2···O11	176.08	Ow3−H2···O23	151.35
N10−H10···Ow4	162.64	Ow5−H1···O24	176.10
Ow5−H2···O6	170.93	Ow6−H2···O3	173.31
Ow7−H1···O2	172.02	N8−H8···Ow8	165.51
Ow9−H1···O14	165.23	Ow9−H2···O1	174.51
Ow10−H1···O14	165.01	Ow10−H2···O20	154.21
Ow11−H1···O9	145.24	Ow12−H2···O15	141.76
N11−H11···Ow12	159.11	Ow1···Ow2···Ow3	120.16
Ow2···Ow3···Ow4	100.52	Ow4···Ow5···Ow6	114.60
Ow5···Ow6···Ow7	124.32	Ow6···Ow7···Ow8	105.29
Ow7···Ow8···Ow9	93.98	Ow10···Ow11···Ow12	106.92

between neighboring water molecules along the chain as well as H-bonding interactions (Table 1) with the available carboxylate O atoms and $dpeH_2^{2+}$ molecules (Figure 2). The $(H_2O)_3$ cluster comes right after each nonamer, and instead of existing as an infinite chain through connecting the trimers and nonamers, they exist separately because of the structural constraints imposed by the host. Optimum water−MOF and water−water interactions for the stability of the overall structure require a separation of 2.6−3.0 Å between water oxygens of the cluster that should also be able to occupy an optimum available space with favorable interactions with the MOF. Both of these are met in the present structure, with the result that water molecules do not behave as single donors and single acceptors but they are rather nonsystematically disposed in terms of H-bond donor/acceptor characteristics. The interaction between the MOF and the water cluster is weak because thermal gravimetric analysis in air shows that weight loss begins[22] at room temperature and without showing any plateau in the thermogram. The FTIR spectrum of **1** shows a broad band centered around 3415 cm^{-1} attributable to the O−H stretching frequency of the water cluster. This broad band vanishes upon heating of the compound under vacuum (0.1 mm) at 140 °C for 2 h, suggesting escape of the water molecules from the lattice. The IR spectrum of ice[23] shows the O−H stretching at 3220 cm^{-1}, while this stretching vibration in liquid water appears at 3490 and 3280 cm^{-1}. This suggests that the water cluster in **1** shows an O−H stretching vibration similar to that of liquid water, and the slight difference is attributable to the environment that the clusters are in. Deliberate exposure to water vapor for 3 days does not lead to reabsorption of water into the lattice, as monitored by FTIR spectroscopy. Powder X-ray diffraction patterns[22] of the compounds before and after water expulsion show major changes in the peak positions as well as their intensities, suggesting breakdown of the host lattice once the water molecules are expelled.

In conclusion, we have identified an acyclic trimeric and a discrete, zigzag nonameric water cluster in an MOF structure. The nonamer provides a rare example of a high-nuclearity, odd-numbered water cluster very different from the one found experimentally or predicted theoretically. The overall structure of the water clusters is commensurate with the MOF. Studies of water clusters of different nuclearity under different surroundings may provide insight into the hydrogen-bonding motif of the aqueous environment in living systems and a clear understanding of the structure of ice and bulk water as well. Water clusters of different sizes and shapes in diverse environments are presently being investigated in our laboratory.

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

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