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Infinite Chains of Quasi-Planar Hexameric Water Clusters Stabilized in a Metal-Organic Framework Built from Co^{II} and Pyrazine-2,3,5,6-tetracarboxylic Acid

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Pyrazine-2,3,5,6-tetracarboxylic acid ($ptcH_4$) reacts with $Co(NO_3)_2 \cdot 6H_2O$ in 1:2 molar ratio in aqueous pyridine (py) at room temperature to form a coordination polymer with the empirical formula, $\{[Co_2(ptc)\cdot(py)_2\cdot 4H_2O]\cdot 4H_2O\}_n$, (**1**). The structure consists of 2D sheets of metal-organic frameworks and infinite chains of cyclic water hexamers that join these sheets to form an overall 3D structure. Thermogravimetry, X-ray powder diffraction and X-ray structural analysis have been used in addition to infrared spectroscopy and elemental analysis to characterize **1**. Crystal data for **1**: monoclinic space group $P2_1$, a = 7.153(4), b = 17.003(2), c = 11.060(5) Å, β = 107.207(5)°, V = 1284.9(11) Å^3, Z = 2, $R1$ = 0.0340, $wR2$ = 0.0875, S = 1.028. This structure demonstrates a new mode of association of water molecules.

Introduction

Identification of small water clusters[1a–1g] in diverse environments continue to be a subject of considerable interest as it provides the key to test and calibrate theoretical studies to understand this liquid. In spite of characterization of a number of clusters of different nuclearity coupled with advances in computational capabilities, some of the properties of liquid water still cannot be accurately described over a significant range of conditions.[2] The advantage of water clusters/networks having different structures is the possibility to correctly describe the many-body interactions among a group of molecules. It also affords to simply vary the size and to investigate the development of properties of the condensed phase in a step-by-step manner.

Supramolecular association of water molecules in the form of chains constitute an important form of water that is poorly understood.[3] However, water chains are generally accepted to play important roles in several biological processes. In membrane-spanning protein gramicidine *A*, the conduction of protons is believed[4] to take place through a chain of hydrogen-bonded water molecules embedded in the protein. Water chains appear to be important[4] in the control of proton fluxes in a variety of biomolecules such as cytochrome b6f, mitochondral ATPase, carbonic anhydrase II, cytochrome c oxidase, bacteriorhodopsin, etc. The highly dynamic water molecules present in membrane channel protein aquaporin I adopt a chain structure for efficient and selective permeation of water across membranes.[5] Although identification of water chains in crystal hydrates is growing, the structural constraints of the host lattice required to stabilize chain structure or the influence of the chain on the host structure remain incomplete.

Water chains can be built either from zig-zag connections of water molecules or through connections of one or more types of cyclic rings. Of particular interest here is the water chains made from hexameric rings. The hexamer has been subjected to a number of experimental[6] and theoretical[7] studies as it is the building block of ice and also exhibits some of the properties of bulk water.[8] Clusters up to pentamers generally have cyclic and quasi-planar structures and the larger clusters have 3D structures. The hexamer behaves as the transitional point from 2D to 3D structures.[9] Theoretical calculations[7] on the $(H_2O)_6$ cluster show five minima in the potential energy surface that correspond to five almost iso-energetic conformers – "cage", "prism", "book", "boat" and "cyclic". The "cage" conformer is the most stable at low temperature and has been observed[10] by vibration-rotation tunneling spectroscopy while a quasi-planar cyclic hexamer was detected[11] in a helium droplet. The lattice of a crystal host offers an environment where a higher energy conformer can be stabilized and this way, chair,[6b,6c,6f] boat[6a,6d] and planar[6e] forms have been characterized in inorganic as well as in organic crystal hosts.

We report here, the X-ray structure of infinite chains of hexameric quasi-planar water molecules present in a metal-organic framework (MOF) built from Co^{II}, pyridine and pyrazine-2,3,5,6-tetracarboxylic acid.[12] Our recent efforts[1d,e,6a,c,13] are directed towards the synthesis of MOFs with voids of different shapes and sizes that can include

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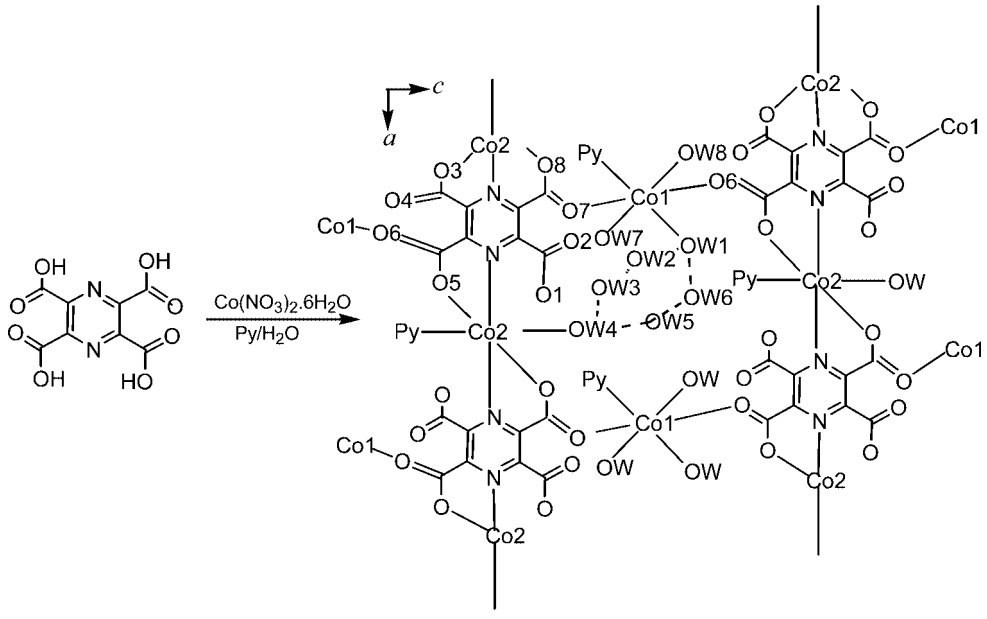
water clusters of different nuclearity. The degree of structuring of water clusters that can be imposed by its environment and vice versa are important in the design of new MOF structures with the ultimate aim(s) of having materials with potentially useful applications.

Results and Discussion

Compound **1** crystallizes in a non-centrosymmetric space group presumably due to unsymmetrical distribution of lattice water molecules. The structure consists of two types of hexacoordinate Co^{II} ions that are bonded to the ligands as shown in Scheme 1. For the ligand, ptc^{4-}, only the carboxylate group at the 2-position is not bonded to a metal. Here, Co2 is equatorially bonded to two pyrazine tetracarboxylate ligands through ring N and one carboxylate O atoms (N_2O_2 donor) and the axial positions on the metal are occupied by a pyridine and a water molecules. Thus, Co2 and ptc^{4-} ligands form a linear coordination polymer extending along the crystallographic *a* axis. The Co1 ion is axially bonded to two carboxylate O atoms belonging to two different polymeric chains thus connecting them to form a 2D coordination polymer in the crystallographic *ac* plane (Figure 1). The equatorial sites of Co1 are occupied by three H_2O and one pyridine molecules. The bond lengths and bond angles involving each Co^{II} center are comparable[13b] with reported values for octahedral Co^{II} complexes. Atoms Ow1 bound to Co1 and Ow4 bound to Co2 are hydrogen-bonded to four other water molecules forming a cyclic hexameric water cluster. The atoms Ow7 and Ow8 are not connected to the cluster. These clusters further assemble the 2D networks along the crystallographic *b* axis into an overall 3D MOF (Figure 2 and Figure 3).

Atom Ow3 of the hexamer is H-bonded to Ow5′′ belonging to another hexamer forming a chain of cyclic hexamers parallel to the *ab* plane and extending along the crystallographic *a* axis (Figure 4). Due to a long distance (3.955 Å) between Ow2′ and Ow6, they are not considered as H-bonded even though one of the H atoms of Ow2 is pointed toward Ow6′. However, the less number of H-bonding interactions among the water molecules are compensated by H-bonding interactions these molecules have with the surroundings (Table 1). Chains of hexameric water clusters with different modes of connectivity present in different crystal hosts are collected[17] in two recent articles. Interconnected hexameric boat conformers are present[18] in hexagonal ice (I_h) and also identified[6g] between the layers of an inorganic polymer constructed from $CdNi(CN)_4$ units. Water molecules forming a hexameric chair conformation and self-assembly of these units into a 1D tape had been found[6f] in an organic host constructed from 5-amino-2,4-dimethylbenzo[*b*]-1,8-naphthyridine. Very recently, 1D chains consisting of cyclic hexameric chair conformers connected by Zn^{II} or Co^{II} have been found[6b] in the complexes, $[M(H_2biim)_2(OH_2)_2](ina)_2{\cdot}4H_2O$ [M = Zn^{II} or Co^{II}, H_2biim = 2,2′-biimidazole, *ina* = isoniconate]. Following the nomenclature suggested by Infantes and Motherwell,[17] the water chain in **1** may be designated as T6(0)A0. Although a structure with the same designation is reported[17] by these authors, the chain is propagated through Ow1 and Ow4 atoms whereas in this case, it is through Ow3′ and Ow5 atoms (Figure 4).

While theoretical calculations[7a] predicts the "cage", "prism", "book", "boat" and "cyclic" conformations that are almost isoenergetic, the lattice of a crystal host may offer an environment for stabilizing a higher energy conformer. In the present structure, the six O atoms of the



Scheme 1. Schematic diagram showing the bonding modes of the ligand with Co^{II}.

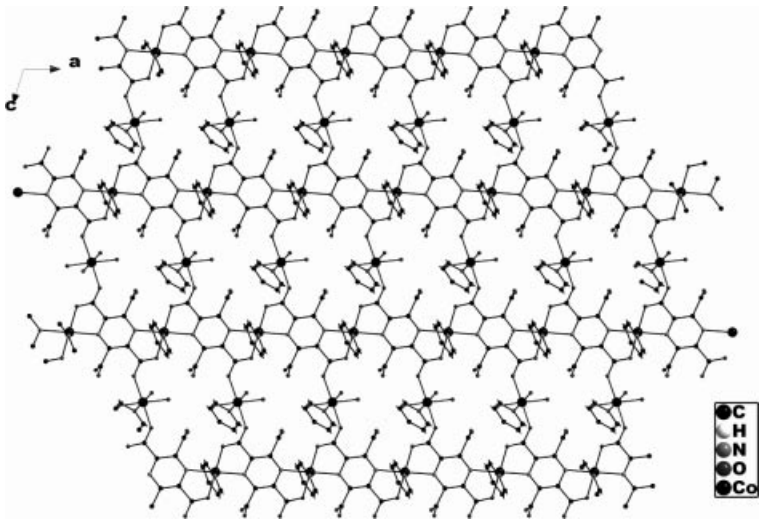


Figure 1. A perspective view of the planar sheet structure of **1** viewed down the *b* axis. Hydrogen atoms are omitted for clarity.

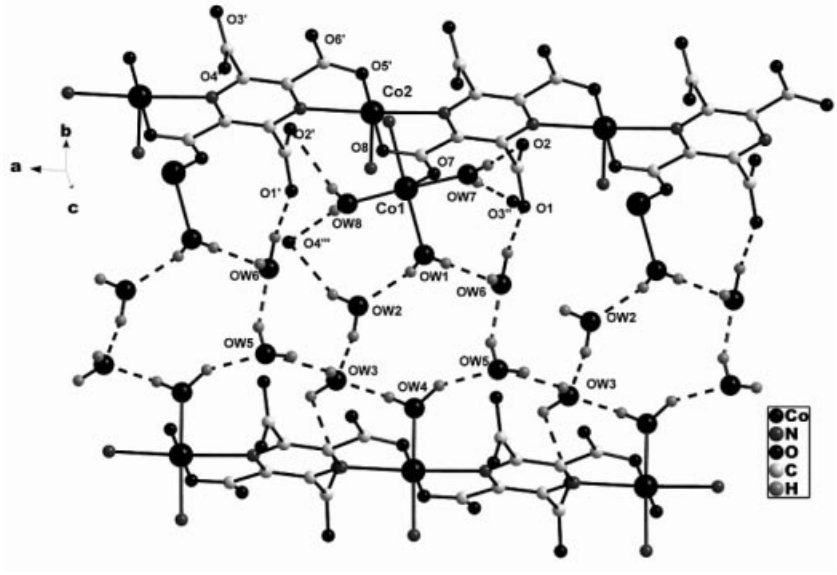


Figure 2. A view showing how water molecules are bound to the MOF. The lone blue spheres are pyridine N atoms. The entire pyridine molecule is not shown for clarity.

hexameric unit assume a slightly puckered conformation and this mode of association results from two factors: (1) the Ow atoms are H-bonded to the carboxylate O atoms which are fixed as almost coplanar in space and (2) the metal-bound pyridine molecules (Figure 3) would obstruct if the conformation is deviated significantly from planarity. Cyclic planar water hexamer is the basic structural motif found[19] in ice II structure under high pressure. This is also a prominent structural unit present[20] in liquid water based on computer simulation while Nauta and Miller detected the "quasi-planar" hexamer within a helium droplet.[11]

The nonbonding Ow···Ow distances (Table 1) show a wide variation commensurate with the MOF structure. The average O···O distance of 2.795 Å is smaller than that of liquid water which shows a value of 2.85 Å from the X-ray diffraction radial distribution curve while for the gas phase, this value is ca. 0.1 Å longer.[18] The water molecules present in clefts of biological/abiological molecules are very different from the gas phase or bulk liquid water. Here, the principle of maximizing H-bonding interactions is followed where the environment plays a major role. Consistent with this principle, the O···O distances in the cluster vary widely for optimized interactions between the water molecules and between a water molecule and its surrounding. For a discrete quasi-planar hexamer[6e] trapped in an organic supramolecular complex with bimesityl dicarboxylic acid, the average O···O distance (2.775 Å) is shorter while in case of a dodecameric[21] water cluster built around a planar cyclic hexamer in a supramolecular complex of a cryptand, the O···O distance (2.801 Å) is similar to the present structure. The nonbonding O···O···O angles (Table 1) in **1** span a wide range [104.8 (3)–132.7(2)°] deviating considerably from an ideal benzene-like structure. In the chain, Ow1 and Ow4 act as double donors, Ow6 as double acceptors while the rest

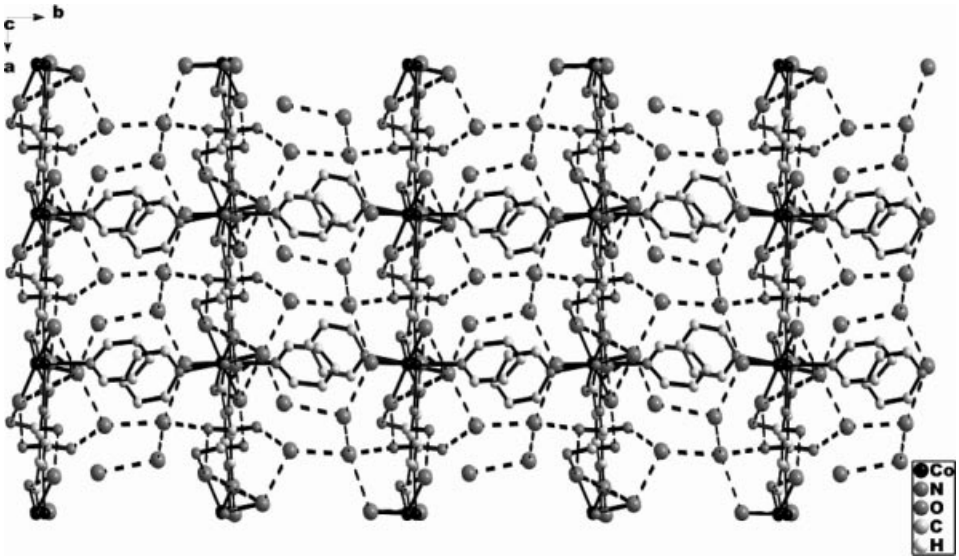


Figure 3. The MOF structure of **1** viewed in the *ab* plane. The chains of quasi-planar water molecules extending along the crystallographic *a* axis.

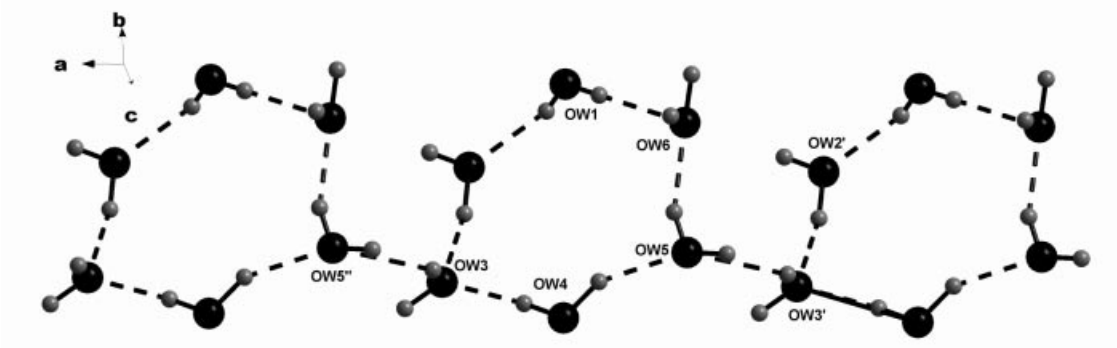


Figure 4. A perspective view of the chain of planar hexamaric water cluster showing the H-bonding Scheme.

Table 1. Non-bonded distances [Å] and angles [°] involving the hexameric water cluster.[a]

Ow1···Ow2	2.691(6)	Ow2···H1–Ow1	175.3(1)
Ow2···Ow3	2.824(3)	Ow3···H1–Ow2	169.2(2)
Ow3···Ow4	2.758(5)	Ow3···H2–Ow4	171.6(2)
Ow4···Ow5	2.808(6)	Ow5···H1–Ow4	162.7(1)
Ow5···Ow6	2.748(2)	Ow6···H1–Ow5	152.4(1)
Ow6···Ow1	2.724(4)	Ow6···H2–Ow1	162.8(1)
Ow3···Ow5′′	3.014(4)	Ow5···H2–Ow3′	129.7(1)
		Ow6···Ow1···Ow2	125.2(2)
		Ow1···Ow2···Ow3	118.2(1)
		Ow2···Ow3···Ow4	104.8(3)
		Ow3···Ow4···Ow5	132.8(2)
		Ow4···Ow5···Ow6	114.3(1)
		Ow5···Ow6···Ow1	113.9(2)
		Ow6···Ow5···Ow3′	91.4(1)
Ow2···O4	2.890(2)	Ow7···O2	2.739(2)
Ow3···O3	2.899(4)	Ow7···O3	2.811(3)
Ow6···O1	2.717(4)	Ow8···O1	2.887(2)
		Ow8···O4	2.759(4)

[a] One H atom in each of Ow4 and Ow5 could not be located in the difference Fourier maps. Their positions were calculated (H2W4 and H2W5) and added to the atom list. Atoms Ow3′ and Ow5′′ are related by 2 – *x*, 1/2 + *y*, 2 – *z* and 2 – *x*, –1/2 + *y*, 2 – *z* respectively.

act both as donors and acceptors of H-bonding. So, every O atom in the unit does not show four coordination. Such hydrogen-bond deficient water molecules are present[22] at the surface of ice while recent X-ray absorption spectroscopy and Raman scattering studies of liquid water also point to the fact that significant number of O atoms show less than tetracoordination in liquid water.[23]

Thermal analysis of the compound shows that onset of water loss starts at ca. 30 °C and complete loss of water takes place within 100 °C without showing any plateau in the thermogram.[24] The FTIR spectrum[24] 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 on heating 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[18a] shows the O–H stretching at 3220 cm^{-1} while this stretching vibration in liquid water[18a] appears at 3490 and 3280 cm^{-1}. This suggests that the water cluster in **1** shows O–H stretching vibration similar to that of liquid water. Deliberate ex-

posure to water vapor for 3 days does not lead to re-absorption of water into the lattice as monitored by FTIR spectroscopy. The spectrum below 2000 cm^{-1} does not change appreciably on heating **1** at 140 °C for 2 h that suggests coordination of ptc^{4-} to Co^{II} is still maintained. However, powder X-ray diffraction[24] patterns of **1** before and after water expulsion show major changes with respect to peak positions and intensities suggesting breakdown of the host lattice once the water molecules are expelled.

Conclusion

In conclusion, we have identified infinite chains of quasi-planar hexameric water clusters in an MOF built from Co^{II} and pyrazine-2,3,5,6-tetracarboxylic acid. Each chain assembles two planar 2D coordination polymeric networks where the structure of the water chain is commensurate with the MOF.

Experimental Section

Materials: The metal salt and phenazene were acquired from Aldrich and used as received.

Physical Measurements: Spectroscopic data were collected as follows: IR (KBr disk, 400–4000 cm^{-1}) Perkin–Elmer Model 1320; X-ray powder pattern (Cu-K_α radiation at a scan rate of 3°/min, 293 K) Siefert ISODEBYEFLEX-2002 X-ray generator; thermogravimetric analysis (heating rate of 5 °C/min) Mettler Toledo Star System. Microanalysis data for the compound were obtained from CDRI, Lucknow.

Synthesis of $\{[Co_2(ptc)\cdot(py)_2\cdot 4H_2O]\cdot 4H_2O\}_n$ (1): $Co(NO_3)_2\cdot 6H_2O$ (0.64 g; 2 mmol) was added to a solution of pyrazine-2,3,5,6-tetracarboxylic acid ($ptcH_4$) (0.26 g; 1 mmol) in 25 mL of aqueous pyridine (1:1, v/v). A dark reddish solution was obtained. After filtering the solution, the solvent was allowed to evaporate slowly at room temperature whereupon (after 10 days) red rectangular parallelopiped crystals of **1** appeared (0.302 g, 45% yield). $C_{18}H_{26}Co_2N_4O_{16}$ (672.29): C 32.16, H 3.89, N 8.33; found C 32.67, H 4.02, N 8.14.

X-ray Structural Studies: Single-crystal X-ray data on **1** were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. The data integration and reduction were processed with SAINT[14] software. The structure was solved by the direct method using SHELXTL[15] and was refined on F^2 by full-matrix least-squares technique using the SHELXL-97[16] program package. All non-hydrogen atoms present were anisotropically refined. All hydrogen atoms except two could be easily located in successive difference Fourier maps and they were treated as riding atoms using SHELXL default parameters. The remaining two H atoms were calculated theoretically and added to the list. Crystal data of **1**: M = 672.29 g mol^{-1}, monoclinic, space group $P2_1$, a = 7.153(5), b = 17.003(5), c = 11.060(5) Å, β = 107.207(5)°, U = 1284.9(11) $Å^3$, Z = 2, $R1$ = 0.0340, $wR2$ = 0.0875, S = 1.028. T = 100 K, D_c = 1.738 g cm^{-3}, μ = 1.376 mm^{-1}, $F(000)$ = 688, crystal size = 0.17 × 0.14 × 0.10 mm^3. A total of 8112 reflections up to θ = 28.30 were collected of which 4482 unique reflections were used.

CCDC-236954 contains the supplementary crystallographic data for this paper. These data can be obtained from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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[24] Supporting Information (for details see footnote on the first page of the contribution): TGA curve, X-ray powder diffraction patterns for **1** before and after exclusion of water and FTIR spectra of **1** before water removal and after water removal.

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