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Article

Coexistence of Water Dimer and Hexamer Clusters in 3D Metal–Organic Framework Structures of Ce(III) and Pr(III) with Pyridine-2,6-dicarboxylic Acid

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$Ce(NO_3)_3 \cdot 6H_2O$ or $Pr(NO_3)_3 \cdot 6H_2O$ and pyridine-2,6-dicarboxylic acid form a linear coordination polymeric structure under hydrothermal conditions. Hexameric water clusters join these linear chains through bonding to the metal ions. Other coordinated water and the carboxylate oxygen form an intricate array of hydrogen bonding resulting in a 3D network where each metal ion shows 9-coordination with an approximate D_3 symmetry. Dimeric water clusters are also located in the void spaces. In the structure containing Pr(III), the water dimers are hydrogen-bonded to the hexamers, whereas in the Ce(III) structure, the dimers and the hexamers are far apart.

Introduction

Characterization of small hydrogen bonded water clusters are important as they not only help in understanding bulk water[1] but also provide clues to understand better how such aggregates influence the overall structure of their surroundings.[2] Hydrogen-bonding involving water molecules along with other noncovalent interactions is capable of guiding the self-assembly processes in chemical systems.[3] In biology, self-assembly depends on many noncovalent interactions where water can play an important role by stabilizing the native conformation of the biomolecules. Thus, studies of small water clusters in crystal hydrates have the ultimate goal(s) of understanding the role(s) played by small water clusters in the stabilization and functioning of biomolecules[4] as well as in designing of new materials.[5] Moreover, hydrogen-bonding interactions and their fluctuations determine the properties of bulk water although correct evaluation of these interactions has been the major impediment in our understanding of the “anomalous” behavior of water. For this, there have been attempts[6−13] to simulate water crystallization in restricted environments such as organic and inorganic host lattices. In these studies, small water clusters, $(H_2O)_n$ where $n = 2-10$, have been reported. Among these clusters, the hexamer is particularly interesting as this cluster can exhibit[14] some of the properties of bulk water. Theoretical calculations[15] have predicted several different isomers for this cluster of which the five low energy ones, viz., “cage”, “prism”, “book”, “boat”, and “cyclic”, are almost isoenergetic (i.e. within $\sim$0.7 kcal mol^{-1}). The “cage” structure, predicted to be the most stable conformation at very low temperature, has been observed[16] by vibration−rotation tunneling spectroscopy while a higher energy quasi-planar cyclic hexamer could be detected[17] in a helium droplet. The lattice of a

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crystal host may offer an environment for stabilizing a higher energy hexamer with a particular topology. Thus far, chair,[18] boat,[19] and planar[20] cyclic hexamers have been characterized in host lattices. Water dimers are the simplest water cluster and have been the focus of attention[21−23] by several groups.

Metal−organic framework (MOF) structures with suitable organic ligands can provide void spaces where discrete water clusters can exist. Metal ions in such structures can act as anchors for holding the water clusters. Precise structural data of such hydrogen-bonded water clusters hold the key to unravel the properties of bulk water. Moreover, the structure of enclathrated water can be an important parameter in understanding the mechanism[5] of formation of different MOFs. Crystal engineering of MOFs has attracted a lot of interest due to potential applications and unusual topologies of these materials. Much of the work has so far been focused on the coordination polymers containing transition elements. However, recent years have seen[24−27] an upsurge in the use of lanthanide elements for constructing MOFs. Due to their high coordination number along with special magnetic and luminescence properties, the MOFs containing lanthanides are likely to provide new materials with desirable properties. We have initiated research in building MOFs with lanthanide elements and different multidentate ligands. We have used pyridine-2,6-dicarboxylate (pdc^{2-}) as a chelating ligand which has limited steric hindrance combined with weak stacking interactions offering possibilities to form homoleptic coordination polymers with concomitant scopes for bridging metal ions through carboxylate groups to propagate the coordination chain. Herein, we describe the presence of both cyclic chairlike hexamer and dimer water clusters in metal−organic frameworks (MOFs) constructed from Ce(III) or Pr(III) and pyridine-2,6-dicarboxylic acid. This is one of the rare examples where two different types of water clusters coexist in the same host lattice. The presence of cyclic hexamers and octamers has been reported[28] recently in an MOF structure built from Er(III) and fumaric acid. An MOF structure of Ce(III) similar to ours has been reported recently[29] although it is silent about the presence of water clusters.

Experimental Section

Materials. $Pr(NO_3)_3\cdot 6H_2O$, $Ce(NO_3)_3\cdot 6H_2O$, and pyridine-2,6-dicarboxylic acid were acquired from Aldrich and used as received.

Synthesis of 1. Standard hydrothermal conditions used for the synthesis of **1** afforded solids not suitable for X-ray crystallography. We adopted a different approach where 1 mmol of $Pr(NO_3)_3\cdot 6H_2O$ and 2 mmol of pyridine-2,6-dicarboxylic acid ($pdcH_2$) were taken in 5 mL of water in a Teflon-lined autoclave. The autoclave was heated under autogenous pressure to 180° C for 3 days and then left to cool to room temperature (RT). On allowing the filtrate from the reaction to evaporate at RT, pale green rectangular parallelepipeds of $[Pr(pdc)(pdcH)2H_2O]0\cdot 4H_2O$ (**1**) could be isolated in ∼65% yield. Anal. Calcd for $C_{14}H_{19}N_2O_{14}Pr$: C, 28.98; H, 3.30; N, 4.83%. Found: C, 29.06; H, 3.38; N, 4.76%.

Synthesis of 2. Compound **2** $[Ce(pdc)(pdcH)2H_2O]0\cdot 4H_2O$ was isolated as pale yellow prismatic crystals following the above procedure using $Ce(NO_3)_3\cdot 6H_2O$ in place of $Pr(NO_3)_3\cdot 6H_2O$. Yield: ∼62%. Anal. Calcd for $C_{14}H_{19}N_2O_{14}Ce$: C, 29.02; H, 3.30; N, 4.83%. Found: C, 28.95; H, 3.41; N, 4.78%.

Measurements. Spectroscopic data were collected as follows: IR (KBr disk, 400−4000 cm^{-1}) Perkin-Elmer model 1320, X-ray powder pattern (Cu Kα radiation at a scan rate of 3 °/min, 293 K) Siefert ISODEBYEFLEX-2002 X-ray generator, thermogravimetric analysis (heating rate of 20° C/min) Perkin-Elmer Pyris 6. Microanalyses were obtained either from IIT Kanpur or from CDRI, Lucknow.

X-ray Structural Studies. Single-crystal X-ray data on **1** and **2** were collected at room temperature on an Enraf-Nonius CAD4 Mach2 X-ray diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The cell parameters in each case were determined by least-squares refinement of the diffractometer setting angles from 25 centered reflections that were in the range $18° \le 2\theta \le 22°$. Three standard reflections were measured every hour to monitor instrument and crystal stability. The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography*.[30] The structures were solved by the direct method using SIR92[31] and refined on F^2 by full-matrix least-squares techniques using the SHELXL-97[32] program package. The H atom positions or thermal parameters were not refined but included in the structure factor calculations. The crystal data for the two structures are collected in Table 1.

Results and Discussion

Both the compounds are stable in air and soluble in water but insoluble in common organic solvents. The structure of each MOF consists of linear chains of M(III) ions where each metal ion shows 9-coordination binding two pdc^{2-} ligands, one bridging carboxylate O atom from a neighbor, and two water molecules (Ow1,Ow2). The asymmetric unit

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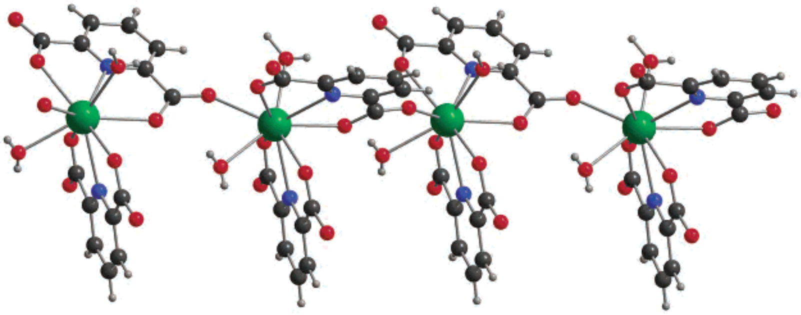

Figure 1. A view of the linear coordination polymeric chain along the crystallographic *a* axis. Carbon: black. Hydrogen: gray. Nitrogen: blue. Oxygen: red. Praseodymium: green.

Table 1. Crystal Data and Structure Refinement for **1** and **2**

	1	**2**
empirical formula	$C_{14}H_{19}N_2O_{14}Pr$	$C_{14}H_{19}N_2O_{14}Ce$
fw	580.21	579.43
temp	293(2) K	293(2) K
radiation, wavelength	Mo Kα, 0.71073 Å	Mo Kα, 0.71073 Å
crystal system	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/a$
a, Å	12.893(3)	12.953 (2)
b, Å	11.200(3)	11.237 (2)
c, Å	14.060(2)	14.007 (3)
β (deg)	102.04(5)	101.86 (5)
V, $Å^3$	1985.6(9)	1995.3(8)
Z	4	4
ρ_{calc} Mg/m^3	1.94	1.93
μ, mm^{-1}	2.53	2.36
F(000)	1152	1148
reflns collected	2586	2598
indep reflns	2289	1752
refinement meth	full-matrix least-squares on F^2	full-matrix least-squares on F^2
GOF	1.04	1.03
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.044 wR2 = 0.112	R1 = 0.044 wR2 = 0.102
R indices (all data)	R1 = 0.052 wR2 = 0.117	R1 = 0.109 wR2 = 0.119

contains one M(III) ion and two ligands besides six H_2O molecules. For charge neutralization, it is suggested that one of the ligands is not deprotonated completely but exists as $(pdcH)^-$. However, we were unable to detect this hydrogen in the difference map. The bridging carboxylate propagates the polymeric chain approximately (Figure 1) along the crystallographic *b* axis. The coordination symmetry around the metal ion is deviated significantly from D_3 symmetry as expected. Bond distances and bond angles involving the metal ion are closely similar to those observed in several related species.[33−35]

The atom Ow1 is hydrogen bonded to two carboxylate O atoms of two other chains while Ow2 is H-bonded to two more water molecules (Ow3, Ow4) forming a hexameric water cluster with three other water molecules related by a center of symmetry and belonging to a different polymeric chain. In addition, two more water molecules, Ow5 and Ow6, are also present in the lattice. In **1**, these two water molecules form a dimer, whereas in **2**, each of Ow5 and Ow6 forms a dimer with an O atom related by a center of symmetry. The water molecules of the dimeric and hexameric clusters are hydrogen bonded to carboxylate O atoms of different polymeric chains resulting in an overall 3D network structure—the water clusters occupying the 3D channels (Figure 2). Once the water molecules are deleted from the packing diagram, zigzag channels can be seen (Figure 3).

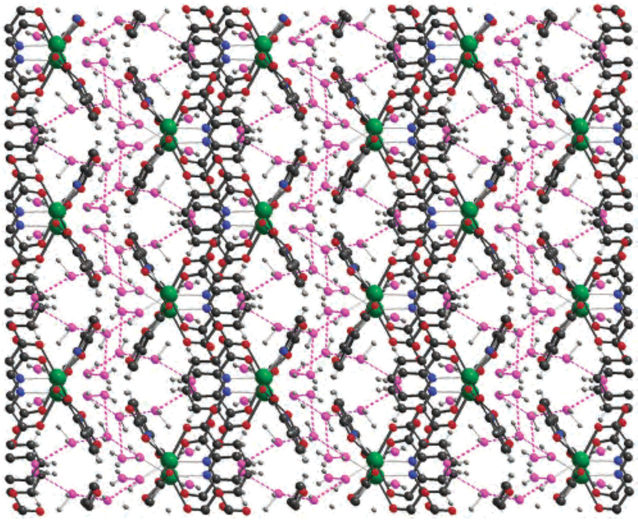

Figure 2. The MOF structure of **1** viewed in the *bc* plane. The dimeric and hexameric water clusters are shown in purple.

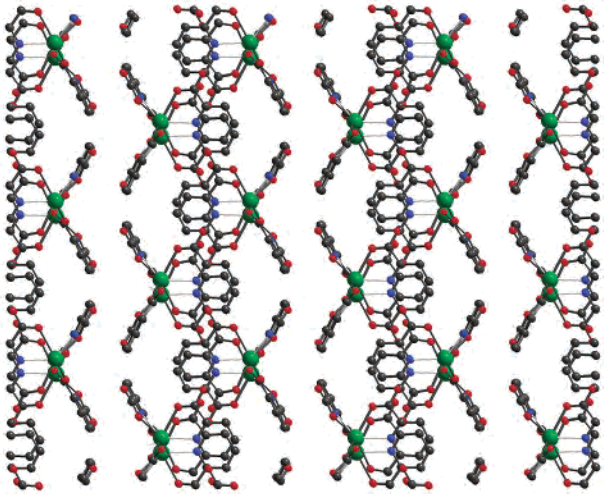

Figure 3. The MOF structure of **1** viewed in the *bc* plane. The water clusters have been omitted to show the zigzag channel along the *b* axis.

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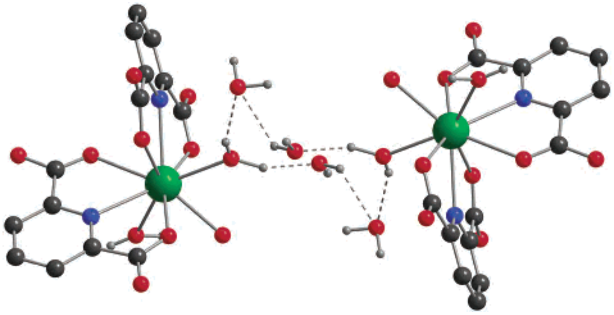

Figure 4. A perspective view of the hexameric water cluster connecting two Pr(III) ions. Each metal ion is showing 9-coordination. Color codes of atoms are same as in Figure 1.

Table 2. Geometrical Parameters of Hydrogen Bonds (Å, deg) for the Water Dimer and the Hexamer and Its Association with the Host in **1** and **2**

1

Ow2···Ow3	2.743	Ow2···Ow3···Ow4′	76.73
Ow3···Ow4′	2.877	Ow3···Ow4′···Ow2′	129.11
Ow5···Ow6	2.829	Ow3···Ow2···Ow4	89.73
Ow2···Ow4	2.702	Pr−Ow2···Ow3	124.70
Ow4···Ow5	3.021	Pr−Ow2···Ow4	144.70
Ow2···Ow4···Ow5···Ow6			−106.33
Ow2···Ow3···Ow4′···Ow5′			−28.51

Ow2−H	1.018	H···Ow4	1.729	Ow2−H···Ow4	159.68
Ow2−H	0.778	H···Ow3	2.149	Ow2−H···Ow3	155.20
Ow4′−H	0.942	H···Ow3	2.189	Ow4′−H···Ow3	130.84
Ow6−H	0.773	H···Ow5	2.223	Ow6−H···Ow5	139.15

2

Ow2···Ow3	2.728	Ow2···Ow3···Ow4′	76.73
Ow3···Ow4′	2.886	Ow3···Ow4′···Ow2′	129.11
Ow2···Ow4	2.700	Ow3···Ow2···Ow4	89.73
Ow5···Ow5′	2.779	Ce−Ow2···Ow3	124.95
Ow6···Ow6′	2.782	Ce−Ow2···Ow4	142.48

The geometrical parameters of the water clusters are collected in Table 2. In the case of **1**, all hydrogen atoms (except one bound to Ow5) bound to water oxygens could be located in the difference maps, which was not the case for **2** apparently because of inferior quality of crystals. The O···O distance in the dimer in **1** is 2.830Å while this distance[36] in regular ice, in liquid water, and in the vapor phase is respectively 2.74, 2.85, and 2.98 Å. In **2**, the dimeric clusters are present in two different types of surroundings showing the O···O distances of 2.779(4) and 2.782(6) Å. Shorter O···O dimer distances in **2** result from the overall compactness of the MOF compared to that of **1**. Thus, the water clusters are sufficiently flexible to respond to small changes in the environment. Recently, the O···O distance of water dimers present in an MOF structure was found[21] to be 2.84 Å where the O−H−O angle was nearly linear (∼170°). In **1**, the O−H−O angle is deviated significantly from linearity (139.15°).

In both the MOFs, the hexameric clusters form an ice-like chair conformation (Figure 4) connecting two M(III) ions in the 1,4-position. The atoms Ow2, Ow3, and Ow4 are connected to the atoms Ow2′, Ow3′, and Ow4′, which are related by the center of symmetry forming the hexamer (Figure 5). These clusters can be regarded as the simplest supramolecular analogue of cyclohexane. As H atoms bound to the O atoms could be located only for **1**, the coordination properties of water O atoms are discussed for this compound. The water molecule Ow2 behaves as H donors, Ow3 as H acceptors, while Ow4 behaves as an acceptor as well as a donor in the hydrogen-bonding scheme. Thus, Ow3 and Ow4 show tetracoordination, and Ow2 which is coordinated to Pr(III) shows tricoordination. The average O···O distances are 2.783 and 2.771 Å in **1** and **2**, respectively. The corresponding value[36] is 2.759 Å in ice I_h at −90 °C. The bond angles in the hexamer vary widely with the average angle being 98.36° and 98.41° in **1** and **2**, respectively, which deviates considerably from the corresponding value of 109.3° in hexagonal ice. The conformational variation from that of ice with the I_h symmetry is due to the constrained environment these clusters are in. Theoretical calculations for the hexamer have revealed the existence of several conformations with energies within 0.7 kcal mol^{-1} of each other. This nearly isoenergetic nature of the different clusters of water hexamers suggests that the conformation that will be detected depends strongly on the chemical environment the cluster is in. The possible effect of the presence of water dimers on the conformation of the hexamer would be minimum in the present structures. This is because the hexamer is weakly hydrogen bonded (Figure 5) to one of the dimers at a O···O distance of 3.024 Å only in structure **1**. In structure **2**, however, none of the dimers are hydrogen bonded to the hexamer, although in both structures, the hexamer forms the same chair conformation.

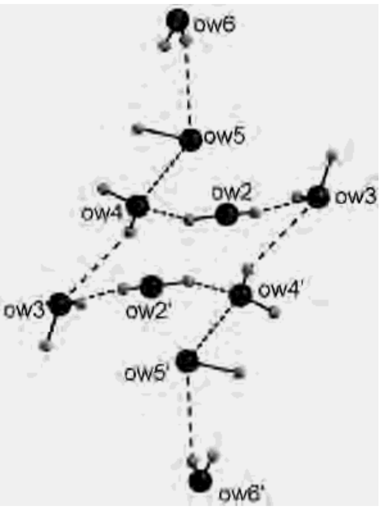

Figure 5. A perspective view of the association of dimeric and hexameric water clusters in **1**. The dimers and hexamers are far apart in **2**.

The 3D structure is largely a consequence of hydrogen bonding interactions among water molecules themselves and the MOF. This association is quite strong as thermal gravimetric analysis of **1** with a 8.75 mg sample in air shows that weight loss occurs in stages beginning at 60° C and the loss 12.8% corresponding to all of the water (calculated 12.1%) takes place above 140° C. Similarly, thermal gravimetric analysis of **2** performed in N_2 atmosphere with 10.34 mg of sample shows that the compound begins to lose weight

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above 50 °C. Water removal continues in several steps giving a total loss of 12.9% at ∼130 °C corresponding to loss of all water molecules (calculated value, 12.2%). The complete decomposition of the compounds is achieved above ∼280 °C. The FTIR spectra of **1** and **2** show a broad band centered around 3400 cm^{-1} attributable[20] to the O−H stretching frequency of the water cluster. This broad band vanishes on heating the compounds under vacuum (0.1 mm) at 140 °C for 2 h, suggesting escape of the water clusters from the lattice. 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 of the compounds before and after water expulsion show major changes in peak positions as well as their intensities, suggesting complete breakdown of the host lattice due to the exclusion of water.

Conclusion

Thus, we have shown that pyridine-2,6-dicarboxylic acid is a suitable ligand to form linear coordination polymers with lanthanide ions under hydrothermal conditions. Here, the metal ion shows 9-coordination with a distorted D_3 symmetry. The 3D structure is largely a consequence of hydrogen bonding interactions among water molecules, and upon removal of water from the lattice, the structures break down. Besides, this is the first set of examples showing the presence of dimeric and hexameric water clusters in the lattice of an MOF. Hydrogen-bonded water clusters can play important roles in stabilizing supramolecular structures quickly without incurring any defects. We are presently probing this aspect of supramolecular chemistry.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of compound **1** and **2**. Table of selected bond distances and angles for **1** and **2**. IR spectra 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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