DOI: 10.1002/ejic.200500735

Octameric Water Clusters of Staircase Structure Present in a Metal-Organic Framework Built from Helical Lanthanide Coordination Polymers

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Keywords: Water chemistry / Supramolecular chemistry / Self assembly / Metal-organic framework / Helical structure

Two lanthanide-carboxylate polymeric complexes containing nine-coordinate lanthanide metal centers, {[Pr(*ptc*$^{-3}$)·$2H_2O$]·$2H_2O$} (**1**), {[Nd(*ptc*$^{-3}$)·$2H_2O$]·$2H_2O$} (**2**) have been prepared by hydrothermal synthesis of $Pr(NO_3)_3·6H_2O$ or $Nd(NO_3)_3·6H_2O$ with pyridine-2,4,6-tricarboxylic acid (*ptc*H_3). These network structures are characterized by X-ray crystallography, powder X-ray diffraction, infrared and thermal gravimetric analyses. Both **1** and **2** form infinite single helical chains with large widths and pitches containing six metal ions per turn. The overall structure consists of two helices connected via discrete octameric water clusters.

Introduction

Water clusters of different nuclearity and structure in both inorganic and organic hydrates continue to attract a lot of attention because such studies facilitate our understanding of the liquid by allowing better description of the many-body interactions in a step by step manner.[1] Of particular interest here is the structure of the $(H_2O)_8$ cluster. Theory predicts[2] two closely related iso-energetic cubane structures with S_4 and D_{2d} symmetries where O atoms occupy the corners and hydrogen bonds along the edges which are supported by experimental proofs in the molecular beam[3] and in gas-phase $C_6H_6(H_2O)_8$ clusters.[4] In crystal hosts, cubane,[5] opened-cubane,[6] cyclic octamer[7] resembling ice I_h and cyclic octamer consisting of a hexamer and two dangling water molecules[8] have been identified. We present here a discrete octamer whose structure is very different from any of these.

The water clusters are present in the voids of 3D metal-organic frameworks built by connecting single helical coordination polymers through carboxylate bridging. Helicate chemistry is not only important in the development and understanding of self-assembly processes, but also to search for new supramolecular architectures endowed with functional properties. The accepted model for helication requires a long multidentate ligand as a molecular thread containing a number of discrete metal-binding sites separated by spacer units. Such a molecular thread can twist around several metal ions controlled by their coordination behavior. Synthesis of only discrete helicates of both transition metals[9] and lanthanides[10] can be achieved following this strategy. We report here formation of open framework structures by connecting infinite single-strand helices[11] made from pyridine-2,4,6-tricarboxylic acid (*ptc*H_3) and either Nd^{III} or Pr^{III} ions.

Results and Discussion

Compounds {[Pr(*ptc*$^{3-}$)·$2H_2O$]·$2H_2O$} (**1**) and {[Nd(*ptc*$^{3-}$)·$2H_2O$]·$2H_2O$} (**2**) were synthesized hydrothermally in ca. 55% yield, by treating the ligand pyridine-2,4,6-tricarboxylic acid[12] (*ptc*H_3) with $Pr(NO_3)_3·6H_2O$ or $Nd(NO_3)_3·6H_2O$, respectively. As both **1** and **2** have an identical structure, only the structure of **1** is discussed.

The asymmetric unit of **1** consists of one *ptc*$^{3-}$ unit, one Pr^{III}, two metal-bound water and two free water molecules. Each metal ion exhibits 9-coordination (Scheme 1) with bonding from six carboxylates of five different ligand units, one ring N atom of one the ligands and two water molecules. All carboxylate groups are bridged to complete the 3D structure. The Pr^{III} ions are arranged in infinite single helices extending along the crystallographic *b* axis (Figure 1) with intervening *ptc*$^{3-}$ ligands. The helical structure is a result of metal–ligand interactions coupled with stereoelectronic characteristics of the ligand and the conditions prevailing during the synthesis. The width of the helix is calculated to be 16.70 Å and the pitch is 11.95 Å and there are six Pr^{III} ions present per turn. Both the width and the pitch are large as a result of the topology of the *ptc*$^{3-}$ ligand and the electrostatic repulsive interactions among the metal ions. The stability of the final helical structure relies on the coordinate bonds that each metal makes with the ligand. Known structures of lanthanide helicates[10] are double- or triple-stranded with long polydentate ligands which are able

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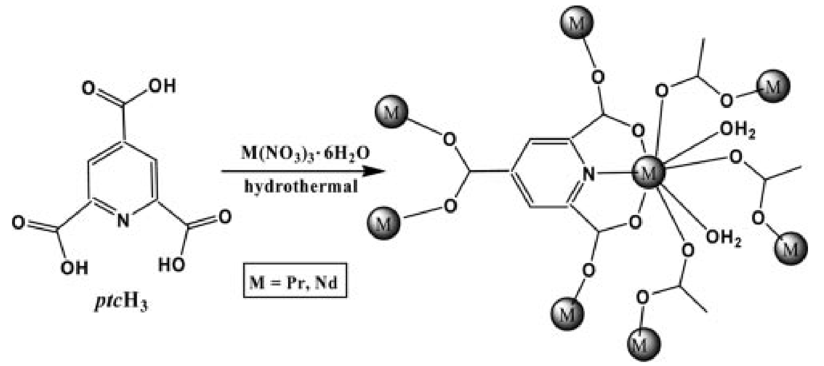

Scheme 1. An illustration showing the binding mode of the ligand.

to wrap around lanthanide ions forming compact helical structures with lower pitch and narrower width. The helices in **1** are further organized into metal-organic framework structures through inter-helix bridging of the carboxylates (Figure 2) with voids occupied by water molecules. Four metal-bound water molecules catch hold of four other water molecules forming an overall discrete octamer. The cluster takes the shape of a staircase-like structure (Figure 3) where only Ow3 and centrosymmetrically related Ow3′ show tetra-coordination while all other water O atoms are tri-coordinated. Such hydrogen-bond deficient water molecules are present[3] at the surface of ice as well as in liquid water.[13] An important feature of this cluster is a very short distance between Ow3 and Ow4′ (2.231 Å). In **2**, this distance is only 1.977 Å although H atoms belong to the water oxygens could not be located in the difference map. Locating these hydrogens by neutron diffraction and probing the nature of Ow···Ow distances in **2** will be another study. Generally, short H bonds are encountered with charged H

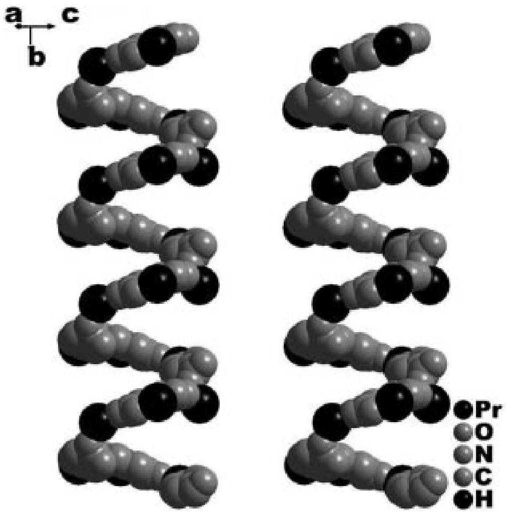

Figure 1. Single helical stereoview of **1**. Other atoms have been omitted for clarity.

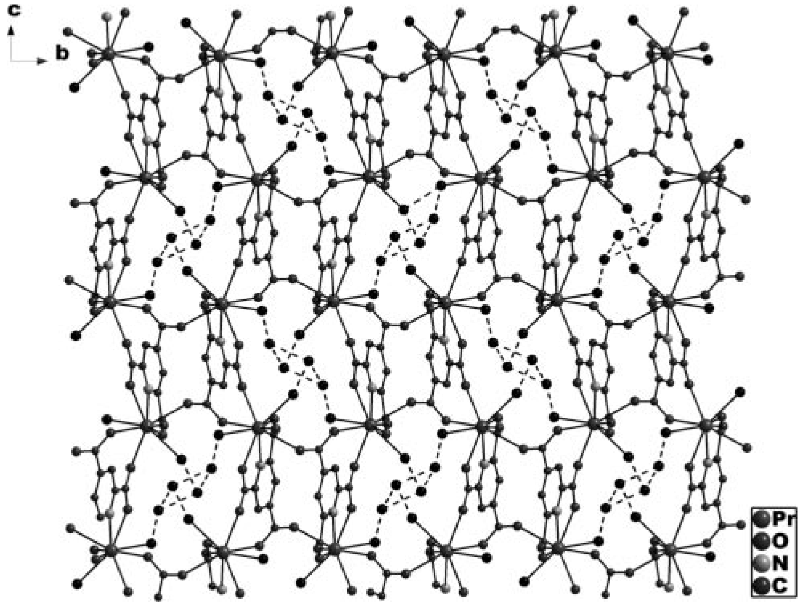

Figure 2. The MOF structure of **1** viewed approximately down the *a* axis. H atoms are omitted for clarity.

bond donors (O^+–H···O) or acceptors (O–H···O^-) such as the Speakman salts[14] with RCOOH···$^-$OOCR hydrogen bonding. In the present case, the metal organic framework pushes the Ow3 and Ow4 atoms closer together. Values of other Ow···Ow distances (range: 2.668–2.903 Å) and O···H–O angles (range: 140.35–175.38°) (Table 1) suggest strong H-bonding interactions among the water molecules. In comparison, bulk water exhibits a short-range O···O order of 2.85 Å in the X-ray diffraction radial distribution curve while for the gas phase, this value is ca. 0.1 Å longer.[15] Hydrogen atoms of Ow2, Ow2′, Ow3 and Ow3′ are also bonded to the nearby carboxylate O atoms cementing the structure further with the MOF and the ultimate symmetry of the octamer results from interactions between the water molecules and between the water molecules and the MOF.

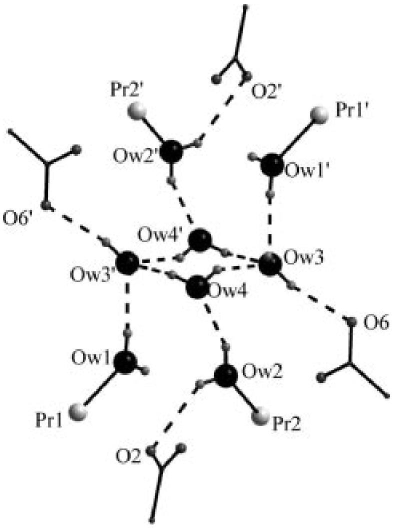

Figure 3. A close view of the water cluster and its surrounding atoms.

Table 1. Geometrical parameters of hydrogen bonds (Å, deg) of the octamer in **1**.

Ow1···Ow4	2.748(2)
Ow2···Ow3	2.868(4)
Ow3···Ow4	2.668(2)
Ow3···Ow4′	2.231(3)
Ow3···O6	2.903(5)
Ow2···O2	2.981(4)
Ow1–H2···Ow4	153.30(5)
Ow2–H1···Ow3	175.38(6)
Ow4–H2···Ow3	145.86(8)
Ow4′–H1···Ow3	140.35(6)
Ow3–H1···O6	165.59(4)
Ow2–H2···O2	155.68(4)
Ow1···Ow4···Ow3	87.29
Ow1···Ow4···Ow3′	109.99
Ow2···Ow3···Ow4	73.21
Ow2···Ow3···Ow4′	109.15
Ow3···Ow4···Ow3′	121.47
Ow4···Ow3···Ow4′	58.53

Thermal gravimetric analyses[16] further corroborate the strong water–MOF interactions. For **1**, with 23.39 mg sample in air shows the loss of first 3 water molecules occur at 145 °C beginning at ca. 100 °C and the loss of all of the water is achieved only above 250 °C and the compound decomposes soon after. Compound **2** shows an almost identical thermogram. The FTIR spectra[16] of **1** and **2** exhibit a broad band centered around 3405 cm^{-1} attributable to the O–H stretching frequency pertaining to the water cluster. All water could be removed by heating either compound at 200 °C for 2 h under 10 mm pressure. However, water expulsion leads to complete breakdown of the 3D lattice as the powder X-ray diffraction patterns[16] of the compounds before and after water expulsion are completely different.

Conclusions

In conclusion, we describe here two open-framework structures formed via carboxylate bridging of infinite single helical coordination polymeric chains. The driving force for helication is the metal–ligand interaction coupled with stereoelectronic characteristics of the ligand and the reaction conditions. Discrete octameric water clusters of hitherto unknown staircase structure occupy the voids in the MOFs.

Experimental Section

Materials and Measurements: The metal salts and 2,4,6-trimethylpyridine were acquired from Aldrich and used as received. 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) Perkin–Elmer Pyris 6. Microanalyses for the compounds were obtained from the Central Drug Research Institute, Lucknow, India. Synthesis of pyridine-2,4,6-tricarboxylic acid (*ptc*H_3): This compound was synthesized in 50% yield by oxidation of 2,4,6-trimethylpyridine with aqueous $KMnO_4$ following a literature method.[12]

Synthesis of {[Pr(*ptc*$^{3-}$)2H_2O]2H_2O}$_n$ (1): This compound is synthesized by mixing 1 mmol of $Pr(NO_3)_3\cdot 6H_2O$ and 1 mmol of pyridine-2,4,6-tricarboxylic acid (*ptc*H_3) in 5 mL of water in a Teflon-lined autoclave. The autoclave is heated under autogenous pressure to 180 °C for 2 days and then kept at 90 °C for a further 12 h period. Upon cooling to room temp. the desired product appeared as long pale green rectangular parallelopipeds in ca. 55% yield. $C_8H_{10}NO_{10}Pr$ (421.08): calcd. C 22.82, H 2.39, N 3.32; found C 22.16, H 2.47, N 3.21.

Synthesis of [Nd(*ptc*$^{3-}$)2H_2O]2H_2O (2): This was prepared in ca. 54% yield as light purple rectangular parallelopipeds crystals on hydrothermal reaction of 1 mmol of $Nd(NO_3)_3\cdot 6H_2O$ with 1 mmol of the ligand in 5 mL H_2O and under identical experimental conditions as above. $C_8H_{10}NO_{10}Nd$ (424.41): calcd. C 22.64, H 2.37, N 3.30; found C 22.31, H 2.46, N 3.23.

X-ray Crystallography. Crystal Data for 1: $C_8H_{10}NO_{10}Pr$, M = 421.08, rectangular parallelopiped, light green crystals, 0.17 × 0.14 × 0.11 mm, monoclinic, space group $P2_1c$, a = 6.754(5) Å, b = 11.937(2) Å, c = 13.456(5) Å, β = 100.381(5)°, U = 1067.1(10) Å^3, T = 100 K, Z = 4. μ(Mo-K_α) = 4.627 mm^{-1}, 6998 reflections measured, 2454 [$I \geq 2\sigma(I)$] unique reflections were used in all calculations. The final R_1 = 0.0312, wR_2 = 0.0773, S = 1.066. **Crystal Data for 2:** $C_8H_{10}NO_{10}Nd$, M = 424.41, rectangular parallelopiped, light purple crystals, 0.18 × 0.14 × 0.11 mm, monoclinic, space group $P2_1c$, $a = 6.751(5)$ Å, $b = 11.916(3)$ Å, $c = 13.457(5)$ Å, $\beta = 103.105(5)°$, $U = 100.427(5)$ Å^3, $T = 100$ K, $Z = 4$. $\mu(\text{Mo-}K_\alpha) = 4.938\ \text{mm}^{-1}$, 6963 reflections measured, 2426 unique $[I \geq 2\sigma(I)]$ reflections were used in all calculations. The final $R_1 = 0.0413$, $wR_2 = 0.0941$, $S = 1.093$.

CCDC-281538 (for **1**) and -281539 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (for details see footnote on the first page of this article): 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.

Acknowledgments

We gratefully acknowledge the financial support received from the Council of Scientific and Industrial Research, New Delhi, India (grant No.1638/EMR II) and a SRF to S.G.

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Received: August 18, 2005