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Structure of Discrete $(H_2O)_{12}$ Clusters Present in the Cavity of Polymeric Interlinked Metallocycles of Nd(III) or Gd(III) and a Podand Ligand

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A new podand ligand has been designed and synthesized which reacts hydrothermally with either Nd(III) or Gd(III) nitrate forming an array of linked metallocycles with void spaces. Discrete dodecameric water clusters occupy the voids in the structures. The structure of the cluster can be described as an open-cube octamer buttressed on two sides by dimers to form the overall dodecamer. These clusters join different arrays of linked metallocycles.

The present upsurge in studying small water clusters is aimed not only at understanding the "anomalous" behavior of bulk water but also in probing its possible role(s) in the stabilization and functioning of biomolecules[1] and in designing new materials.[2] Hydrogen-bonding interactions and their fluctuations determine the properties of water in bulk as well as in molecular confinements although they still remain as ill-understood phenomena.[3] The key to unravel this is precise structural data of water clusters in diverse environments, and therefore, several studies of water clusters in restricted environments such as organic and inorganic host lattices have been made recently.[4−10] In these studies, small water clusters $(H_2O)_n$, where $n = 2-10$, have been reported.

Formation of metal−organic framework (MOF) structures has attracted a lot of interest due to potential applications and unusual topologies of these materials. While much of the work involves transition metals, recent years have seen considerable interest in the use of lanthanide elements for constructing[11−16] MOF structures. 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. Our research efforts in this area are directed toward the synthesis of open frameworks with high porosity and thermal stability. For this, we have designed and synthesized a tripodal ligand **L** (see Scheme 1), bearing one carboxylate group at each terminal and a long linker from the bridgehead nitrogen. The position of the carboxylate groups in this ligand excludes the formation of a homoleptic metal complex, and provides a platform to assemble more than one metal ion, leading to an open-framework structure.

We report here the synthesis and characterization of Nd(III) and Gd(III) structures with the podand ligand **L**. The structures have void spaces as expected. These voids are occupied by discrete $(H_2O)_{12}$ clusters of hitherto unknown geometry, showing yet another new mode of association of water molecules.

Compounds $\{Nd(ptaH)^{1}/_{2}ox)\cdot 6H_2O\}_n$ (**1**) and $\{Gd(ptaH)^{1}/_{2}ox)\cdot 6H_2O\}_n$ (**2**) were synthesized[17] hydrothermally in 55% yield, by treating the tripodal ligand $ptaH_3$ in water, with $Nd(NO_3)_3\cdot 6H_2O$ or $Gd(NO_3)_3\cdot 6H_2O$, respectively. We speculate that under prevailing reaction conditions, the ligand $ptaH_3$

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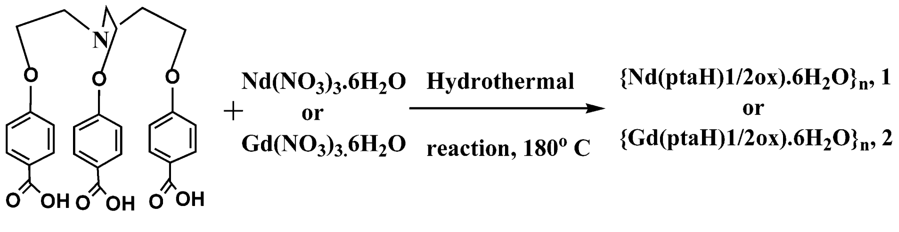
Scheme 1. Synthetic Scheme for the Compounds



ptaH$_3$

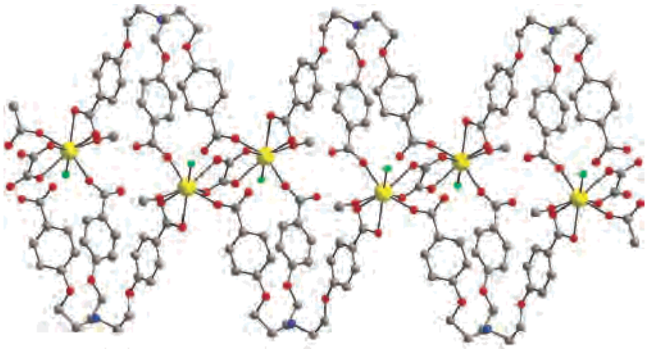


Figure 1. A perspective view of the interlinked metallocycles. Hydrogen atoms are omitted for clarity. Color code: carbon, gray; nitrogen, blue; oxygen, red; water oxygen, green; neodymium/gadolinium, yellow.

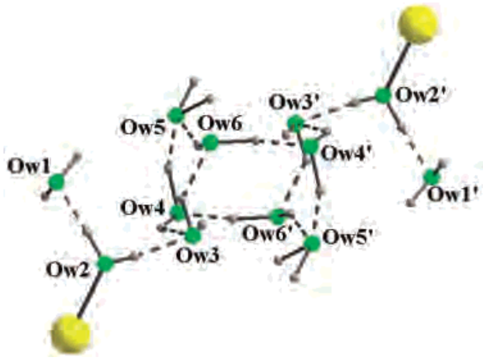


Figure 2. A perspective view of the water cluster bound to two metal ions showing all hydrogen-bonding interactions.

is partially converted to oxalate (ox^{2-}) and gets coordinated to the metal along with ptaH^{2-} forming the MOF structures.[18]

Both **1** and **2** show identical structure, and so, only the structure of **1** is described here. In this structure, each metal is bonded to four carboxylates from four different ligand units. One carboxylate donates both its O atoms, and two carboxylates donate one O atom each (the other O atom in each case is donated to a different Nd(III)) while the fourth carboxylate is protonated and donates a single O atom. Each metal ion is also bonded to an oxalate group and a water molecule (Ow2) showing an overall eight coordination. The bridging carboxylates propagate the 3D MOF. The overall structure looks like an array of metallomacrocycles (Figure 1) joined via the bridgehead N of the podand. In every alternate metallocycle, the two Nd(III) ions are connected through ox^{2-} bridging showing a distance of 6.317 Å between the metals. The bond distances and bond angles involving the metal ion in both **1** and **2** are within[19] normal statistical errors. The atom Ow2 bound to Nd(1) is a part of six water molecules present in the asymmetric unit. The other six water molecules, associated with a Nd(III) ion of a centrosymmetrically related polymeric chain, are connected to these forming an overall $(H_2O)_{12}$ cluster (Figure 2). The cluster can be considered as derived from a cubic arrangement of eight water molecules with opening of two edges. The hydrogen-bonded O···O distances within the octamer span the range 2.951−2.696 Å (Table 1) while the oxygen atoms are separated by 3.41 Å along the opened edge. The metal-bound water molecule Ow2 is hydrogen-bonded to Ow1 and the octamer. None of the hydrogens of Ow1 and Ow5 are involved in hydrogen bonding. Both hydrogens of Ow2, Ow4, and Ow6 act act as donors while Ow3 acts as a single donor of hydrogen bonds. Such hydrogen bond deficient water molecules are present[20] at the surface of ice as well as liquid water. The overall structure of the water cluster can be described as an "opened-cube" octamer buttressed on two sides by two water dimers. While an opened-cube $(H_2O)_8$ cluster has been reported[21] in $[V(phen)_2SO_4]_2O(H_2O)_4$ (phen = 1,10-phenanthroline), an opened-cube $(H_2O)_{10}$ cluster was detected[22] in molecular beams with different hydrogen-bonding schemes for the octamer compared to the present $(H_2O)_{12}$ cluster. These dodecameric water clusters occupy the voids in the MOF (Figure 3).

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(17) Synthesis of **1**: An aqueous mixture of the tripodal ligand ptaH$_3$ (0.13 g; 0.25 mmol) was placed in a Teflon-coated stainless steel vessel, and $Nd(NO_3)_3 \cdot 6H_2O$ (0.16 g; 1.5 × 0.25 mmol) was added to it. The vessel was sealed and heated to 180 °C for 48 h and then cooled to room temperature at a rate of 1 °C/min. Small light yellow rectangular parallelepiped crystals were collected from the residue. Anal. Calcd for $C_{28}H_{37}NO_{17}Nd$: C, 41.84; H, 4.64; N, 1.74. Found: C, 41.96; H, 4.59; N, 1.76. Compound **2** was isolated following the above procedure. Anal. Calcd for $C_{28}H_{37}NO_{17}Gd$: C, 41.17; H, 4.55; N, 1.71. Found: C, 41.11; H, 4.62; N, 1.74.

(18) Crystal data for **1**: $C_{28}H_{37}NO_{17}Nd$; $M = 803.83$, rectangular parallelepiped, light yellow crystals, 0.18 × 0.16 × 0.13 mm, triclinic, space group $P\bar{1}$, $a = 10.888(3)$ Å, $b = 11.638(3)$ Å, $c = 13.793(3)$ Å, $\alpha = 95.367(2)°$, $\beta = 103.259$ (2)°, $\gamma = 108.532(3)°$, $V = 1586.5(6)$ Å^3, $T = 100$ K, $Z = 2$. $\mu(\text{Mo K}\alpha) = 1.72$ mm^{-1}, 10635 reflections measured, 7308 ($I \geq 2\sigma(I)$) unique reflections were used in all calculations. The final R1 = 0.031, WR2 = 0.083, $S = 1.055$. Crystal data for **2**: $C_{28}H_{37}NO_{17}Gd$; $M = 816.84$, rectangular parallelepiped, light brown crystals, 0.16 × 0.14 × 0.11 mm, triclinic, space group $P\bar{1}$, $a = 10.861(5)$ Å, $b = 11.600(5)$ Å, $c = 13.806(5)$ Å, $\alpha = 95.385(5)°$, $\beta = 103.105(5)°$, $\gamma = 108.467(5)°$, $V = 1580.8(11)$ Å^3, $T = 100$ K, $Z = 2$. $\mu(\text{Mo K}\alpha) = 2.14$ mm^{-1}, 10607 reflections measured, 7214 unique ($I \geq 2\sigma(I)$) reflections were used in all calculations. The final R1 = 0.028, WR2 = 0.0751, $S = 1.061$.

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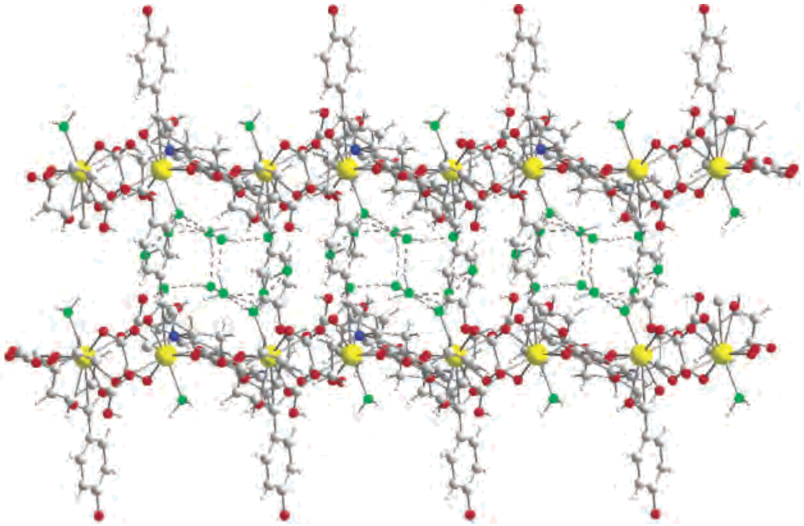

Figure 3. A view of the MOF showing the dodecameric water clusters in red. Color code as in Figure 1.

Table 1. Geometrical Parameters of Hydrogen Bonding (Å, deg) for **1** and **2**

	1		
Ow1···Ow2	2.713	Ow1···Ow2···Ow3	101.81
Ow2···Ow3	2.696	Ow2···Ow3···Ow4	99.91
Ow3···Ow4	2.951	Ow3···Ow4···Ow5	88.46
Ow3···Ow6	2.729	Ow4···Ow5···Ow6	87.63
Ow4···Ow5	2.858	Ow5···Ow6···Ow3	93.32
Ow5···Ow6	2.842	Ow6···Ow3···Ow4	87.92
Ow6···Ow4′	2.910	Ow6···Ow4′···Ow5′	89.80
Ow4···Ow6′	2.910	Ow4···Ow6′···Ow5′	122.48
Ow2−H···Ow1	175.97	Ow4−H···Ow5	163.31
Ow2−H···Ow3	172.06	Ow6−H···Ow5	169.21
Ow3−H···Ow6	145.76	Ow6′−H···Ow4	145.59
Ow4−H···Ow3	132.33	Ow6−H···Ow4′	145.59
	2		
Ow1···Ow2	2.716	Ow1···Ow2···Ow3	102.69
Ow2···Ow3	2.736	Ow2···Ow3···Ow4	97.20
Ow3···Ow4	2.913	Ow3···Ow4···Ow5	88.38
Ow3···Ow6	2.735	Ow4···Ow5···Ow6	88.08
Ow4···Ow5	2.856	Ow5···Ow6···Ow3	96.05
Ow5···Ow6	2.674	Ow6···Ow3···Ow4	87.92
Ow6···Ow4′	3.019	Ow6···Ow4′···Ow5′	75.19
Ow4···Ow6′	3.019	Ow4···Ow6′···Ow5′	124.45
Ow2−H···Ow1	170.04	Ow4−H···Ow5	163.41
Ow2−H···Ow3	176.34	Ow3−H···Ow6	154.46
Ow6′−H···Ow4	155.94	Ow4−H···Ow3	123.58
Ow6−H···Ow4′	159.05		

The association of the water molecules with the MOF is quite strong as thermal gravimetric analysis of **1** with an 11.725 mg sample in air shows that weight loss occurs in stages beginning at 80 °C and the loss 13.6% corresponding to all of the water (calculated 13.44%) takes place above 260 °C when the compound decomposes. Compound **2** shows an almost identical thermogram. The FTIR spectra of **1** and **2** exhibit a broad band centered around 3400 cm^{-1} attributable[7] to the O−H stretching frequency pertaining to the water cluster. Powder X-ray diffraction patterns of the compounds before and after water expulsion show major changes. Therefore, the loss of water from the lattice leads to breakdown of the 3D structure, which is in support of the thermal analysis results.

In summary, we have characterized the MOF structures of Nd(III) and Gd(III) with a new tripodal ligand. This ligand is partly oxidized under hydrothermal conditions, to oxalate ion which also gets coordinated to the metal. The large voids present in the MOF are not empty but contain (H$_2$O)$_{12}$ clusters with yet another new mode of association of water molecules. These water clusters act as “glue” to reinforce the coordination polymeric chains forming an overall 3D structure. Replacement of the water molecules keeping the structure intact is not possible as the water clusters are very tightly held. We are presently building MOF structures with this ligand and a number of transition as well as lanthanide metal ions by hydro- and solvothermal techniques.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of compounds **1** and **2**, TGA curves, 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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