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# Template Trapping and Crystal Structure of the Magic Number $(H_2O)_{21}$ Cluster in the Tetrahedral Hole of a Nanoscale Global Ion Packed in a Face-Centered Cubic Pattern

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Water clusters, because of their fundamental importance in chemical and biological processes[1−4] and as promising materials for hydrogen storage,[5] have received considerable attention. Among them, the $(H_2O)_{21}$ cluster is more dominant than its neighboring sizes in mass spectra and has long been known as a magic number cluster since it was first identified by Lin in 1973.[6] Since then, great efforts have been made to verify the existence of the magic number water cluster in solution and the gas phase.[7] There has been much speculation about the structure and the formation mechanism of the magic number cluster.[8] Indeed, a regular dodecahedral cage structure encaging a $H_2O$ molecule in the cavity has been proposed, with support from theoretical calculations and the known polyhedral clathrate hydrates.[7,9] However, isolation and detailed structural information on a discrete $(H_2O)_{21}$ cluster in a condensed phase has still been lacking.[10]

In the past decades, considerable attention has been paid to the theoretical and experimental studies of water clusters.[11] An efficient approach for trapping and studying the precise structure and behavior of condensed-phase water clusters involves confinement and stabilization of the water molecules inside predesigned hosts, such as organic materials,[12] inorganic microporous materials,[13] and metal−organic frameworks.[14] Although various water clusters have been investigated by X-ray diffraction methods, the design of an appropriate host in which to embed a discrete, high-nuclearity $(H_2O)_n$ cluster ($n > 20$) is still a big challenge.[11,15] Fortunately, we successfully employed a nanoscale, global ionic cluster $[Co(H_2O)_6\subset Co_8L_{12}]^{6+}$ [HL = 4,6-di(2-pyridyl)-1,3,5-triazine-2-ol] as a template to trap a $(H_2O)_{21}$ cluster, in which the ionic spheres pack in a face-centered cubic (fcc) pattern as "hosts" and the water clusters are embedded in the tetrahedral holes as "guests". This provides a new approach for trapping high-nuclearity water clusters and offers precise structural information on the magic number water cluster, which was always assumed when its structural features were discussed.

Reaction of $[Co(H_2O)_6\subset Co_8L_{12}](NO_3)_6\cdot 12H_2O$[16] with imidazole (Him) and KBr (or KCl) in EtOH gave compounds $[Co(H_2O)_6\subset Co_8L_{12}]Br_6\cdot[(H_2O)_{21}]_2\cdot 12Him\cdot 14H_2O$ (**1**) or $[Co(H_2O)_6\subset Co_8L_{12}]Cl_6\cdot[(H_2O)_{21}]_2\cdot 12Him\cdot 16H_2O$ (**2**) (see the Supporting Information). Microanalyses and X-ray diffraction experiments were employed to identify their composition and structural properties.[17] As shown in Figure 1, the Co2 ion is coordinated by six aqua molecules in an ideal octahedral geometry and is located as a guest in the center of the $[Co(H_2O)_6\subset Co_8L_{12}]^{6+}$ cluster, which is assembled into a cube-like nanocage via the formation of 12 hydrogen bonds between the aqua ligands and the oxygen atoms of the L ligands (O1W···O1 = 2.685 Å for **1** and 2.674 Å for **2**). Compounds **1** and **2** adopt a rock-salt structure based on an fcc array of the $[Co(H_2O)_6\subset Co_8L_{12}]^{6+}$ nanocage ions with a radius of ~10 Å, in which the disordered anions and water molecules occupy all of the octahedral holes (Figure 2). X-ray analysis clearly showed that the $(H_2O)_{21}$ clusters, of which there are two per cation, are trapped in the tetrahedral holes, because their sizes and shapes match. Moreover, 12 Him are symmetrically placed around each $(H_2O)_{21}$ cluster via the formation of 12 hydrogen bonds (N4···O4W = 2.927 Å in **1** and 2.951 Å in **2**) (Figure 3) and further connect the water clusters into a 3D hydrogen-bonding network. Alternatively, the compounds can be viewed as a primitive cubic (α-Po) structure in which the $(H_2O)_{21}$ clusters occupy lattice points located at the corners of a cube and the disordered $\{Br_6(H_2O)_{14}\}^{6-}/\{Cl_6(H_2O)_{16}\}^{6-}$ and $[Co(H_2O)_6\subset Co_8L_{12}]^{6+}$ ions are alternately encapsulated in the centers of the cubic holes. At this point, it is worth emphasizing that the Him plays an indispensable role in the formation and stabilization of the $(H_2O)_{21}$ cluster.[16]

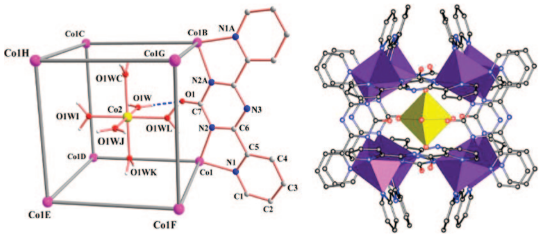

***Figure 1.*** Views of the structure of $[Co(H_2O)_6\subset Co_8L_{12}]^{6+}$, with only one bridging ligand shown for clarity (left) and with polyhedrons for Co(II) ions (right).

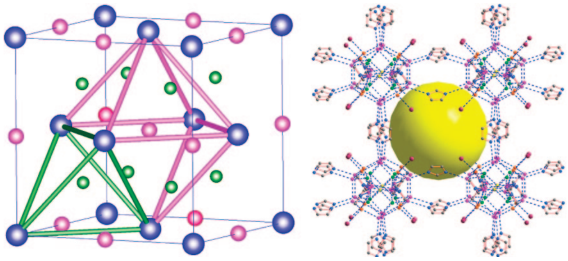

***Figure 2.*** (left) Packing diagram of $[Co(H_2O)_6\subset Co_8L_{12}]^{6+}$ ions (blue) in an fcc pattern as hosts, with the guests $(H_2O)_{21}$ (green) and $\{Br_6(H_2O)_{14}\}/\{Cl_6(H_2O)_{16}\}$ (pink) embedded in the tetrahedral and octahedral holes, respectively. (right) Three-dimensional H-bonded framework formed by Him molecules and $(H_2O)_{21}$ clusters, with a $[Co(H_2O)_6\subset Co_8L_{12}]^{6+}$ nanocage cation (yellow ball) in the center of the cavity.

The most interesting feature of the compounds is that each $(H_2O)_{21}$ cluster is trapped in a tetrahedral hole as a "guest". X-ray structure analysis revealed that it crystallizes in the higher-symmetry cubic space group $Fm\bar{3}$, with $^1/_{12}$ of the cluster being crystallographically independent. The occupancies of O2W, O3W, O4W,

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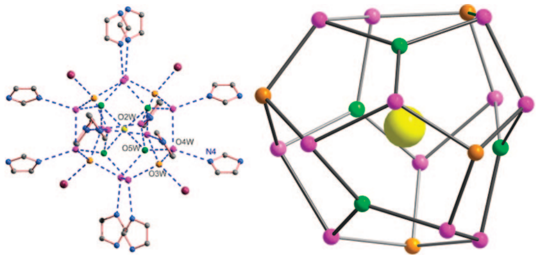

***Figure 3.*** Perspective views of (left) the $(H_2O)_{21}$ cluster with its hanging Br and Him and (right) the pentagonal dodecahedron shell formed by four O3W (orange), four O5W (green), and 12 O4W (purple), with O2W (yellow) in the center of the cavity. Selected distances (Å) and angles (deg) for **1** (**2**): O2W···O5W, 2.85 (2.79); O3W···O4W, 2.72 (2.76); O4W···O4WA, 2.96 (2.96); O4W···O5W, 2.70 (2.72); O3W···X, 3.19 (2.90); O4W···N4, 2.93 (2.95); O3W−O4W−O5W, 102.0 (102.3); O4W−O5W−O4WA, 120.0 (120.0); O5W−O4W−O4WA, 89.0 (88.2); O4WA−O4W−O3W, 116.6 (118.1); O4W−O3W−O4WA, 103.5 (101.6); O5W−O2W−O5WA, 109.5 (109.5); O2W−O5W−O4W, 89.8 (91.1).

and O5W are $^{1}/_{12}$, $^{1}/_{3}$, 1, and $^{1}/_{3}$, respectively. The 20 water molecules (four O3W, 12 O4W, and four O5W) on the surface of the cluster are generated by the symmetry operation and connect each other via hydrogen bonding, resulting in a distorted pentagonal dodecahedron (Figure 3), one of the most stable and important structural units in clathrate hydrates. Furthermore, O2W, with a specific position ($^{1}/_{4}$, $^{3}/_{4}$, $^{3}/_{4}$), sits in the center of the cage. The distances from O2W to the surface O5W, O4W, and O3W are 2.85, 3.92, and 4.20 Å for **1**, and 2.79, 3.93, and 4.30 Å for **2**, respectively, indicating the hydrogen-bonding interaction between O2W and O5W. The size of the $(H_2O)_{21}$ cluster observed here is slightly larger than that obtained from the theoretical simulation (3.9 Å radius).[18] The pentagonal water on the surface of the cluster is a puckered ring because of the departure of O5W from the plane to form a hydrogen bond with the center O2W, in agreement with both experimental and theoretical studies by Saykally and co-workers.[19] The average O···O distances and O−O−O angles within the pentamer are 2.76 Å and 106.2° for **1** and 2.78 Å and 106.1° for **2**, respectively, which are very comparable with the values obtained from experiments (2.73−2.8 Å)[20] and calculations.[21]

The oxygen atoms in the $(H_2O)_{21}$ cluster, which feature a dodecahedral structure with a water molecule in the cavity, are well-resolved according to the results of the X-ray structure analysis. Though the positions of the hydrogen atoms cannot be located directly, a reasonable assignment can be made on the basis of hydrogen bonding. In the $(H_2O)_{20}$ shell, 10 hydrogen atoms from four O3W and six O4W hang on the surface of the water cluster and further donate hydrogen bonds to four anions (O3w···Br1 = 3.192 Å and O3w···Cl1 = 2.900 Å) and six Him, respectively, and the other six O4W accept hydrogen bonds from six Him molecules. Moreover, the residual 30 hydrogen atoms of the 20 water molecules hydrogen bond within the shell, forming a closed dodecahedron. Two hydrogen atoms of O2W in the cavity are disordered into four positions and donate hydrogen bonding to four O5W. It should be pointed out that the central O2W molecule, acting as a guest to prevent the cage from collapsing, plays an important role in the formation and stabilization of the dodecahedral clathrate hydrate via formation of hydrogen bonds with the O5W on the surface.

PXRD experiments showed that the dehydration and rehydration processes of complexes **1** and **2** are reversible, though the complexes lose their single-crystal character in the dehydrated phase.

In summary, a nanoscale global ion $[Co(H_2O)_6{\subset}Co_8L_{12}]^{6+}$ packed in an fcc pattern was constructed, in which $(H_2O)_{21}$ clusters were captured and stabilized in the tetrahedral holes. The X-ray diffraction study suggests that the $(H_2O)_{21}$ cluster is a pentagonal dodecahedron with one water molecule in the center of the cage. This new structural characterization of the water cluster definitely enhances the understanding of the structural aspects and formation of the clathrate hydrates in both the atmosphere and biosphere.

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**Supporting Information Available:** Synthetic details; EA, TGA, IR, PXRD, and X-ray structural data; and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Crystal data for **1**: $M_r = 5946.53$, cubic, $Fm\bar{3}$ (No. 202), $a = 30.1073(2)$ Å, $V = 27290.8(3)$ Å$^3$, $Z = 4$, $D_{calcd} = 1.440$ g/cm$^3$, $T = 100(2)$ K, $R_1$ [$I > 2\sigma(I)$] = 0.0682, $wR_2$ (all data) = 0.2023, GOF = 1.005, $R_{int} = 0.053$. For **2**: $M_r = 5715.85$, cubic, $Fm\bar{3}$ (No. 202), $a = 30.165(3)$ Å, $V = 27448(5)$ Å$^3$, $Z = 4$, $D_{calcd} = 1.375$ g/cm$^3$, $T = 100(2)$ K, $R_1$ [$I > 2\sigma(I)$] = 0.0523, $wR_2$ (all data) = 0.1730, GOF = 1.009, $R_{int} = 0.033$.
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