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Authors

Doedens, Robert J
Yohannes, Elizabeth
Khan, M Ishaque

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Novel water clusters in the crystalline state: structures of a symmetrical, cyclic hexamer and an 'opened-cube' octamer

Robert J. Doedens,^{*a} Elizabeth Yohannes^b and M. Ishaque Khan^b

^a Department of Chemistry, University of California, Irvine, CA 92697, USA. E-mail: rdoedens@uci.edu

^b Department of Biological, Chemical, and Physical Sciences, Illinois Institute of Technology, Chicago, IL 60616, USA

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Six- and eight-membered hydrogen-bonded water clusters of novel structure types have been found in crystalline hydrates.

Small water clusters, $[(\text{H}_2\text{O})_n, n = 2-10]$, have been a topic of considerable recent interest.^{1,2} Studies of water clusters can yield insight into the properties of water in various environments and clusters have played a role in theoretical approaches to understanding the properties of bulk water.³ The most stable conformations for water clusters of various degrees of aggregation have been predicted on the basis of *ab initio* electronic structure calculations.⁴ A number of clusters, including hexamers and octamers, have been characterized spectroscopically in the gas phase,⁵⁻⁷ in molecular beams⁸ and in liquid helium droplets.⁹ Clusters with $n = 6, 8$ and 10 have been found in crystalline hydrates.¹⁰⁻¹⁴

For $n = 6$, the calculated minimum-energy structure is a three-dimensional cage,⁴ which is consistent with experimental data for isolated clusters.⁵ Cyclic hexamers, predicted to be only slightly higher in energy, have been found in liquid helium droplets⁹ and in three solid-state systems. In chiral crystals of tris-(2'-methylbenzamidazol-1'-yl)methane, the $(\text{H}_2\text{O})_6$ rings have an envelope conformation and are linked into chains by a seventh water molecule. The racemic form of the same compound contains isolated six-membered rings with a chair conformation.¹⁰ Water hexamers, linked into one-dimensional tapes, have been found to occupy the channels in crystals of a π -stacked benzonaphthyridine derivative.¹¹

Here, we describe a symmetrical, cyclic hexameric water cluster observed in the crystalline framework material $\text{Li}_6\text{-}[\text{Ni}_3\text{V}_{18}\text{O}_{42}(\text{H}_2\text{O})_{12}(\text{SO}_4)]\cdot 24\text{H}_2\text{O}$ **1**,¹⁵ derived from the cage-like polyoxovanadate cluster $\{\text{V}_{18}\text{O}_{42}(\text{SO}_4)\}$. Compound **1** is isomorphous with our previously reported Fe and Co analogs,¹⁶ but forms higher quality crystals that permit observation of more complete details of the water cluster.¹⁷ The body-centered cubic unit cell contains eight equivalent hydrogen-bonded $(\text{H}_2\text{O})_6$ clusters with a chair configuration and crystallographic $3m$ symmetry. Fig. 1 is an edge-on view of the unit cell in which four of the water clusters are visible and Fig. 2 shows the structure of a single hexameric water cluster. The hydrogen atoms within the $\{\text{H}_2\text{O}\}_6$ ring display a twofold disorder and the axial hydrogen atom is hydrogen-bonded to one of the terminal oxygen atoms of the $\{\text{V}_{18}\text{O}_{42}(\text{SO}_4)\}$ cage.

The chair configuration and the disordered hydrogen atoms of the $(\text{H}_2\text{O})_6$ ring are also found in hexagonal ice (ice I_h) as well as in the metastable cubic ice I_c .¹⁸ The intra-ring O...O distance of 2.759 Å in deuterated ice I_h ¹⁹ is close to the value of 2.769 Å that we find. However, the torsion angle of the chair in the present case (77.7°) is considerably larger than the corresponding value of 60.2° in ice. Among crystallographically characterized six-membered clusters, ours is the first example to display the full symmetry and the hydrogen atom disorder of the hexagonal building block of ice.

For $n = 8$, theory predicts two closely related isomers of nearly identical energy with S_4 and D_{2d} symmetries.⁴ Each of these isomers has oxygen atoms at the corners of a cube with hydrogen bonds along each edge; they differ only in the details of the hydrogen bonding. Evidence for the presence of both of

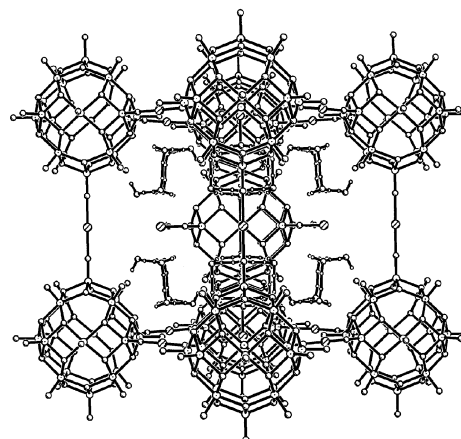


Fig. 1 An edge-on view of the body-centered unit cell of **1**, showing the $\{\text{V}_{18}\text{O}_{42}(\text{SO}_4)\}$ cages, the Ni^{2+} ions linking them, and the hexameric water clusters. For clarity, the encapsulated sulfate ions, the water molecules bound to the nickel ion and the Li^+ ions have been omitted. Four of the eight water clusters are clearly visible; the others are obscured by the cages.

these isomers has been found in gas-phase $\text{C}_6\text{H}_6(\text{H}_2\text{O})_8$ clusters⁷ and in molecular beams.⁸ An octameric cluster with a cubic arrangement of oxygen atoms has also been reported in a solid-state hydrate, but in this case the hydrogen atoms were not located.¹² Very recently, a cyclic $(\text{H}_2\text{O})_8$ cluster that closely resembles a portion of the ice I_c structure has been found in an organic supramolecular complex.¹⁴

We have now found a new type of octameric cluster in crystalline $[\text{V}(\text{phen})_2\text{SO}_4]_2\text{O}(\text{H}_2\text{O})_4$ (phen = 1,10-phenanthroline) **2**, (Fig. 3).^{17,20} As shown in Fig. 4, this compound adopts a structure in which alternating layers of the oxygen-bridged complex and water clusters are stacked perpendicular to the a -axis. The water molecules, which are hydrogen-bonded to oxygen atoms of metal-coordinated sulfate groups, form centrosymmetric octameric clusters.

A view of a single $(\text{H}_2\text{O})_8$ cluster and its immediate environment in **2** is shown in Fig. 5. The cluster can be considered as derived from a cubic arrangement by the opening of two edges, resulting in the folding of two opposite faces into

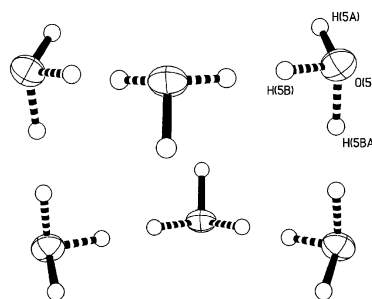


Fig. 2 The cyclic water cluster in **1**, showing the disorder of the equatorial hydrogen atoms. Each equatorial hydrogen atom is hydrogen bonded to the adjacent oxygen atom.

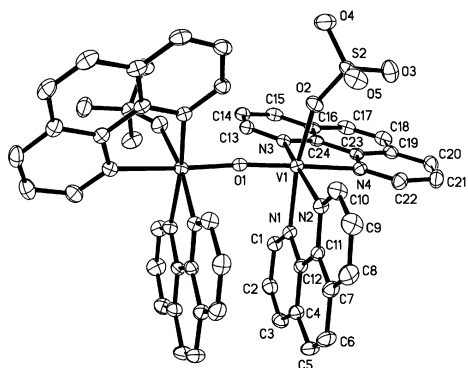


Fig. 3 A view of the oxygen-bridged dimer of **2**. The two halves of the molecule are related by a twofold symmetry axis.

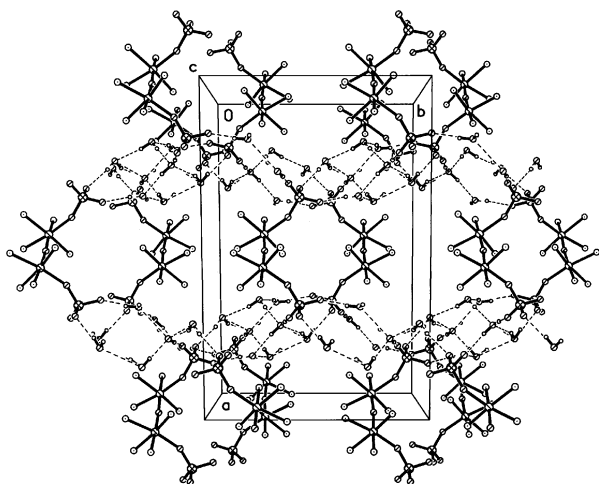


Fig. 4 The crystal packing of **2**, viewed down the *c*-axis and showing the alternating layers of O-bridged dimers and water clusters. For clarity, the carbon atoms of the 1,10-phenanthroline ligands have been omitted.

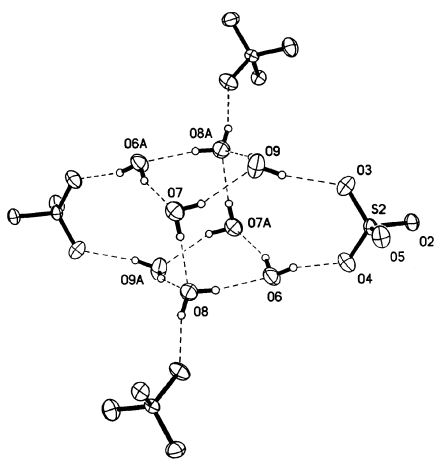


Fig. 5 A centrosymmetric, octameric water cluster and its immediate environment as found in **2**. All hydrogen bonds are shown.

a 'butterfly' shape with a folding angle of 29.5°. The hydrogen-bonded O...O distances within the octamer range from 2.76 to 2.91 Å, while the oxygen atoms are separated by 3.92 Å along the opened edge. Each of the four independent water molecules donates one hydrogen atom to a hydrogen bond within the four-membered folded face. Three of these water molecules use their second hydrogen to form a hydrogen bond to a sulfate oxygen atom and the fourth forms a hydrogen bond to a water oxygen atom from the opposite face. One water oxygen atom serves as

an acceptor for two hydrogen bonds and the others are single acceptors. A similar 'opened-cube' configuration with a different arrangement of hydrogen bonds is found at the core of the cage structure observed for the (H₂O)₁₀ cluster in molecular beams.⁸

These results further illustrate the structural diversity of water clusters and the sensitive dependence of their structures upon the details of their environment.

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- 17 *Crystal data*: for **1**: H₇₂Li₆Ni₃O₈₂SV₁₈, *M* = 2551.33, cubic, space group *Im*3̄*m* (no. 229), *a* = 15.4344(4) Å, *U* = 3676.8(2) Å³, *T* = 163 K, *Z* = 2, $\mu(\text{Mo-K}\alpha)$ = 3.077 mm⁻¹, 12057 reflections measured, 488 unique (*R*_{int} = 0.021) which were used in all calculations. The final *R*1 was 0.0353 (all data). The SO₄²⁻ group is disordered and encapsulated within the polyoxovanadate cage. Some of the H₂O molecules bound to Ni²⁺ and some of the Li⁺ ions are disordered. For **2**: C₂₄H₂₄N₄O_{8.5}SV, *M* = 587.47, monoclinic, space group *C2/c* (no. 15), *a* = 21.2997(12), *b* = 14.1986(8), *c* = 16.3825(9) Å, β = 98.0460(10)°, *U* = 4905.7(5) Å³, *T* = 158 K, *Z* = 8, $\mu(\text{Mo-K}\alpha)$ = 0.551 mm⁻¹, 25833 reflections measured, 5962 unique (*R*_{int} = 0.0382) which were used in all calculations. The final *R*1 value (all data) was 0.0548. A full report on the preparation, characterization and properties of the compound **2** will be included in a future publication. CCDC reference numbers 171785 and 171786. See <http://www.rsc.org/suppdata/cc/b1/b108866a/> for crystallographic data in CIF or other electronic format.
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- 20 The hydrothermal reaction of vanadium pentoxide, 1,10-phenanthroline, hydrazinium sulfate, zinc sulfate heptahydrate and water in the molar ratio 1:2:1:1.5:444 for 120 h at 160 °C gave a deep colored liquid that was allowed to stay at room temperature for 24 h to yield purple crystals of **2** in moderate yield.