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

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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, $[(H_2O)_n, n = 2–10]$, 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 beams[8] 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 droplets[9] and in three solid-state systems. In chiral crystals of tris-(2′-methylbenzamidazol-1′-yl)methane, the $(H_2O)_6$ 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 benzonapthyridine derivative.[11]

Here, we describe a symmetrical, cyclic hexameric water cluster observed in the crystalline framework material $Li_6[Ni_3V_{18}O_{42}(H_2O)_{12}(SO_4)]\cdot 24H_2O$ **1**,[15] derived from the cage-like polyoxovanadate cluster $\{V_{18}O_{42}(SO_4)\}$. 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 $(H_2O)_6$ clusters with a chair configuration and crystallographic $\bar{3}m$ 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 $\{(H_2O)_6\}$ ring display a twofold disorder and the axial hydrogen atom is hydrogen-bonded to one of the terminal oxygen atoms of the $\{V_{18}O_{42}(SO_4)\}$ cage.

The chair configuration and the disordered hydrogen atoms of the $(H_2O)_6$ 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 these isomers has been found in gas-phase $C_6H_6(H_2O)_8$ clusters[7] 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 $(H_2O)_8$ cluster that closely resembles a portion of the ice I_c structure has been found in an organic supramolecular complex.[14]

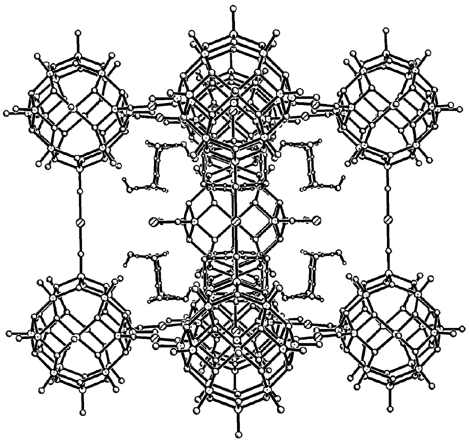

Fig. 1 An edge-on view of the body-centered unit cell of **1**, showing the $\{V_{18}O_{42}(SO_4)\}$ cages, the Ni^{2+} ions linking them, and the hexameric water clusters. For clarity, the encapsulated sulfate ions, the water molecules bound to the nickel ion and the Li^+ ions have been omitted. Four of the eight water clusters are clearly visible; the others are obscured by the cages.

We have now found a new type of octameric cluster in crystalline $[V(phen)_2SO_4]_2O(H_2O)_4$ (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 $(H_2O)_8$ 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

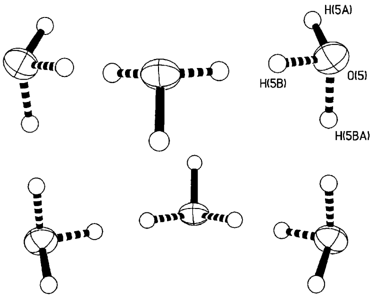

Fig. 2 The cyclic water cluster in **1**, showing the disorder of the equatorial hydrogen atoms. Each equatorial hydrogen atom is hydrogen bonded to the adjacent oxygen atom.

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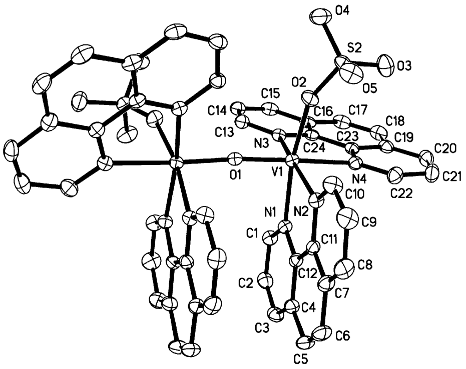

Fig. 3 A view of the oxygen-bridged dimer of **2**. The two halves of the molecule are related by a twofold symmetry axis.

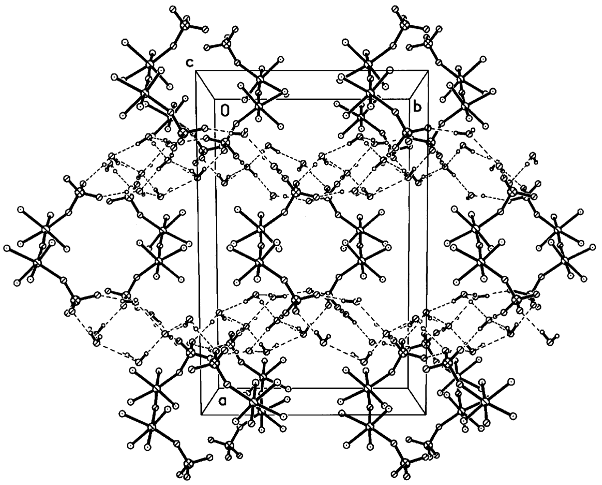

Fig. 4 The crystal packing of **2**, viewed down the *c*-axis and showing the alternating layers of O-bridged dimers and water clusters. For clarity, the carbon atoms of the 1,10-phenanthroline ligands have been omitted.

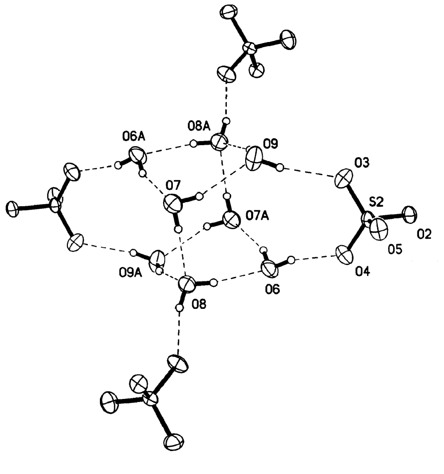

Fig. 5 A centrosymmetric, octameric water cluster and its immediate environment as found in **2**. All hydrogen bonds are shown.

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 $(H_2O)_{10}$ 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**: $H_{72}Li_6Ni_3O_{82}SV_{18}$, M = 2551.33, cubic, space group $Im\bar{3}m$ (no. 229), a = 15.4344(4) Å, U = 3676.8(2) Å^3, T = 163 K, Z = 2, μ(Mo-Kα) = 3.077 mm^{-1}, 12057 reflections measured, 488 unique (R_{int} = 0.021) which were used in all calculations. The final $R1$ was 0.0353 (all data). The SO_4^{2-} group is disordered and encapsulated within the polyoxovanadate cage. Some of the H_2O molecules bound to Ni^{2+} and some of the Li^+ ions are disordered. For **2**: $C_{24}H_{24}N_4O_{8.5}SV$, 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) Å^3, T = 158 K, Z = 8, μ(Mo-Kα) = 0.551 mm^{-1}, 25833 reflections measured, 5962 unique (R_{int} = 0.0382) which were used in all calculations. The final $R1$ 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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