Vertex-Sharing Water Tape Consisting of Cyclic Hexamers

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Keywords: Water aggregates / Cyanides / Hydrogen bonds

A 1D water tape consisting of vertex-sharing cyclic water hexamers has been observed, which represents a subunit of ice structure.

Introduction

Water is recognized as being essential for life processes, but its actual role in these processes is relatively poorly understood.[1] The obstacle lies in the diversity of hydrogen-bonding associations of water molecules, as reflected by a large number of polymorphous forms of ice. Discrete small clusters, as the basic units of water structure, have been widely investigated both experimentally and theoretically, because their structural information holds considerable promise for the understanding of the behavior of bulk water and processes in biological systems.[2] This realization has prompted enormous studies on the water structures trapped in different environments and great progress has been made regarding structural characterization in hydrate clathrates.[3–7]

One-dimensional water morphologies including chains and tapes constitute an important form of water, which plays a significant role in many fundamental biological processes as "proton wires".[8] Helical water chains have also been observed in crystal hosts.[9] From a structural point of view, the polymeric water morphologies have a close relationship with bulk water, especially those containing a cyclic water hexamer, which is one of the dominant components in liquid water and the building unit of ice I_h. Two-dimensional water layers consisting of hexameric rings with different conformations such as boat, chair, or hybrid chair/boat have been observed in several cases.[10] Although extended tapes containing hexamers have been reported recently, they actually comprise fused tetramers and hexamers[11] rather than sole hexamers. In this context, we report herein a 1D tape-like water structure consisting of vertex-sharing cyclic hexamers, which is hosted within the complex $[Fe(bipy)_2(CN)_2]\cdot 2.5H_2O$ (**1**) (bipy = 2,2′-bipyridine). The tape is a fragment of ice I_h and can be viewed as a simple model of ice structure.

Results and Discussion

Description of the Structure of 1

An ORTEP view of compound **1** is shown in Figure 1. Selected bond lengths and angles are given in Table 1. The compound consists of one $Fe(bipy)_2(CN)_2$ moiety and two and a half water molecules. The ferricyanide moiety has been widely used for the preparation of molecule-based magnetic materials[12] and recent interest has been focused on the versatile cyanide fragments with capping ligands to diversify the structures and properties.[13] The Fe atom in **1** is coordinated by four N atoms from two chelating 2,2′-bipy molecules [Fe–N1 = 2.004(2); Fe–N2 = 1.978(2); Fe–N3 = 1.987(2); Fe–N4 = 1.962(2) Å] and two C atoms from two *cis* cyanide groups [Fe–C21 = 1.915(2); Fe–C22 = 1.910(2) Å], forming an essentially octahedral coordination environment, which is similar to its analogue, $[Fe(1,10\text{-}phen)_2(CN)_2]\cdot 3H_2O$.[14] The corresponding bond lengths are in agreement with those in $[Fe(1,10\text{-}phen)_2(CN)_2]\cdot 3H_2O$. The Fe atom and cyanide groups are almost linear, with the Fe–C21–N5 and Fe–C22–N6 bond angles being 176.6(8) and 176.0(8)°, respectively. The C21–Fe–C22 bond angle is

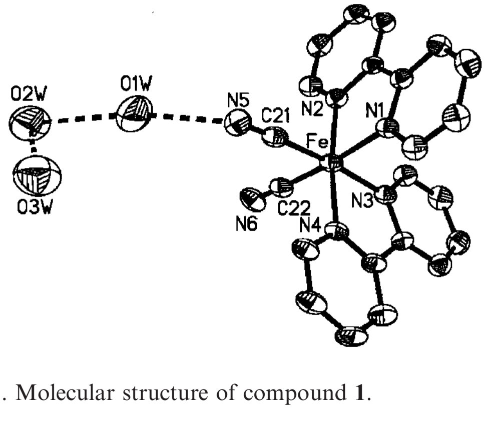

Figure 1. Molecular structure of compound **1**.

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DOI: 10.1002/ejic.200500374

87.52°, consistent with that in complex [Fe(1,10-phen)$_2$-(CN)$_2$]·3H_2O (88.61°). The dihedral angles between the two pyridine rings of each 2,2′-bipy (N1–N2; N3–N4) are 7.88(62) and 5.17(21)°, respectively, and the two 2,2′-bipy molecules are almost perpendicular, with an intersecting angle of 86.37°.

Table 1. Selected bond lengths [Å] and angles [°] for **1**.

Fe–C(22)	1.9103(18)	Fe–C(21)	1.9154(14)
Fe–N(4)	1.9617(14)	Fe–N(2)	1.9776(14)
Fe–N(3)	1.9867(10)	Fe–N(1)	2.0035(14)
N(5)–C(21)	1.1447(18)	N(6)–C(22)	1.153(2)
C(22)–Fe–C(21)	87.51(7)	C(22)–Fe–N(4)	92.44(7)
C(21)–Fe–N(4)	93.83(6)	C(22)–Fe–N(2)	93.31(7)
C(21)–Fe–N(2)	91.69(6)	N(4)–Fe–N(2)	172.19(5)
C(22)–Fe–N(3)	91.50(6)	C(21)–Fe–N(3)	174.48(7)
N(4)–Fe–N(3)	80.79(5)	N(2)–Fe–N(3)	93.78(5)
C(22)–Fe–N(1)	174.13(7)	C(21)–Fe–N(1)	92.17(6)
N(4)–Fe–N(1)	93.43(6)	N(2)–Fe–N(1)	80.83(6)
N(3)–Fe–N(1)	89.37(5)	N(5)–C(21)–Fe	176.42(17)
N(6)–C(22)–Fe	177.20(17)		

Interestingly, two and a half independent water molecules associated with hydrogen bonds form a cyclic hexamer, which is center-symmetric and adopts a chair conformation (Figure 2a). The average O···O distance of 2.89 Å is close to the value in liquid water (2.85 Å),[15] but longer than that in ice I$_h$ (2.759 Å).[16] Compared with those discrete water hexamers recently observed in the solid states, the distance is slightly shorter than that found in a planar hexamer (2.905 Å)[5b] trapped in an organic compound, however it is longer than that housed in a metal-organic framework.[17] The bond angles in the hexamer vary from 80.5 to 132.9°, which considerably deviates from the corresponding value of 109.3° for preferred tetrahedral geometry in hexagonal ice, implying that the flexibility of hydrogen bonds allows efficient perturbation enforced by the surrounding environments.

Theoretical calculation predicts that hexamer represents the transition from 2D cyclic to 3D cage structure with a cage isomer as a stable configuration.[2a] Other less stable conformers including boat, chair, and quasiplanar, have also been experimentally observed. The chair-shaped hexamers described here are not discrete, but self-assembled into a one-dimensional tape by sharing a vertex, which is located on a twofold axis parallel to the [010] direction (Figure 2a). The adjacent hexamers are tilted with an intersecting angle of 28°. The shared water serves as double hydrogen-bond donors and acceptors with a tetrahedral geometry, which is a quite common configuration for the oxygen atom in ice and liquid water. The remaining two water molecules participate in three hydrogen-bonding interactions as double donors and single acceptor, reminiscent of the water surface or interface, where deficient hydrogen-bonded water molecules are present. Recent spectroscopic experiments also demonstrated that significant numbers of oxygen atoms in liquid water are less than four coordinate.[18] As imposed by the symmetry (space group *C*2/*c*), the hydrogen atoms, except for those bonded to a peripheral host, are disordered, as commonly found in ice structure, and there are four possible hydrogen-bonding patterns, as illustrated in Figure 2b. This reflects the anomalous nature of water due to flexible hydrogen bonds. Four hydrogen atoms related by a twofold axis on O3W have half occupancy. O1W and O2W water molecules each have a full-occupancy hydrogen atom that is hydrogen bonded to the host, while the intratape hydrogen atoms are positionally disordered with half occupancy. The bridging O3W has a typical tetrahedral geometry for a water molecule with O3W···O1W and O3W···O2W distances being 2.904(4) and 2.799(3) Å, respectively.

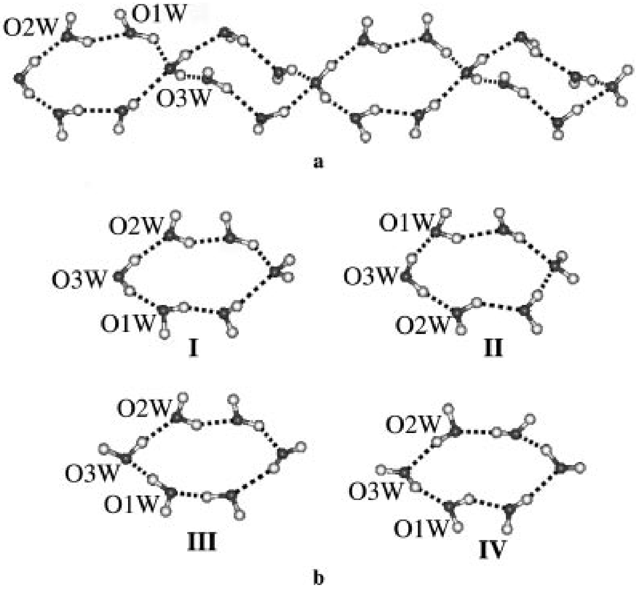

Figure 2. (a) 1D water tape assembled from cyclic hexamers by sharing one vertex. Hydrogen bonds [Å]: O1W···O2W*a* = 2.952(4); O1W···O3W = 2.920(3); O2W···O3W = 2.808(3); *a* = –*x*, –*y* + 1, –*z*. (b) Four different hydrogen-bonding patterns presented in the water tape due to imposed symmetry restriction.

In contrast to frequently observed discrete water tetrameric, pentameric, and hexameric clusters, the connection of these clusters into a tape-like motif is relatively rare. Very recently, a 1D tape consisting of vertex-sharing water tetramers has been reported[19] and we discovered two water tapes made up of vertex-sharing and edge-sharing pentamers.[6a,20] Water tapes consisting of mixed water rings including fused hexamers and tetramers trapped in an organic compound, 2,4-bimethyl-5-aminobenzo[*b*]-1,8-naphthyridine,[11a] and a metal-organic complex, [Ag_2(ophen)$_2$]$_2$·6H_2O [Hophen = 1*H*-[1,10]phenanthrolin-2-one], have also been observed.[11b] The currently described water tape built from vertex-sharing hexamers represents an important development of this kind of motif. We are unaware of any other reported water tapes made of sole water hexamers, though 1D chains consisting of cyclic hexameric chair conformers linked by metal ions have been reported in the complexes [M(H_2biim)$_2$(H_2O)$_2$](ina)$_2$·4H_2O (M = Zn, Co; H_2biim = 2,2′-biimidazole; ina = isoniconate).[21] Considering a pivotal position of the hexamer in the water structure, our water tape could provide insight into the mysterious veil

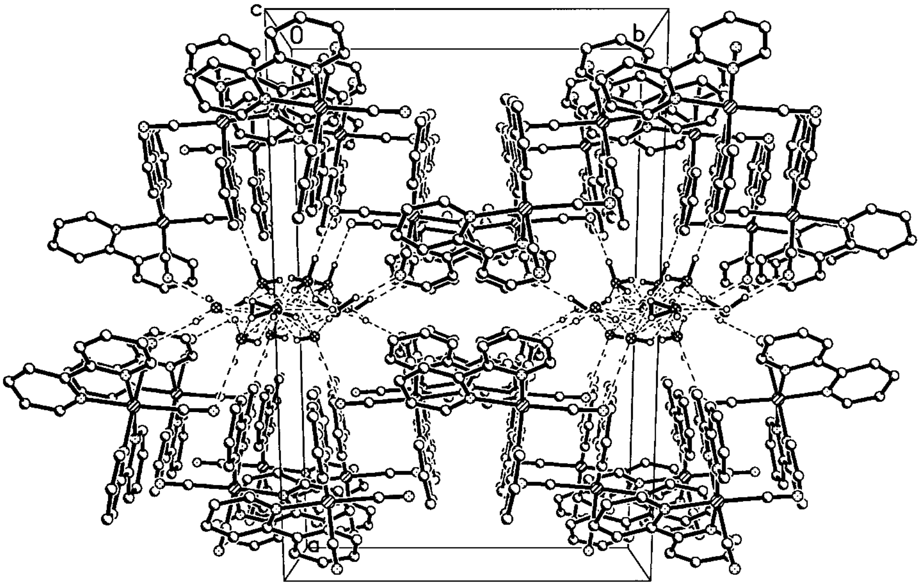

Figure 3. The packing diagram of **1** viewed along crystallographic *c* axis, showing 1D channels in which water tapes are included. Hydrogen atoms on the host are omitted for clarity. Hydrogen bonds [Å]: O1W···N5 = 2.850(3); O2W*a*···N6 = 2.918 (2); *a* = –*x*, –*y* + 1, –*z*.

of water. To simplify the ice structure, one can reduce its dimension to 2D sheet, to 1D tape, to 0D cluster. The 1D tape lies in between 2D sheet and 0D cluster and can be either edge- or vertex-sharing, which not only is a simple model with respect to 2D sheet, but also has close approximation to ice with respect to the discrete hexameric cluster.

These 1D water tapes are anchored within the channels produced by the host packing. The perpendicular arrangement of the two coordinated 2,2′-bipy molecules around the Fe atom in **1** leads to a rectangular channel with approximate dimensions of 5 × 8 Å parallel to the [001] direction (Figure 3). This channel size appears to adapt the water tape well, as opposed to the "armchair" and zigzag water chains which are hosted within the channels of 6.63 × 3.44 Å and 4.80 × 3.02 Å, respectively.[22] By comparison, a linear water trimer cluster is filled within the channel formed in the compound [Fe(1,10-phen)$_2$(CN)$_2$]·3H$_2$O,[14] which has a similar structure to **1**. The small channel size due to the presence of the bulky 1,10-phen ligands prevents further aggregation of water clusters, and no water tape was observed, indicating the influence of the host environment on the water structure. The cyanide groups from [Fe(2,2′-bipy)$_2$(CN)$_2$] units point inward to the channels and form hydrogen bonds with the free hydrogen atoms available to O1W and O2W water molecules. The O···N separation from water tapes to cyanide groups are 2.850(3) and 2.918(2) Å, which are comparable to those in the interior of the tape.

Thermogravimetric Analysis

Thermogravimetric analysis was done with an LT-1 model thermobalance. Compound **1** showed a weight loss of 9.59% below 100 °C, which corresponds to the lattice water molecules, in agreement with the calculated value of 9.62%. It also demonstrates that water tapes are loosely anchored within the host. At 220 °C, the complex began to lose the ligands and decomposed completely at 355 °C. The processes of decomposition are very complicated. The final residue (observed 18.84%) is assigned as Fe_2O_3 (calculated 18.20%).

Conclusions

A novel water tape structure featuring vertex-sharing cyclic hexamers has been structurally determined. Characterization of water morphologies in crystal hydrates is rapidly growing into a new field. Although the control of water clusters of different nuclearity is impossible at the current stage, a judicious choice of hosts could be helpful to trap novel water morphologies. This study and our recent finding of an octameric cluster in a cyanide-bridged f-d complex[23] imply that the cyanide compound might be a good promoter to induce water aggregations.

Experimental Section

Synthesis of 1: Compound **1** was prepared by the literature method.[24] Column-shaped single crystals suitable for X-ray diffraction were obtained through recrystallization of **1** in methanol after 2 weeks.

Crystallography: Crystal data and refinement parameters are summarized in Table 2. Data collection was performed with an Enraf–Nonius CAD-4 Mach3 diffractometer with graphite-monochromated Mo-K_α radiation. A dark red single crystal with approximate dimensions of 0.12 × 0.15 × 0.30 mm^3 was chosen. Unit cell was determined from 25 indexed reflections in the range 8.32–14.97°. Intensity data were collected using ω-2θ-scan mode in the range $1.67 \le \theta \le 27.02°$. Of the 5793 reflections measured, 4624 were found to be unique (R_{int} = 0.1146). An absorption correction based on ψ scan was applied to the data during data reduction. No decay correction was applied. The structure was solved by the heavy atom method and refined by a full-matrix least-squares technique based on F^2 using the SHELXL 97 program[25]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on 2,2′-bipy molecules were placed in geometrically calculated positions and refined isotropically. Hydrogen atoms on water molecules were located from difference Fourier maps and refined by fixing the O–H bond length to 0.96 Å and the isotropic temperature factors to a value of 1.5 times that of the oxygen atoms. CCDC-255296 contains 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.

Table 2. Crystal data and structure refinement for **1**.

Formula	$C_{22}H_{21}FeN_6O_{2.5}$
Formula mass	465.30
Crystal system	monoclinic
Space group	*C*2/*c*
a [Å]	23.5045(13)
b [Å]	14.7424(12)
c [Å]	13.2038(10)
β [°]	112.246(5)
V [Å^3]	4234.7(5)
Z	8
$D_{calcd.}$ [Mg/m^3]	1.460
μ [mm^{-1}]	0.747
Unique reflections	4624
Observed reflections $[I > 2(I)]$	2620
Gof	1.069
F(000)	1928
R_1, wR_2 $[I > 2\sigma(I)]$	0.0677/0.1290
R_1, wR_2 [all data]	0.1500/0.1536

Acknowledgments

This work was supported by the National Science Fund for Distinguished Young Scholars (20125104) and NSFC Nos. 20221101, 20490210.

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Received: April 27, 2005