

Comments on Proton Cascade in a Molecular Solid: H/D Exchange on Mobile and Immobile Water

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Abstract. Following a previous report of proton transport in a channel-free molecular solid possessing a complex set of water wires, the mechanisms implied by the available neutron diffraction measurements are further developed. Three specific proton transfer pathways along an experimentally observed water wire are proposed. The first is proton transfer involving two aqua ligands coordinated to the same Mn(II) unit and one free water acting as a shuttle. The second mechanism consists of proton transfer between coordinated aqua ligands of distinct molecules, with no shuttle. The third mechanism involves a component of vehicle transport, involving a water molecule that changes position during the process. Geometric parameters of the proposed mechanisms are given.

1. Introduction

Many biological and technological processes (*e.g.*, Adenosine triphosphate (ATP) synthesis in the former case or hydrogen fuel cells for the latter), require the presence of protons. Acid-base, redox and enzymatic reactions are based on proton transfer from one reagent to another. Proton mobility in bulk water is much higher, about 4.5 times greater than the mobility of other cations in different solvents, including water. Greater insight into the mechanism through which protons are transferred in bulk water can facilitate the understanding and development of other processes involving ionic movement.¹

It has been observed in biological systems that the presence of a one dimensional H-bonded water chain (or "water wire" or "proton wire") facilitates proton transport through membranes. The associated transport mechanism, commonly called the Grotthuss mechanism,² is based on concepts put forward by Grotthuss in 1806 in the context of electrolysis. The mechanism, as conceived for proton transport, consists of the movement of an excess proton along the H-bonded water chain while the oxygen atoms of the water molecules remain in place. Materials showing this behaviour are known as proton conductors. Specific proposals involving Eigen and Zundel cations have been put forward for this process,³ although there is still debate on the details.

A two-stage process is generally accepted as the basis of the Grotthuss mechanism of proton transport in liquid electrolytes and solids.⁴ The process begins with the transfer of a proton from one molecule of water to an adjacent one, with both molecules being links in a water wire. This proton jump involves the rupture and formation of several covalent and hydrogen bonds in the neighbourhood of the molecules involved. Figure S1 represents the approach of a proton to the terminal water molecule of a chain (a).



The water molecule that binds the newly incorporated proton shares one of its H atoms with an adjacent water molecule, forming a Zundel dimer (b). As this shared proton becomes fully bonded to the O atom of the neighbouring water molecule, the latter in turn loses one of its original H atoms to the next water molecule along the chain (c). This process is repeated along the water chain and finally an H⁺ exits the chain (b-d). This process inverts the dipole moments of the water molecules, and the original state is restored by reorientation of the molecules (e). Once the conformation of the water molecules is identical to that of the original state, the system can host a new proton jump (f).

Another feasible mechanism, the “vehicle mechanism,” entails protons traveling on a host molecule. A host molecule, the carrier, is a species that can interact with protons, such as H₂O or NH₃, so the transfer takes place as an H₃O⁺ or an NH₄⁺, instead of as an H⁺. The substance behaves as a Brønsted base and its diffusion coefficients are the limiting factors in proton conduction. The main difference here is that an H-bonded chain is not required and stronger basic species such as NH₃ can be used, which has helped for example in the preparation of new materials based on zeolites showing proton conductivity.⁵

2. Experimental

Full details of the measurements on which this discussion is based are given in Reference 6a and its accompanying Supporting Information.

3. Discussion

Compound **1** has been described in detail.⁶ It is a 1-D coordination polymer that crystallizes in the monoclinic system, space group $P2_1/n$. The structural building block of the polymer is an [Mn₄(citrate)₄]⁸⁻ cubane, which together with bridging [Mn(H₂O)₄]₂⁺ units, forms a chain that is propagated along a crystallographic n -glide plane. Balancing the negative charge of the polymer are one pendant [Mn(H₂O)₅]₂⁺ unit coordinated to the periphery of each cubane and two freestanding [Mn(H₂O)₆]₂⁺ units between the polymer chains. In addition, there are nine free water sites per asymmetric unit, two of which are half-occupied. There are thus a total of 21 coordinated water molecules and, stoichiometrically, eight crystallization water molecules per unit of the polymer. The crystal is not porous and presents no channels in its structure. Nevertheless, when it is exposed to the atmosphere it undergoes a reversible dehydration in which three molecules of water (occupying four crystallographic sites) are lost, but with preservation of the crystallinity of the sample (compound **2**). There is a reduction of about 250 Å³ in the volume of the unit cell, but the crystal still belongs to the monoclinic space group $P2_1/n$. When a crystal of **2** is left inside a closed vial, with a humid atmosphere created using moist cotton (among other methods), the initial derivative is fully restored (compound **1'**). This reversible process was characterized using single crystal X-ray and neutron diffraction (Figure S2).

As described previously,⁶ when the rehydration is carried out using D₂O instead of H₂O, the structure of **1'** shows deuteration not only at the four crystallographic sites from which water egress takes place, but also at all of the remaining 26 water sites, including the 21 that are coordinated to Mn centers. This fact was definitively established using neutron diffraction, whose H/D isotope contrast provides irrefutable experimental characterization of the affected sites.

It is the purpose of the following discussion to expand on the mechanism that was proposed in Reference 6a, with more detail of the proton transport pathways that can operate in this crystal.

In compound **1**, as characterized by neutron diffraction, a significant H-atom disorder is observed for a number of the water molecules, with the 58 H atoms of the asymmetric unit occupying 72 crystallographic sites. The key to a cogent description of the mechanism through which such massive H/D substitution can take place in a non-porous molecular crystal, without loss of crystallinity, is the presence of an extensive H-bonded water structure: Several continuous motifs traverse a complete unit cell, with O...O distances of between 2.5 and 3.3 Å. (Figure S3). As mentioned above, such a proton wire, or water wire, is a characteristic feature of proton conductors, and it is along such pathways that proton transport can take place.

Our original report^{6a} described an H-bonded chain of water molecules presenting two different types of disorder (Figure S4). The first disorder pattern is present in eight of the 30 water fragments and consists of an oxygen atom [Ox (s.o.f. 1; s.o.f. = total site occupancy factor)] surrounded by three H atoms, one fully occupied [Hxa (s.o.f. 1)] and the remaining two with half occupancy each [Hxb and Hxc (s.o.f. 0.5)]. This can be split into two congeners with good geometry for a water fragment, Hxa-Ox-Hxb and Hxa-Ox-Hxc. The second type of disorder, found for two of the 30 sites, presents an oxygen atom attached to four half-occupied H sites [Hxa, Hxb, Hxc and Hxd (s.o.f. 0.5)]. This pattern can be split into two congeners, each with appropriate H-O distances and H-O-H angle for a water fragment, Hxa-Ox-Hxc and Hxb-Ox-Hxd. Each of the two congeners would be present half of the time. Proton movement along this 1-D chain is explained in terms of the Grotthuss mechanism. The proposed mechanism accounts for the splitting of each water site into two congeners as described above. One of these congeners, a, would be present in the first step, when the excess proton enters the chain (Figure S1). Note that the sites occupied by the hydrogen atoms in the b congeners are vacancies when congener a is present. The excess proton jumps from one water molecule to a second one, occupying a vacancy. This transfer is coordinated with the exit of one proton from the second water molecule; this proton is transferred to the next water molecule in the chain. Once protons have traversed the H-bonded water chain, the extra hydrogen leaves the chain. At this point, the dipole moment of the water molecules is inverted with respect to the starting state of the chain (b congeners). In order to restore the original situation and enable a new proton jump, a simple rotation and reorientation of the water molecules is needed.

Based on neutron diffraction results of the initial derivative, it was possible to identify three pathways through which protons were transferred from one molecule of water to an adjacent one. For these three situations, the experimental disorder observed for the H atoms matches the proposed mechanism, and a full description of the proton interchange can be given on the basis of the split of the disordered molecules into two congeners. All of the H-atom sites described in the following mechanisms were observed in the neutron diffraction analysis of compound **1**.

Mechanism 1: Proton transfer involving three water molecules, two coordinated to the same Mn(II) unit and one free water acting as a shuttle (Figure 1). This process involves O14w, attached to Mn(II) and surrounded by four half-occupied H sites; O30w, a crystallization water molecule; and the coordinated aqua O10wⁱ, both of the latter two having three H-atom sites, one fully occupied and the remaining two with half occupancies. In the initial arrangement, the congeners present are those formed by H14b-O14w-H14d, H30a(sof 1)-O30w-H30c(sof 0.5) and H10aⁱ(sof 1)-O10wⁱ-H10cⁱ(sof 0.5). The process starts with transfer of the half-occupied H14d to the H30b site bonded to O30w, a distance of 1.39(4) Å, Table S1. The distance H14d...O30w, 1.93(3) Å, is within the range considered acceptable for the Grotthuss mechanism. Concomitant with this proton jump, H30c hops to the site of H10bⁱ [distance: 0.73(3) Å] attached to O10wⁱ [H30c...O10wⁱ 1.74(4) Å]. At the same time H10cⁱ is transferred to another water molecule as will be described presently.

The loss of H14d at O14w is compensated by an incoming H atom that occupies the vacant H14c site. In the Grotthuss mechanism, proper geometry is maintained about O14w through rotation of this aqua ligand about the vicinal Mn7-O14w bond, which moves H14b to the H14a site.

To restore the initial situation and enable a new proton jump, some readjustments are needed. A rotation around the Mn7-O14w bond of about 90° would place H14a at the site of H14d, and of 104° will transform H14c into H14b. In a similar way, rotation of 109° around the H30a-O30w axis restores the initial H30a-O30w-H30c congener. Finally, a rotation of 110° around the H10aⁱ-O10wⁱ axis would move H10bⁱ to the site of H10cⁱ. This concerted set of rotations is the second step of the Grotthuss mechanism.

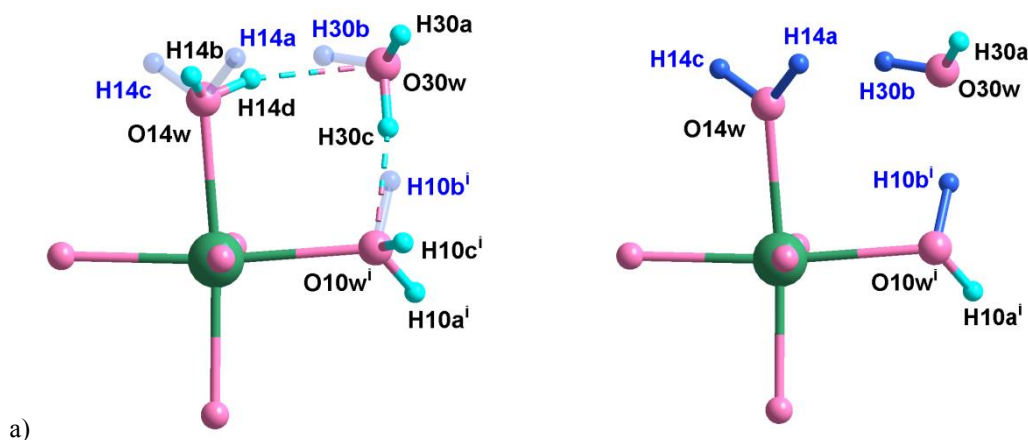


Figure 1. First pathway: proton transfer between two water fragments coordinated to the same Mn(II) unit mediated by a free water molecule. a) Complete disorder observed around the water molecules. Atoms represented as solid spheres are present in the initial configuration. b) Final situation after the proton transfer.

Mechanism 2: Proton transfer between two water fragments coordinated to different Mn(II) units, with no intermediary. Figure 2 shows the disorder at the water sites involved in the transfer. This process, beginning with the H10aⁱ-O10wⁱ-H10cⁱ and H10aⁱⁱ-O10wⁱⁱ-H10bⁱⁱ congeners present, involves transfer of H10cⁱ to O10wⁱⁱ concomitant with the arrival of H10bⁱ as described for Mechanism 1 above. The aqua-complexes between which the proton jump occurs are related by a crystallographic inversion center. The H10cⁱ hopping distance to H10cⁱⁱ is 0.94(4) Å. As a consequence, H10bⁱⁱ exits O10wⁱⁱ, whose proton component now consists of H10aⁱⁱ and H10cⁱⁱ. After the proton jump, rotations around the H10a-O10w axes of the water molecules involved would restore the initial situation, moving H10bⁱ to the H10cⁱ site and H10cⁱⁱ at H10bⁱⁱ. A more complex development of this mechanism is possible, accounting for the bi-directionality implied by a crystallographic inversion center.

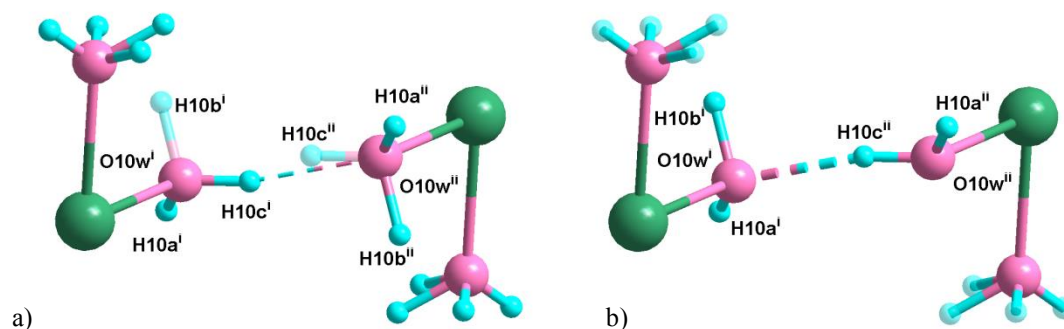


Figure 2. Second pathway: direct transfer between two water fragments coordinated to different Mn(II) units. a) Initial situation, only the congeners present before the proton jump are represented for O10w. b) Final situation after the proton jump between O10wⁱ and O10wⁱⁱ. i: -x, 1-y, -z; ii: 1+x, y, z.

Mechanism 3: Proton transfer between different Mn(II) units through an external water molecule acting as a shuttle. In this process the free water molecule, O28w, plays a crucial role. It is one of the water molecules that exit the sample when it is exposed to the air. Figure 3 shows the disorder in this region of the structure. O28wⁱⁱ is half occupied and is related by a crystallographic center of inversion

at (1,1/2,0) with its congener O28wⁱⁱⁱ at a distance of 1.94(3) Å. Several options can be considered to explain the observed disorder at the site of O28w. It could be that occupation of the two sites is randomly distributed throughout the solid; or it may be that the separate dispositions are required for proton movement in opposite directions in different regions of the crystal. Another possibility is that O28w changes its disposition in concert with the proton movement. This would impute the second mechanism for proton transport described in the Introduction, known as the vehicle mechanism.⁷

The proton movement observed in this third pathway is necessarily coordinated with the proton movements described in the first two mechanisms. First, at O14wⁱⁱ, H14cⁱⁱ jumps to O28wⁱⁱⁱ [1.94(3) Å], coincident with the arrival of H30bⁱⁱⁱ at the H14dⁱⁱ site on O14wⁱⁱ (Mechanism 1), as H14aⁱⁱ rotates to the H14bⁱⁱ site (H14bⁱⁱ and H14dⁱⁱ are semi-transparent in Figure 3a). Then, H28aⁱⁱⁱ jumps to O14wⁱⁱⁱ, occupying the site of H14cⁱⁱⁱ. This second transfer is coordinated with the jump of H14dⁱⁱⁱ to O30w, and the subsequent rotation of H14bⁱⁱⁱ to the site of H14aⁱⁱⁱ, with the final configuration at O14wⁱⁱⁱ consisting of H14aⁱⁱⁱ and H14cⁱⁱⁱ atoms.

The rotations of H14bⁱⁱ and H14dⁱⁱ (Figure 3b) to the H14aⁱⁱ and H14cⁱⁱ positions (Figure 3a) and of H14aⁱⁱⁱ and H14cⁱⁱⁱ to the H14bⁱⁱⁱ and H14dⁱⁱⁱ sites leave O14wⁱⁱⁱ ready to host a new hydrogen atom at the H14cⁱⁱⁱ site and H14cⁱⁱ ready to jump in a subsequent cycle.

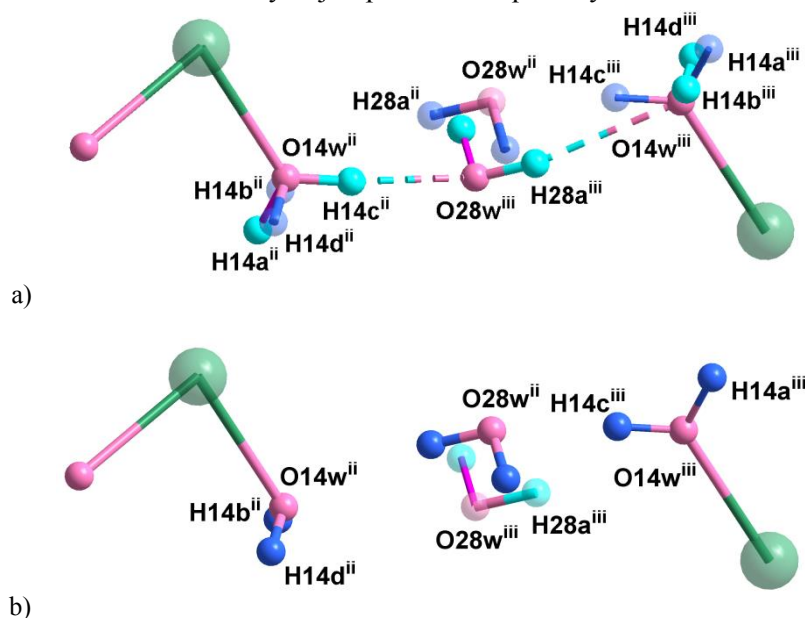


Figure 3. Third pathway: Proton jump between two water molecules coordinated to different Mn(II) units. a) Experimentally observed disorder of the water molecules is shown. The atoms represented as solid spheres are present in the initial arrangement. b) Final disposition of the water molecules after the proton transfer. The two congeners of O28w are represented. i: -x, 1-y, -z; ii: 1+x, y, z; iii: 1-x, 1-y, -z.

The H...H jump distances for these proposed mechanisms are collected in Table S1, together with the distances from the initial H positions to the respective O atoms to which the protons are transferred. The jump distances range from 0.73(3) to 1.55(4) Å, with the larger distances corresponding to the pathway that involves O-atom motion.

4. Conclusions

Neutron diffraction reveals several pathways through which protons can be transferred between water fragments in compound **1**. The complexity of the mechanisms presents a challenge for constructing a fully detailed explanation of the proton movements and their coordination. What can be stated with certainty is that all water-bound H atoms, including those present on immobile waters bonded to Mn

atoms, are substituted by deuterium in this non-porous molecular crystal. The presence of a complex system of H-bonded water wires provides an entry point to a description of possible proton-transfer mechanisms. The further presence of H-atom disorder, revealed accurately by neutron diffraction and compatible with the expected proton positions in a putative Grotthuss mechanism, permits a more detailed mechanistic description compatible with the experimental results and with a proposed proton transport protocol.

We propose mobile protons as the fundamental feature of this system, so it is important to emphasize that in experimental terms, with the diffraction measurements conducted at a temperature of 20 K, the protons are assumed to have occupied minimum-energy positions that permit this snapshot of what we conclude are stopping points in the Grotthuss mechanism.

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Supplementary Material

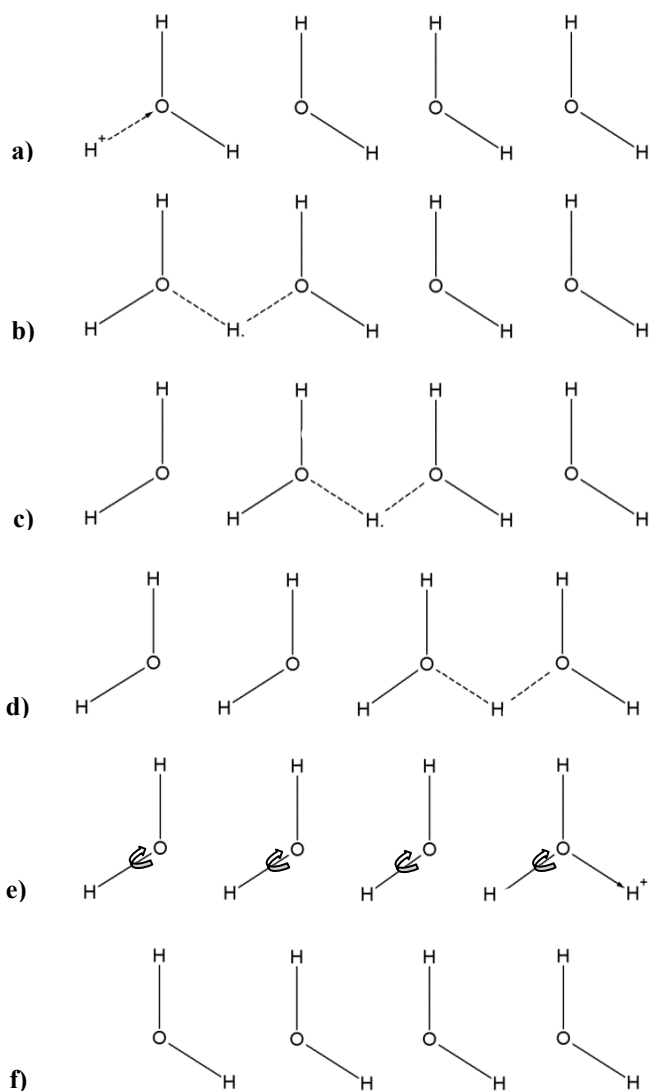


Figure S1. Schematic representation of a proton jump along an H-bonded water chain through the Grotthuss Mechanism. Extracted from reference 6b.

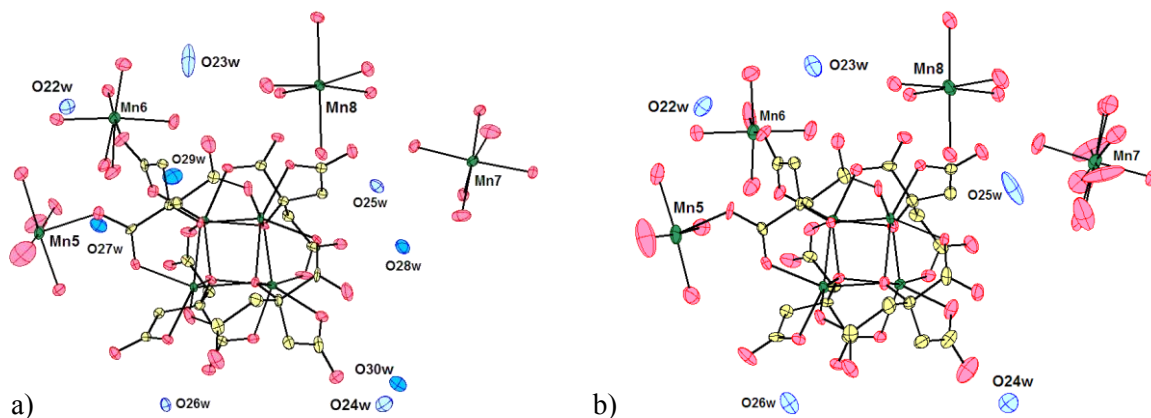


Figure S2. A complete cubane attached to a bridging and a pendant Mn(II) unit and two $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ as counterions and free water molecules for compounds **1** and **1'**. Single crystal X-ray diffraction data. Displacement ellipsoids: 50%

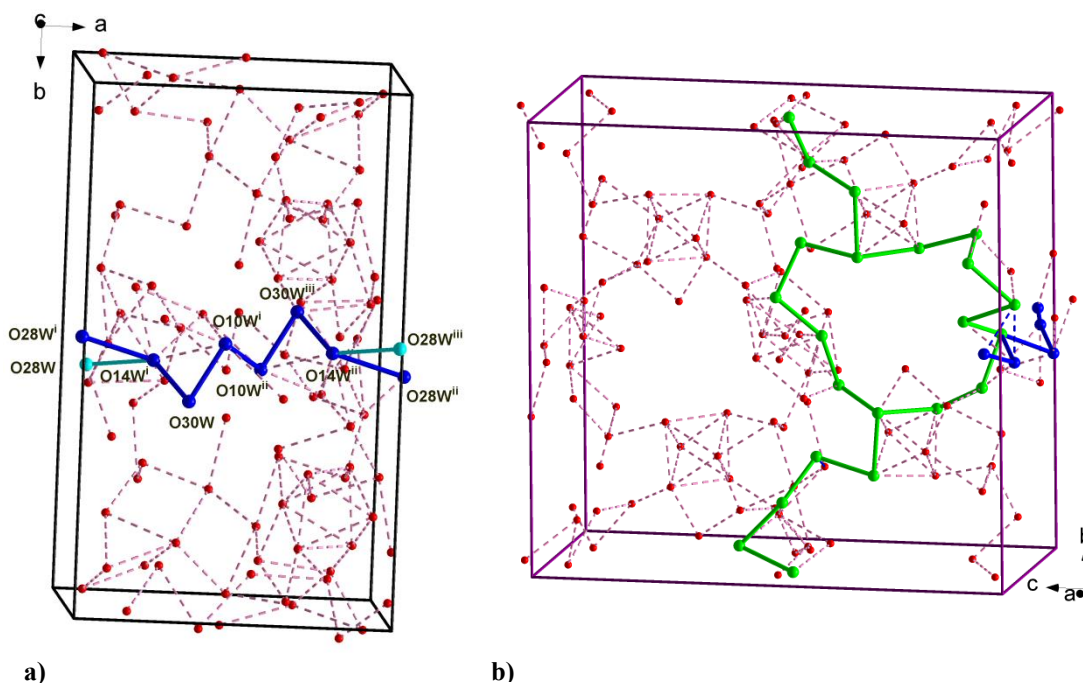


Figure S3. Different H-bonded water pathways traversing the unit cell of **1**. a) 1D chain and b) cyclic motif. i: $-x, 1-y, -z$, ii: $1+x, y, z$, iii: $1-x, 1-y, -z$.

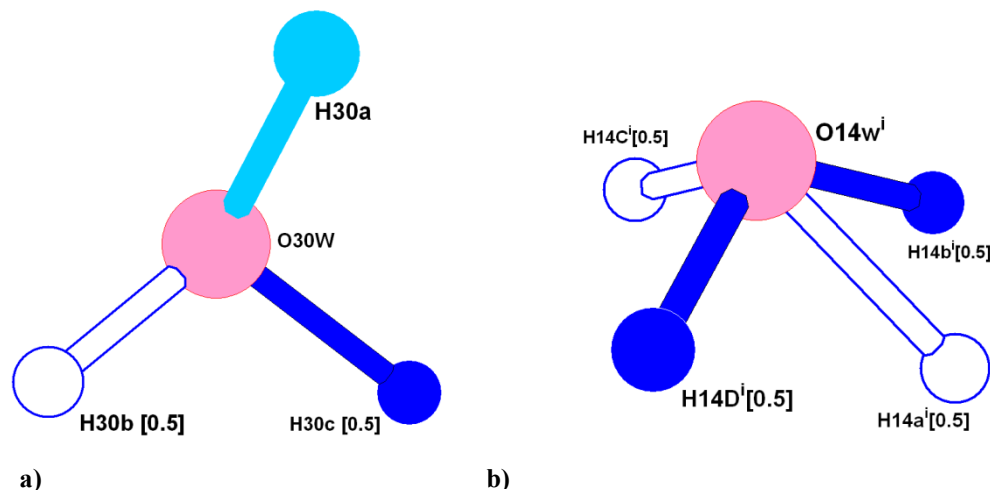


Figure S4. Experimental disorder found around water oxygen atoms. Occupancies are in brackets.
 i: -x, 1-y, -z.

Table S1. Distances and angles between the atomic sites involved in the mechanisms detailed in the text. Symmetry operations: i: -x, 1-y, -z; ii: 1+x, y, z; iii: 1-x, 1-y, -z.

Atom A ... Atom B	Distance (Å)
H14d ... O30w	1.93 (3)
H14d ... H30b	1.39 (4)
H30c ... O10w ⁱ	1.74 (4)
H30c ... H10b	0.73 (3)
H10c ⁱ ... O10w ⁱⁱ	1.88 (2)
H10c ⁱ ... H10c ⁱⁱ	0.94 (4)
H14c ⁱⁱ ... O28w ⁱⁱⁱ	1.94 (3)
H28a ⁱⁱⁱ ... O14w ⁱⁱⁱ	2.18 (3)
H28a ⁱⁱⁱ ... H14c ⁱⁱⁱ	1.55 (4)
O28w ⁱⁱⁱ ... O28w ⁱⁱ	1.94 (3)