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Proton Hopping in Crystals | Hot Paper

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

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Orderly movement of water and of protons through confined spaces is at the heart of a number of areas of science and technology. In the case of water, its movement into and out of living cells, mediated by the aquaporins, is an example of the sophistication that nature applies to the problem of selective transport.[1] The related topic of proton transport is widely studied, for example in proton exchange membranes for use in fuel cells.[2] Systems capable of transporting water or protons—zeolites, aquaporins, Nafion—have pores, channels, or some other identifiable pathway for the movement of their substrates. Synthetic materials aimed at molecular storage, such as the metal–organic frameworks (MOF),[3] are prepared to have channels. However, in a few cases, non-porous solids have shown reversible uptake and release of small molecules,[4] water among them;[5] and under some conditions this can involve reversible chemical reactions,[6–9] suggesting that the solid itself is more than just a passive support in the transit of molecules through its interior. Mechanisms have been put forward for the dehydration of non-porous crystals.[10,11]

The nature of ionic or molecular uptake and release pathways is thus not limited to the presence of open space that guest entities can traverse. Among the transport mechanisms found in living systems is the movement of H^+ ions in a cascade involving concerted proton "hand-off" from one water molecule to the next. This "proton wire," whose working is based on a construct known as the Grotthuss mechanism,[12–14] founded on ideas proposed two centuries ago, involves the jumping of protons between water molecules followed by reorientation of the molecules in the chain. The model is simple in concept, but the difficulty in obtaining detailed experimental information has limited its direct observation. Most studies of the Grotthuss mechanism have been theoretical or based on modeling; their conclusions can be compared to secondary experimental observations.[15,16] New technologies such as multidimensional optical[17] and NMR spectroscopies[18] have been applied recently, but comparison to theoretical models is still necessary.

We report herein the complete exchange of protium for deuterium on mobile and immobile water molecules in a non-porous crystal of a manganese citrate coordination polymer (citrate, $C_6H_4O_7^{(4-)}$, Figure 1 A), when a partially dehydrated crystal is exposed to D_2O vapor at room temperature. This total exchange, observed through single-crystal neutron diffraction analyses, reveals an unprecedented motion of protons through a crystal that has no pores, defined channels, or voids. Furthermore, a chain of double-minimum hydrogen wells has been identified, which fits the expected geometric properties of the two steps of a Grotthuss mechanism, and which involves both coordinated (immobile) and unligated (free) water molecules.

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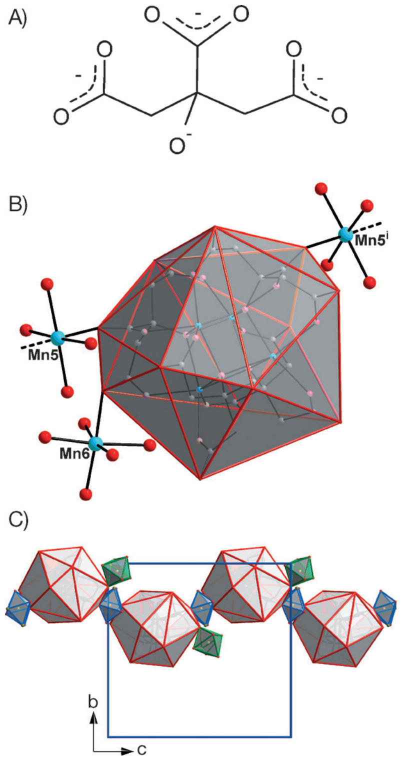

Figure 1. Components of the chemical environment of compound **2**. A) Structural formula of citrate. B) Crystal structure showing one $[Mn_4(citr)_4]^{8-}$ unit with its pendant Mn^{II} centers and their ligands. The second congeners of three disordered H_2O ligands are not shown. The polymer is propagated at Mn5 and $Mn5^{i}$. (i: $-1/2+x$, $3/2-y$, $-1/2+z$). C) One-dimensional polymer formed by the cubane fragments (pink and red), bridging Mn^{II} units (blue), and pendant octahedrally coordinated Mn^{II} (green). The chain is propagated by the *n*-glide plane perpendicular to the b-axis of the unit cell. From structure **2a**.[24]

A complex reaction procedure, described in the Supporting Information, first yields a known manganese citrate complex of formula $[Mn_3(Hcitr)_2(H_2O)_6]_n{\cdot}4n(H_2O)$ (**1**)[19] and then produces crystals of the compound $[Mn(H_2O)_6]_{2n}\{[Mn(H_2O)_5]Mn_4(citr)_4[\mu\text{-}Mn(H_2O)_4]\}_n{\cdot}8nH_2O$ (**2**) as the second of at least four crystalline products that can be harvested from the reaction mixture. The basic building block of **2** is an $[Mn_4(citr)_4]^{8-}$ cluster, whose core is a cubane and whose outermost O atoms form an enneakaidecahedron (Figure 1B). This is assembled into a polymer (Figure 1C) through bridging, octahedrally coordinated Mn^{II} centers (Mn5, Figure 1B). A further octahedrally coordinated Mn^{II} center is attached to the cluster but is terminal (Mn6). A single link of the polymer chain has a charge of 4−, which is balanced by two $[Mn(H_2O)_6]^{2+}$ ions.

There are stoichiometrically 29 H_2O units per formula unit, 21 of them in the form of aqua ligands attached to four independent Mn^{II} centers—four waters at the bridging Mn5, five at terminal Mn6 and 12 on the two cations. There are also nine free water sites in the crystallographic asymmetric unit, two of which are half-occupied.

There is an extended net of hydrogen bonds between the coordinated and free water molecules, and no empty channels or voids are found in the crystal.

When crystals of **2** are placed in a desiccator for 36 h, three formula units of H_2O, one of which is disordered over two sites in the crystal, are removed, giving crystals of stoichiometry $[Mn(H_2O)_6]_{2n}\{[Mn(H_2O)_5]Mn_4(citr)_4[\mu\text{-}Mn(H_2O)_4]\}_n{\cdot}5nH_2O$ (**2.1**), in which the only substantive difference from **2** is that there are three fewer free waters (four fewer sites) per formula unit. The sites from which H_2O is lost are not contiguous in the crystal; and there is no obvious exit path for these water molecules. All four sites are close to the Mn citrate polymer, not embedded in a free-water environment. Each has one of its nearest hydrogen-bonding interactions with either a citrate oxygen atom or with a manganese-bound water molecule.

When **2.1** is exposed to a humid atmosphere, for example, by enclosing a crystal in a sealed tube with wet cotton for 24 h, the original product **2** is restored, still in single-crystal form. The crystal structure of the product following this treatment, which we call **2b**, is nearly identical to the structure of a newly formed crystal of **2**.

X-ray structure analysis was carried out on the original product **2** (X-ray analysis **2a**), on the dehydrated product **2.1**, and on the rehydrated **2** (**2b**).

In an experiment intended to elucidate the H_2O exit and re-entry paths for the partial dehydration and rehydration processes, single-crystal neutron diffraction analyses were conducted first on **2** (neutron analysis **2n**) and then, following partial dehydration, on the rehydrated product **2**, but with the rehydration having been conducted under pure D_2O vapor (product **2.2**). The most striking result to emerge from the neutron analyses is that when **2.1** is exposed to D_2O vapor, all 30 of the bound and free water sites in the structure are fully deuterated. This unforeseen result is clearly established on the basis of the scattering length contrast between H (−3.742 fm) and D (6.674 fm), even with the weaker diffraction data measured from the rehydrated sample (**2.2**).

The pristine and D_2O- and H_2O-rehydrated samples are isostructural, and the structural parameters of the non-hydrogen atoms are in good agreement between the X-ray and neutron analyses. In addition, both of the neutron analyses reveal the positions of all of the hydrogen atoms, including those that are partially occupied as a result of disorder. The presence of disorder helps explain why the water H atoms were not located in the X-ray analyses.

The pronounced scattering length contrast between protium and deuterium makes isotopic substitution an effective tool in neutron-scattering analysis.[20,21] The hydrogen atoms of the CH_2 groups of the citrate ligands, whose inertness to substitution makes them a control group, were found still to be protium after exposure to a D_2O atmosphere. The hydrogen disorder found in the pristine crystal was also observed, but with some modification, after deuteration. For the 21 H_2O moieties bound to Mn^{II}, the possibility of full-water mobility in the absence of channels with retention of crystallinity, is sufficiently remote on both energetic and steric grounds that we prefer an explanation based on a proton cascade, which, while common in other contexts, has not to our knowledge been invoked for molecular crystals. This explanation is consistent with both the observation of full H/D substitution and the observed H-atom disorder.

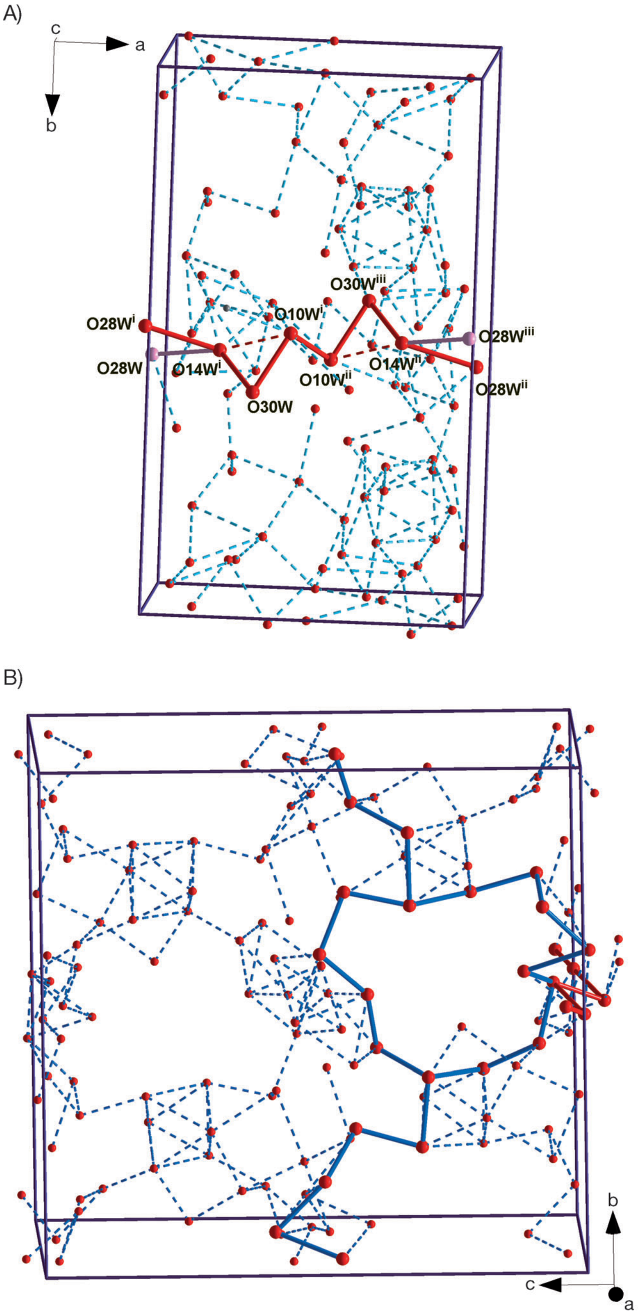

Figure 2. Hydrogen-bonded chains of ligated and free water through one unit cell in **2**. A) Unit-cell water content, showing one of the hydrogen-bonded water chains (red line). O28W is half-occupied. Interatomic distances [Å]: O28W···O28W$^{\text{i}}$ 1.94(3); O28W···O14W$^{\text{i}}$ 2.760(15); O28W$^{\text{i}}$···O14W$^{\text{i}}$ 3.057(15); O14W$^{\text{i}}$···O30W 2.813(11); O14W$^{\text{i}}$···O10W$^{\text{i}}$ 3.211(10); O30W···O10W$^{\text{i}}$ 2.760(10); O10W$^{\text{i}}$···O10W$^{\text{ii}}$ 2.830(13). Symmetry codes i: $-x$, $1-y$, $-z$; ii: $1+x$, y, z; iii: $1-x$, $1-y$, $-z$. B) Linear H-bonded chain propagated parallel to [010], with an attached cyclic motif joining this chain to that shown in A).[24]

Water connectivity through hydrogen bonds is critical to proton transport. Although there are no channels present, the manganese-bound aqua ligands and unligated water molecules do form unbounded hydrogen-bonded chains. Figure 2 A shows one of these, a topologically linear aggregate propagated parallel to the crystallographic a-axis.

Other, more elaborate hydrogen-bonded pathways exist through this crystal. Figure 2 B is a view down the a-axis of the unit cell, showing a cyclic motif appended both to a linear pathway parallel to the crystallographic b-axis (blue), and to the linear pathway along the a-axis (red). These H-bonded chains are topologically similar to previously observed patterns.[22]

A model derived from the experimentally observed hydrogen disorder and involving just one of several proton-conduction pathways, the chain shown in Figure 2 A, describes the fundamental character of the process involved. A fuller modeling study would be needed to complete and fine-tune the model.

With reference to the structure of the untreated, H-containing crystal, of the 30 water sites, eight had hydrogen atoms that were disordered in such a way that one H atom was common to the two disordered congeners. This assembly appears as a fully occupied oxygen atom with one fully occupied and two half-occupied H sites at bonding distances from O. Further, two of the water molecules were each observed as a single O atom surrounded by four half-occupied H sites, separable into two pairs of H forming good H_2O geometry. This is another commonly observed disorder, seen, for example, in neutron studies of cyclodextrins where it was described as resulting from a flip-flop of the water molecules.[23]

The observed pattern of atomic positions in the water chain of Figure 2 A is consistent with the Grotthuss mechanism,[12–14] a concerted hopping of protons between neighboring water molecules (Figure 3 A,B) with posterior rotation of the water molecules to regenerate their initial orientations in preparation for repetition of the transfer-reorientation cycle. The hydrogen disorder along the water chain of Figure 2 A (Supporting Information Figure S5 A) can be interpreted as a superposition of the two dispositions of the respective water molecules (congeners A and B in Figure 4), frozen in place at the data collection temperature, 20 K, and averaged over the entire crystal. The separate patterns describe geometrically valid water structures.

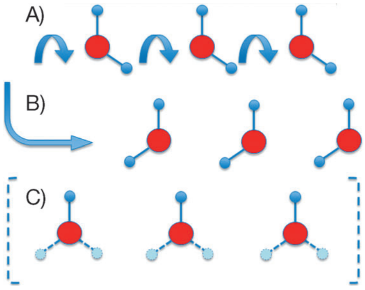

Figure 3. Simplified drawing of the Grotthuss mechanism. A) Water molecules at the beginning of the process with the arrows showing how the hydrogen atoms jump to the neighboring water sites; B) Final situation after the hydrogen atoms jump; C) Superposition of the initial and final situations, giving disorder of the mobile hydrogen atoms.

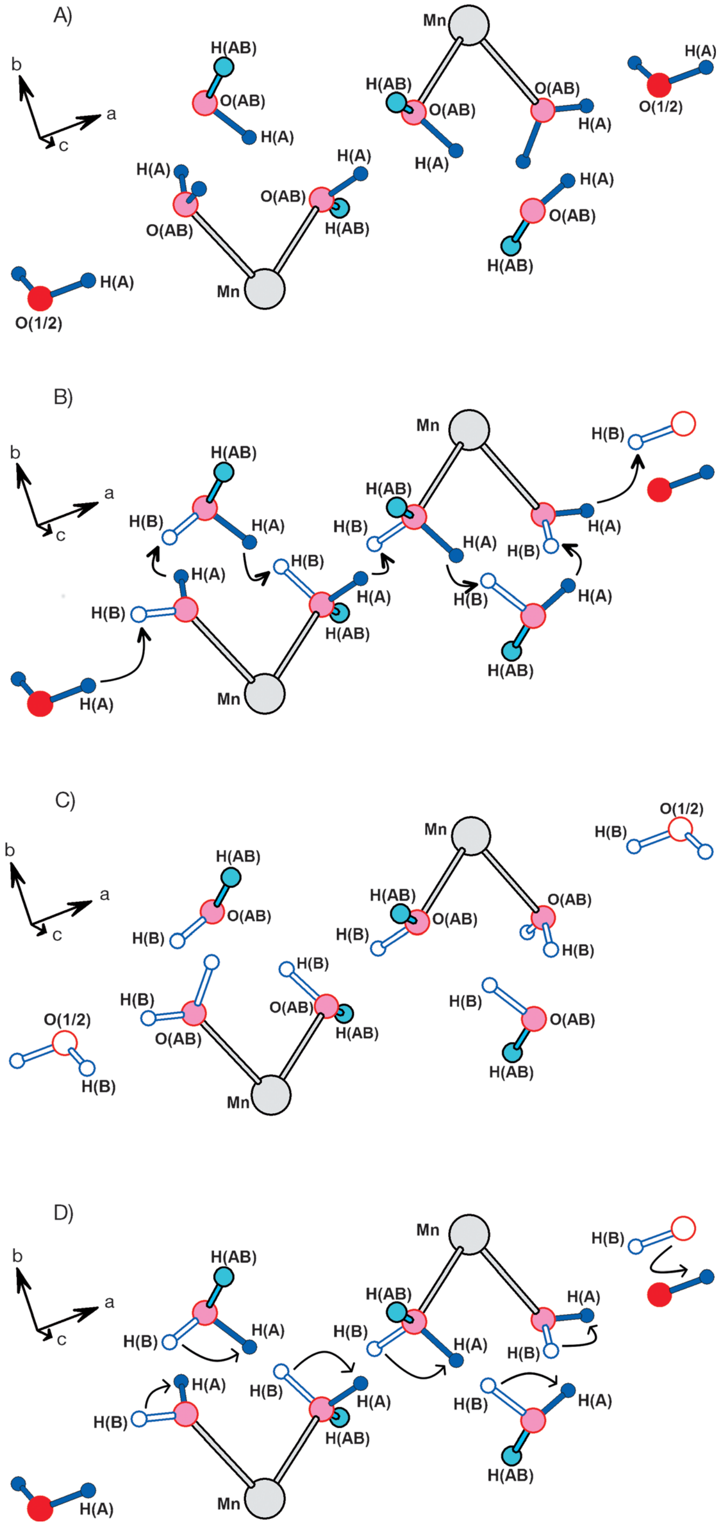

Figure 4. One cycle of the Grotthuss mechanism, consisting of proton hopping followed by water-molecule reorientation. A) One of the valid H-atom structures, congener A (solid blue) through the length of one unit cell along the a-direction. B) First stage of the Grotthuss mechanism, consisting of short hops between neighboring water molecules, from positions in congener A (solid blue) to the positions of congener B (open blue). C) The second valid H-atom structure, congener B (open blue). D) Second stage of the Grotthuss mechanism, consisting of rotations of the H_2O molecules of congener B to return the system to its initial condition (congener A, Figure 4 A).[24]

The proton transport mechanism for this segment of the structure is summarized in Figure 4. Figure 4 A shows one of the valid H-atom structures, which we call congener A and which gives good geometry and H-bonding through the length of one unit cell along the a-direction. Short hops between neighboring water molecules are shown in Figure 4 B; these produce the second valid H_2O structure, congener B, shown in Figure 4 C. The well-to-well distances traversed by H atoms during this process range from 0.73(3) to 1.55(4) Å (Figure S5 A caption), with the corresponding O⋯O distances varying from 2.760(11) to 3.057(15) Å. The hopping from one set of positions to another is the first part of the Grotthuss mechanism; and the second part, Figure 4 D, consists of rotations of the resulting H_2O molecules to return the system to its initial condition (congener A), Figure 4 A. This completes one cycle of the mechanism and is a single step in the proton transfer necessary for the full H/D replacement that we observe.

The identification of this proton wire shows that a proton can be transferred through at least three mechanisms: The first consists of movement inside the coordination sphere of a *cis*-aqua complex (O10W^{ii}, O14W^{ii}, Figure S5A) mediated by an external water molecule, O30W^{iii}. Secondly, H^+ is also transferred directly between two aqua complexes (O10W^{i}, O10W^{ii}) without the need for an external water molecule as mediator. The third mechanism is H-atom transfer between neighboring aqua complexes (two congeners of O14W) with mediation by a disordered external lattice water molecule (O28W).

The situation before the concerted hopping of protons as in the proposed processes (Figure 3 A, 4 A) and the situation after the proton transfer (Figure 3 B) can be superposed to give the observed disorder of Figure 3 C and 4. This is equivalent to the simple representation of the Grotthuss mechanism of Figure 3, but now the pattern is derived from experimental data and involves free and coordinated water molecules in specific transfer and reorientation mechanisms.

Mass transport in molecular solids has been conceived as taking place mainly through channels; however, flexible crystals without clear channels and with few free water molecules not only can exhibit extended proton transfer phenomena, as the present results demonstrate, but they may be the best option for its study. The present results demonstrate that in molecular crystals the subtler mechanisms used by living systems can also operate. The observation of proton transport in confined space in this Mn citrate coordination polymer opens a conceptually new area of study for molecular crystals.

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[24] CCDC 940521 (**2a**), CCDC 940522 (**2.1**), CCDC 940523 (**2b**), CCDC 940768 (**2n**), CCDC 940769 (**2.2**) contain 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.