Crystal Structure and Proton Conductivity of a One-dimensional Coordination Polymer, {Mn(DHBQ)(H_2O)$_2$}

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{Mn(DHBQ)(H_2O)$_2$} (H_2DHBQ = 2,5-dihydroxy-1,4-benzoquinone) was investigated by X-ray diffraction, thermogravimetry, sorption isotherm of water, and proton conductivity measurements. It showed a one-dimensional coordination-polymer structure with axial coordination waters, which is the first report on the crystal structure of a one-dimensional coordination polymer with the DHBQ ligand. It also exhibited reversible structural change associated with desorption/sorption of the waters. The proton conductivities of the anhydride and dihydrate states were measured. The dihydrate showed a high proton conductivity of 4×10^{-5} S cm^{-1}, while the anhydride was below the lower limit of the measurable range ($<10^{-13}$ S cm^{-1}).

Coordination polymers (CPs) have received considerable attention[1] because of their fascinating properties, such as magnetic,[2] optical,[3] catalytic,[4] and gas-storage properties.[5] CPs have highly ordered frameworks composed of a wide variety of metal species and organic ligands. In addition, hydrogen-bond networks and nanospaces can be introduced into the frameworks of CPs. Maier and co-workers have reported that ionic conduction is greatly enhanced when the conduction pathway is restricted to nanosize.[6] CPs have, therefore, advantages for developing proton conductors.

However, few proton-conductive properties of CPs have been reported in the past.[7] Recently, ferrous oxalate dihydrate {Fe(ox)(H_2O)$_2$} was reported to show high proton conductivity at room temperature, where coordination waters to the Fe^{II} ions play the role of a Lewis acid and contribute to the high proton conduction.[8] The detailed mechanism of the proton conduction is still under discussion.

2,5-Dihydroxy-1,4-benzoquinone (H_2DHBQ) is known to be a bis-bidentate ligand with a π-electron system. Divalent metal ions (M) and DHBQ are expected to form one-dimensional (1-D) CPs, MDHBQ, consisting of an alternating arrangement of M and DHBQ.[9] The study of MDHBQ should offer further information about the conduction mechanism of metal oxalates. However, no crystal structures have so far been reported for MDHBQ by single-crystal X-ray diffraction. Herein, we report the first crystal structure of an example of {MDHBQ(H_2O)$_2$} and discuss its proton-conductive properties.

{Mn(DHBQ)(H_2O)$_2$} (**1**·2H_2O) was synthesized by slow diffusion in an H-shaped tube of aqueous solutions containing manganese sulfate pentahydrate (241.08 mg, 1 mmol) and H_2DHBQ (140.01 mg, 1 mmol), respectively, at room temperature. After several days, red plate-like crystals were obtained. The crystal structure of **1**·2H_2O was determined by X-ray diffraction.[10] A powdered sample of **1**·2H_2O was synthesized by mixing manganese sulfate pentahydrate (2.411 g, 10 mmol) and H_2DHBQ (1.400 g, 10 mmol) in water. A red powder immediately precipitated and was washed with water and ethanol several times (yield: 96%). The obtained powdered sample was characterized by X-ray powder diffraction and elemental analysis. The powder diffraction pattern observed for the powdered sample was in good agreement with the simulated pattern for the structure obtained from the crystal structure analysis for **1**·2H_2O. {Mn(DHBQ)(H_2O)$_2$} Anal. Calcd for $C_6H_6O_6Mn$: C, 31.46; H, 2.64%. Found: C, 31.06; H, 2.60%. The sorption isotherm of water was measured at 25 °C by a volumetric adsorption apparatus, BELSORP 18-PLUS. Before the measurement, **1**·2H_2O was evacuated at 50 °C for 24 h. The thermal behavior of **1**·2H_2O was evaluated by thermogravimetric analysis (TGA).

As shown in Figure 1, **1**·2H_2O has a 1-D chain structure composed of Mn^{II} ions and DHBQ ligands. Each Mn^{II} ion is equatorially coordinated to four oxygen atoms of two DHBQ ligands, and two water molecules axially coordinate to the metal site. As explained below (Figure 4), hydrogen bonds are formed between a coordination water and an oxygen atom of DHBQ of the adjacent chain (2.724 Å).

From the TGA of **1**·2H_2O, it was found that the weight loss up to 120 °C corresponds to two equivalents of water (Figure 2a). Weight loss above 300 °C originates from decomposition of **1**. The water vapor pressure–composition isotherm (PCT curve) for **1** is shown in Figure S1 (see Supporting Information).[11] From the PCT measurement, it was found that **1** absorbs two equivalents of water with humidification, indicating that **1**·2H_2O loses two coordination waters by evacuation at 50 °C and that the sample was totally dehydrated under those conditions. To reveal the structural changes accompanied by water desorption and absorption, X-ray powder diffraction patterns of as-synthesized, dehydrated, and rehydrated samples were measured (Figure 2b). The dehydrated sample showed a totally different pattern from the as-synthesized sample, indicating that structural change occurred during the dehydration process. The diffraction pattern of the as-synthesized product was reproduced after dehydration followed by rehydra-

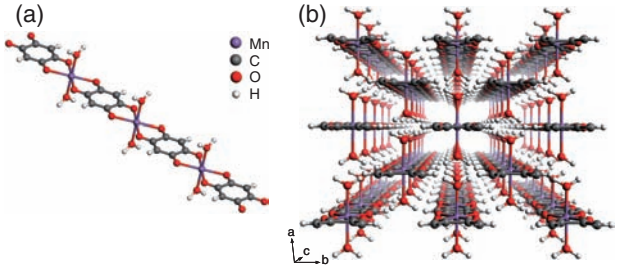

Figure 1. (a) Crystal structure of a 1-D chain of **1**·2H_2O and (b) perspective view of **1**·2H_2O along the *c* axis.

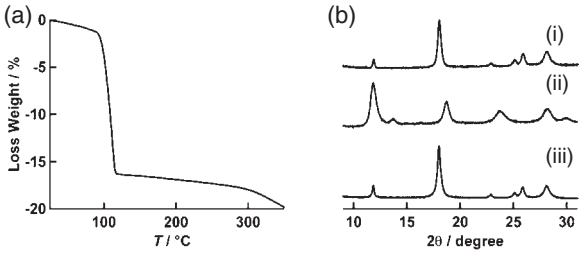

Figure 2. (a) Thermogravimetric analysis for **1**·2H_2O. (b) X-ray powder diffraction patterns for **1** (i) as-synthesized, (ii) after heating at 50 °C for 24 h, and (iii) under saturation vapor pressure at 25 °C for 24 h.

tion, demonstrating that **1** can absorb and desorb two coordination waters reversibly without destruction of the 1-D framework. It is known that 1-D metal oxalate dihydrates show reversible structural change during dehydration and rehydration with rearrangement of hydrogen bonds between the 1-D CP chains.

Proton conductivities of **1** and **1**·2H_2O were evaluated by an AC impedance method. As an anhydride sample, powder of **1** was compressed to a pellet and heated at 50 °C in vacuo for 24 h. Gold wires were attached to both sides of the pellet with gold paste. To measure the proton conductivity of the hydrated phase, the pellet was exposed to humidified conditions (98% RH) for 24 h. AC impedance measurements were carried out both for hydrated and dehydrated specimens at various frequencies and temperatures. The diffraction patterns of the pellets before and after humidification were measured and agreed with those for **1** and **1**·2H_2O, respectively. The conductivity of anhydrous **1** was found to be below the lower limit of the measurable range ($<10^{-13}$ S cm^{-1}), showing that **1** is insulating in proton conduction. With water vapor uptake, however, the proton conductivity of **1** increased drastically by more than eight orders of magnitude up to 4×10^{-5} S cm^{-1}. The coordination waters are, therefore, considered to play an important role in the proton-conductive properties of **1**·2H_2O. It is notable that **1**·2H_2O exhibits extremely high proton conductivity in spite of having no acidic functional groups such as sulfonic acid groups. The manganese ion in **1**·2H_2O is assumed to act as a Lewis acid, and it can be expected that some of the protons in the coordination waters dissociate and migrate by hopping.

The temperature dependence of proton conductivity for **1**·2H_2O at 98% RH is shown in Figure 3. Proton conductivity increased with temperature and the activation energy (E_a) was estimated to be 0.26 eV, comparable to that of superprotonic conductors such as Nafion.[12] The proton conductivity is lower by one order of magnitude in **1**·2H_2O than that of {Fe(ox)(H_2O)$_2$}. The distance between the water molecules of **1**·2H_2O is longer than that in {Fe(ox)(H_2O)$_2$} because of the introduction of a benzene ring. If protons migrate by hopping from coordination water to the neighbors along the 1-D chain, the hopping distance becomes longer in **1**·2H_2O. In contrast, **1**·2H_2O has a smaller value for E_a than does {Fe(ox)(H_2O)$_2$} (0.37 eV). As shown in Figure 4, hydrogen bonds between coordination water and frameworks exist perpendicular to the 1-D chain. Although the geometry and distance of the hydrogen bonds are similar to {Fe(ox)(H_2O)$_2$}, the O···O intra-ligand distance (2.656 Å) in DHBQ of **1**·2H_2O is significantly shorter than that (2.755 Å) in ox of {Fe(ox)(H_2O)$_2$}, resulting in a smaller E_a value. Therefore, the conductive pathways are believed to be networks composed

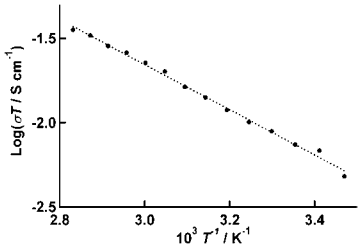

Figure 3. Arrhenius-type plot for **1** under 98% relative humidity.

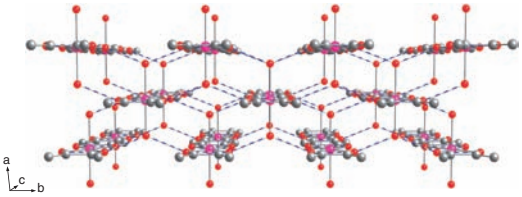

Figure 4. Hydrogen bonds lie perpendicular to the 1-D chain in **1**·2H_2O.

of hydrogen bonds and O···Os, running perpendicular to the 1-D chain. The somewhat lower conductivity in **1**·2H_2O may be derived from the weaker Lewis acidity of Mn^{II} compared with the Fe^{II} ion, that is, a lower carrier concentration of protons.

In summary, we have investigated the 1-D coordination polymer {Mn(DHBQ)(H_2O)$_2$} and determined the first crystal structure of this type of CP with a DHBQ ligand. Absorption and desorption of water vapor were examined with TGA and PCT measurements, and reversible structural change accompanied by coordination and dissociation of axial water molecules was observed by X-ray powder diffraction. Proton conductivity was increased from $<10^{-13}$ to 4×10^{-5} S cm^{-1} by the coordination of water to the Mn^{II} ions. The proton carriers are considered to be generated from the coordinated waters and migrate along networks composed of interchain hydrogen bonds and O···Os in DHBQ.

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