Hydrogen bond network involving water molecules in the crystal of a protonated Anderson-type polyoxometalate and the tetraphenylphosphonium cation

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Introduction
Protonated polyoxometalates, which are capable of both accepting and donating hydrogen bonds at programmable sites, are potentially good candidates as structure guiding building blocks for the rational design of hydrogen bond networks. We are trying to further tailor the crystal structure by the use of the tetraphenylphosphonium cation, another structure guiding building block through the C–H···π and π···π interactions.

In this context, we have prepared a tetraphenylphosphonium salt of hexaprotonated hexamolybdoaluminate, [(C₆H₅)₄P][Al(OH)₆Mo₆O₁₈]·17.5H₂O, whose detailed hydrogen-bond network structure has been successfully determined by the synchrotron X-ray diffraction at NW2A beamline of PF-AR, KEK.

Results and Discussion
Preparation of the samples
A 1.52 g sample of Na₅[Al(OH)₆Mo₆O₁₈]·17.5H₂O was dissolved in distilled water whose pH had been adjusted to 2.5 with hydrochloric acid. To this solution was added 40 mL aqueous solution dissolving 1.02 g [(C₆H₅)₄P]Br, when white precipitate was obtained. The crude product was recrystallized from the mixed solvent of water and acetone.

X-ray diffraction
A preliminary diffraction experiment using MoKα radiation from a rotating target generator allowed us to determine the location of non-hydrogen atoms. However, the positions of the hydrogen atoms could not be determined, which prevented us from analyzing the hydrogen bond networks in the crystal. In order to elucidate the hydrogen atom positions, we conducted a diffraction experiment at AR NW2A beamline. Crystal data is summarized in Table 1.

Hydrogen bond network
The synchrotron diffraction data allowed us to reveal the positions of the hydrogen atoms and to discuss on the hydrogen bond network in detail.

Two characteristic features were observed in the hydrogen bond network in [(C₆H₅)₄P][Al(OH)₆Mo₆O₁₈]·17.5H₂O as shown in Figure 1. One is the pentagonal water arrangement attached on the molybdoaluminate anion with hexagonal symmetry. The mismatch in symmetry, derived from the mismatch in the O···O interatomic distances between those within the polyoxometalates and those among the hydrogen-bonded water oxygen atoms, is expected to lead to fluxional behaviors of the water molecules surrounding the polyoxanion in the solution. Another feature is a dangling hydrogen atom that does not contribute to any hydrogen bond. This geometry is stabilized by three hydrogen bonds in which the water molecule is involved: it is donating one hydrogen bond to its neighboring polyoxometalate and accepting two hydrogen bonds from its surrounding water molecules.