Crystallography

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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, $[(C_6H_5)_4P]_3[Al(OH)_6Mo_6O_{18}]\cdot 17.5H_2O$, 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 $Na_5[Al(OH)_6Mo_6O_{18}]\cdot 17.5H_2O$ 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 $[(C_6H_5)_4P]Br$, 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.

Table 1: Crystal data for $[(C_6H_5)_4P]_3[Al(OH)_6Mo_6O_{18}]\cdot 17.5H_2O$

Formula weight		2324.1
Crystal size / mm		0.06×0.04×0.04
Crystal system		monoclinic
Space group		*P* -1
Z		2
Unit cell dimensions	*a* / Å	15.1362(1)
	b / Å	16.3640(2)
	c / Å	20.5423(2)
	α / °	100.685(1)
	β / °	102.909(1)
	γ / °	106.968(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 $[(C_6H_5)_4P]_3[Al(OH)_6Mo_6O_{18}]\cdot 17.5H_2O$ 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 polyoxoanion 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.

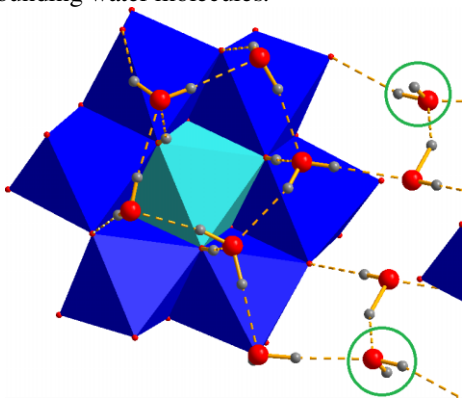

Figure 1: Hydrogen bond network in $[(C_6H_5)_4P]_3[Al(OH)_6Mo_6O_{18}]\cdot 17.5H_2O$, showing the pentagonal water ring attached onto the molybdoaluminate polyoxoanaion and water molecules with dangling hydrogen atoms (designated with green circles).

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