

Dynamics of the water included in $[\text{H}_{11}\text{O}_5][\text{ZnCu}(\text{CN})_4]$

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The title compound $[\text{H}(\text{H}_2\text{O})_5][\text{ZnCu}(\text{CN})_4]$ is a bimetal cyanide complex with a 3D framework structure built by bidentate behavior of cyanide linking tetrahedral Cu(I) and Zn(II) ions. The structure of the 3D framework is the tridymite-like structure as shown in Fig. 1 and the framework has negative electric charges. Inside the 3D framework void space is formed and water molecules and protons are included. The water molecules and protons are considered to form a hydrogen bonding network which penetrates the 3D framework of the bimetal cyanide complex. Although our previous X-ray structure analysis revealed the 3D framework structure, the structure of the hydrogen bonding network was unclear. The water molecules and protons are expected to be in a dynamic state. DSC measurement showed phase transitions at 160K-170K and 240K. 2H-NMR powder patterns, which were measured using a deuterated sample, suggested a flip-flop motion about the C2 axis of a water molecule below 168K, a rotational motion about the C2 axis between 178K and 233K and an isotropic rotational motion above 253K for the water molecules. Although considerably activated rotational motion was confirmed near room temperature, there was no information about translational diffusion of the protons. If translational diffusion is observed, a possibility as a proton conductor comes up. In order to obtain information about such translational diffusion, we have carried out quasi-elastic neutron scattering (QENS) measurement on the title compound.

The sample was powdered and packed in a double walled cylindrical cell made of Al. The shape of the packed sample was a cylinder with a 13 mm diameter,

a 50 mm height and a 1 mm thickness. The QENS measurement was carried out in the temperature range of 200K-323K on a time-flight type spectrometer AGNES(C3-1-1) installed at JRR-3M on JAEA(Tokai).

The data obtained were analyzed using the Chudley-Elliott model after several trials. This model is a jump diffusion model in which an atom stays and vibrates at a given position for an interval time and after that time the atom jumps rapidly to another position. In the case of a powder sample the jump direction is isotropic but the jump distance is fixed to a constant value. In our case, considering the results of the 2H-NMR experiments, we assumed that during the interval time the proton is undergoing reorientation among the four apexes of a tetrahedron which is a part of the hydrogen bonding network formed with the water molecules. At the center of the tetrahedron the O atom of a water molecule is positioned and the distance between the O and each apex is 0.97 Å, which is the bond length of O-H. Fig.2 shows the HWHM vs Q plot and the best fit results based on our Chudley-Elliott model for the translational diffusion. From this fitting, the jump distance, the interval time, the diffusion constant and the activation energy were derived to be 2.9(1) Å, $9(3) \times 10^{-15}$ sec, $6(3) \times 10^{13}$ Å²/sec and 16(1) kJ/mol, respectively. Considering the O-O distance in a O-H-O type hydrogen bond is 2.72(15) Å, the jump distance obtained here means that the proton diffuses by a jump to an adjacent water molecule. The correlation time and the activation energy for the 4-site reorientation during the interval time were calculated to be $1.7(3) \times 10^{-12}$ sec and 11.2(5) kJ/mol, respectively.

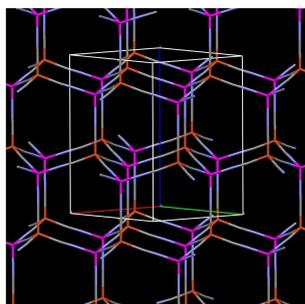


Fig. 1

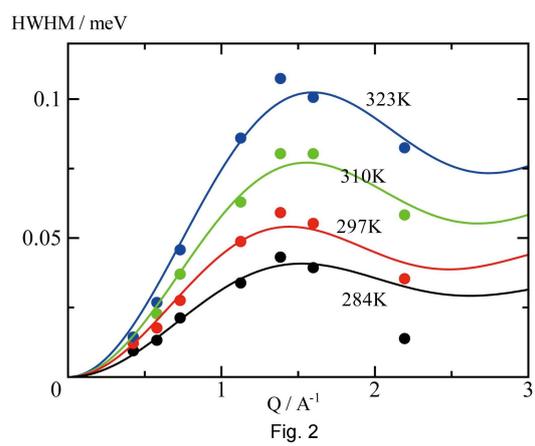


Fig. 2

Fig. 1. Fig.1. The structure of the 3D framework of [ZnCu(CN)₄]. Fig.2. HWHM vs Q plot and curve fitting using the Chudley-Elliott model for the translational diffusion.