## Tridymite-like host clathrate [K(H<sub>2</sub>O)<sub>n</sub>][CuZn(CN)<sub>4</sub>] : crystal structure, guest molecular motion and properties

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## **Electronic Supplementary Information (ESI)**



Fig. S1 (a) Crystal structure of HT-Cristobalite SiO<sub>2</sub> (b) Structure of Cd(CN)<sub>2</sub> host of the Cristobalite type Cd(CN)<sub>2</sub>·G clathrate. The orientation of the cyanide bridges is disordered. X is a hybrid atom of 50%C and 50%N.[1] (c) Structure of  $[CuZn(CN)_4]^-$  host of the  $[N(CH_3)_4][CuZn(CN)_4]$ ·G clathrate. The gravity centre of  $N(CH_3)_4^+$  is indicated with a small green point.[1] (d) Crystal structure of HT-Tridymite SiO<sub>2</sub>, (e) Structure of Cd(CN)<sub>2</sub> host of the Tridymite type Cd(CN)<sub>2</sub>·G clathrate. The orientation of the cyanide bridges is disordered. X is a hybrid atom of 50%C and 50%N.[2] (f) Structure of  $[CuZn(CN)_4]^-$  host of  $[K(H_2O)_n][CuZn(CN)_4]$  found in this study.



Fig.S3 DSC graph of the samples which reabsorbed H<sub>2</sub>O (a), CH<sub>3</sub>OH (b) and CH<sub>3</sub>CN (c). The measurements were carried out using a Perkin Elmer Diamond DSC instrument.

## <sup>2</sup>H-NMR powder pattern

A brief outline of the line shape analysis of <sup>2</sup>H-NMR powder patterns in a fast speed region (>10<sup>7</sup> Hz) is presented here. <sup>2</sup>H-NMR spectra in solids are ruled by the first-order perturbation to the Zeeman effect, which comes from the interaction between the nuclear electric quadrupole moment and the electric field gradient. The electric field gradient (EFG) around a D atom is represented with an EFG tensor V, and V described in its principal axis system or diagonalized V is denoted by V<sub>pas</sub>. <sup>2</sup>H-NMR powder patterns have characteristic line widths  $\Delta v_{xx}$ ,  $\Delta v_{yy}$  and  $\Delta v_{zz}$  as shown in Fig. S4. The relations among  $\Delta v_{xx}$ ,  $\Delta v_{yy}$ ,  $\Delta v_{zz}$ , the quadrupole coupling constant *Qcc* in Hz, the asymmetric parameter  $\eta$  and the principal values of V<sub>pas</sub>,  $V_{xx}$ ,  $V_{yy}$ ,  $V_{zz}$  are

$$\eta = \frac{\Delta v_{yy} - \Delta v_{xx}}{\Delta v_{zz}}$$

$$\Delta v_{xx} = \frac{3}{4}Qcc(1-\eta) = \frac{3}{4}Qcc|V_{xx}|$$

$$\Delta v_{yy} = \frac{3}{4}Qcc(1+\eta) = \frac{3}{4}Qcc|V_{yy}|$$

$$(1)$$

$$\Delta v_{zz} = \frac{3}{2}Qcc = \frac{3}{4}Qcc|V_{zz}|$$



Fig. S4 <sup>2</sup>H-NMR powder pattern and its characteristic line widths  $\Delta v_{xx}$ ,  $\Delta v_{yy}$  and  $\Delta v_{zz}$ .

The characteristic line widths of <sup>2</sup>H-NMR powder pattern in a fast speed region(  $>10^7$  Hz ) can be calculated by averaging V tensors of a D atom at all sites distributed by the molecular motion. V orientated to a direction at a site in the motion is described as

$$\mathbf{V}(\alpha,\beta,\gamma) = \mathbf{R}(\alpha,\beta,\gamma)^{-1} \mathbf{V}_{\text{pas}} \mathbf{R}(\alpha,\beta,\gamma) \qquad \cdots (2)$$

where **R** is a matrix of a rotating operation and  $\alpha$ ,  $\beta$ ,  $\gamma$  are Euler angles indicating the direction of **V**.

$$\mathbf{R}(\alpha,\beta,\gamma) = \begin{pmatrix} \cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma & \sin\alpha\cos\beta\cos\gamma + \cos\alpha\sin\gamma & -\sin\beta\cos\gamma \\ -\cos\alpha\cos\beta\sin\gamma - \sin\alpha\cos\gamma & -\sin\alpha\cos\beta\sin\gamma + \cos\alpha\cos\gamma & \sin\beta\sin\gamma \\ \cos\alpha\sin\beta & \sin\alpha\sin\beta & \cos\beta \end{pmatrix} \cdots (3)$$

In the case of an equivalent *n*-site reorientation, the averaged EFG tensor ( $\overline{\mathbf{V}}$ ) is

$$\overline{\mathbf{V}} = \frac{1}{n} \sum_{i=1}^{n} \mathbf{V}(\alpha_i, \beta_i, \gamma_i) \quad \cdots \quad (4)$$

From the principal values of  $\overline{V}_{pas}$ , which is diagonalized  $\overline{V}$ , the characteristic line widths are calculated using the above relations and the prediction of the resultant line shape is possible. However, spectra in an intermediate speed region (10<sup>6</sup>-10<sup>4</sup> Hz) show deformed and complicated line shapes depending on a motional mode and speed, and for their simulation numerical calculation using a computer is necessary. For further details of <sup>2</sup>H-NMR spectra in solids and their line shape analysis, see papers written by experts.[3] Homemade programs were used for drawing simulated line shapes shown below.[4]

Two-site reorientation of a D<sub>2</sub>O molecule

Fig. S5 shows a coordinates setting for two-site reorientation of a D<sub>2</sub>O molecule. The *z* axis bisects the D-O-D angle and is the central axis for the two-site reorientational motion. D atom is undergoing reorientation between Site-1, whose Euler angles are  $\alpha = 0^{\circ}$ ,  $\beta = D$ -O-D angle/2,  $\gamma = 0^{\circ}$ , and Site-2, whose Euler angles are  $\alpha = 180^{\circ}$ ,  $\beta = D$ -O-D angle/2,  $\gamma = 0^{\circ}$ . Namely, two D atoms exchange their positions in this orientational motion. *Qcc* and  $\eta$  values for a static state were estimated to be 226 kHz and 0.12, respectively, from the line shape at 123 K. Using these *Qcc* and  $\eta$  data and the above calculation scheme, line widths and line shapes were simulated. Fig S6 shows the results obtained.



In the case that  $\eta$  is not 0, 0° and 90° are possible for  $\gamma$ . Comparison between the observed and calculated line widths suggested that 0° is more suitable in our case. When 52.3°, which is half the well known H-O-H angle of 104.5°, was adopted as the  $\beta$  value, small discrepancy between the observed and calculated line widths generated. The line width  $\Delta v_{xx}$ , which is the narrowest width at the centre of the spectrum, is sensitive around this  $\beta$  angle region. In the simulations shown in Fig. S6 54.4° was used for  $\beta$ , which was determined from the agreement between the observed and calculated widths. 54.4° is closer to half the tetrahedral angle of 109.5°.



Fig. S6 (a) and (b) are a simulated line shape for a static state and that for a fast two-site reorientation, respectively. (c), (d) and (e) are observed (left) and simulated (right) line shapes at 133K, 153K and 163K. The simulated line shapes are superpositions of (a) and (b). The ratio of (a):(b) is 1:0.7 in (c), 1:1.6 in (d) and 1:6 in (e).

Rotation of a D<sub>2</sub>O molecule

In our case, it is natural to consider rotation of the D<sub>2</sub>O molecule about the *z* axis in Fig. S5. The line widths for rotation about a fixed central axis can be calculated by use of an *n*-site reorientation model, in which the number of the sites must be more than two and all sites must be equivalent about the fixed axis. The simplest way is considering three sites whose  $\alpha$  are 0°, 120°, 240°, and  $\beta$  and  $\gamma$  are common to all sites. In general, the powder pattern for rotation about an axis is a so-called axial pattern, whose  $\eta$  is 0, namely,  $\Delta v_{xx} = \Delta v_{yy}$  and  $\Delta v_{zz} = 2\Delta v_{xx}$ . The line widths depend on only the  $\beta$  value. Especially, around  $\beta$  = magic angle(54.7°) the line widths are very narrow. In the model shown in Fig. S5  $\beta$  is close to the magic angle and the spectra observed in 193-233 K were deformed axial patterns with very narrow line widths. Fig. S7 shows the spectrum at 233 K and its simulation based on the rotation model. In the simulation the  $\beta$  value of 56.0° was used for realizing good agreement.



Fig. S7 Line shape observed at 233K and its simulation based on the rotation model.

Rotation of a CD<sub>3</sub> methyl group

The situation that a CD<sub>3</sub> group is undergoing rotation about its  $C_3$  axis is illustrated in Fig. S8, where the  $C_3$  axis is on the *z* axis. Similarly to the case of the rotation of D<sub>2</sub>O, an equivalent 3-site reoreintaional model is applicable and the resultant line shape is an axial pattern. In general, the rotation of a methyl group has sufficient fast speed near liquid nitrogen temperature and observed spectra are axial patterns already narrowed by the fast rotational motion. Their observed effective *Qccs* are *ca*. 50-55 kHz, which corresponds to line width  $\Delta v_{xx}$  of 37.5-41.3 kHz.[5] Fig. S9(a) and (b) show the spectra of the CD<sub>3</sub> part observed in the case of CD<sub>3</sub>OD and CD<sub>3</sub>CN, respectively, and (c) shows line shape simulated assuming that the effective *Qccc* is 55 kHz.



Fig. S9 (a) the CD<sub>3</sub> part in the spectrum observed for the sample absorbing CD<sub>3</sub>OD, (b) observed spectrum for the sample absorbing CD<sub>3</sub>CN, (c) spectrum simulated assuming  $Qcc_{eff} = 55$  kHz.

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