Nature of Hydration Water in (±)-Tris(ethylenediamine)cobalt(III) Chloride Hydrate, (±)-$[Co(en)_3]Cl_3{\cdot}nH_2O$, as Studied by ^1H, ^2H, and ^{17}O Solid State NMR

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Z. Naturforsch. **55 a,** 362–368 (2000); received August 23, 1999

Presented at the XVth International Symposium on Nuclear Quadrupole Interactions, Leipzig, Germany, July 25 - 30, 1999.

The static and dynamics properties of hydration water molecules in (±)-$[Co(en)_3]Cl_3$ were studied by means of ^1H, ^2H, and ^{17}O solid state NMR. By ^1H pulsed field gradient (PFG) NMR the apparent diffusion coefficient of mobile water through a micropore along the crystalline unique *c*-axis was found to be 1.0×10^{-9} m^2 s^{-1}. The ^2H NMR spectrum at 141 K consists of two components, one being a Pake doublet corresponding to a quadrupole coupling constant (QCC) of (226 ± 2) kHz and an asymmetry parameter of the electric field gradient η of 0.08 ± 0.01, and another being a Gaussian line with a linewidth of 3.5 kHz. The ^{17}O NMR spectrum at 300 K also consists of a narrow Gaussian peak and a broad powder pattern with a second order quadrupole effect corresponding to QCC = (6.3 ± 0.5) MHz and η = 0.55±0.02. The broad and narrow components are assigned to water molecules accommodated at general 12g positions and special 2a and 2b positions in the trigonal lattice with space group $P\bar{1}c1$. From the ratio of the populations at these positions their potential energy difference was estimated to be between (2.7 ± 0.1) and (3.5 ± 0.1) $kJmol^{-1}$. The ^2H NMR spectrum at room temperature indicates a finite quadrupole interaction which is attributable to the rapid rotation of water molecule about the molecular C_2-axis. When the water content exceeds 2.7, the QCC is reduced sharply to (5.0 ± 0.1) kHz at 285 K, suggesting that there occurs rapid rotation of water and rapid exchange of ^2H between nonequivalent positions.

Key words: (±)-$[Co(en)_3]Cl_3$; Absorbed Water; Molecular Motion; Hydrogen Bond; Quadrupole Interaction.

Introduction

Recently, various kinds of micro- and meso-porous materials have been developed for the use as ion-exchange agents, molecular sieves, catalysts, catalyst supports, the reaction field, and so on for small molecules which are absorbed in the micro- and/or meso-pores [1 - 3]. The variety of the sizes and shapes of these pores provides absorbed molecules with a variety of much specified spaces, and so the accommodated molecules show a specific behavior which is different from that in the usual open space or in solution. The molecular dynamics and the structure of the adsorbed molecules in such a restricted space concerns a great variety of physical situations including surfaces, lamella systems, polymers, membranes, glasses and biomolecular systems. Water is one of the most interesting guest small molecules in these various pore systems, and its behavior has recently been studied extensively by neutron scattering [4], X-ray diffraction [5], and NMR [6].

(±)-$[Co(en)_3]Cl_3{\cdot}nH_2O$ crystal is known to form uniform and homogeneous one-dimensional micropores. Its crystal structure was determined by X-ray diffraction using single crystals [7, 8]. This complex compound crystallizes in a trigonal $P\bar{3}c1$ unit cell of the dimensions, $a = 1.150 \pm 0.002$ nm and $c = 1.552 \pm 0.004$ nm, with $Z = 4$ at 290 K. $Co(en)_3{}^{3+}$ cations are stacked along the *c*-axis, and a micropore is formed along the *c*-axis. This micropore can accommodate

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water molecules up to 4 per formula unit or 12 per unit cell, at general 12g positions and the special 2a and 2b positions. The water molecules are linked to each other by hydrogen bonds. The water sorption and desorption behavior in this compound is zeolitic. According to the isotherm measured at 289 K, the water content suddenly increases at 2.85 Torr, suggesting that capillary condensation of the water vapor take place. The Kelvin equation for this pressure gives a reasonable pore radius of 0.58 nm [9].

This compound has much homogeneous micropores in which the positions of the water molecules are well defined. Therefore it is an ideal model system for studies of guest water molecules in micro- or mesopores. The molecular motion of water in this compound was studied by dielectric measurements [10]. It was found that the water molecules undergo hindered rotation between –150 °C and room temperature, and that the activation energy depends strongly on the water content. It was also predicted that proton jumps along the crystallographic *c*-axis through the hydrogen-bonded network take place. However, the excitation of such a specific proton motion has not yet been confirmed.

In the present work we have measured ^{1}H, ^{2}H, and ^{17}O solid state NMR spectra of H_2O and D_2O accommodated in micropores of (±)-$[Co(en)_3]Cl_3 \cdot nH_2O$ with n between 0.5 and 4.0, in order to study the dynamics of water molecules confined in such a unique micropore. We examine the long-range hopping of the proton or water molecule in the micropore by measuring the diffusion coefficient of water by ^{1}H PFG (pulsed field gradient) NMR. Based on ^{2}H and ^{17}O solid state NMR spectra, we discuss the mechanism of the local motion as well as the long-range hopping of water molecules.

Experimental

(±)-$[Co(en)_3]Cl_3$ was synthesized according to [7]. The crystalline sample was obtained by recrystallization three times from aqueous solution. Chemical analysis. Found: H, 7.37; C, 19.19; N, 22.56%; calcd. for (±)-$[Co(en)_3]Cl_3$ anhydrate: H, 7.00; C, 20.85; N, 24.32%, and for (±)-$[Co(en)_3]Cl_3H \cdot 1.86H_2O$: H, 7.37; C, 19.01; N, 22.17%. The XRD diffraction pattern was found to be consistent with the reported trigonal unit cell with space group $P\bar{3}c1$ [7, 8]. Single crystals were grown by slow evaporation of aqueous solution at room temperature. Hexagonal prismatic crystals about 30 mm long and 9 mm across were obtained. The dehydrated specimen was prepared by the heating at 393 K under a vacuum of 10^{-3} Torr. The water content in the specimen was adjusted by keeping the dried sample in a moist atmosphere for given times. For the NMR measurements, each specimen was sealed into a glass ampoule under the equilibrium water vapor pressure. The water content was determined within an uncertainty of ±0.1 by comparing the weight of the hydrated specimen to its original dry weight. For the ^{17}O NMR measurements ^{17}O enriched water (10%, ICON Inc. U.S.A.) was absorbed into the completely dried compound.

All NMR measurements were carried out with Bruker Model DSX-200 pulsed spectrometer operating at the Larmor frequency of 200.13 MHz for proton. The temperature of sample was controlled using Bruker BVT-3000 unit within ±1 K by flowing heated N_2 gas. The ^{1}H, ^{2}H, and ^{17}O NMR spectra were measured using the solid echo pulse sequence with an interval of 20 μs between the first and the second pulses. The width of the 90° pulse was 2.2 μs for ^{1}H, 3.0 μs for ^{2}H, and 5.7 μs for ^{17}O. For ^{17}O this width corresponds to the 90° pulse for the central transition ($-1/2 \leftrightarrow 1/2$). A pulse width of 17 μs is necessary to excite all spins in the four energy states. Bulk ^{17}O-enriched water (10 atom%) was used as the external standard for the ^{17}O chemical shift. In order to measure the diffusion coefficient of the zeolitic water molecule, ^{1}H pulsed-field gradient (PFG) NMR measurements were carried out with a conventional pulse sequence with the separation of 20 ms or 120 ms between the 90° and 180° pulses and by changing the strength of the gradient pulse from 0 to 1.10×10^{-4} T m. The strength of the field gradient pulse is calibrated by referring to the diffusion coefficient of 2.14×10^{-9} m^{2}s^{-1} at 298 K in bulk water [11]. The experimental error for the diffusion coefficient was estimated to be within 10%.

Results and Discussion

^{1}H NMR

Figure 1 shows the ^{1}H NMR spectra for the powdered and single crystal specimens with water contents of $n = 3.8$ and 3.6 at 299 K, respectively. The spectrum of the powdered specimen consists of the superposition of a Pake doublet and a Lorentzian

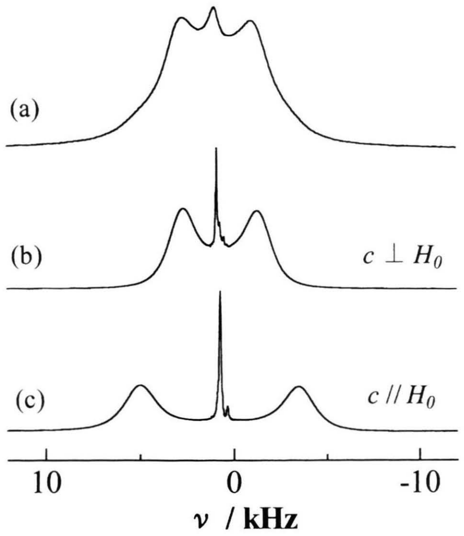

Fig. 1. ^{1}H NMR spectra of (±)-$[Co(en)_3]Cl_3 \cdot nH_2O$ for the powdered sample (a), single crystals with the c-axis perpendicular to (b) and parallel to (c) the applied field. The water content is n = 3.8 for the powdered specimen and ca. 3.6 for the single crystal. The spectra were measured at 299 K.

peak, suggesting the existence of two kinds of water in the compound. The peak-to-peak width of the Pake doublet is 3.7 kHz, which corresponds to an apparent dipolar interaction of 2.5 kHz. The spectrum of the single crystal consists of two distinct peaks; their splitting is 4.0 kHz when the applied static field H_0 is parallel to the crystallographic c-axis and amounts to 8.4 kHz when H_0 is perpendicular to the c-axis. In a two-spin system where the inter-spin vector makes an angle θ with H_0, the dipolar interaction is proportional to $(3\cos^2\theta - 1)/2$ [12]. The fact that the splitting for $c \perp H_0$ is twice that for $c \parallel H_0$ implies that the proton-proton vector in the zeolitic water molecule is in a plane perpendicular to the c-axis.

In addition to the typical Pake doublet a very narrow component appeared at the center of the spectrum, corresponding to the Lorentzian peak observed in the powdered specimen. We consider that such a very narrow line comes from some mobile protons. In order to clarify the behavior of these protons, we conducted pulse field gradient (PFG) NMR experiments and obtained the following results: When the separation between the 90° and 180° pulses is set to be 20 ms, the apparent diffusion coefficient of water along the c-axis is 1.2×10^{-9} m^{2}s^{-1}, whereas the diffusion in the perpendicular direction to the c-axis is 1.0×10^{-9} m^{2}s^{-1}. These values may be compared with the diffusion coefficient of the bulk water [11]. When the separation between the 90° and 180° pulses is longer, i. e., 120 ms, the apparent diffusion coefficients of water in the direction of and the perpendicular to the c-axis are 1.0×10^{-9} m^{2}s^{-1} and 4.5×10^{-10} m^{2}s^{-1}, respectively. This implies that there exist water molecules which are very mobile in the pore along the c-axis, and that the diffusion of these along the pore is very fast but highly hindered in the c-plane.

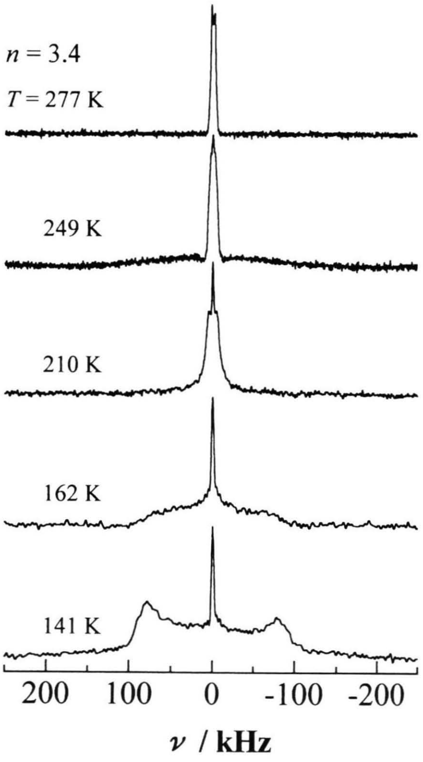

Fig. 2. Temperature dependence of the ^{2}H NMR spectrum of (±)-$[Co(en)_3]Cl_3 \cdot nD_2O$ with water content of n = 3.4.

^{2}H NMR Spectra

Figure 2 shows the temperature dependence of the ^{2}H NMR spectrum for D_2O absorbed into dehydrated (±)-$[Co(en)_3]Cl_3$ at a heavy water content of n = 3.4. At 141 K the spectrum consists of two components; a Pake doublet which can be reproduced by a spectral simulation with QCC = (226 ± 2) kHz and η = 0.08 ± 0.01, and a narrow Gaussian line with a linewidth of 3.5 kHz. D_2O molecules will be distributed among twelve general positions (12g, symmetry 1), two special a positions (2a, symmetry 32) and two special b

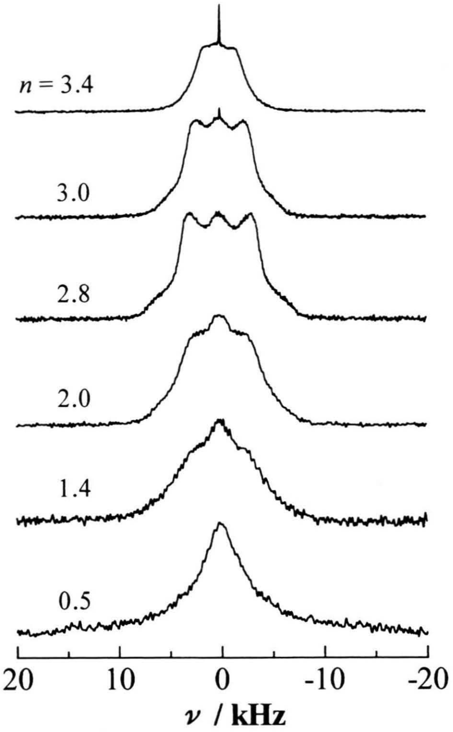

Fig. 3. Water content dependence of the ^2H NMR spectrum of (±)-$[Co(en)_3]Cl_3 \cdot nD_2O$ at 285 K.

positions (2b, symmetry $\bar{3}$) in the crystalline unit cell in the same manner as H_2O [7, 8]. Thus, it is reasonable to assign the broad peak with the large QCC value to D_2O at general positions, and the narrow peak to D_2O at both or either of two special positions. The spectral pattern at 162 K indicates that $\eta = 1$, implying that the 180° flip of the water molecule about the C_2-axis takes place above 141 K and become rapid at 162 K. The bisector angle of D-O-D was evaluated to be 112° [13], being smaller than 130° which has been determined by the crystal structural analysis for water at 12g sites [8]. Between 162 K and 210 K the spectral pattern changes again from $\eta = 1$ to 0, and the amount of the peak splitting decreases drastically to a value corresponding to QCC = (17 ± 1) kHz. This change in the spectrum is attributed to the rapid rotation or reorientation of D_2O molecules about the molecular C_2-axis. When the rate of the rotation is much larger than the QCC value for the static water, the QCC is reduced by a factor of $(3\cos^2\alpha - 1)/2$ in which 2α is the D-O-D angle [14]. Thus the rapid C_2-rotation may results in the reduction of the QCC values to 6.2 kHz. The QCC value, (17 ± 1) kHz, at 210 K is larger than this predicted one, suggesting that the rate of rotation is still too slow for the quadrupole interaction to be completely averaged. On the other hand, the narrow component remains unchanged on heating from 141 K to 210 K, but its intensity decreases on further heating. This change in the spectrum is certainly brought about by the onset of the site exchange of water molecules among the three distinct sites (12g, 2a, and 2b).

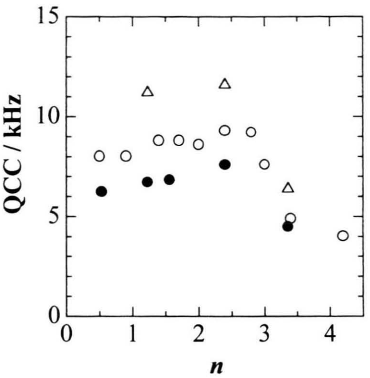

Fig. 4. Water content dependence of the ^2H QCC in (±)-$[Co(en)_3]Cl_3 \cdot nD_2O$ at 277 K (Δ), 285 K (○) and 300 K (●).

Figure 3 shows the dependence of the ^2H NMR spectrum of D_2O on the content of the hydration water n at 285 K. In the samples with $n \geq 3$, the spectrum consists of three components and could be deconvoluted into a very weak and narrow Lorentzian line, a slightly broad Lorentzian line, and a Pake doublet. The fact that a weak and very narrow Lorentzian line appears implies the existence of traces of D_2O molecules with high mobility; such water molecules may be assigned to an adsorbed water on the crystal surface. In the compounds with $n < 3$, except for $n = 0.5$ each spectrum consists of two components, i. e., a slightly broad Lorentzian line and a Pake doublet. In the specimen with $n = 0.5$ another Lorentzian line must be added to reproduce the spectrum, of which the appreciable width may be brought about by the overall rotation of the water molecules. It is noted that the relative intensities of the Lorentzian line and the Pake doublet depend on the water content. However, the Pake doublet with a relatively small QCC value is always the major component with more than 85% of the total intensity of the spectrum, except for the compound with $n = 0.5$. The QCC value elucidated from the Pake doublet lies in the range between (4.0 ± 0.1) and (9.5 ± 0.1) kHz at 285 K, and decreases systematically on heating from 277 to 300 K, as can be seen in Figure 4. The QCC value seems to depend also on the water content. The QCC value at 285 K increases gradually from (8.0 ± 0.1) to (9.5 ± 0.1) kHz as the water content increases from 0.4 to 2.7. On increasing the water content from $n = 2.7$ at 285 K, QCC begins to decrease and reaches 5.0 kHz at $n =$ *ca.* 3.4, and finally ~4.0 kHz for $n > 4$. At 277 and 300 K similar change in QCC was observed. We mentioned above that the rotation of water about the molecular C_2-axis takes place above 210 K; this motion works to average partially the QCC down to 6.2 kHz. The observed QCC for $n < 2.7$ is larger than this predicted value even at 285 K, and so the rate of rotation may be not fast enough to average the quadrupole interaction completely. The steep decrease of QCC with n implies that the rotation of water molecules is suddenly accelerated when the water content n exceeds 2.7. Furthermore, the observed value of QCC is lower than the predicted one for $n = 3$, implying that rapid exchange of D_2O molecules can take place among the crystallographically nonequivalent positions, i. e., 12g, 2a, and 2b, when these water sites are fully occupied.

^{17}O NMR

Figure 5 shows the central transition (−1/2 ↔ 1/2) in the ^{17}O broad line NMR spectrum of hydration water for $n = 3.1$ at 300 K. The spectrum consists of two components: A narrow resonance line near 0 ppm, and a broad line spreading over about 2500 ppm. The former is represented by a Gaussian line with the linewidth of 4.6 kHz, and any finite quadrupole interaction works on it. Hence it may be assigned to water occupying 2a and/or 2b positions in the pore. The latter is represented by a typical powder pattern perturbed by second order quadrupole interaction of QCC = (6.3 ± 0.5) MHz and $\eta = 0.55 \pm 0.02$, and so is assigned to the water occupying the 12g positions in the pore. The value of QCC can be compared with the (6.525 ± 0.015) MHz for water in normal ice, whereas η is smaller than 0.925 ± 0.020 [15]. This is due probably to the rapid 180° flipping of water molecule, which brings about the effective asymmetry parameter η_{eff}. Using the η value in the rigid lattice, the η_{eff} value is given by $|(3 - \eta)\cos 2\beta/(1 + \eta)|$, where β is the angle between the flipping axis and the principal z-axis of the EFG tensor [16]. When $\eta \sim 1$, the 180° flip of water molecule with $\beta = 69°$ results in $\eta_{\text{eff}} \sim 0.55$. It is noted that the two components are observed separately from each other at room temperature, suggesting that the exchange of water between the nonequivalent sites is slower than 6 MHz.

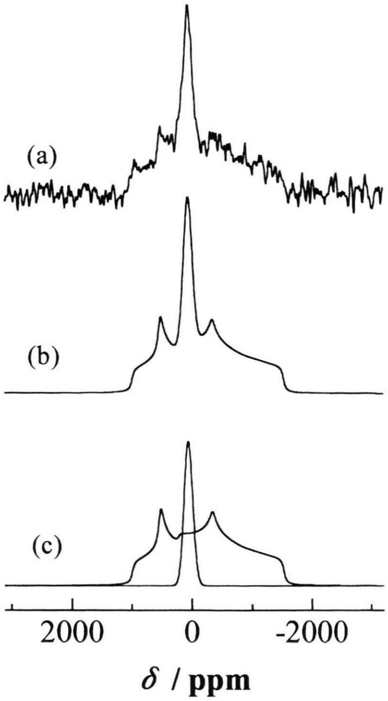

Fig. 5. ^{17}O NMR spectra of (±)-$[Co(en)_3]Cl_3 \cdot nH_2O$ with a water content of $n = 3.1$ at 300 K. Experimental (a), simulated (b) and the individual components of simulated spectra (c).

The Stability and Dynamics of Water Molecule in the Compound

As we mentioned in the above sections, the water molecules occupying 12g and 2a and/or 2b positions are distinguished in the ^2H NMR spectrum at 141 K and ^{17}O NMR spectrum at room temperature. These facts suggest that the rate of the exchange of water among these positions is much smaller than the linewidth in each of the spectra at the specified temperature. Since in general the integrated intensity of individual line component in the NMR spectrum is proportional to the population of water in each site, we can obtain information on the energy relation between these crystallographically nonequivalent positions. First of all, assuming that D_2O molecules are distributed between the special (2a and/or 2b) and the general (12g) positions according to the Boltzmann

Table 1. Potential energy difference between 12g and 2a and 2b positions for hydration water molecules in $[Co(en)_3]Cl_3 \cdot nH_2O$.

n	p_s/p_g	ΔE/kJmol^{-1}	T/K	Method
1.2	0.10	2.7	143	^{2}H NMR
2.4	0.051	3.5	141	^{2}H NMR
3.4	0.050	3.5	141	^{2}H NMR
3.1	0.12	~ 5	300	^{17}O NMR

distribution, the ratio of the relative populations of the water molecules at the special positions s and the general one g, p_s and p_g, is given by

$$\frac{p_s}{p_g} = \exp\left(-\frac{\Delta E}{RT}\right), \quad (1)$$

where ΔE denotes the potential energy difference between these positions. Analysis of the ^{2}H NMR spectrum led to the relative population and the energy difference between the two sites, ΔE, as listed in Table 1. On the other hand, the ^{17}O NMR spectrum was analyzed to evaluate the population at 300 K by taking account of both effects of the pulse length and the ratio of the peak intensities between all and central transitions for 5/2 nuclei. The 90° pulse for the central transition reduces the intensity of the narrow signal to be 1/2, whereas the resonance peak from the central transition contributes 26% of all transition [17]. Therefore, the p_s/p_g is reduced by a factor of 0.5/0.26 (~ 2). The deduced ΔE from the ^{17}O NMR spectrum may contain a large uncertainty because of the extremely broad line shape and many corrections on the quantitative analysis. Thus, ΔE from the ^{17}O NMR spectrum is somewhat larger than that from the ^{2}H NMR spectrum, but it seems to be reasonable in the order (see in Table 1). The values of ΔE in Table 1 suggest that the 12g general position is much preferable for the water molecule to the 2a and/or 2b special positions. The amount of the potential energy difference happens to be nearly the same as 3.7 kJ mol^{-1} except for ΔE evaluated from the ^{17}O NMR spectrum, which was deduced from the dielectric relaxation measurements above 183 K and assigned to the energy difference between different hydrogen bond configurations of water molecules in the pore [10].

The present compound can accommodate up to 3 water molecules at 12g positions, 0.5 at 2a and 0.5 at 2b positions per formula unit. Regarding this point, the above NMR experiments revealed that the hydration water molecules are distributed among at least two energetically different water sites in the pore. Here we recognized that the general 12g positions are energetically more favorable for a water molecule to be accommodated than either of the special 2a or 2b positions; it is now desirable to specify which position, i. e., a or b, is more favorable. In the specimen with $n = 3.4$, the above energy consideration indicates that 3.2 water molecules occupy more preferable sites and 0.2 molecules occupy unfavorable sites; the former exceeds 3, the maximum number of available 12g sites. Therefore, we must consider that either the 2a or the 2b position can be populated by water with a similar probability to that at the 12g positions, and that the remaining one is less populated. In the ^{2}H NMR spectra, a narrow component was observed separately from a very broad component and attributed to the water occupying the 2b position. Thus it is reasonable to consider that water at the 2a position contributes to the broad component in a similar manner to that at the 12g position.

D_2O molecules at the 2a and 12g positions undergo rotation about the molecular C_2-axis and so have a motionally averaged small but finite QCC, whereas those at 2b positions give nearly zero QCC when they undergo a rapid rotation because of the high site symmetry. When the sample temperature is above 210 K, a rapid exchange of D_2O between the b position and a or g position occurs, and this causes a decrease of the apparent QCC values. This mechanism can explain the temperature and the water content dependence of the ^{2}H spectrum.

We now discuss the possibility of single proton transfer or exchange between water molecules instead of the exchange of water molecules. Water molecules at the 12g, 2a and 2b positions in the pore are linked by hydrogen bonds [7, 8, 10]. Hence there may be a proton transfer between water molecules located at these positions through the hydrogen-bond network. In our present study the ^{1}H PFG NMR experiments revealed that there occurs a very fast diffusion of "protons". ^{2}H NMR found that exchange of ^{2}H between non-equivalent water sites takes place above 210 K, whereas ^{17}O NMR indicated that no exchange of ^{17}O takes place at the same temperature. These findings may be accounted for by the transfer of single protons instead of molecules; however, we do not have any clue to distinguish these two mechanisms at the present stage.

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