Temperature Dependence of ^2H Quadrupole Coupling Constants in ^2H_2O and Ionic Motions in Crystalline $[M(^2H_2O)_6][SnCl_6]$ (M: Mg, Ca), Studied by ^2H NMR and Neutron Powder Diffraction *

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The temperature dependence of ^2H NMR spectra was measured at 130–430 K on $[M(D_2O)_6][SnCl_6]$ (M: Mg, Ca) (rhombohedral, space group: $R\bar{3}$), and neutron powder diffraction on the Mg salt was performed at room temperature. Based on the accurate orientation of D_2O molecules in an octahedral cation, spectra with a large asymmetry parameter η, observed around 200 K, were explained by a model of 180° flip of water molecules. Another motional narrowing observed above room temperature was assigned to a cationic overall reorientation about the C_3-axis.

Key words: ^2H NMR; Neutron Diffraction; Molecular Motion; Quadrupole Coupling Constant; Spectrum Lineshape.

1. Introduction

^{35}Cl NQR studies [1–4] on $[M^{II}(H_2O)_6][M^{IV}Cl_6]$ (M^{II}: Mg, Ca, Zn, Cu, Co, Ni; M^{IV}: Pt, Sn), consisting of octahedral cations and anions with an isomorphous rhombohedral structure (space group $R\bar{3}$), have been investigated to reveal inter-molecular paramagnetic interactions and molecular motion in both ions. In such ^{35}Cl NQR relaxation measurements [5–10] several kinds of motion in the cations and anions were found to be excited above ca. 200 K. Onset of anionic overall reorientation was found above room temperature from measurement of the ^{35}Cl spin-lattice relaxation time (T_{1Q}) exhibiting a rapid exponential decrease at high temperatures. On the other hand, motions in cations were studied by measurement of the ^1H NMR linewidth and relaxation times (T_{1H}, $T_{1\varrho}$) on diamagnetic complexes of M^{II} = Mg and Ca [11, 12]. In these studies, the minima of T_{1H} observed around 200 K were attributed to a 180° flip motion of H_2O molecules, and the T_{1H}-decrease observed above room temperature in $[M(H_2O)_6][SnCl_6]$ (M: Mg, Ca) and $T_{1\varrho}$ minima were interpreted as C_3 or C_4 reorientation and overall reorientation of cations.

^2HNMR spectra give information about the motional modes of molecules containing hydrogen. In this study we have measured the temperature dependence of the ^2H NMR spectra of $[M(D_2O)_6][SnCl_6]$ (M: Mg, Ca) and the neutron powder diffraction of the Mg complex, and have determined the modes of cationic motion, based on the crystal structure data.

2. Experimental

$[M(D_2O)_6][SnCl_6]$ (M: Mg, Ca) were prepared by mixing equivalent amounts of $SnCl_4$ and MCl_2, both dissolved in 2 M HCl. These solutions were warmed on a hot-plate until crystallization starts, and crystals were obtained by cooling slowly down to room temperature. The crude crystals were recrystallized form 0.2 M HCl by gradual evaporation of the solvent for ca. 1 month in a desiccator over P_2O_5. The deuteration of these complexes was carried out by successive crystallization three times from D_2O. The prepared crystals were identified by X-ray powder diffraction at room temperature and by comparing the obtained data with the reported ones.

^2H NMR spectra were measured by a Bruker MSL300 spectrometer operated at 46.073 MHz using the quadrupole echo method. Pulse widths of a $\pi/2$-pulse of 3.0 μs and 10 μs were employed for the measurements on a 5 mm diameter sample tube at 130–250 K and a 10 mm tube above 250 K, respectively.

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The time-of-flight neutron diffraction experiment on $[Mg(D_2O)_6]$ $[SnCl_6]$ was carried out at room temperature using the powder diffractometer VEGA [13] at the KENS pulsed neutron source. A TOF range of 0.5–4.3 ms, corresponding to a d-spacing range of 0.5–4.3 Å, was covered in the measurement. The resolution of the data ($\Delta d/d$) was 0.2%.

The measurement of X-ray powder diffraction was performed at 305 K for both complexes, using a Philips X'Pert PW 3040/00 diffractometer with Cu Kα radiation.

3. Results and Discussion

3.1 Thermal and Powder X-ray Measurement

We performed differential scanning calorimetric measurements on the Mg and Ca salts at 170–435 and 170–380 K, respectively. We scanned several times with a rate of 2 K min^{-1}, but no anomaly due to phase transitions was observed.

X-ray powder diffraction of the Mg and Ca salts was carried out to identify the prepared crystals by comparing the results with the reported data [2, 14] and to obtain the lattice parameters of both complexes at the same temperature. The lattice constants determined at 305 K are shown in Table 1 together with the reported values.

3.2 Neutron Powder Diffraction

The Rietveld refinement [15], using the program RIETAN-96T [16], was carried out to determine the orientation of the D_2O molecules in $[Mg(D_2O)_6]$ $[SnCl_6]$ [17]. The lattice parameters determined by the preliminal X-ray powder diffraction of $[Mg(D_2O)_6]$ $[SnCl_6]$ and the atomic coordinates calculated on the basis of the reported structure of $[Ca(H_2O)_6]$ $[SnCl_6]$ [2] were used as starting model for the refinement of the structure. In the initial stage of the refinement, the bond length and angle of the D_2O molecule was constrained to be within (1.0 ± 0.2) Å and $(107.0 \pm 2.5)°$, respectively. The next stage of the refinement was performed without any constraint on the structural parameters. In the late stages, anisotropic displacement parameters were introduced except for the Mg and Sn atoms. Rapid convergence was obtained to give an excellently small S value ($=R_{wp}/R_e$) of 0.83. For a detailed discussion on the structure refinement see [17]. The final lattice parameters are $a = 10.6829(2)$ and $c = 10.9566(2)$ Å. The final results of the profile fitting are illustrated in Figure 1.

Table 1. Lattice parameters in the hexagonal unit cell for $[M(D_2O)_6]$ $[SnCl_6]$ (M: Mg, Ca) determined at 305 K by X-ray powder diffraction with Cu Kα radiation together with the reported data. The space group is $R\bar{3}$.

Compound	$[Mg(H_2O)_6]$ $[SnCl_6]$		$[Ca(H_2O)_6]$ $[SnCl_6]$	
	Present work	[14]	Present work	[2]
a/Å	10.652	10.79	10.737	10.750
c/Å	10.903	10.97	11.485	11.474

The structure of $[Mg(D_2O)_6]$ $[SnCl_6]$ at room temperature is shown in Figure 2. The D_2O molecules are orientationally ordered. The D–O bond lengths of 0.91(1) and 0.94(1) Å, and the D–O–D bond angle of 107(1)°, which were calculated from the refined fractional coordinates, are both reasonable compared with the literature values. Some geometrical values, which are essential for the analysis of ^2H NMR spectra, were also calculated (see below).

3.3 ^2H NMR Spectra observed below 200 K

^2H NMR spectra of $[Mg(D_2O)_6]$ $[SnCl_6]$ observed at 130, 167, and 200 K are shown in Figure 3. A clear spectrum narrowing, assignable to some molecular motion, was observed in this temperature range. The spectrum observed at 130 K resulted in a quadrupole coupling constant (qcc) of $e^2Qq = 247 \pm 2$ kHz and an asymmetry parameter of the electric field gradient (efg) $\eta = 0.118 \pm 0.005$. These data are comparable to $e^2Qq =$ 213.2 kHz and $\eta = 0.100$ reported for deuterated ice at 77 K [18]. The nearly equal qcc values obtained in the present complex and ice indicate that the D_2O molecules in $[Mg(D_2O)_6]$ $[SnCl_6]$ are almost rigid at 130 K. The observed qcc value, smaller than that in ice, can be attributed to the difference in the H-bond between O–D · · · Cl in the present salt and O–D · · · O in ice.

With increasing temperature from 130 K, a marked narrowing of the spectrum was observed, and a typical spectrum with a large η was obtained at 200 K. By fitting the simulated spectra to the observed one, we determined qcc $= 136 \pm 1$ kHz and $\eta = 0.860 \pm 0.005$ at 200 K. The remarkable increase of η is attributable to the onset of a two-site jump of the O–D bond axis in all D_2O molecules of the cation upon heating. Here, we take coordinate systems representing the efg prin-

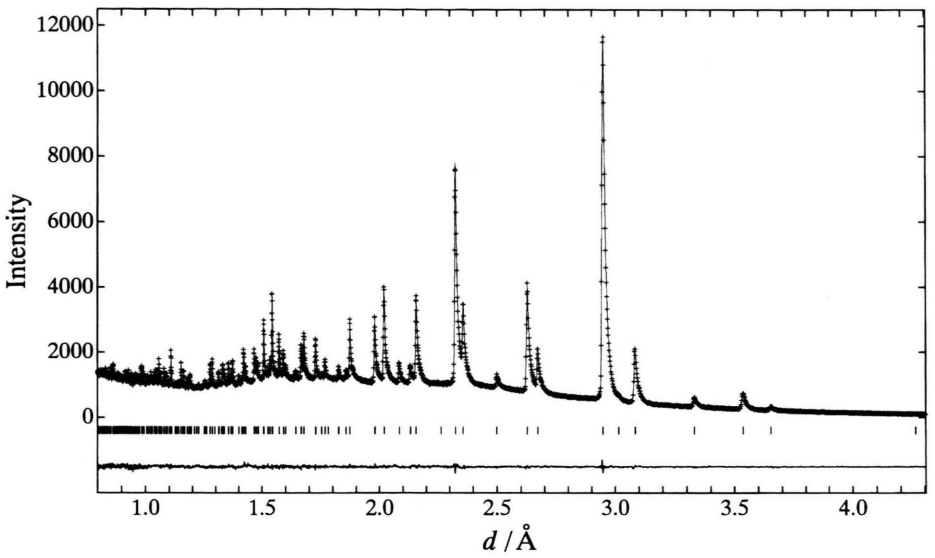

Fig. 1. Neutron powder diffraction pattern of $[Mg(D_2O)_6]$ $[SnCl_6]$ crystal at room temperature. Plus marks denote the observed intensities, and the solid line is calculated from the final structure determined by the Rietveld refinement. The calculated peak positions are given by the tick marks, and differences between the observed and calculated intensities are shown at the bottom.

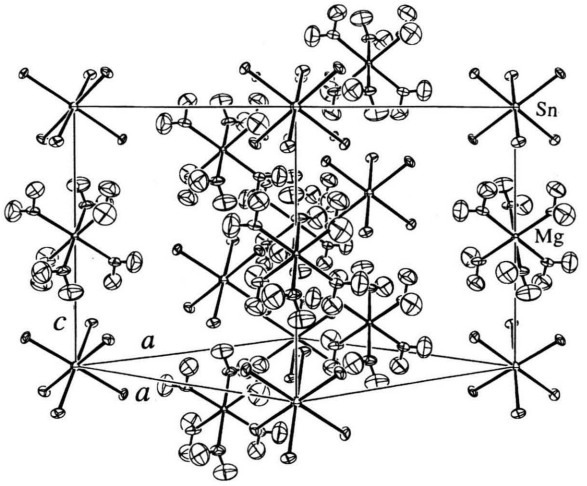

Fig. 2. A perspective view of the hexagonal unit cell of $[Mg(D_2O)_6]$ $[SnCl_6]$ determined by neutron powder diffraction at room temperature.

cipal axes in the rigid state and in the fast jumping state as (x, y, z) and (x', y', z'), respectively. We assume the direction of the principal axis z along the O–D bond in the rigid state and take 2θ as the jump angle of the O–D bond. If the jump of the O–D bond is rapid enough, the new principal axis z' is along the bisector of the two O–D orientations, and the axis y', which can be taken parallel to the y axis, is perpendicular to the jumping plane, as shown in Figure 4. The relationship between the quadrupole parameters in the rigid and jumping states are given by [19]

$$e^2Qq_{x'} = \frac{e^2Qq_s}{2}[(\eta_s - 3)\cos^2\theta + 2], \tag{1}$$

$$e^2Qq_{y'} = -\frac{e^2Qq_s}{2}(\eta_s + 1), \tag{2}$$

$$e^2Qq_{z'} = \frac{e^2Qq_s}{2}[(\eta_s - 3)\sin^2\theta + 2], \tag{3}$$

where $e^2Qq_{x'}$, $e^2Qq_{y'}$, and $e^2Qq_{z'}$ are three principal values of qcc in the new coordinate system, and e^2Qq_s and η_s denote the qcc and η values in the rigid state, respectively. By substituting the values of e^2Qq_s and η_s observed at 130 K into (2), we obtained $|e^2Qq_{y'}| =$ 138.1 kHz, in good agreement with 136 kHz observed at 200 K. This result implies that the y'-axis parallel to the y-axis became the main axis of the efg tensor in the new coordinate system. Since the new asymmetry parameter $\eta_m = 0.860$ observed at 200 K is expressed as

$$\eta_m = \frac{|q_{x'} - q_{z'}|}{q_{y'}}, \tag{4}$$

we can determine the jump angle $2\theta = 109°$ (or 71°). This result suggests that this two-site jump is an 180°-flip of D_2O molecules because this angle is very close

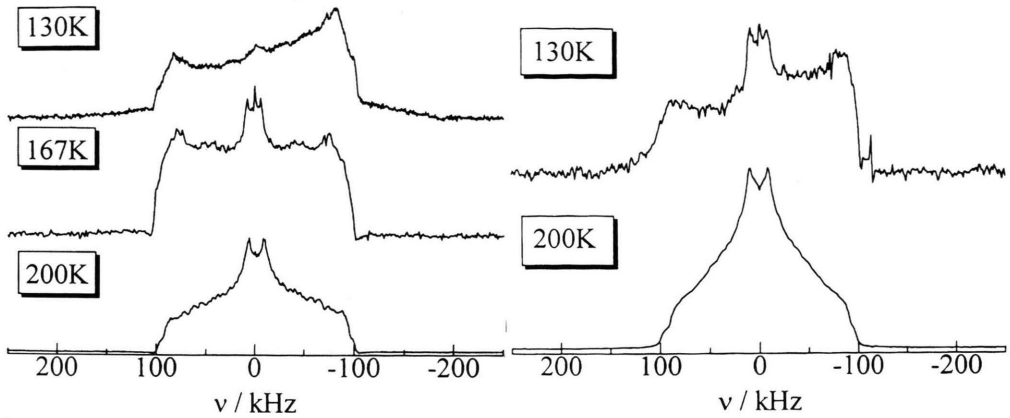

Fig. 3. ^2H NMR spectra of $[M(D_2O)_6]$ $[SnCl_6]$ where M = Mg (left), Ca (right) observed between 130 and 200 K.

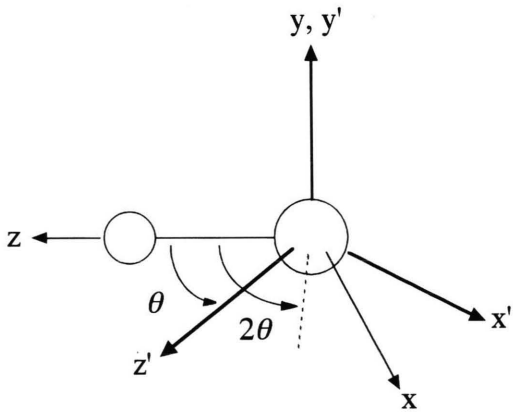

Fig. 4. Coordinate systems for the model of the two-side jump of an O–D bond by the angle of 2θ.

to the bond angle D–O–D as obtained to be 107° in the present neutron diffraction study at room temperature. The onset of this motion is also supported by the structure at room temperature, where no disordered position of deuterium was observed. The assignment to an 180°-flip of water molecules is in good agreement with the analysis of ^{35}Cl NQR and ^1H NMR relaxation studies on Mg and Ca salts [8, 11, 12]. The other possible angle of 71° is unacceptable because a jump over this angle results in disordered O–D orientations, inconsistent with the neutron diffraction result.

Quite a similar temperature dependency of ^2H spectra was observed for the Ca salt, as shown in Figure 3. A qcc of 119.6 ± 0.5 kHz and $\eta = 0.804 \pm 0.005$ were obtained at 200 K. From the difference in the spectra at 130 K observed in the Mg and Ca salts, the 180°-flip motion of D_2O takes more easily place in the Ca salt than in the Mg salt. This difference is attributed to the Mg–O bond which is stronger than the Ca–O bond because of the difference in the ion sizes.

3.4 ^2H NMR Spectra observed above Room Temperature

The observed lineshapes of both salts were essentially the same up to ca. 330 and ca. 250 K for the Mg and Ca salt, respectively. Of course we observed a gradual narrowing of the spectrum for both complexes upon heating, attributable to the increase of the thermal vibration amplitude. With further heating above these temperatures, the doublet observed at the centre of the spectra gradually disappeared and a broad single peak appeared at the centre, suggesting the onset of a new motion. With further increase of the temperature, we observed a clear spectrum change above 360 and 280 K in Mg and Ca salts, respectively, as shown in Figure 5. Since these temperatures agree with those of the NMR T_{1H} decrease observed in fully protonated complexes [11, 12], this spectrum change can be correlated with the motional processes detected in ^1H NMR. Our observation that almost temperature-independent lineshapes were obtained for the Mg and Ca salts around 435 and 385 K, respectively, implies that this motional process occurs fast enough compared with the linewidth observed around these temperatures. These spectra, analogous with each other, give almost vanishing values of η and qcc of 41.1 (435 K) and 35.2 ± 0.5 kHz (380 K) for Mg and Ca salts, respectively.

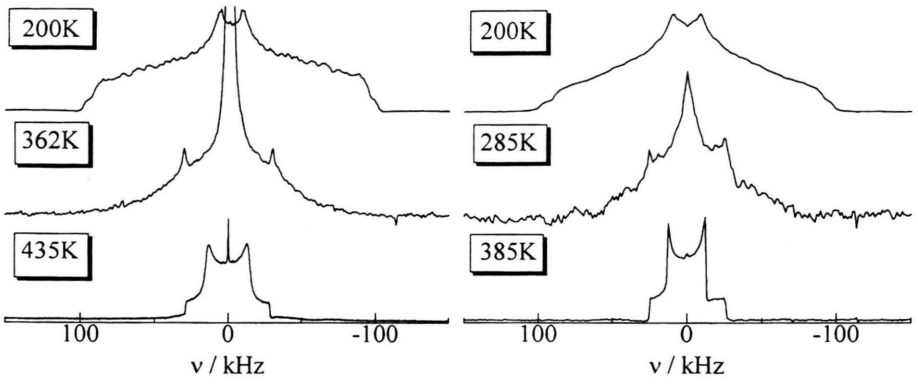

Fig. 5. ^2H NMR spectra of $[M(D_2O)_6]$ $[SnCl_6]$ where M = Mg (left), Ca (right) observed above 200 K.

We tried to analyse the observed spectra by applying several kinds of cationic motional modes expected in the analysis of ^1H NMR T_{1H} and $T1\varrho$ [7, 11, 12]:

(1) Isotropic rotation of D_2O about its C_2-axis (The C_2-axis bisects the D–O–D angle).
(2) Overall reorientation of cations about the C_3 or C_4-axes (These axes are shown in Figure 6 b),
(3) Isotropic rotation of the cations.

We can easily exclude the possibility of model 3 because this motion results in a spherically symmetric efg around the D nuclei, whereas a finite value of qcc was observed at 435 K.

Model 1 is also unacceptable because, if this motion takes place quite frequently, the new principal axis with the largest efg value is along the C_2-axis. From the quadrupole parameters determined in the Mg salt at around 200 K we obtain a qcc of 9.67 kHz along the C_2-axis (the new principal axis). This value is much smaller than the 41.1 kHz observed in the Mg salt at 435 K.

As for the discussion of model 2, we need information on the orientation of the D_2O molecules in an octahedral cation. From the present neutron diffraction study we found that the six O-atoms sit on the corners of a regular octahedron, and that the position of the D-atoms of every D_2O can be found in the following way: Starting from the fictive situation that every two D-atoms sit symmetrically outside the octahedron in a plane through four O-atoms, one turns this plane by ca. 6° about the corresponding C_4-axis (cf. Figure 6 a). Then one tilts this plane about the O-atom by 24° with respect to the C_4-axis (cf. Figure 6 b).

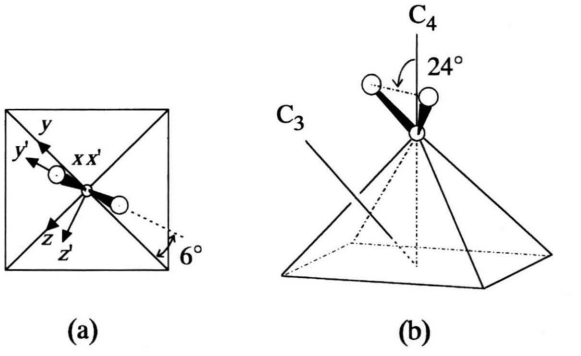

Fig. 6. The orientation of D_2O molecules on a cationic octahedron determined by the neutron powder diffraction at room temperature.

The atomic arrangement in a cation, projected along the C_3- and C_4-axis, is shown in Figure 7. For the rotation about the C_3-axis all D_2O molecules in a cation are equivalent, whereas the rotation about the C_4-axis brings about three kinds of nonequivalent D_2O molecules, i.e., the pair of D_2O molecules located along the C_4-axis and the two pairs of D_2O molecules in the plane perpendicular to the C_4-axis. Applying simple coordinate transformations by Eulerian angles, using the D_2O orientation angles given in Fig. 6, we evaluated the three kinds of qcc values, averaged by the rapid C_4-rotational motion of the cation, starting from the quadrupole parameters in D_2O molecules performing fast 180°-flip about the C_2-axis at 200 K [20]. The qcc values, averaged by the C_4-rotation, were calculated to be 11.07, 103.9, and 123.8 kHz for

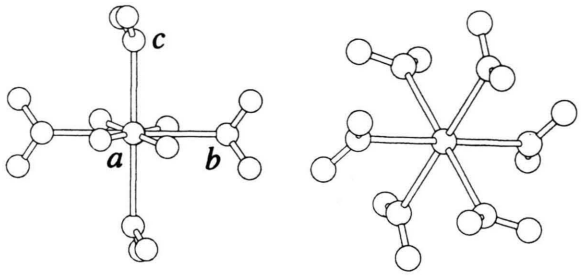

Fig. 7. Structure of a cation projected along the octahedral C_4- (left) and C_3-axes (right) determined by neutron diffraction.

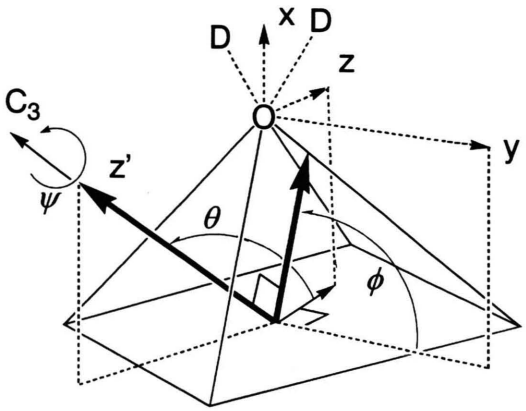

Fig. 8. Coordinate transformation of Eulerian angles (ϕ, θ) for the C_3-rotation of the octahedral $[Mg(D_2O)_6]^{2+}$ ion from (x, y, z) to (x', y', z') system.

the D_2O molecules *a*, *b*, and *c*, respectively, named in Figure 7. Since this result conflicts with the observed spectrum at 430 K consisting of a single qcc value of 41 kHz, the C_4-axis rotation model is unacceptable.

For the C_3-rotation we calculated the motionally averaged qcc values by applying the transformation of Eulerian angles (ϕ, θ, ψ) as shown in Fig. 8, where the angle ψ takes three different values at the rotation. In the rapid rotation limit, ψ is averaged and the relations between the quadrupolar parameters before and after the onset of the rotation are given by [20]

$$q_{z'} = (q_z/2)\,[\eta\{2\cos^2\phi - 1) - 3\}\,\sin^2\theta + 2], \quad (5)$$

$$q_{x'} = q_{y'} = -(q_z/4)\,[\eta\{2\cos^2\phi - 1) - 3\}\,\sin^2\theta + 2], \quad (6)$$

where q_z and η are values in the limit of slow motion, $q_{z'}$, $q_{x'}$ and $q_{y'}$ are principal efg tensor values averaged by this motion. We obtained a motionally averaged qcc value of 46.9 kHz for the model of the rapid reorientations about the cationic C_3-axis parallel to the crystallographic unique C_3-axis by using Eulerian angles ($\phi = 40.0°$, $\theta = 76.3°$) calculated from the crystal data of D_2O orientation given above, together with the eQq_z and η data of 180°-flipping D_2O observed at 200 K. This value is comparable to that of the Mg salt at 430 K. The difference of the observed and calculated values is attributable to the thermal vibration of the D_2O molecules, which should increase upon heating from 200 to 430 K. The marked thermal factors of D atoms obtained in the present neutron diffraction study at room temperature supports the decrease of the qcc value at high temperatures.

Quite an analogous analysis is applicable to the Ca salt. The spectrum change due to the onsets of 180°-flip and the cationic C_3-reorientation take place in the range 130–200 K and of room temperature, respectively. These temperature ranges, lower than those for the Mg salt, are attributable to the larger molar volume of the Ca salt which enables the cations to move more easily.

4. Conclusion

Temperature dependences of ^{2}H NMR spectra in $[M(D_2O)_6]\,[SnCl_6]$ (M : Mg, Ca) were measured in a range of 130–430 K. Also neutron powder diffraction measurement was carried out for the Mg salt at room temperature to determine the orientation of the D_2O molecules. Marked ^{2}H spectrum narrowings were observed at 130–200 K and above room temperature. The narrowed spectra with large η values observed at low temperatures were well explained by the model of 180°-flip of D_2O about its C_2-axis, in agreement with the reported results of ^{35}Cl NQR and ^{1}H NMR studies. The high temperature spectra with almost vanishing η values were compared with several possible models of cation motion calculated by use of D_2O orientations determined by neutron diffraction. Among them, the model of cationic reorientation about the C_3-axis can be shown to explain the spectrum of the Mg salt observed at 430 K.

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