Chlorine Nuclear Spin-Spin Relaxation Mechanism in Mg(H₂O)₆SnCl₆ as Studied by NQR and NMR Techniques*  
Keizo Horiuchi  
Department of Chemistry, Division of General Education, University of the Ryukyus,  
Nishihara, Okinawa 903-01, Japan  
Daiyu Nakamura*  
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464-01, Japan  

The ³⁵Cl NQR spin-lattice relaxation time \( T_{1Q} \), spin-spin-relaxation time \( T_{2Q} \), and \(^1\)H NMR 
spin-lattice relaxation time in the rotating frame \( T_{1R} \) in Mg(H₂O)₆SnCl₆ were measured as functions 
of temperature. Above room temperature \( T_{2Q} \) increased rapidly with increasing temperature, which 
can be explained by fluctuations of the local magnetic field at the chlorine nuclei due to cationic 
motions. From the \( T_{1R} \) experiments, these motions are found to be attributable to uniaxial and 
overall reorientations of [Mg(H₂O)₆]²⁺ ions with activation energies of 95 and 116 kJ mol⁻¹, 
respectively. Above ca. 350 K, \( T_{1Q} \) decreased rapidly with increasing temperature, which 
indicates a reorientational motion of [SnCl₆]²⁻ ions with an activation energy of 115 kJ mol⁻¹.  

**Key words:** Complex compounds, Molecular dynamics, Nuclear relaxation, Nuclear quadrupole 
resonance, Nuclear magnetic resonance.

**Introduction**

Previously, we studied the temperature variation of the \( ^{35}\)Cl NQR frequencies in M(II)(H₂O)₆SnCl₆ (M(II) = Ca, Mg, Mn, Co, Ni) and M(II)(D₂O)₆SnCl₆ (M(II) = Ca, Co, Ni) crystals [1]. The crystal structure of the 
Ni and the Ca salts at room temperature were determined by X-ray diffraction measurements [2, 3]. The 
crystals were found to be trigonal with a space group R3 and the slightly distorted CsCl type structure 
consisting of an [M(II)(H₂O)₆]²⁺ octahedron and an [SnCl₆]²⁻ octahedron. The other compounds are iso-
morphous with the two salts [1]. All these complexes yielded a single \(^{35}\)Cl NQR signal and showed unusual 
temperature dependences with a positive temperature coefficient [1], which were assigned to weak Cl • • • H–O 
type hydrogen bonds [1]. In these compounds three hydrogen atoms are close to a chlorine atom. These 
Cl • • • O bond distances are 3.344, 3.352, and 3.550 Å in Ca(H₂O)₆SnCl₆ [3].

Recently, we have studied the dynamics of molecular ions in pyridinium tetrachloroaurate(III) and pyri-
dinium hexachlorometallates(IV) by chlorine NQR and proton NMR experiments [4–7]. In these 
complexes, an unusual relaxation mechanism was found on measuring the \(^{35}\)Cl NQR spin-lattice relaxation 
time \( T_{1Q} \) and the \(^1\)H NMR spin-lattice relaxation time \( T_{1R} \). That is, it was shown that the relaxation mecha-
nisms of the chlorine and hydrogen nuclei are fluctuations of the electric field gradient (EFG) due to cationic 
motions and fluctuations of the local magnetic field due to anionic motions, respectively.

In the present work, the \(^{35}\)Cl NQR \( T_{1Q} \) and spin-spin relaxation time \( T_{2Q} \), and the \(^1\)H NMR spin-latt-
ice relaxation time in the rotating frame \( T_{1R} \) were measured as functions of temperature. By these mea-
surements, we can investigate whether the fluctuation (modulation) of inter-nuclear interactions due to 
cationic motions affects the chlorine nuclear relaxation mechanism in Mg(H₂O)₆SnCl₆.

**Experimental**

The sample was synthesized in the same way as described in [1]. For the NQR measurements, the 
polycrystalline sample was sealed in a glass tube and
annealed at ca. 410 K for 24 hours to strengthen the intensity of the NQR signal. For the NMR measurements the sample was powdered and dried in a desiccator with silica gel for one day before being sealed in a sample tube.

$T_{1Q}$ and $T_{2Q}$ were measured by means of a pulsed NQR spectrometer [8]. The temperature of the specimen was controlled within ±0.5 K, and determined with an accuracy of ±1 K. $T_{1Q}$ was determined by a $180^\circ-\tau-90^\circ-\tau_e-180^\circ$ pulse sequence, in which $\tau_e$ was fixed throughout a measurement at 200–400 μs and $T_{2Q}$ by a $90^\circ-\tau-180^\circ$ pulse sequence.

The measurements of $T_{1e}$ were made by employing a standard spin-locking technique [9]. The Larmor frequency was 32 MHz and the spin-locking field 6.8 G. The sample temperature was estimated to be accurate within ±1 K.

Results

The obtained $^{35}\text{Cl}$ NQR $T_{1Q}$ and $T_{2Q}$ in Mg(H$_2$O)$_6$SnCl$_6$ are shown in Figure 1. The most interesting feature is the temperature variation of $T_{2Q}$ above room temperature. $T_{2Q}$ below 167 K was almost constant (ca. 450 μs). Above 167 K, $T_{2Q}$ increased very slowly on heating. However, between 250 and 345 K $T_{2Q}$ showed a nearly constant value of ca. 580 μs. When the temperature increased further, $T_{2Q}$ increased rapidly and then exhibited a sharp maximum (1.29 ms) around 390 K. Between 352 and 366 K, log $T_{2Q}$ depended linearly on $T^{-1}$. With further increasing temperature $T_{2Q}$ decreased steeply. The temperature dependence of $T_{2Q}$ above ca. 330 K is shown in detail in an insert of Figure 1.

The temperature variation of $T_{1Q}$ is divided roughly into two regions. Above ca. 350 K $T_{1Q}$ decreases very rapidly with increasing temperature and log $T_{1Q}$ vs. $T^{-1}$ plots are almost linear between ca. 370 and 420 K. Below ca. 350 K $T_{1Q}$ increases gradually with decreasing temperature.

The $^1\text{H}$ NMR free induction decay (FID) signal in Mg(H$_2$O)$_6$SnCl$_6$ at room temperature can be interpreted in terms of a typical dipolar interacting two-proton system. With increasing temperature the FID shape changed gradually, and above ca. 360 K the FID signal decayed monotonously. Figure 2 shows the temperature dependence of the $^1\text{H}$ NMR $T_{1e}$ between 295 and 495 K. The log $T_{1e}$ vs. $T^{-1}$ curve yields a broad and unsymmetrical minimum around 380 K.

$T_{1e} \approx$ 120 μs between 370 and 420 K. The temperature dependence of $T_{1e}$ at the high temperature side of the minimum is slightly steeper than that at the low temperature side.

Discussion

$^1\text{H}$ NMR Spin-Lattice Relaxation Time in the Rotating Frame $T_{1e}$

In general, $T_{1e}$ is expressed as

$$T_{1e}^{-1} = \sum_i C_i \left( \frac{3}{2} \frac{\tau_{ci}}{1 + 4 \omega_0^2 \tau_{ci}^2} + \frac{5}{2} \frac{\tau_{ci}}{1 + \omega_0^2 \tau_{ci}^2} \right),$$

(1)

where $\omega_0$ is the angular resonance frequency of the nucleus and $\omega_1 = \gamma H_1$, $\gamma$ is the nuclear gyromagnetic ratio and $H_1$ is a spin locking field [10]. $C_i$ is the $i$-th motional constant, which is related to the second mo-
ments reduction $\Delta M_{2i}$ caused by the $i$-th motional mode [11]:

$$C_i = (2/3) \gamma^2 \Delta M_{2i}. \tag{2}$$

According to the measurements of the $^1$H NMR second moments $M_2$ [12], it decreases from 23.6 $G^2$ at ca. 330 K to 1.8 $G^2$ at 412 K. This second moments reduction can be related to the observed $T_{1e}$ minimum. The temperature variation of the shape of the FID signal is considered to result from an averaging of the dipolar interaction between a pair of protons in a water molecule. Moreover, from the fact that $M_2$ decreases to a very small value we can assume that a Brownian motion of the proton pair is activated. The motional constant for this mode is given by

$$C = \frac{2}{5} \frac{\gamma^4 h^2}{r^6} I(I+1), \tag{3}$$

where $r$ is the inter-nuclear distance and $I$ the nuclear spin quantum number [13]. We assume that the distance of two protons is 1.6 Å, which is the normal value in a water molecule and also the value reported for Ca(H$_2$O)$_6$SnCl$_6$ [3]. With this value, $\Delta M_2$ is calculated to be 21.3 $G^2$ from (2) and (3). This value agrees quite well with the observed value of $22 \pm 3 G^2$.

By use of the observed $\Delta M_2$ value, we can calculate the minimum value of $T_{1e}$ from (1). The value of 22 $G^2$ leads to $T_{1e, \text{min}} = 47 \mu s$, which does not agree with the measured value of ca. 100 $\mu s$. Moreover, judging from the unsymmetrical minimum of the $T_{1e}$ curve it is very hard to interpret this result by a single motional mode. Hence we tentatively assume that two motional modes are activated above room temperature. Since the term containing $\omega_2$ is dominant in (1) around the temperature at which the $T_{1e}$ minimum is observed, we have calculated the least squares fit of the equation

$$T_{1e}^{-1} = a_1 \frac{\tau_{01} \exp(E_{a1}/RT)}{1 + 4 \omega_1^2 \tau_{01} \exp(E_{a1}/RT)} + a_2 \frac{\tau_{02} \exp(E_{a2}/RT)}{1 + 4 \omega_2^2 \tau_{02} \exp(E_{a2}/RT)}, \tag{4}$$

where $a_i(=\gamma^2 \Delta M_{2i})$, $\tau_{0i}$, and $E_{ai}$ ($i = 1, 2$) are fitting parameters and $\omega_1 = 2 \pi \times 29 \text{ kHz}$. The resulting best fitted curve is depicted in Fig. 2, and the obtained numerical values are listed in Table 1. The sum of $(\Delta M_2)_{\text{fit}}$ obtained from this fitting calculation was $15.1 \pm 4 \text{ G}^2$, which agrees with the observed $\Delta M_2$ value of $22 \pm 3 \text{ G}^2$ within the experimental errors. From this result we conclude that two motional modes of cations are activated above room temperature.

The same features were also reported for Ca(H$_2$O)$_6$SnCl$_6$ [14], in which the motions with a low and a high activation energy were identified as a reorientation about the $C_3$ or $C_4$ axes and an isotropic tumbling motion of the entire cation, respectively. We also adopt this identification for the present compound. The activation energy of the uniaxial motion derived from $T_1$ measurements was $83 \pm 5 \text{ kJ mol}^{-1}$, which agrees well with our result of $95 \pm 10 \text{ kJ mol}^{-1}$.

The activation energies observed for the Ca complex were 38 and 48 kJ mol$^{-1}$ for the uniaxial and the overall reorientation, respectively [14]. These values are only 40% of those of the present complex. Since these two compounds are isomorphous, such energy differences seem to be too large. However these energy
Table 1. Motional parameters of [Mg(H₂O)₆]²⁺ ions and [SnCl₆]²⁻ ions in Mg(H₂O)₆SnCl₆. These values were determined by the fitting calculation of ⁳⁵Cl NQR T₁ data.

<table>
<thead>
<tr>
<th>Motional mode</th>
<th>a × 10⁹/s⁻²</th>
<th>Eₜ/kJ mol⁻¹</th>
<th>τ₀/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O 180° flips</td>
<td>–</td>
<td>22±2</td>
<td>7.0 × 10⁻¹⁵</td>
</tr>
<tr>
<td>Cation C₃ or C₄</td>
<td>4.6</td>
<td>95±10</td>
<td>6.4 × 10⁻²⁰</td>
</tr>
<tr>
<td>Cation overall</td>
<td>6.2</td>
<td>116±6</td>
<td>6.6 × 10⁻²¹</td>
</tr>
<tr>
<td>Anion reorient.</td>
<td>–</td>
<td>115±4</td>
<td>3.5 × 10⁻¹⁸</td>
</tr>
</tbody>
</table>

* Ref. [12].

The observed steep decrease of T₂Q with increasing temperature above 400 K can be explained in terms of the non-adiabatic part because in this temperature region T₁Q is nearly equal to T₂Q. These temperature variations of T₁Q and T₂Q above 400 K result from a reorientational motion of the anions [17].

Below 370 K, however, T₁Q is longer than T₂Q, and so the adiabatic part must be dominant in T₂Q. Moreover, we find that the observed temperature dependence of T₂Q below 370 K is very similar to the one observed in NMR experiments [18]. According to the BPP theory, this temperature dependence of T₂Q arises from the secular part and is explained as follows. We assume that the fluctuation of the inter-nuclear interactions due to a molecular motion is the dominant relaxation mechanism. When the correlation time of the motion τc is longer than T₂Q (T₂Q being the time characterizing the spin-spin coupling in the rigid lattice and being nearly equal to the inverse of the linewidth) then T₂ = T₂Q = const. Since τc decreases with increasing temperature, it becomes shorter than T₂Q at some temperature. Above this temperature, the inter-nuclear interactions are averaged by this motion, and T₂ increases linearly with τc⁻¹ with increasing temperature (motional narrowing). Hence, we find that log T₂ depends linearly on ¹/² as long as the motional correlation time can be expressed by (5a).

Judging from the similarity between the temperature dependence of T₂ and the observed one of T₂Q below 370 K, we can infer that in Mg(H₂O)₆SnCl₆ there exists the same relaxation mechanism as mentioned above.

Among the motional modes thought to exist in this complex, anionic motions cannot be responsible for this relaxation mechanism. The reason is as follows. If the reorientational motion of the ions containing the resonant nuclei is effective on the spin-lattice relaxation, T₁Q becomes nearly equal to τc [17]. Hence around the temperature at which τc becomes shorter than T₂Q, T₁Q already decreases to the value nearly equal to T₂Q and the non-adiabatic part dominates in T₂Q. In this case T₂Q decreases with increasing temperature as observed in general [8]. On the other hand, cationic motions can be responsible for the temperature dependence of T₂Q. Furthermore, from the measurements of T₁e we have found that two motions of cations are activated above room temperature in this compound. These motions could be responsible for the chlorine nuclear relaxation.

The rapid increase of T₂Q and the decrease of the ¹H NMR M₂ with increasing temperature occurred at nearly the same temperature of ca. 340 K. The correlation time of the uniaxial motions around this temper-
ature is ca. $10^{-4}$ s, which satisfies the motional narrowing condition. These results suggest that the same cationic motions are responsible for the temperature variation of $T_{2Q}$ and $M_2$ above room temperature. Therefore we can conclude that the temperature dependence of $T_{2Q}$ below 370 K is caused by the modulation effect due to the cationic motions.

Next, let us examine whether magnetic interactions can be responsible for $T_{2Q}$ observed below 370 K. It is difficult to calculate exactly the local magnetic field $H_{loc}$ at a chlorine nucleus, so we are satisfied with estimating an order of $T_{2Q}$. In this case, it is enough to take into account only $H_{loc}$ produced by three protons close to the chlorine nuclei. A rough estimate for $T_{2Q}$ due to the magnetic interactions is given by

$$(T_{2Q})^{-1} = \frac{1}{\gamma_C H_{loc}} = \frac{\gamma_H h}{r^3},$$

(7)

where $\gamma_C$ and $\gamma_H$ are the gyromagnetic ratio of the chlorine nucleus and the proton, respectively, and $r$ is the inter-nuclear distance [19]. On the basis of the reported value of the O⋯Cl bond distance in Ca(H$_2$O)$_6$SnCl$_6$ [3], we can assume $r = 2.6$ Å. This value gives $T_{2Q} = 0.08$ ms, which is somewhat shorter than the measured value of 0.45 ms below ca. 170 K. This difference is considered to be partly caused by the averaging due to the motion of water molecules and partly to lattice vibrations of anions. Accordingly, it can be concluded that the $T_{2Q}$ values below 370 K are attributed to the magnetic interactions between chlorine nuclei and protons of the cations. In some $T_{1Q}$ measurements of the $^{14}$N NQR, a distinct minimum such as observed in NMR [18] was observed [20]. Such a minimum has been interpreted, in the same way as discussed above, in terms of the fluctuation of the dipolar field caused by the reorientation of nearby groups containing nuclei which produce the dipolar field at the resonant nuclei.

On carefully looking at the $T_{2Q}$ results shown in the insert of Fig. 1, we find that in the temperature region between 370 and 400 K, $T_{2Q}$ is nearly constant. This seems to result from the fluctuation due to lattice vibrations being effective over other relaxation mechanism in this temperature region. Hence in all three relaxation mechanisms probably contribute to $T_{2Q}$ in Mg(H$_2$O)$_6$SnCl$_6$:

$$(T_{2Q})^{-1} = T_{2Q,\text{latt}}^{-1} + T_{2Q,\text{mod}}^{-1} + T_{2Q,\text{reorient}}^{-1}. \quad (8)$$

Here, $T_{2Q,\text{latt}}$, $T_{2Q,\text{mod}}$, and $T_{2Q,\text{reorient}}$ are the spin-spin relaxation times due to lattice vibrations, the cationic motions, and the anionic motions, respectively. In order to estimate $T_{2Q,\text{latt}}$, we will fit the above equation to the $T_{2Q}$ data.

$T_{2Q,\text{latt}}^{-1}$ is assumed to take a constant value,

$$T_{2Q,\text{latt}}^{-1} = b. \quad (9a)$$

In the temperature region where $T_{2Q,\text{mod}}$ is dominant, the correlation time of the uniaxial motion is faster than that of the overall reorientation, so it is adequate to consider only the contribution from the $C_3$ or $C_4$ reorientations,

$$T_{2Q,\text{mod}}^{-1} = d\tau_{e2}, \quad (9b)$$

where $\tau_{e2}$ is the correlation time of the uniaxial motion of cations.

Above 400 K, $T_{2Q}$ is nearly equal to $T_{1Q}$, so we can assume

$$T_{2Q,\text{reorient}} = P\tau_{ea}. \quad (9c)$$

where $\tau_{ea}$ is the correlation time for the anionic motion. $P$ is 1 and 2/3 for $C_4$ and $C_3$ reorientations, respectively [21]. We assumed $C_3$ reorientations for convenience.

The $T_{2Q}$ data above 350 K were analyzed by (9a)–(9c), where $b$ and $d$ are fitting parameters. We used the $\tau_{e2}$ values obtained by the analysis of the $T_{1e}$ data and the $\tau_{ea}$ values which was derived from $T_{1Q}$ data (see Table 1). The results are shown in the insert of Fig. 1, where the best fitted curve is given by

$$T_{2Q,\text{latt}}^{-1} = 635 + 1.2 \times 10^8 \tau_{e2} + (3/2) \tau_{ea}^{-1}. \quad (10)$$

$T_{2Q,\text{latt}}$, which is ascribed to the fluctuation due to lattice vibrations, was estimated to be 1.58 ms. Since the local magnetic field produced by protons is averaged by cationic motions, the interaction being fluctuated due to lattice vibrations is probably the local magnetic field produced by the chlorine and tin nuclei. We can estimate the one at a chlorine nucleus due to nearby four chlorine and one tin nuclei using (7). Since the Cl⋯Cl and Sn⋯Cl internuclear distances in the present complex are not available, average distances in some compounds including SnCl$_2^-$ ions [22] were used. Internuclear distances of $r$(Cl⋯Cl) = 3.44 Å and $r$(Sn⋯Cl) = 2.43 Å lead to $T_{2Q} = 1.0$ ms. This value agrees well with $T_{2Q,\text{latt}}$ of 1.58 ms.

According to the BPP theory, an inverse of a square root of $d$, which is a fitting parameter of (9b), has to be nearly equal to $(\gamma H_{loc})^{-1}$ or $T_2^*$ [18]. The resulting value was 0.1 ms, which is nearly equal to the estimated values (0.08 ms) of $T_{2Q}$ and $T_{2Q}$ observed at low temperatures (0.45 ms).
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