Motion of Water Molecules and Hydrogen Bonds in Zinc Hexachlorostannate (IV) Hexahydrate as Studied by $^1$H NMR and $^{35}$Cl NQR *

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The $^1$H NMR spin-lattice relaxation time $T_1$, $^{35}$Cl NQR frequency $v_Q$, and $^{35}$Cl NQR spin-lattice relaxation time $T_{1Q}$ of [Zn(H$_2$O)$_6$][SnCl$_4$] (zinc hexachlorostannate(IV) hexahydrate) have been measured at temperatures between 77 and 350 K. The NQR spin echo signal with $v_Q=15.689$ MHz at 77 K showed a positive temperature coefficient attributable to O-H-Cl type H-bonds in the crystal. $v_Q$ at 77 K is strongly correlated with the electronegativity $\chi_M$ of the metal M in the series of stannates [M(H$_2$O)$_6$][SnCl$_4$] (M = Mg, Ca, Mn, Co, Ni, Zn). A $T_1$ minimum observed for the Zn salt is ascribed to 180° flips of water molecules with an activation energy of 20 kJ mol$^{-1}$. The motion is influenced by repulsive forces among the water molecules within a cation rather than by attractive forces between the H-bonded H and Cl atoms. $T_{1Q}$ proved to be mainly governed by lattice vibrations, weakly modulated by the fluctuating electric field gradient caused by the 180° flip motions.

Key words: $^1$H NMR spin-lattice relaxation, $^{35}$Cl NQR frequency, $^{35}$Cl NQR spin-lattice relaxation, H-bonding, Electronegativity.

Introduction

Metal hexachlorostannate(IV) hexahydrates [M(H$_2$O)$_6$][SnCl$_4$] (M = Mg, Ca, Mn, Co, Ni) have been extensively studied by NQR. The $^{35}$Cl NQR frequencies $v_Q$ in these complexes show positive temperature coefficients [1-4]. The lowering of $v_Q$ at low temperatures has been attributed to the formation of O-H-Cl H-bonds [2, 3]. Recently, the understanding of the dynamic properties of the H-bonds has been deepened through studies on the motions of water molecules, hydrated cations, and complex anions by pulsed NMR and NQR techniques applied to the Ca [5], Mg [6-9], and Ni [7, 8] salts. However, no clear relations have been obtained between the nature of the molecular motions and the H-bonds. In order to further elucidate the nature of the molecular motions related to the H-bonds in this series of stannates we have extended the NMR and NQR works to diamagnetic [Zn(H$_2$O)$_6$][SnCl$_4$] (zinc hexachlorostannate(IV) hexahydrate).

Experimental

A home made pulsed spectrometer [9] was employed for the determination of the $^1$H NMR spin-lattice relaxation time $T_1$, the $^{35}$Cl NQR frequency $v_Q$, and the $^{35}$Cl NQR spin-lattice relaxation time $T_{1Q}$. Measurements of $T_1$ and $T_{1Q}$ were performed with the pulse sequences 180°-90°-T-90° and 180°-180°, respectively, where $\tau_e$ was 200 μs throughout the measurements. An exponential decay of the signal amplitude as a function of $\tau$ was observed for $T_1$ and $T_{1Q}$ at all temperatures studied. The second moments $M_2$ of the $^1$H NMR absorption spectra were determined by using a JEOL JNM-MW-40S NMR spectrometer operated at 40 MHz. The sample temperatures were estimated to be accurate within ± 1 K. [Zn(H$_2$O)$_6$][SnCl$_4$] was prepared in a similar as in [3, 10]. The NQR signal for the Zn salt had not been observed by a cw spectrometer [3]. In the present study, a polycrystalline sample of the Zn salt was pulverized in a dry atmosphere to avoid spurious signals. The X-ray powder patterns of Zn and Ni salts were recorded on a model 2012 diffractometer from Rigaku Denki Co. equipped with a copper anticathode.

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Results

$^1H$ NMR $T_1$ and $M_2$

The temperature dependence of $^1H$ NMR $T_1$ for $[\text{Zn}(\text{H}_2\text{O})_6][\text{SnCl}_6]$ yielded the typical BPP curves at the Larmor frequencies 19.5 and 27 MHz as shown in Figure 1. At these frequencies, $T_1$ minima and $T_1$ minimum temperatures were determined as follows: 232 ms, 188 K (19.5 MHz); 332 ms, 193 K (27 MHz). $T_1$ was independent of the Larmor frequency at the higher temperature side of the minima and was dependent on the square of the Larmor frequency at the lower temperature side. The temperature dependence of $^1H$ NMR $M_2$ is given in Figure 2. $M_2$ was nearly constant ($21 \pm 2 \text{ G}^2$) above 200 K and showed a slight increase below 200 K.

$^{35}\text{Cl NQR } v_0$ and $T_{1Q}$

At 290 K a single $^{35}\text{Cl NQR}$ spin echo signal arising from the Zn salt was observed at 15.735 MHz, indicating that all chlorine atoms in the crystal are equivalent (A $^{37}\text{Cl NQR}$ signal was observed at 12.402 MHz). This value of $v_0$ occurs in a narrow frequency range covered by the series of $[\text{M}(\text{H}_2\text{O})_6][\text{SnCl}_6]$ having isomorphous crystal structure [3]. Graybeal et al. [1] reported the appearance of a doublet NQR line around 15.74 MHz on a superregenerative spectrometer. Our X-ray powder patterns have shown that the Zn salt is isomorphous with Ni salt [11] and belongs to the space group $R3$ [2] with the lattice constants $a = 10.65$ and $c = 10.98$ Å as a hexagonal cell. With this crystal symmetry all chlorine atoms are equivalent, supporting the validity of our present NQR experiments.

The $^{35}\text{Cl NQR}$ frequencies $v_0$ are plotted against temperature in Figure 3. In agreement with very similar temperature dependence of other salts in the series, $v_0$ occurred at frequencies between those of the Co and Ni salts at all temperature studied [3], until the NQR line disappeared at the melting point of ca. 340 K. Open circles in Fig. 4 show the temperature dependence of $^{35}\text{Cl NQR } T_{1Q}$ in the Zn salt. $T_{1Q}$ depends almost linearly on $T$ between 100 and 330 K but is accompanied with a shallow and broad dip around 180 K.
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**Fig. 4.** Temperature dependence of $^{35}$Cl NQR spin-lattice relaxation time $T_{1Q}$. The observed $T_{1Q}$ values are indicated by the open circles. The broken lines $T_{1Q,I}$ and $T_{1Q,m}$ show the contributions to $T_{1Q}$ from the lattice vibration and from the EFG modulation by the 180° flips of water molecules, respectively. The solid line represents the calculated overall $T_{1Q}$. These lines are expressed in (3-5).

**Discussion**

**Motion of the Water Molecules**

The observed $^1$H NMR $M_2$ and $T_1$ for the Zn salt are similar to those for [Mg(H$_2$O)$_6$][SnCl$_6$] [9]. The intramolecular contribution to the proton dipole-dipole interaction $M_2 = 21 \pm 1$ G$^2$ is calculated on an assumption of $160 \pm 1$ pm as the interprotonic distance within a water molecule in agreement with the observed value above 200 K (Figure 2). The interprotonic distance in a water molecule ranges from 156 to 161 pm in several hydrated crystals [12]. The observed $M_2 \sim 25$ G$^2$ at 100 K, therefore, may contain the intermolecular contribution as well. When the water molecules begin the 180° flips, the intermolecular interactions average out to zero, so that only the intramolecular contribution remains as observed at present above 150 K. Since the 180° flips fluctuate the intermolecular dipole interactions, the motions are also responsible for the spin-lattice relaxation. The observed $T_1$ curves (Fig. 1), assignable to the 180° flips, are expressed by the equations [13]

\[ 1/T_1 = C \left[ \tau_0/(1 + \omega^2 \tau^2) + 4 \tau_0/(1 + 4 \omega^2 \tau^2) \right] \quad (1) \]

and

\[ \tau = \tau_0 \exp(E_a/RT), \quad (2) \]

where $C$, $\omega$, and $\tau$ represent the motional constant, the angular Larmor frequency of the proton, and the correlation time, respectively. It is assumed that $\tau$ obeys the Arrhenius relation (2). The broken and the solid lines in Fig. 1 are the best fits of the data with (1) and (2) by using the parameters $\tau_0$ and $E_a$ listed in Table 1 and $C = 3.59 \times 10^2$ s$^{-2}$. The observed $E_a$ for the 180° flips of water molecules in the Zn salt is nearly the same as in the Mg salt, while $E_a$ for Ca salt is lower (Table 1). Figure 5 shows the relationship between $E_a$ of the 180° flips and the ionic radius (Pauling scale) of the metal M$^{2+}$ ion [14]. The smaller the M$^{2+}$ ion, the higher is $E_a$ for the 180° flips. With decreasing ionic radius of M$^{2+}$ ions and the activation energy $E_a$ for the 180° flips of the water molecules coordinated to M$^{2+}$.

**Table 1.** Motional modes and parameters for [M(H$_2$O)$_6$][SnCl$_6$] (M = Mg, Ca, Ni, and Zn).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_a/\text{k} \cdot \text{mol}^{-1}$</th>
<th>$\tau_0/\text{s}$</th>
<th>Motional mode</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>21</td>
<td>$1.2 \times 10^{-14}$</td>
<td>H$_2$O 180° flips</td>
<td>[9]</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>$6.4 \times 10^{-20}$</td>
<td>Cation (C$^3$ or C$^4$)</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>116</td>
<td>$1.6 \times 10^{-21}$</td>
<td>Cation (isotropic)</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>115</td>
<td>$3.5 \times 10^{-18}$</td>
<td>Anion (reorientation)</td>
<td>[6]</td>
</tr>
<tr>
<td>Ca</td>
<td>13.7</td>
<td>$1.5 \times 10^{-13}$</td>
<td>H$_2$O 180° flips</td>
<td>[5]</td>
</tr>
<tr>
<td></td>
<td>38.1</td>
<td>$1.8 \times 10^{-13}$</td>
<td>Cation (C$^3$ or C$^4$)</td>
<td>[5]</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>$2.0 \times 10^{-14}$</td>
<td>Cation (isotropic)</td>
<td>[5]</td>
</tr>
<tr>
<td></td>
<td>29.5</td>
<td>$\sim 10^{-7}$</td>
<td>Anion (reorientation)</td>
<td>[5]</td>
</tr>
<tr>
<td>Ni</td>
<td>44</td>
<td>$8.6 \times 10^{-17}$</td>
<td>Cation (C$^3$ or C$^4$)</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td>52</td>
<td>$9.9 \times 10^{-17}$</td>
<td>Cation (isotropic)</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td>86</td>
<td>$7.5 \times 10^{-14}$</td>
<td>Anion (reorientation)</td>
<td>[8]</td>
</tr>
<tr>
<td>Zn</td>
<td>20 $\pm$ 1</td>
<td>$1.4 \times 10^{-14}$</td>
<td>H$_2$O 180° flips</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5. Relation between the ionic radius of M$^{2+}$ ions and the activation energy $E_a$ for the 180° flips of the water molecules coordinated to M$^{2+}$.
radius, the distance between the neighboring water molecules within a hydrated cation is reduced. The observed linear relationship between \( E_a \) and the ionic radius, therefore, suggests that \( E_a \) is mainly influenced by the repulsive forces among the water molecules within a hydrated cation.

**Strength of the Hydrogen Bonds**

The \(^{35}\text{Cl} \) NQR frequencies \( v_0 \) for \([\text{Zn(H}_2\text{O)}_6]\) \([\text{SnCl}_6] \) yielded a positive temperature coefficient. Such positive temperature coefficients of \( v_0 \) in various compounds containing \( \text{NH}_4^+ \) ions have been interpreted in terms of breaking of H-bonds caused by the motion of \( \text{NH}_4^+ \) ions [15–19]. It has been suggested that in the case of \([\text{M(H}_2\text{O)}_6]\) \([\text{SnCl}_6] \), the positive temperature coefficients of \( v_0 \) are attributable to the weakening of the O-H-Cl H-bonds caused by molecular motions of water molecules [2–5, 17]. The present Zn salt shows a similar temperature dependence of \( v_0 \) at 77 K for \([\text{M(H}_2\text{O)}_6]\) \([\text{SnCl}_6] \) (\( \text{M} = \text{Mg, Ca, Mn, Co, Ni} \)) [3]. At low temperatures, the influence of the molecular motion on \( v_0 \) is relatively small \((\tau^{-1} \text{ for the } \text{180° flips is smaller than } v_0) \) so that the contribution to the EFG at the chlorine from the H-bonded hydrogen is important. The hydrogen interacts electrostatically with the lone pair electrons of the chlorine atom causing polarization of the chlorine atoms to lower \( v_0 \) at low temperatures as observed for \([\text{M(H}_2\text{O)}_6]\) \([\text{SnCl}_6] \) [3]. Estimates of \( \tau \) for the \( 180^\circ \) flips by using the parameters listed in Table 1 show that \( \tau^{-1} \) becomes comparable to \( v_0 \) at ca. 160 K, above which temperature a sharp increase of \( v_0 \) is observed (Figure 3). The positive temperature coefficient observed for the present Zn salt is, therefore, attributable to the breaking of the H-bonds caused by the \( 180^\circ \) flips of water molecules.

In the series of \([\text{M(H}_2\text{O)}_6]\) \([\text{SnCl}_6] \), \( v_0 \) shows a tendency to converge around 15.85 MHz near 400 K [3]. Therefore we assume that \( v_0 \) at 77 K has a close relation to the relative strength of the H-bonds in these complexes. A plot of the reported [3] and newly determined \( v_0 \) at 77 K for \([\text{M(H}_2\text{O)}_6]\) \([\text{SnCl}_6] \) against the electronegativity (Allred-Rochow scale) \( \chi_M \) of \( \text{M} \) [20] gives rise to a good correlation, as shown in Figure 6. Smaller values of \( \chi_M \) will induce larger positive charges on the hydrogens because the total charge +2 on a whole hydrated cation will be preserved irrespective of the kind of M in these complexes. A larger positive charge on hydrogens will have the stronger effect on the polarization of chlorine and will lower \( v_0 \) to a larger extent. In the present type of the crystals, \( v_0 \) at 77 K offers a good measure for the strength of the H-bonds. For the \( 180^\circ \) flips of the water molecules, \( E_a \) has been determined on the diamagnetic Mg and Ca salts (Table 1). Including \( E_a \) of the Zn salt and \( E_a \) of the various complexes for other motional modes listed in Table 1, no clear correlation can be observed between \( E_a \) and the strength of the H-bond. The magnitude of \( E_a \) for the \( 180^\circ \) flips is not concerned with the breaking of the H-bonds, instead it is strongly related to the rotational hindrance among the water molecules within a cation.

**The Symmetry of the Axis of the 180° Flips of Water Molecules**

The temperature dependence of \( T_{1Q}^{-1} \) for the Zn salt (Fig. 4) is attributable to the EFG fluctuation caused by the lattice vibration involving the chlorine nuclei \( (T_{1Q}, ) \), and by the \( 180^\circ \) flips of water molecules \( (T_{1O,m}) \) \([7]\):

\[
T_{1Q}^{-1} = T_{1Q,1}^{-1} + T_{1O,m}^{-1}.
\]  

The first term is given as

\[
T_{1Q,1}^{-1} = a \, T^*,
\]
where, \(a\) represents a constant and usually \(n \sim 2\). The second term has the effect of modulating EFG and has the following form for a nucleus with \(I = 3/2\) and asymmetry parameter \(\eta = 0\):

\[
T_{1Qm}^{-1} = (1/3) (q'/q)^2 [4\pi^2 v_0^2 \tau / (1 + 4\pi^2 v_0^2 \tau^2)],
\]

where \(q'/q\) is a fluctuating fraction of EFG caused by the 180° flips and \(\tau\) is the correlation time as defined in (2). If we employ \(\tau\) as specified by \(E_a\) and \(\tau_0\) in Table 1, the observed \(T_{1Q}\) dip around 180 K is explained satisfactorily, as shown with the solid line (3) in Figure 4. The parameters have been determined as follows: \(a = 2.30 \times 10^5\), \(n = 2.52\), \(q'/q = 1.1 \times 10^{-4}\), \(v_0 = 15.6870 \times 10^6\). These parameters are close to those reported for the Mg salt [7]. The small but nonzero magnitude of the fluctuation in EFG, arising from the 180° flips, suggests that the water molecules flip about the pseudo \(C_2\) and not the \(C_2\) axes [8].

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