Uniaxial Reorientation of Octahedral Complex Anions
Excited in Triethylammonium Hexachlorostannate (IV) Crystals

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The temperature dependence of the $^{35}$Cl NQR spin-lattice relaxation time $T_{1Q}$ has been determined for three resonance lines observed in $[[C_2H_5)_3NH]_2SnCl_5]$. The higher frequency lines fade out around 150 K upon heating, whereas the lowest line shows up to room temperature no anomaly, although these three lines are assigned to chlorines belonging to the same complex anion. The $T_{1Q}$ values of the higher two lines decrease exponentially around the fade-out temperature, where $T_{1Q}$ of the lowest line shows no such behavior. These results are explained by the onset of uniaxial reorientations of the octahedral complex ions by $90^\circ$ about the Cl–Sn–Cl axis containing the lowest frequency chlorines. The activation energy ($E_a$) of this reorientation ($22–24$ kJ mol$^{-1}$) is the lowest so far reported for $[SnCl_3]^{2–}$ ions. $E_a$ about the other axes is $67$ kJ mol$^{-1}$, indicating a remarkable anisotropic reorientation.

Key words: Spin-Lattice Relaxation, NQR, NMR, Reorientational Motion, Hydrogen Bond.

Introduction

The “fade-out” of NQR signals on heating has often been observed in the temperature dependence of resonance lines, and the mechanism of this interesting phenomenon has been investigated.

Recently, Borchers and Weiss [1] have measured the temperature dependence of $^{35}$Cl NQR lines in $[[C_2H_5)_3NH]_2SnCl_5]$ and found that two of the observed three resonance lines fade out at ca. 150 K, whereas the other line was detected up to room temperature. The observed three resonance lines could be assigned to the crystallographically nonequivalent three chlorine sites belonging to the same complex ion.

In the present study, we report a measurement of $^{35}$Cl NQR and $^1$H NMR spin-lattice relaxation times of $[[C_2H_5)_3NH]_2SnCl_5]$ to reveal the mechanism of the fade-out of resonance lines.

Experimental

$[[C_2H_5)_3NH]_2SnCl_5]$ was prepared by mixing $SnCl_4$ dissolved in hydrochloric acid with the stoichiometric amount of $[[C_2H_5)_3NH]_2HCl$. The colorless crystals obtained were recrystallized from hydrochloric acid by evaporating the solvent in a desiccator. The spin-lattice relaxation times $T_{1Q}$ and resonance frequencies of $^{35}$Cl NQR were measured in a spectrometer previously reported [2, 3]. $T_{1Q}$ was determined using a pulsed spectrometer at a Larmor frequency of 60 MHz. Differential thermal analysis (DTA) was carried out to detect possible phase transitions between ca. 100 K and room temperature, using an apparatus reported in [4]. Sample temperature was determined by copper-constantan thermocouples within an accuracy of $\pm 1$ K.

Results

The frequencies of three chlorine NQR lines above ca. 85 K agreed well with those of $^{35}$Cl nuclei reported

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by Borchers and Weiss [1]. With increasing temperature, these frequencies gradually decreased, and the high and middle frequency lines, designated as \( v_1 \) and \( v_2 \), respectively, faded out around 150 K, while the low frequency one \( (v_3) \) persisted up to room temperature in good agreement with the reported results [1]. The temperature dependence of the three lines is depicted in Figure 1.

The \( ^{35}\text{Cl} \) NQR spin-lattice relaxation times \( T_{1\text{Q}} \) of these lines on increasing the temperature are shown in Figure 2. The \( T_{1\text{Q}} \) values of \( v_1 \) and \( v_2 \) are very close in the whole temperature range studied, and, below ca. 100 K, they increased only slowly with decreasing temperature. Above this temperature, the log \( T_{1\text{Q}} \) vs. \( T^{-1} \) plots of \( v_1 \) and \( v_2 \) showed sharp exponential decreases, and a \( T_{1\text{Q}} \) shorter than 1 ms was reached above ca. 140 K. \( T_{1\text{Q}} \) of the \( v_3 \) line was much greater than the two others; its temperature dependence below room temperature is also moderate like the other lines at low temperatures; above room temperature, a rapid exponential decay with increasing temperature was obtained, and \( T_{1\text{Q}} \) became less than 1 ms above ca. 310 K.

The \( ^1\text{H} \) NMR spin-lattice relaxation time \( T_{1\text{H}} \) observed at a Larmor frequency of 60 MHz is shown in Fig. 3; a \( T_{1\text{H}} \) minimum of 75 ms was detected around 170 K. On the both sides of the minimum, the log \( T_{1\text{H}} \) values increased almost linearly against \( T^{-1} \).

**Discussion**

The crystal structure of the present complex at room temperature has been determined by X-ray diffraction [5]. According to this study, the structure is of a distorted antifluorite-type with the space group P2\(_1\)/n and \( Z = 2 \). Each octahedral complex anion is centrosymmetric and contains three kinds of nonequivalent chlorine atoms. This result agrees well with the observation of the NQR lines with roughly the same intensity. At least two of the three chlorines are expected to form Cl· · · H–N type H-bonding. Borchers and
Weiss have reported that the chlorine with the shortest $N \cdots Cl$ (333 pm) and longest $Sn-Cl$ (245.8 pm) distance corresponds to the lowest frequency line $v_3$; $v_2$ is assigned to the chlorine with the next shorter $N \cdots Cl$ (346 pm) and intermediate $Sn-Cl$ (242.7 pm) distance, and $v_1$ to that of the shortest $Sn-Cl$ (240.7 pm) distance. These assignments seem reasonable, and the observed marked frequency differences which cannot be explained by crystal field effects alone, can be attributed to differences in the H-bond strength. However, the origin of the fade-out observed only in $v_1$ and $v_2$ but not in $v_3$ cannot be directly related to this H-bond structure.

As possible reasons for this phenomenon we considered (i) the onset of a structural phase transition and (ii) excitations of motions including triethylammonium cations and complex anions.

The first possibility was investigated by careful differential thermal analysis (DTA) between 100 and 350 K, but no sign of a phase transition was observed. The fact that the $v_1$ frequency changes continuously in this temperature range supports this DTA result.

The second possibility was studied by measuring the $^1H$ NMR spin-lattice relaxation time $T_{1H}$ minimum is attributed to the fluctuation of magnetic dipolar interactions between protons caused by cationic motions. This relaxation process can be explained by the BPP equation expressed as [6]

$$T_{1H}^{-1} = C \left( \frac{\tau_c}{1 + \omega^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega^2 \tau_c^2} \right),$$

where $C$, $\tau_c$, and $\omega$ denote the motional constant, the correlation time of the motion, and the angular Larmor frequency, respectively. The temperature dependence of $T_{1H}$ can be obtained by introducing the Arrhenius relationship between $\tau_c$ and temperature

$$\tau_c = \tau_0 \exp(E_a/RT),$$

where $E_a$ is the activation energy. The facts that the $T_{1H}$ minimum was observed very close to the fade-out temperature of NQR signals, and also the temperature of rapid decrease of $T_{1Q}$ of the $v_1$ and $v_2$ lines, suggest the presence of a close relation between the cationic motion and the chlorine NQR. A possible mechanism for the fade-out of resonance lines, and at the same time the $T_{1Q}$ decreases, is the fluctuation of the electric field gradient (efg) at the $v_1$ and $v_2$ chlorines (Cl(1) and Cl(2), respectively) caused by some cationic motion. In case the efg fluctuation contributes to the NQR relaxation, $T_{1Q}$ can be written as [7]

$$T_{1Q}^{-1} = \frac{2}{3} \omega_Q^2 \left( \frac{q'}{q} \right)^2 \tau_c \frac{\tau_c}{1 + \omega^2 \tau_c^2},$$

where $\omega_Q$ and $q'/q$ are the angular NQR frequency and the modulation fraction of the efg, respectively. Assuming that the $T_{1Q}$ decrease for Cl(1) and Cl(2) observed above ca. 100 K is explainable by (2) and (3), the activation energy $E_a$ was evaluated from the log $T_{1Q}$ slope in Fig. 2 as ca. 20 kJ mol$^{-1}$. On the other hand, $E_a$ for the cationic motion derived from Fig. 3 applying (1) and (2) became ca. 12 kJ mol$^{-1}$. Because of the large difference between these two $E_a$ values, we could not attribute the fade-out of NQR signals to the efg fluctuation associated with cationic motions.

The reorientations of the octahedral complex anion by 120° or 90° about its $C_3$ or $C_4$ axes, respectively, could also be an acceptable relaxation process for the fade-out phenomenon. In most cases reported, the fade-out of NQR lines caused by whole molecular rotations takes place at temperatures close to each other [2, 8]. It is unusual in the present complex that the $v_1$ and $v_2$ lines disappear around 150 K whereas $v_3$ was observed up to room temperature, although these three lines are assigned to chlorines belonging to the same complex anion.
To get information on the anionic motions, we quantitatively analyse the observed $T_{1Q}$ values by assuming that the relaxation rate is expressed as the sum of two processes,

$$T_{1Q}^{-1} = (T_{1Q})_{\text{vib}}^{-1} + (T_{1Q})_{\text{rot}}^{-1},$$

(4)

where $(T_{1Q})_{\text{vib}}$ and $(T_{1Q})_{\text{rot}}$ denote the NQR relaxation times contributed from lattice vibrations and anionic reorientations, respectively. The former mainly contributes at low temperatures, while the latter explains the rapid decrease at high temperatures. These two components are written as $[9, 10]$

$$(T_{1Q})_{\text{vib}}^{-1} = a T^n,$$

(5)

$$(T_{1Q})_{\text{rot}}^{-1} = \frac{3}{2} b \tau_0^{-1} \exp(-E_a/RT),$$

(6)

where $a$ and $n$ are constants. $b$ denotes the number of sites allowed by a 90° reorientation of the complex anion $[10]$ and is taken $b = 2$ for Cl(1) and Cl(2), and $b = 4$ for the $v_3$ chlorine Cl(3) by assuming $W_{12} \gg W_{23} = W_{31}$ for the transition probabilities $W_{ij}$ between Cl(i) and Cl(j). Equations (4)–(6) were fitted to the observed $T_{1Q}$ data by the least-squares method. The calculation was performed using SALS $[11]$ in the Computation Center of Nagoya University. The best fitted theoretical $T_{1Q}$ curves are shown in Fig. 2, the parameters of which are listed in Table 1.

The exponent $n$ has been reported to be close to 2.0 if the contribution from lattice vibrations is important $[9]$. The value obtained, $n = 2.9$, for the $v_3$ line implies that this mechanism is operative for Cl(3). The rapid $T_{1Q}$ decrease upon heating, observed for all resonance lines, could be expressed by the exponential function. This means that an Arrhenius-type excitation of anionic motions contributes to the relaxation much more than the lattice vibrations. According to Alexander and Tzalmona $[12]$, this relaxation can be explained by random jumps of the spin-quantization axis of chlorine nuclei due to the reorientations of complex anions. Accepting this mechanism, we can understand the reason of the fade-out, which is attributable to the line broadening associated with $T_{1Q}$ decrease caused by reorientational jumps of the complex ions. Since $v_1$ and $v_2$ faded out at nearly the same temperature, and also $T_{1Q}$ of these two chlorines became almost the same in this temperature range, the anionic reorientation is expected to take place about the Cl(3)–Sn–Cl(3) axis perpendicular to the plane made by Cl(1) and Cl(2). Onset of this motion seems easier to occur than about the other Cl–Sn–Cl axes in a complex ion because Cl(3), forming the strongest Cl⋯H–N H-bond, is fixed in this motional process. The very close values of $E_a$ for 22 and 24 kJ mol$^{-1}$ for Cl(1) and Cl(2), respectively, support the adequacy of this motional mode; a small difference between these $E_a$ values is attributable to experimental errors. It is quite unusual that the bulky complex ions reorient at such low temperatures with a small activation energy. In Table 2, activation energies for [SnCl$_4$]$^{2-}$ reorientations in crystals so far reported are summarized. A surprising result is that $T_{1Q}$ of Cl(3) is little affected by this motion and shows a gradual decrease up to room temperature. This indicates that the reorientation is only uniaxial about the Cl(3)–Sn–Cl(3) axis, and the rotations about the other axes are strongly hindered. This anisotropy in motion can be seen in the $E_a$ values derived from Cl(3), $T_{1Q}$ being about three times larger than those of Cl(1) and Cl(2). This difference is attributable to the formation of weak H-bonding in Cl(1) and Cl(2) compared with that in Cl(3). However, the N⋯Cl distances determined by X-ray
diffraction [5] are 333 and 346 pm for Cl(3) and Cl(2), respectively, which values cannot be said to be markedly different. It is supposed that the cationic motions, which seem to be C₃ reorientations of the triethylammonium group as well as CH₃ groups, are closely connected with this anisotropic anionic reorientations, because the cationic motions are excited in the temperature range of T_{1Q} decrease. It is possible that the onset of the triethyl reorientation triggers the bulky anionic motion.