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-latticew relaxation time T_{1Q} has been determined for the three resonance lines observed in $[(C_2H_5)_3NH]_2SnCl_6$. 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° 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 reportd for $[SnCl_6]^{2-}$ 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 $[(C_2H_5)_3NH]_2SnCl_6$ 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 $[(C_2H_5)_3NH]_2SnCl_6$ to reveal the mechanism of the fade-out of resonance lines.

Experimental

$[(C_2H_5)_3NH]_2SnCl_6$ was prepared by mixing $SnCl_4$ dissolved in hydrochloric acid with the stoichiometric amount of $(C_2H_5)_3NHCl$. 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 by a $\pi-\tau-\pi/2-\tau_e-\pi$ pulse sequence, where τ was varied while τ_e was set constant (ca. 100 μs). The ^{1}H NMR spin-lattice relaxation time T_{1H} 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 ± 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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Fig. 1. Temperature dependences of three resonance frequencies (v_1, v_2, and v_3) of ^{35}Cl NQR in $[(C_2H_5)_3NH]_2SnCl_6$.
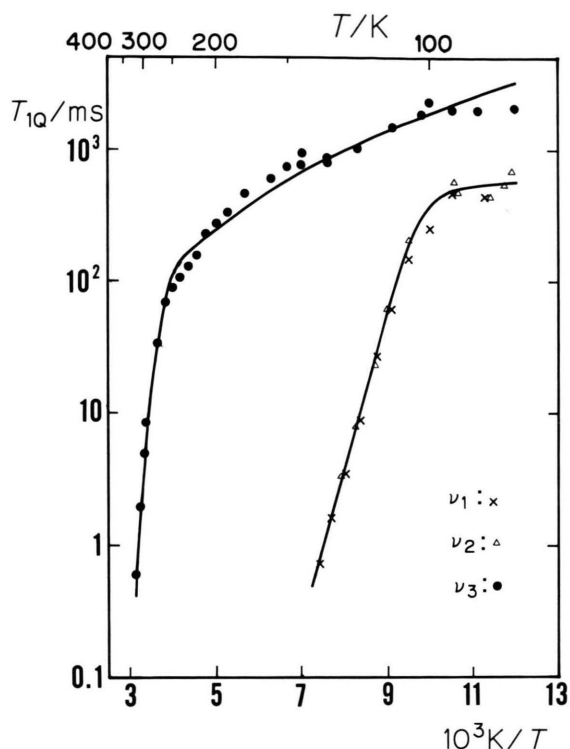
Fig. 2. Temperature dependences of the ^{35}Cl NQR spin-lattice relaxation time T_{1Q} for three resonance lines of $[(C_2H_5)_3NH]_2SnCl_6$. The solid curves are fitted (cf. Table 1).

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}Cl NQR spin-lattice relaxation times T_{1Q} of these lines on increasing the temperature are shown in Figure 2. The T_{1Q} 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_{1Q} vs. T^{-1} plots of v_1 and v_2 showed sharp exponential decreases, and a T_{1Q} shorter than 1 ms was reached above ca. 140 K. T_{1Q} 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_{1Q} became less than 1 ms above ca. 310 K.

The ^1H NMR spin-lattice relaxation time T_{1H} observed at a Larmor frequency of 60 MHz is shown in Fig. 3; a T_{1H} minimum of 75 ms was detected around 170 K. On the both sides of the minimum, the log T_{1H} 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 $Cl \cdots H-N$ type H-bonding. Borchers and
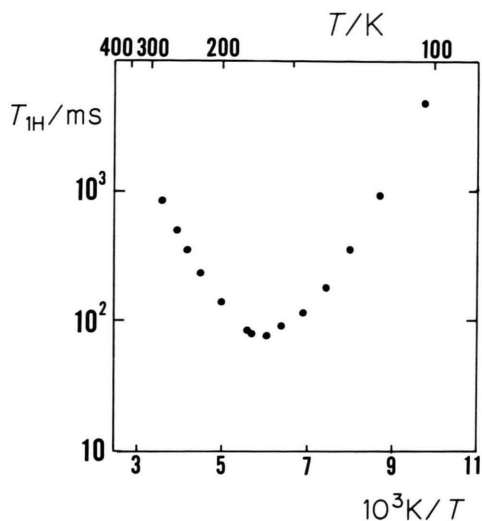
Fig. 3. Temperature dependence of the ^{1}H NMR spin-lattice relaxation time T_{1H} observed at a Larmor frequency of 60.0 MHz for $[(C_2H_5)_3NH]_2SnCl_6$.

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_3 frequency changes continuously in this temperature range supports this DTA result.

The second possibility was studied by measuring the ^{1}H NMR spin-lattice relaxation time T_{1H}. The observed 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]

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

where C, τ_c, and ω 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 τ_c and temperature

$$\tau_c = \tau_0 \exp(E_a/RT), \qquad (2)$$

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]

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

where ω_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,

$$T_{1Q}^{-1} = (T_{1Q})_{vib}^{-1} + (T_{1Q})_{rot}^{-1}, \qquad (4)$$

where $(T_{1Q})_{vib}$ and $(T_{1Q})_{rot}$ 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]

$$(T_{1Q})_{vib}^{-1} = a\,T^n, \qquad (5)$$

$$(T_{1Q})_{rot}^{-1} = \tfrac{3}{2}\,b\,\tau_{0Q}^{-1}\exp(-E_{aQ}/RT), \qquad (6)$$

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

Table 1. Relaxation parameters obtained from temperature dependences of the spin-lattice relaxation time T_{1Q} of ^{35}Cl NQR contributed from lattice vibrations and anionic reorientations expressed as (4)–(6) in the text.

^{35}Cl NQR line	$a/\mathrm{s}^{-1}\,\mathrm{K}^{-1}$	n	τ_0/s	$E_a/\mathrm{kJ\,mol}^{-1}$
v_1	(0.2)*	(0.5 ± 2)*	5×10^{-12}	22 ± 1
v_2	(0.4)*	(0.3 ± 1)*	2×10^{-12}	24 ± 1
v_3	8×10^{-7}	2.9 ± 0.1	9×10^{-14}	67 ± 2

* Parameters in parentheses are roughly estimated from a small number of data below ca. 100 K.

Table 2. Activation energies (E_a) for reorientations of $[SnCl_6]^{2-}$ ions in crystals, determined ny chlorine NQR.

Counter cation	$E_a/\mathrm{kJ\,mol}^{-1}$	Ref.
K	48.5	[13]
NH$_4$	83	[14]
CH$_3$NH$_3$	77	[15]
(CH$_3$)$_2$NH$_2$	33	[2]
	38	
(CH$_3$)$_3$NH	65	[16]
(CH$_3$)$_3$S	60	[16]
(C$_2$H$_5$)$_3$NH	22	present
	24	work
	67	
Ca · 6 H$_2$O	29.5	[17]
Mg · 6 H$_2$O	115	[18]

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_{aQ}, 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_{aQ} 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 $[SnCl_6]^{2-}$ 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_{aQ} 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 C_3 reorientations of the triethylammonium group as well as CH_3 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.

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