Reorientational Motion of Hydrogen Bonded Octahedral Complex Anions in Hydrazinium Hexachlorostannate(IV), $(N_2H_5)_2SnCl_6$, as Studied by ^{35}Cl NQR Spin-Lattice Relaxation Measurements*

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The temperature dependences of NQR frequencies and spin-lattice relaxation times, T_{1Q}, of ^{35}Cl in $(N_2H_5)_2SnCl_6$ were measured. Four NQR signals distributed in a fairly wide frequency range were observed, the lowest-frequency line exhibiting an anomalous positive temperature coefficient. The highest-frequency line showed a steep temperature dependence. These results could be interpreted by considering the intermolecular interaction between Cl and $-NH_2$ in $N_2H_5^+$. Below ca. 250 K, T_{1Q} of the upper three signals exhibited a gradual decrease upon heating, explainable by lattice vibrations, while a shallow T_{1Q} minimum, ascribable to the modulation of electric quadrupole interaction, was observed at ca. 110 K for the lowest-frequency signal. The reorientation of $[SnCl_6]^{2-}$ was elucidated to be highly anisotropic, in that it reorients about one of the Cl–Sn–Cl axes much more frequently than about the other two axes. The activation energies were determined to be 62 and 94 kJ mol^{-1} for the respective reorientations.

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

Introduction

In previous papers we reported the halogen NQR and the hydrogen NMR of methylammonium hexahalometallates(IV) [1–4]. In the low temperature region, methylammonium ions reorient as a whole about the triad axis, together with the independent $-NH_3^+$ and $-CH_3$ reorientations in the cation, and also complex anions reorient above room temperature. Although the univalent hydrazinium ion has similar molecular structure to the methylammonium ion, the hydrazinium ion is expected to make more easily a hydrogen bond(H-bond) with electron-donors like halide ions. In this study, we investigate the chlorine NQR in hydrazinium(+1) hexachlorostannate(IV) and clarify the motions of $[SnCl_6]^{2-}$ in the crystalline state.

Experimental

Hydrazinium(+1) hexachlorostannate(IV) $(N_2H_5)_2SnCl_6$ was prepared according to [5]. The crystals obtained were recrystallized from aqueous solution and dried on disphosphorus pentaoxide.

The temperature dependence of the ^{35}Cl NQR frequencies and quadrupole relaxation times T_{1Q} were measured with the pulsed NQR spectrometer already reported [6]. T_{1Q} was determined with the usual pulse sequence, $180°-\tau-90°-\tau'-180°$, for the detection of the echo-signal.

The spin-lattice relaxation time, T_1, of ^{1}H NMR was determined at 20 MHz and 30 MHz with a $180°-\tau-90°$ pulse sequence by a pulsed spectrometer.

Results and Discussion

Four ^{35}Cl NQR lines were observed in the whole temperature range studied. Figure 1 shows temperature dependences of the observed resonance frequencies. There exists no discontinuity in both frequencies and temperature coefficients. The frequencies of the upper two lines ν_1 and ν_2 are ca. 3 MHz higher than

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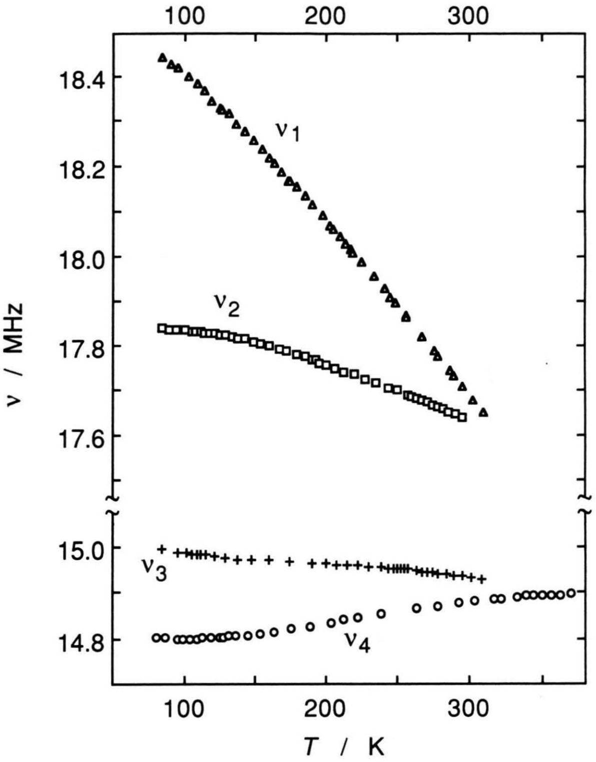

Fig. 1. Temperature dependences of ^{35}Cl NQR frequencies, ν_1, ν_2, ν_3, and ν_4, observed for $(N_2H_5)_2SnCl_6$.

those of the other two lines ν_3 and ν_4. This shows that there are four crystallographically inequivalent chlorines, two of which have fairly different circumstances from the other two chlorines in the crystals.

According to the X-ray diffraction study [7], at room temperature this complex salt has the crystal structure, Pbcn, $a = 11.84$, $b = 8.23$, $c = 11.84$ Å, $Z = 4$, and there are four inequivalent chlorines in a complex anion $[SnCl_6]^{2-}$, two of which exist on the crystallographic diad axis C_2 parallel to b axis. These two chlorines, Cl(1) and Cl(2), can be regarded as forming no H-bond with $N_2H_5^+$ ions, although Cl(1) is sited very close to the nitrogen, N(2): the Cl(1)–N(2) distance is 2.71 Å. This is because Cl(1) approaches to N(2) not from the expected N–H bond direction but approximately from the N–N bond direction. The others, Cl(3) and Cl(4), being on the *a-c* plane perpendicular to the C_2 axis, form weak H-bonds whose directions are roughly perpendicular to the Sn–Cl bonds. Short Cl–N contacts less than 3.4 Å (the van der Waals radii of Cl and N atoms are 1.75 and 1.55 Å, respectively [8]) are Cl(1)–N(2): 2.71, Cl(3)–N(1): 3.17, Cl(3)–N(2): 3.25, Cl(4)–N(1): 3.30 and 3.36, Cl(4)–N(2): 3.04 Å. Except for the Cl(1)–N(2) contact, the others are assignable to H-bonds because, putting an H atom on these N–Cl vectors, a reasonable molecular geometry can be otained for the $N_2H_5^+$ ion. Since N(1) and N(2) have three and two H-bonds, respectively, in this model, we assigned them to the $-NH_3^+$ and $-NH_2$ nitrogens, respectively.

Figure 2 shows the temperature dependence of the ^{1}H NMR spin-lattice relaxation time, T_1. The deep minimum (13 ms) at 116 K is attributable to the reorientation of the $-NH_3^+$ group by taking into account the results obtained in $Li(N_2H_5)SO_4$ [9, 10]. The activation energy of this reorientation was evaluated from the solid line in Fig. 2 by assuming the Arrhenius relationship. The value obtained, 10.9 kJ mol^{-1}, is reasonable for the reorientation of weakly H-bonded $-NH_3^+$ group in the crystal [3, 10, 11]. The reorientational motions of the $-NH_2$ group are not so frequent at room temperature, suggesting that hydrogens of the $-NH_2$ group form stronger H-bonds; with the neighbouring chlorines than hydrogens of $-NH_3^+$ group. This is consistent with the above assignment of the nitrogens, where N(2), i.e. $-NH_2$ nitrogen, has the shortest H-bond.

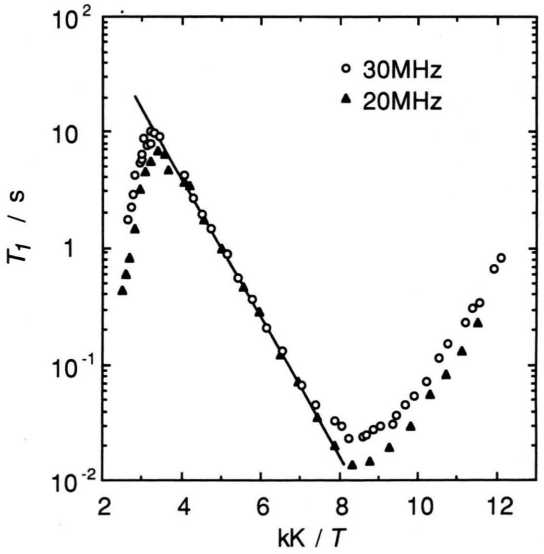

Fig. 2. Temperature dependence of the proton magnetic resonance spin-lattice relaxation time, T_1, at two Larmor frequencies (○: 30 MHz and ▲: 20 MHz) in $(N_2H_5)_2SnCl_6$. The solid line is drawn for getting the activation energy in the rapid-motion limit.

In Table 1, the resonance frequencies and the temperature coefficients at 250 K are listed. The temperature coefficient of ν_1 was quite large as compared to those of normal chlorines in $[SnCl_6]^{2-}$ [12, 13], while ν_4 exhibited anomalous positive values. The anomalous temperature dependence of ν_3, having a inflection point as shown in Fig. 1, is unexplainable by the Bayer-Kushida theory [14]. This feature can be explained by the crystal structure of this complex salt.

When a covalently bonding chlorine atom forms a H-bond from the direction perpendicular to the covalent bond, the NQR frequency of the chlorine is lowered compared with the chlorine with no H-bond because of the decrease of the unbalanced p-electron [12, 15]. Since the effect of the hydrogen bond on the NQR frequency becomes gradually weaker with increasing temperature due to the molecular motion in the crystal, the frequency of chlorines with such H-bonds may increase upon heating by overcoming the normal behaviour of the negative temperature coefficient caused by lattice and molecular motions. In case the chlorine atom is approached by an electron-donor or a lone pair of electrons from the direction perpendicular to the covalent bond, the effects of this situation on the frequency and the temperature coefficient are reversed to the case of the H-bond.

Based on the above discussion, the lower two lines ν_3 and ν_4 with anomalous temperature coefficients can be assigned to the chlorines, Cl(3) and Cl(4), on the *a-c* plane. Further it is plausible to assign the lowest ν_4 line to Cl(4) having the shortest H-bond. From the positive temperature coefficient observed for ν_4 it is concluded that the H-bond with the $-NH_2$ group is strongly affected by the thermal excitation of lattice vibrations. The upper two lines ν_1 and ν_2 can be assigned to the chlorines on the C_2 axis. If the ν_1 line is assigned to Cl(1), the large negative temperature coefficient can be explained by taking into account an electrostatic interaction between the chlorine and the lone pair electrons of the amino nitrogen, N(2).

Table 1. The NQR frequencies (ν) and temperature coefficients $[(1/\nu)(d\nu/dT)]$ at 250 K.

	ν/MHz	$10^3 \frac{1}{\nu}\frac{d\nu}{dT} \Big/ K^{-1}$
ν_1	17.885 ± 0.001	−0.219
ν_2	17.695 ± 0.001	−0.068
ν_3	14.952 ± 0.001	−0.027
ν_4	14.858 ± 0.002	0.032

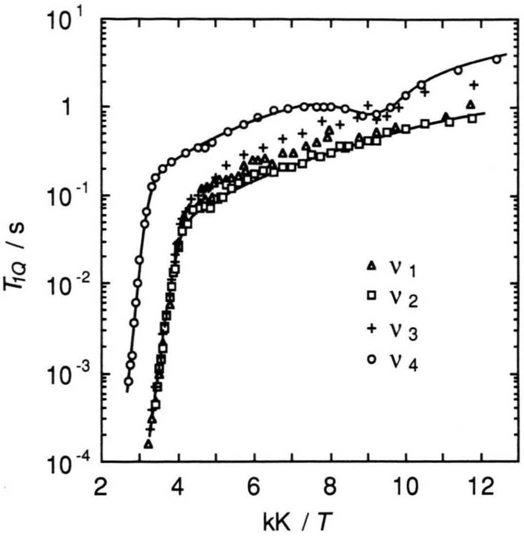

Fig. 3. Temperature dependences of NQR spin-lattice relaxation times, T_{1Q}, observed for ν_1, ν_2, ν_3, and ν_4 lines in $(N_2H_5)_2SnCl_6$. Solid lines indicate the best fitted curves for ν_2 and ν_4.

Figure 3 shows temperature dependencies of spin-lattice relaxation times T_{1Q} of four ^{35}Cl NQR signals. T_{1Q} of ν_1, ν_2, and ν_3 rapidly decreased with increasing temperature above ca. 250 K, resulting in almost the same values at given temperatures. The rapidly decreasing part in high temperature range can be attributed to reorientation [16–18] of $[SnCl_6]^{2-}$ ions, and the gently decreased part in the low temperature range to lattice vibrations [18, 19]. The relaxation rate T_{1Q}^{-1} consisting of two mechanisms is expressed as

$$T_{1Q}^{-1} = T_{1Q}^{-1}(\text{vib.}) + T_{1Q}^{-1}(\text{reo.}), \tag{1}$$

where T_{1Q}^{-1} (vib.) and T_{1Q}^{-1} (reo.) express the contributions from the lattice vibration and the reorientation of the complex ions, respectively. These are given by the equations [16–18]

$$T_{1Q}^{-1}(\text{vib.}) = a\,T^n, \tag{2}$$

$$T_{1Q}^{-1}(\text{reo.}) = \tfrac{3}{2}\,p\,\tau_0^{-1}\exp(-E_a/R\,T), \tag{3}$$

where a and n are constants [18] which are determined from the data at low temperatures. τ_0 and E_a denote the correlation time at the limit of infinite temperature and the activation energy for the reorientation of $[SnCl_6]^{2-}$ ions, respectively. Here, for the chlorines which give ν_1, ν_2, and ν_3, the number of sites, p, allowed by a one-step 90° reorientation of the complex ion was taken as $p = 2$, instead of $p = 4$ for the

Table 2. The Optimal Parameters determined by Least Squares Fitting.

	Lattice vibration		Modulation			Reorientation	
	n	$a/s^{-1}\,K^{-n}$	c/s^{-2}	τ_{0m}/s	$E_{am}/kJ\,mol^{-1}$	τ_0/s	$E_a/kJ\,mol^{-1}$
ν_1	2.5 ± 0.1	19×10^{-6}	–	–	–	2×10^{-14}	61 ± 1
ν_2	2.5 ± 0.1	16×10^{-6}	–	–	–	5×10^{-15}	65 ± 2
ν_3	2.9 ± 0.1	1×10^{-6}	–	–	–	5×10^{-14}	60 ± 1
ν_4	2.4 ± 0.1	8×10^{-6}	12×10^7	4×10^{-15}	13 ± 2	2×10^{-16}	94 ± 2

isotropic 90° reorientation [16, 17], since the long T_{1Q} observed for ν_4 suggests a very small transition probability to the ν_4 chlorine site. Least squares fitting calculation to the observed T_{1Q} values was performed by the SALS program [20] using (1)–(3). The optimal fitting yielded the values of a, n, τ_0 and E_a as listed in Table 2. The fitted curve for ν_2 is, as an example, drawn in Figure 3.

The temperature dependence of T_{1Q} for ν_4 has two different characteristics from the others: one is that the starting temperature (ca. 300 K) of the rapid decrease of T_{1Q} is higher than those of the others, suggesting the ν_4 chlorine, Cl(4), is more strongly bound in the crystals. The other is that there exists a shallow minimum at ca. 110 K, indicating another relaxation mechanism. The observed deep T_1 minimum at 116 K for ^1H NMR at 20 MHz suggests strongly that the reorientation of the $-NH_3^+$ group affects T_{1Q}: there exist also weak interactions between the $-NH_3^+$ group and Cl(4), which has the shortest H-bond with the $-NH_2$ group. The reorientation of the cations can affect T_{1Q} by modulating the spin state of the quadrupole nucleus. There are two kinds of modulation, one of which is the modulation of the magnetic dipole-dipole interaction [21, 22] and the other is the modulation of the electric field gradient at the quadrupole nucleus [22, 23]. These modulation effects can be expressed as

$$T_{1Q}^{-1}\,(\text{mod.}) = c \cdot \tau_m / (1 + 4\pi^2 \nu^2 \tau_m^2)\,, \tag{4}$$

$$\tau_m = \tau_{0m} \exp(E_{am}/R\,T)\,, \tag{5}$$

where c is a parameter which contains contributions of the two modulation mechanisms and ν denotes the resonance frequency of NQR. τ_{0m} and E_{am} are the correlation time at the limit of infinite temperature and the activation energy for the reorientation of $-NH_3^+$, respectively. Thus the whole relaxation rate T_{1Q}^{-1} for ν_4 is expressed as

$$T_{1Q}^{-1} = T_{1Q}^{-1}\,(\text{vib.}) + T_{1Q}^{-1}\,(\text{reo.}) + T_{1Q}^{-1}\,(\text{mod.})\,. \tag{6}$$

In this case, T_{1Q}^{-1} (reo.) is given as

$$T_{1Q}^{-1}\,(\text{reo.}) = 6\,\tau_0^{-1} \exp(-E_a/R\,T)\,, \tag{7}$$

assuming that the 90° reorientation to the ν_1, ν_2, and two ν_3 chlorine sites are equally possible. Here, τ_0 and E_a have the same meanings as in (3). We performed the last squares fitting to the observed T_{1Q} values for ν_4 using (2) and (4)–(7), where it was assumed that ν is constant (at 14.9 MHz). The best fitted values of a, n, τ_0, E_a, τ_{0m}, E_{am}, and c are listed in Table 2. The fitted T_{1Q} curve is indicated by a solid line in Figure. 3. The E_a for ν_4 is larger than the others, indicating that the chlorine Cl(4) is hindered more strongly than the other chlorines. The E_a value evaluated for ν_4 (94 kJ mol^{-1}) is much larger than the corresponding values in $[(CH_3)_2NH_2]_2SnCl_6$ (35 kJ mol^{-1}) [6] and K_2SnCl_6 (49 kJ mol^{-1}) [24] and is still slightly large compared to those reported for $(CH_3NH_3)_2SnCl_6$ (77 kJ mol^{-1}) [4] and $(NH_4)_2SnCl_6$ (83 kJ mol^{-1}) [25]. This indicates that the Cl(4) is bound more tightly in the crystals than chlorines in the above complex salts. The jumping rate can also be calculated using $\tau^{-1} = \tau_0^{-1} \exp(-E_a/R\,T)$. According to the results, $[SnCl_6]^{2-}$ anions perform rotatory jumps about the Cl(4)–Cl(4) axis at a rate of ca. 10^3 per second at 300 K, while the jumping rate of Cl(4) is 0.2 s^{-1} at 300 K. This indicates that the reorientation of the complex anions in this salt is highly anisotropic.

The derived E_{am} value (13 kJ mol^{-1}) from the T_{1Q} data for the reorientation of neighbouring cations causing the modulation to the electric quadrupole interaction agreed well with 10.9 kJ mol^{-1} determined by ^1H NMR as the activation energy for the reorientations of the $-NH_3^+$ group. This agreement indicates that the reorientations of the $-NH_3^+$ group influence the NQR of Cl(4). For ν_3, assigned to Cl(3) which is located more closely to $-NH_3^+$, a similar T_{1Q} minimum could be seen around the same temperature to that of ν_4, although there exist wide variations in the observed T_{1Q} values compared with ν_4.

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