1H NMR Studies on Cationic Motions in Solid tert-Butylammonium Hexachlorostannate (IV)

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The temperature dependences of the 1H spin-lattice relaxation time (T1) and the second moment (M2) of 1H NMR absorptions were measured for anhydrous tert-butylammonium hexachlorostannate (IV) and its partially deuterated analogs [(CD3)3CNH3]2SnCl6 and [(CH3)3CD2]3SnCl4. Three kinds of cationic motions were revealed: the reorientations of the CH3 group about their C–C bonds, the NH3 group about its C–N bond, and the tert-butyl group about the C–N bond. Their motional parameters were determined. Among the three motions, the NH3 motion occurs at the lowest temperature with quite a small activation energy (9.9–10.0 kJ mol–1).

1. Introduction

Recently we have studied the 1H NMR spin-lattice relaxation time (T1) and the second moment (M2) of 1H NMR absorption of tert-butylammonium hexachloro- and hexabromotellurate (IV) in the temperature range of 77–405 K [1]. In these crystals, tert-butylammonium ions were found to perform composite motions consisting of C3 reorientations of CH3 and NH3 groups about C–C and C–N bonds, respectively, and the C3 reorientation of the tert-butyl group about the C–N bond. The activation energies obtained for these motions are quite small compared with those in halides [2–4], implying that the cations are loosely bound in the crystals. Among the three motions, the NH3 motion occurs at the lowest temperature with activation energies (7.9–10.1 kJ mol–1) smaller than those for CH3 groups (7.9–16.7 kJ mol–1), indicating that the NH3 group rotates more easily than the CH3 groups in these complexes. The X-ray structural analysis of [(CH3)3CNH3]2SnCl6 recently performed [5] shows no particular distortion of the cation nor unusual contact between ions such as to make the NH3 group more movable than the CH3 groups. Therefore, the above result may suggest that, in case the cations are quite loosely bound in the crystal lattice, the NH3 group can perform less hindered rotation than the CH3 groups.

[(CH3)3CNH3]2SnCl6, abbreviated hereafter (t-BA)2SnCl6, belongs to the [(CH3)3CNH3]2MX4 (M = quadrivalent metal, X = halogen) group, and the cations in this complex are expected to move freely like in [(CH3)3CNH3]2SnCl6. The present investigation of (t-BA)2SnCl6 and its partially deuterated analogs by using continuous and pulsed 1H NMR techniques has been undertaken to elucidate the cationic motions in the crystal.

2. Experimental

The second moment (M2) of 1H NMR absorption was determined with a JEOL JNM-MW-40S spectrometer. 1H NMR T1 was measured at 32 MHz using a pulsed spectrometer [6]; the 180°–t–90° pulse sequence was employed. Differential thermal analysis (DTA) was performed with a home-made apparatus similar to that reported previously [7]. Thermogravimetric analysis (TGA) was carried out using an apparatus from Rigaku Denki Co.

tert-Butylammonium hexachlorostannate (IV) was prepared by mixing tert-butylammonium chloride with a stoichiometric amount of SnCl4, both dissolved in concentrated hydrochloric acid. The result-

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ing colorless crystals were recrystallized from concentrated hydrochloric acid. The obtained crystals effloresce easily in dry air, its color becoming white and opaque. TGA showed that the compound contains five molecules of crystal water. The dehydrated samples were obtained by drying the hydrated crystals under vacuum (ca. 1 × 10⁻³ Torr) for 12 h at ca. 60 °C. Calculated for [(CH₃)₂CNH₃]₂SnCl₆; C, 20.01; H, 5.00; N, 5.84%. Found: C, 20.00; H, 4.95; N, 5.83%.

[(CD₃)₃CNH₂]₂SnCl₆ ((t-Bd₃A)₂SnCl₆) was synthesized in a similar manner by use of (CD₃)₃CNH₂Cl prepared by neutralization of (CD₃)₃CNH₂ purchased from MSD Isotopes with hydrochloric acid. [(CH₃)₂CNH₂]₂SnCl₆ ((t-Bd₂A)₂SnCl₆) was obtained from purified [(CH₃)₂CNH₂]₂SnCl₆ by crystallizing three times from deuterated hydrochloric acid.

3. Results and Discussion

X-ray powder patterns of (t-BA)₂SnCl₆ taken at room temperature are very complicated and quite different from those of (t-BA)₂TeCl₆ [1], indicating that these complexes are not isomorphous at room temperature. DTA measurements performed in the range 100 ≤ T/K ≤ 300 showed a heat anomaly attributable to a phase transition. The transition temperatures determined for (t-BA)₂SnCl₆, (t-Bd₂A)₂SnCl₆, and (t-Bd₃A)₂SnCl₆ are 196, 189, and 195 K, respectively.

The temperature dependence of M₂ of ¹H NMR absorption is shown in Figure 1. The M₂ value of 32 ± 1 G² (1 G = 1 × 10⁻⁴ T) observed at 77 K is close to 28.7 G² calculated for the rigid t-BA⁺ ion reported on (t-BA)₂TeCl₆ [1]. With increasing temperature, M₂ decreased rapidly and almost a constant value of 2.8 ± 0.2 G² was obtained above ca. 200 K. This value can be explained by rapid C₃ reorientations of the NH₃⁺ and three CH₃ groups as well as the C₃ reorientation of the tert-butyl group, although the observed value is somewhat small as compared with the calculated M₂ of 4.8 G² [1] for the cation performing these three motions. This difference is attributable to the contribution to M₂ from large amplitude librations of the cation about its C–C and/or C–N bond axis, as pointed out previously [1, 8].

The temperature variations of ¹H T₁ are shown in Figs. 2 and 3 for (t-BA)₂SnCl₆ and its partially deuterated analogs, respectively. No detectable changes of T₁ were observed at the transition temperatures of these complexes determined by DTA. In the following analysis of T₁, thus, we assume that the cationic motions are not influenced by the phase transition.

A slightly asymmetric T₁ minimum at ca. 140 K observed for (t-Bd₂A)₂SnCl₆ can be attributed to the reorientation of the NH₃⁺ groups, by referring to the M₂ results. Since the asymmetric shape of the T₁ minimum can be ascribed to successively overlapped T₁ minima, we can expect the presence of crystallographically nonequivalent NH₃⁺ groups in the crystal.

Here we suppose for simplicity, two kinds of nonequivalent cations in the crystal. Then ¹H T₁ for
Fig. 3. Temperature dependences of the spin-lattice relaxation time $T_1$, observed at 32 MHz in [(CD$_3$)$_3$CNH$_3$]$_2$SnCl$_6$ (△) and [(CH$_3$)$_3$CND$_3$]$_2$SnCl$_6$ (○). Solid lines indicate the best fitted theoretical values. The dotted and broken lines are the separated $T_1$ curves according to (1) and (8), respectively. 189 K and 195 K in the figure are the transition temperatures determined by DTA for [(CD$_3$)$_3$CNH$_3$]$_2$SnCl$_6$ and [(CH$_3$)$_3$CND$_3$]$_2$SnCl$_6$, respectively.

(t-BAd$_2$)SnCl$_6$ can be written as [9]

$$ T_1^{-1} = A f(\tau') + B f(\tau'') , $$

where

$$ f(\tau) = \tau / (1 + \omega^2 \tau^2) + 4 \tau / (1 + 4 \omega^2 \tau^2) , $$

where $\tau'$, $\tau''$, $\gamma$, $r$, and $\omega$ denote the correlation times of the reorientation for the two kinds of NH$_3^+$ groups, the protonic gyromagnetic ratio, the inter-proton distance in an NH$_3^+$ group, and the resonance angular frequency, respectively. An Arrhenius-type relationship between $\tau^i$ ($i = I, II$) and the activation energy ($E'_i$) for the motional process of the i-th NH$_3^+$ group was assumed:

$$ \tau^i = \tau_0^i \exp(E'_i/RT) . $$

Equations (1)–(4) were least-squares fitted to the observed $T_1$ values. The optimum values of $A$, $B$, $\tau_0^i$, and $E'_i$ are shown in Table 1, and the best fitted curves are shown in Fig. 3; the agreement between the calculated and observed $T_1$ is quite good. Since almost the same values of $A$ and $B$ were obtained, the nonequivalent cations in the crystal can be classified into two groups with an abundance ratio of 1:1.

A deep $T_1$ minimum at ca. 190 K and a shoulder at ca. 270 K were observed for (t-BAd$_2$)$_2$SnCl$_6$, as shown in Figure 3. These are assignable to the reorientations of the CH$_3$ and tert-butyl groups from the $M_2$ results mentioned above. Since two kinds of cations have been revealed to exist in the crystal, we should consider at least four relaxation processes corresponding to the reorientations of the CH$_3$ and tert-butyl groups in the two different cations under the assumption that all CH$_3$ groups in each cation are equivalent. Then, $^1$H $T_1$ for these motions can be expressed as [2, 10, 11]

$$ T_1^{-1} = (1/2) [ A \{ f(\tau_1^i) + f(\tau_2^i) \} + B \{ f(\tau_3^i) + f(\tau_4^i) \} + C \{ f(\tau_5^i) + f(\tau_6^i) \} , $$

where

$$ \tau_1^i = 1/\tau_2^i + 1/\tau_2^i \quad (i = I, II) $$

and

$$ A = (9/80) (\gamma^2 h^2 r^{-6}) (3/2) \sin^4 \delta , $$

$$ B = (9/80) (\gamma^2 h^2 r^{-6}) (\sin^2 2 \delta + \sin^4 \delta) + (27/20) \gamma^4 h^2 R^{-6} , $$

$$ C = (9/80) (\gamma^2 h^2 r^{-6}) (1/2) (8 - 3 \sin^4 \delta) . $$

Here $\tau_1^i$, $\tau_2^i$ ($i = I, II$, $r$, $R$, and $\delta$ stand for the reorientational correlation times of the CH$_3$ and tert-butyl groups in the i-th cation, the inter-proton distance in a CH$_3$ group, the distance between the centers of three protons in each CH$_3$ group, and the angle between the C–C and C–N bond axes, respectively. It is difficult, however, to analyse the observed $T_1$ values using (4)–(7) because of too many unknown parameters to be optimized. Thus, we assume that $^1$H $T_1$ can be written conventionally by a sum of the three BPP
equations as
\[ T_1^{-1} = C_a f(\tau_a) + C_b f(\tau_b) + C_c f(\tau_c), \]
where the first term, \( C_a f(\tau_a) \), corresponds to the \( T_1 \) shoulder while \( C_b f(\tau_b) \) and \( C_c f(\tau_c) \) contribute to the asymmetric \( T_1 \) minimum on its high and low temperature side, respectively. A fitting calculation using (4) and (8) was successful as shown in Fig. 3 and its results are listed in Table 1. We obtained \( C_a = 1.3 \times 10^9 \), \( C_b = 3.4 \times 10^9 \), and \( C_c = 5.7 \times 10^9 \) s\(^{-2}\) as the optimum values for the motional constants, which are close to \((B/2) = 1.30 \times 10^9\), \((A+C)/2 = 3.81 \times 10^9\), and \((A+B+C)/2 = 5.11 \times 10^9\) s\(^{-2}\), respectively calculated from (7a)–(7c) using the evaluated most probable values, \( r = 1.797 \) Å, \( R = 3.593 \) Å, and \( \delta = 70.73^\circ\). Since the presence of two kinds of cations has been revealed, the above result can be interpreted as follows: 1) the \( T_1 \) shoulder at ca. 270 K and the \( T_1 \) in the high temperature region of the asymmetric minimum are attributed to the \( C_3 \) reorientation of the tert-butyl group and the \( C_3 \) reorientation of the three CH\(_3\) groups, respectively, in one of the two different cations, and 2) the reorientations of the CH\(_3\) and tert-butyl groups in the other cation occur at almost the same temperature and contribute together to \( T_1 \) in the low temperature region of the minimum.

From the results of the partially deuterated analogs, the \( T_1 \) minimum in (t-BA)\(_2\)SnCl\(_6\) is assigned to the motions of all CH\(_3\) groups in the crystal and the tert-butyl group in one of the two cations, while the two \( T_1 \) shoulders observed at ca. 270 and 130 K are attributed to the tert-butyl group motion in the other cation and the NH\(_3^+ \) motion, respectively. For the fully protonated t-BA\(^+\) cation, \( T_1 \) is approximately expressed as
\[ T_1^{-1} = (1/4) \{ T_1 (NH_3^+) \}^{-1} + (3/4) \{ T_1 (\text{tert-butyl}) \}^{-1}, \]
where \( T_1 (NH_3^+) \) and \( T_1 (\text{tert-butyl}) \) are given by (1) and (5), respectively. In Fig. 2, the calculated \( T_1 \) curves using (9) by substituting the parameters obtained for the partially deuterated analogs are shown. A satisfactory agreement between the experimental and calculated \( T_1 \) is obtained. The discrepancy in the high temperature region can be explained by the interaction between protons in the NH\(_3^+\) and CH\(_3\) groups.

In the present investigation we obtained quite small activation energies \((9.9-10.0 \text{ kJ mol}^{-1})\) for the NH\(_3^+ \) motion, comparable to \(7.9-10.1 \text{ kJ mol}^{-1}\) for the same motion obtained in (t-BA)\(_2\)TeX\(_6\) \((X = Cl, Br)\) [1]. This indicates that the cations in the present complex form very weak, if any, hydrogen bonds of N–H ••• Cl, as expected for the loosely packed cation in the crystal. Moreover, we found that the NH\(_3^+ \) motion occurs at lower temperatures than the CH\(_3\) motion, namely, the activation energy for the NH\(_3^+ \) groups is smaller than for the CH\(_3\) groups. This is the same result as obtained in (t-BA)\(_2\)TeX\(_6\) \((X = Cl, Br)\), although the tin and tellurium complexes are not isomorphous. This suggests that the NH\(_3^+ \) group can rotate more easily than the CH\(_3\) groups, if the cation is completely free or packed loosely in the crystal.