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

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Z. Naturforsch. **47a**, 1087–1090 (1992); received July 8, 1992

The temperature dependences of the $^1$H spin-lattice relaxation time ($T_1$) and the second moment ($M_2$) of $^1$H NMR absorptions were measured for anhydrous tert-butylammonium hexachlorostannate(IV) and its partially deuterated analogs $[(CD_3)_3CNH_3]_2SnCl_6$ and $[(CH_3)_3CND_3]_2SnCl_6$. Three kinds of cationic motions were revealed: the reorientations of the $CH_3$ group about their C–C bonds, the $NH_3^+$ 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 $NH_3^+$ 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 $^1$H NMR spin-lattice relaxation time ($T_1$) and the second moment ($M_2$) of $^1$H 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 $C_3$ reorientations of $CH_3$ and $NH_3^+$ groups about C–C and C–N bonds, respectively, and the $C_3'$ 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 ar loosely bound in the crystals. Among the three motions, the $NH_3^+$ motion occurs at the lowest temperature with activation energies (7.9–10.1 kJ mol$^{-1}$) smaller than those for $CH_3$ groups (7.9–16.7 kJ mol$^{-1}$), indicating that the $NH_3^+$ group rotates more easily than the $CH_3$ groups in these complexes. The X-ray structural analysis of $[(CH_3)_3CNH_3]_2TeCl_6$ recently performed [5] shows no particular distortion of the cation nor unusual contact between ions such as to make the $NH_3^+$ group more movable than the $CH_3$ groups. Therefore, the above result may suggest that, in case the cations are quite loosely bound in the crystal lattice, the $NH_3^+$ group can perform less hindered rotation than the $CH_3$ groups.

$[(CH_3)_3CNH_3]_2SnCl_6$, abbreviated hereafter (t-BA)$_2$SnCl$_6$, belongs to the $[(CH_3)_3CNH_3]_2MX_6$ (M = quadrivalent metal, X = halogen) group, and the cations in this complex are expected to move freely like in $[(CH_3)_3CNH_3]_2TeCl_6$. The present investigation of (t-BA)$_2$SnCl$_6$ and its partially deuterated analogs by using continuous and pulsed $^1$H NMR techniques has been undertaken to elucidate the cationic motions in the crystal.

## 2. Experimental

The second moment ($M_2$) of $^1$H NMR absorption was determined with a JEOL JNM-MW-40S spectrometer. $^1$H NMR $T_1$ 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 $SnCl_4$, 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. $1 \times 10^{-3}$ Torr) for 12 h at ca. 60 °C. Calculated for $[(CH_3)_3CNH_3]_2SnCl_6$; C, 20.01; H, 5.00; N, 5.84%. Found: C, 20.00; H, 4.95; N, 5.83%.

$[(CD_3)_3CNH_3]_2SnCl_6$ ($(t\text{-}Bd_9A)_2SnCl_6$) was synthesized in a similar manner by use of $(CD_3)_3CNH_3Cl$ prepared by neutralization of $(CD_3)_3CNH_2$ purchased from MSD Isotopes with hydrochloric acid. $[(CH_3)_3CND_3]_2SnCl_6$ ($(t\text{-}BAd_3)_2SnCl_6$) was obtained from purified $[(CH_3)_3CNH_3]_2SnCl_6$ by crystallizing three times from deuterated hydrochloric acid.

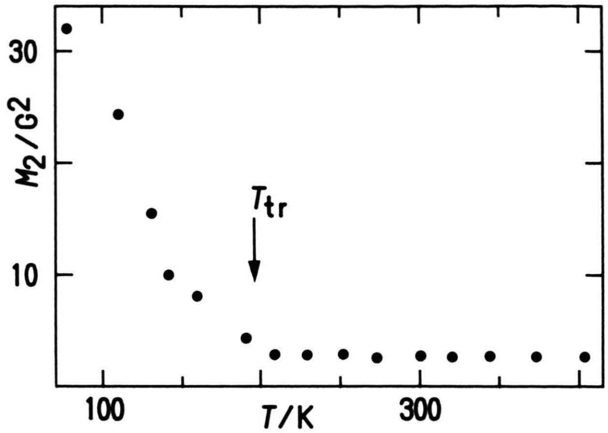

Fig. 1. Temperature dependence of the $^1$H NMR second moment $M_2$ observed for $[(CH_3)_3CNH_3]_2SnCl_6$. $T_{tr}$ is the transition temperature determined by DTA.

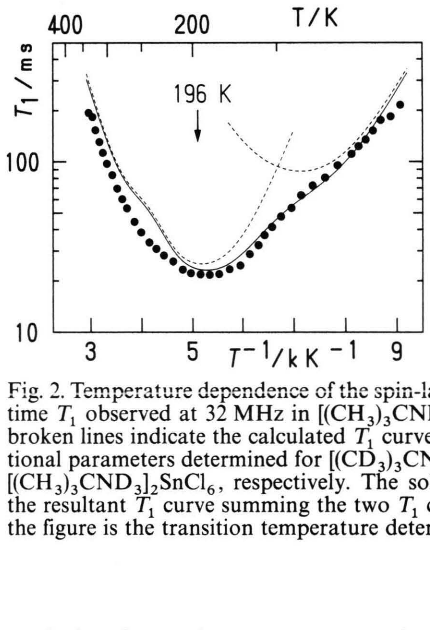

Fig. 2. Temperature dependence of the spin-lattice relaxation time $T_1$ observed at 32 MHz in $[(CH_3)_3CNH_3]_2SnCl_6$. The broken lines indicate the calculated $T_1$ curves using the motional parameters determined for $[(CD_3)_3CNH_3]_2SnCl_6$ and $[(CH_3)_3CND_3]_2SnCl_6$, respectively. The solid line denotes the resultant $T_1$ curve summing the two $T_1$ curves. 196 K in the figure is the transition temperature determined by DTA.

## 3. Results and Discussion

X-ray powder patterns of $(t\text{-}BA)_2SnCl_6$ taken at room temperature are very complicated and quite different from those of $(t\text{-}BA)_2TeCl_6$ [1], indicating that these complexes are not isomorphous at room temperature. DTA measurements performed in the range $100 \leq T/K \leq 300$ showed a heat anomaly attributable to a phase transition. The transition temperatures determined for $(t\text{-}BA)_2SnCl_6$, $(t\text{-}Bd_9A)_2SnCl_6$, and $(t\text{-}BAd_3)_2SnCl_6$ are 196, 189, and 195 K, respectively.

The temperature dependence of $M_2$ of $^1$H NMR absorption is shown in Figure 1. The $M_2$ value of $32 \pm 1$ G$^2$ (1 G = $1 \times 10^{-4}$ T) observed at 77 K is close to 28.7 G$^2$ calculated for the rigid t-BA$^+$ ion reported on $(t\text{-}BA)_2TeCl_6$ [1]. With increasing temperature, $M_2$ decreased rapidly and almost a constant value of $2.8 \pm 0.2$ G$^2$ was obtained above ca. 200 K. This value can be explained by rapid $C_3$ reorientations of the $NH_3^+$ and three $CH_3$ groups as well as the $C_3'$ reorientation of the tert-butyl group, although the observed value is somewhat small as compared with the calculated $M_2$ of 4.8 G$^2$ [1] for the cation performing these three motions. This difference is attributable to the contribution to $M_2$ 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 $^1$H $T_1$ are shown in Figs. 2 and 3 for $(t\text{-}BA)_2SnCl_6$ and its partially deuterated analogs, respectively. No detectable changes of $T_1$ were observed at the transition temperatures of these complexes determined by DTA. In the following analysis of $T_1$, thus, we assume that the cationic motions are not influenced by the phase transition.

A slightly asymmetric $T_1$ minimum at ca. 140 K observed for $(t\text{-}Bd_9A)_2SnCl_6$ can be attributed to the reorientation of the $NH_3^+$ groups, by referring to the $M_2$ results. Since the asymmetric shape of the $T_1$ minimum can be ascribed to successively overlapped $T_1$ minima, we can expect the presence of crystallographically nonequivalent $NH_3^+$ groups in the crystal.

Here we suppose for simplicity, two kinds of nonequivalent cations in the crystal. Then $^1$H $T_1$ for

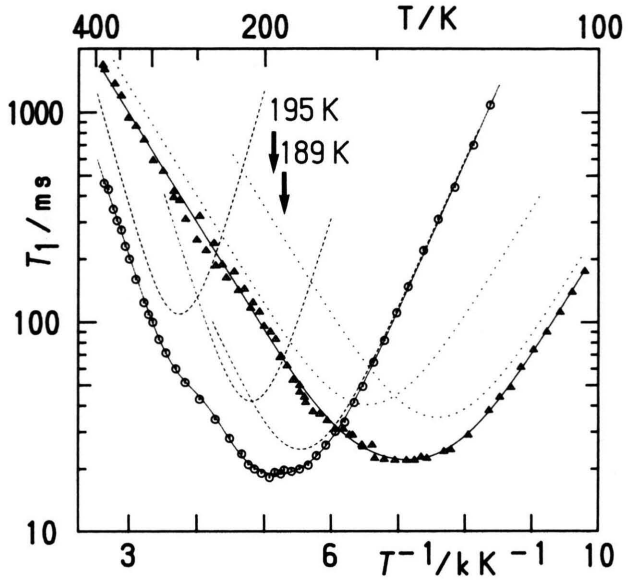

Fig. 3. Temperature dependences of the spin-lattice relaxation time $T_1$ observed at 32 MHz in $[(CD_3)_3CNH_3]_2SnCl_6$ (△) and $[(CH_3)_3CND_3]_2SnCl_6$ (○). Solid lines indicate the best fitted theoretical values. The dotted and broken lines are the separated $T_1$ curves according to (1) and (8), respectively. 189 K and 195 K in the figure are the transition temperatures determined by DTA for $[(CD_3)_3CNH_3]_2SnCl_6$ and $[(CH_3)_3CND_3]_2SnCl_6$, respectively.

$(t\text{-}Bd_9A)_2SnCl_6$ can be written as [9]

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

$$A + B = (9/20)\,\gamma^4\,\hbar^2\,r^{-6}, \tag{2}$$

$$f(\tau) = \tau/(1+\omega^2\tau^2) + 4\tau/(1+4\omega^2\tau^2), \tag{3}$$

where $\tau^{I}$, $\tau^{II}$, $\gamma$, $r$, 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 ($E_a^i$) for the motional process of the $i$-th $NH_3^+$ group was assumed:

$$\tau^i = \tau_0^i \exp(E_a^i/RT)\,. \tag{4}$$

Equations (1)–(4) were least-squares fitted to the observed $T_1$ values. The optimum values of $A$, $B$, $\tau_0^i$, and $E_a^i$ 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.

Table 1. Motional parameters of tert-butylammonium ions in partially deuterated tert-butylammonium hexachlorostannate(IV).

| $E_a$/kJ mol$^{-1}$ | $\tau_0/10^{-13}$ s | $C/10^9$ s$^{-2}$ | Reorienting group |
|---|---|---|---|
| **$[(CD_3)_3CNH_3]_2SnCl_6$** | | | |
| 9.9 ± 0.5 | 4.0 ± 1.0 | 4.0 ± 1.0 | $NH_3^+$ |
| 10.0 ± 0.5 | 1.2 ± 0.2 | 3.5 ± 1.0 | $NH_3^+$ |
| **$[(CH_3)_3CND_3]_2SnCl_6$** | | | |
| 21.7 ± 0.7 | 1.7 ± 0.4 | 1.3 ± 0.2 | tert-butyl |
| 19.7 ± 1.0 | 0.4 ± 0.1 | 3.4 ± 0.5 | $CH_3$ |
| 13.6 ± 0.1 | 3.6 ± 0.3 | 5.7 ± 0.5 | $CH_3$ and tert-butyl |

A deep $T_1$ minimum at ca. 190 K and a shoulder at ca. 270 K were observed for $(t\text{-}BAd_3)_2SnCl_6$, 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, $^1H$ $T_1$ for these motions can be expressed as [2, 10, 11]

$$T_1^{-1} = (1/2)\,[A\,\{f(\tau_1^{I}) + f(\tau_1^{II})\} + B\,\{f(\tau_2^{I}) + f(\tau_2^{II})\} + C\,\{f(\tau_3^{I}) + f(\tau_3^{II})\}]\,, \tag{5}$$

where

$$1/\tau_3^i = 1/\tau_1^i + 1/\tau_2^i \qquad (i = \text{I, II}) \tag{6}$$

and

$$A = (9/80)\,(\gamma^4\hbar^2 r^{-6})\,(3/2)\sin^4\delta\,, \tag{7a}$$

$$B = (9/80)\,(\gamma^4\hbar^2 r^{-6})\,(\sin^2 2\delta + \sin^4\delta) + (27/20)\,\gamma^4\hbar^2 R^{-6}, \tag{7b}$$

$$C = (9/80)\,(\gamma^4\hbar^2 r^{-6})\,(1/2)\,(8 - 3\sin^4\delta)\,. \tag{7c}$$

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 $^1H$ $T_1$ can be written conventionally by a sum of the three BPP equations as

$$T_1^{-1} = C_a f(\tau_a) + C_b f(\tau_b) + C_c f(\tau_c) , \qquad (8)$$

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 $C_c = 5.7 \times 10^9\ \mathrm{s}^{-2}$ 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 $(A+B+C)/2 = 5.11 \times 10^9\ \mathrm{s}^{-2}$, respectively calculated from (7a)–(7c) using the evaluated most probable values, $r = 1.797$ Å, $R = 3.593$ Å, and $\delta = 70.73°$. 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 $(\text{t-BA})_2SnCl_6$ 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

$$T_1^{-1} = (1/4)\,\{T_1(NH_3^+)\}^{-1} + (3/4)\,\{T_1(\text{tert-butyl})\}^{-1} , \qquad (9)$$

where $T_1(NH_3^+)$ and $T_1$(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 kJ mol$^{-1}$) for the $NH_3^+$ motion, comparable to 7.9–10.1 kJ mol$^{-1}$ for the same motion obtained in $(\text{t-BA})_2TeX_6$ (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 $(\text{t-BA})_2TeX_6$ (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.

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