Chlorine Nuclear Quadrupole Relaxation and Cationic Motion in Trimethylsulfonium Hexachloroselenate(IV): $[(CH_3)_3S]_2SeCl_6$*

Makoto Kaga, Tetsuo Asaji, Ryuichi Ikeda[a], and Daiyu Nakamura[b]

Department of Chemistry, Faculty of Science, Nagoya University,
Nagoya 464-01, Japan

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The ^{35}Cl NQR spin-lattice and spin-spin relaxation times, T_{1Q} and T_{2Q}, respectively, and the ^{1}H NMR spin-lattice relaxation time T_{1H} at 32 and 60 MHz were determined for $[(CH_3)_3S]_2SeCl_6$ as functions of temperature. The rapid decrease of T_{1Q} observed above ca. 250 K with increasing temperature was attributed to the onset of reorientation of the $[SeCl_6]^{2-}$ complex anion with the activation energy $E_a = 42 \pm 5$ kJ mol^{-1}. When cooled from ca. 250 K, T_{1Q} showed an anomalous decrease. This T_{1Q} decrease was explained by electric field gradient modulation related to some cationic motion. Possible origins of the cationic motion are discussed.

Key words: Spin-lattice relaxation, NQR, NMR, EFG modulation, Molecular motion.

1. Introduction

A new relaxation mechanism of chlorine NQR, unexplainable by reorientation or lattice vibrations of complex anions containing the resonant nuclei, has been observed in trimethylsulfonium hexachlorometallates(IV), $[(CH_3)_3S]_2MCl_6$ (M = Sn, Pt) [1]. This mechanism, giving rise to relaxation maximum with decreasing temperature, is expected to be related with some motion of the counter cation. The C_3 reorientation of CH_3 group about its triad axis seems to be little important because no such relaxation anomaly has been observed in trimethylammonium hexachlorostannate(IV), $[(CH_3)_3NH]_2SnCl_6$, and tetramethylphosphonium hexachlorostannate(IV), $[(CH_3)_4P]_2SnCl_6$, having crystal structures very close to that of the trimethylsulfonium salt.

In order to obtain further information about the electric field gradient (EFG) modulated by cationic motions, ^{35}Cl NQR spin-lattice and spin-spin relaxation times, T_{1Q} and T_{2Q}, respectively, and the ^{1}H NMR spin-lattice relaxation time T_{1H} are measured for $[(CH_3)_3S]_2SeCl_6$ as functions of temperature.

2. Experimental

Using a pulsed NQR spectrometer described elsewhere [2, 3], T_{1Q} and T_{2Q} were determined from the height of echo signals observed after the pulse sequences, $\pi - \tau - \pi/2 - \tau_e - \pi$ and $\pi/2 - \tau - \pi$, respectively, where the echo height was observed at various interpulse spacing time τ, while τ_e was set constant (ca. 150 µs). The length of a π pulse was ca. 30 µs. Recovery and decay of the echo amplitude against τ and 2τ in the T_{1Q} and T_{2Q} measurements, respectively, could be fitted to the simple exponential law usually employed in pulsed NMR experiments [4]. A pulsed NMR spectrometer [5] was employed to determine T_{1H} at Larmor frequencies of 32 and 60 MHz, using the usual $\pi - \tau - \pi/2$ method. The error of the relaxation times is expected to be less than ca. 10 and 20% in NMR and NQR measurements, respectively. The sample temperature was controlled within ± 0.5 K and estimated to be accurate within ± 1 K. Differential thermal analysis (DTA) was performed employing a homemade apparatus [6]. The sample, which was used in the previous NQR study [7], was employed in the present NQR measurements. The sample for the NMR measurements was newly prepared in a similar way as in [7].

3. Results

The temperature dependence of the ^{35}Cl NQR frequencies observed for $[(CH_3)_3S]_2SeCl_6$ agreed well

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[a] Present address: Department of Chemistry, University of Tsukuba, Tsukuba 305, Japan.

[b] Deceased.

Reprint requests to Dr. Tetsuo Asaji, Department of Chemistry, Faculty of Science, Nagoya University, Nagoya 464-01, Japan.

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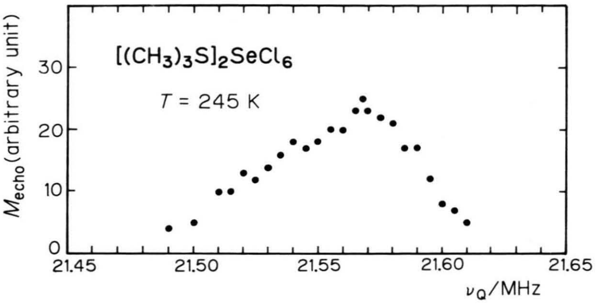

Fig. 1. The frequency dependence of the spin-echo-height observed for $[(CH_3)_3S]_2SeCl_6$ at $T = 245$ K.

with those reported earlier [7]. The signal could be observed only in the restricted temperature range of ca. 150–350 K. However, no phase transition was observed in DTA measurements. Since NQR signals with a very broad line-width (50–100 kHz) were observed, the resonance frequency was determined by plotting echo-heights against the irradiated rf frequencies at each temperature. One such plot, bearing a marked asymmetry, is shown in Figure 1. The frequencies at the maximum echo-heights are plotted as functions of temperature in Figure 2. The bar shows the half-height width of the echo-envelope.

The temperature dependences of ^{35}Cl T_{1Q} and T_{2Q}, determined at the frequencies with the maximum echo-heights, are shown in Fig. 3 together with that of T_{1H}. The shortening of T_{2Q} is responsible for the disappearance of the NQR signal both at low and high temperatures. The rapid decrease of T_{1Q} observed above ca. 250 K with increasing temperature is attributable to the onset of reorientation of the $[SeCl_6]^{2-}$ complex anions with the activation energy $E_a = 42 \pm 5$ kJ mol^{-1} [8]. When cooled from ca. 250 K, T_{1Q} decreased to 3 ms at ca. 170 K. This T_{1Q} decrease is much steeper than those in the corresponding Pt and Sn complexes [1].

The 32 MHz T_{1H} showed two minima of 27 ms (at ca. 130 K) and 48 ms (at ca. 370 K) describable by the C_3 reorientations of the CH_3 groups and the whole cation about their triad axes, respectively, by referring to the reported assignments of ^{1}H NMR observed in the analogous complexes $[(CH_3)_3S]_2MCl_6$ (M = Pt, Sn, Te) having the isomorphous structure with the present complex [7]. The activation energy $E_a = 6 \pm 0.5$ kJ mol^{-1} evaluated for the CH_3 reorientation in the temperature range of ca. 150–250 K disagrees with $E_a = 9 \pm 1$ kJ mol^{-1} derived from the slope of log T_{1Q} vs. T^{-1} plot below ca. 250 K.

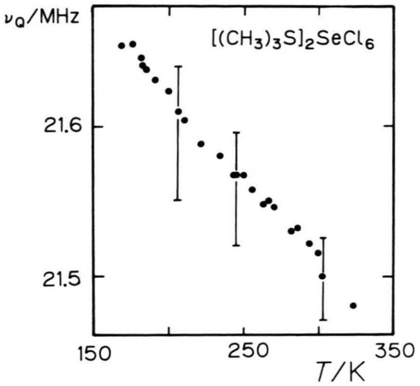

Fig. 2. The temperature dependence of ^{35}Cl NQR frequency of $[(CH_3)_3S]_2SeCl_6$. The bar shows the half-height width of the echo-envelope.

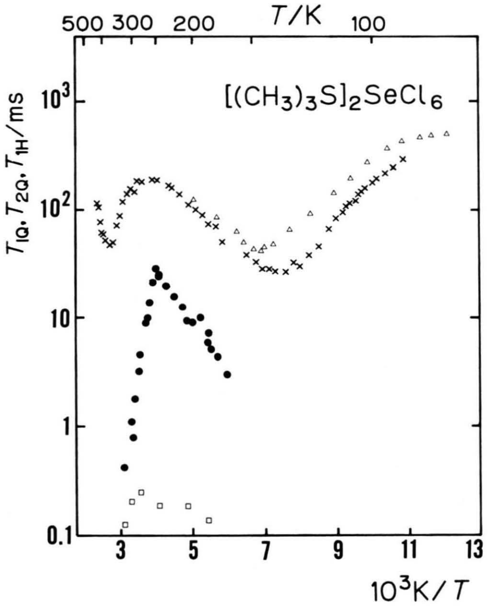

Fig. 3. The temperature dependences of ^{35}Cl NQR spin-lattice and spin-spin relaxation times, T_{1Q} (●) and T_{2Q} (□), respectively, compared with that of ^{1}H NMR spin-lattice relaxation times T_{1H} at Larmor frequencies of 32 (×) and 60 (△) MHz.

4. Discussion

The above mentioned new relaxation mechanism of chlorine NQR observed in the low-temperature range for $[(CH_3)_3S]_2MCl_6$ (M = Pt, Sn, Se) is explainable by the EFG modulation due to some cationic motion. This motion was expected in the previous report [1] to be characteristic for the $[(CH_3)_3S]^+$ cation having lone-pair electrons and not attributable to a simple CH_3 reorientation by 120° about the S–C bond. This is because the chlorine relaxations were quite normal in $[(CH_3)_3NH]_2SnCl_6$ and $[(CH_3)_4P]_2SnCl_6$, and moreover, for $[(CH_3)_3S]_2PtCl_6$, the correlation time of the motion responsible for the EFG modulation was elucidated to be much shorter than that of the CH_3 reorientation [1]. It has recently been reported that a similar EFG modulations due to cationic motions is operative also in $[(CH_3)_4N]_2MCl_6$ (M = Pb, Sn, Te), in which a detailed analysis of the chlorine relaxation is prevented by the existence of a structural phase transition [9]. Now, our question is what is the origin of the cationic motion which causes the EFG modulation. To answer this question, the cationic orientations in the crystal lattice are compared for the series of complexes so far studied in Table 1. In the compounds in which chlorine EFG modulation was observed, at least some cations $[(CH_3)_3YL]^+$, where L is CH_3, H or lone-pair electrons and Y is N or S, are located at a high symmetry site and the Y–L vector points at an empty site of the complex ions in the cubic structure. This cationic orientation may be related to a possible disorder in the cationic position, which is suggested by the very broad NQR linewidth observed. When the CH_3 group or the whole cation reorients among the disordered sites, the chlorine EFG is very likely to be modulated. Repulsion between the lone-pair electrons of $[(CH_3)_3S]^+$ ions and chlorines is expected to be one of the reasons why the lone-pair axis of the cation prefers to point at an empty site.

Table 1. The cationic orientation in the crystal lattice of $[(CH_3)_3YL]_2SnCl_6$ and chlorine EFG modulation due to cationic motions.

Compounds	Crystal symmetry	Y–L vector orientation	Chlorine EFG modulation
$[(CH_3)_3NH]_2SnCl_6$	cubic Pa3, $Z = 4$[a]	N–H vector pointed at a $[SnCl_6]^{2-}$ site	No
$[(CH_3)_3S]_2SnCl_6$	cubic Pa3, $Z = 4$[b]	lone-pair axis pointed at an empty site	Yes
$[(CH_3)_4N]_2SnCl_6$	cubic Fd3c, $Z = 32$[c]	cation at 23 site: N–CH_3 vectors pointed at empty sites; cation at $\bar{4}$ site: N–CH_3 vector pointed at one particular halogen	Yes
$[(CH_3)_4P]_2SnCl_6$	lower than cubic[d]	unknown	No

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As an experimental fact that supports the above disorder model of the cationic position, in our preliminary measurements we observed a shallow T_{1H} minimum of ^1H NMR in $[(CH_3)_3S]_2PtCl_6$ at a temperature close to that for the minimum of Cl NQR T_{1Q} reported previously [1]. This result suggests that a small-angle reorientation of the CH_3 group or the whole cations, which makes EFG modulation at the chlorines, takes place in the $[(CH_3)_3S]^+$ cation. However, the X-ray diffraction analysis of $[(CH_3)_3S]_2SnCl_6$ [10] does not show any remarkable sign of disorder of the cationic position. Therefore, a possible disorder will be of hydrogen atoms in the CH_3 groups.

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