Electric field Gradient Modulation by Motion of Lone-Pair Electrons in $[(CH_3)_3S]_2MCl_6$ (M = Pt, Sn) as a Possible Relaxation Mechanism of Chlorine Nuclear Quadrupole Resonance

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Z. Naturforsch. **45a**, 1033–1037 (1990); received May 26, 1990

The temperature dependence of the chlorine NQR spin-lattice relaxation time T_{1Q} was observed for trimethylsulfonium hexachlorometallates(IV), $[(CH_3)_3S]_2MCl_6$ (M = Pt, Sn), trimethylammonium hexachlorostannate(IV), $[(CH_3)_3NH]_2SnCl_6$, and tetramethylphosphonium hexachlorostannate(IV), $[(CH_3)_4P]_2SnCl_6$. The quadrupolar relaxation in $[(CH_3)_3NH]_2SnCl_6$ and $[(CH_3)_4P]_2SnCl_6$ can be described by the usual librational and reorientational motion of the complex anion at lower and higher temperatures, respectively. Besides T_{1Q} due to these two mechanisms, T_{1Q} minimum was observed at ca. 90 and 120 K for $[(CH_3)_3S]_2PtCl_6$ and $[(CH_3)_3S]_2SnCl_6$, respectively, which is attributable to the electric field gradient modulation by the motion of the $[(CH_3)_3S]^+$ cation having lone-pair electrons. The activation energies for the isotropic reorientation of the complex anion were determined as 46, 65, 59, and 60 kJ mol^{-1} for $[(CH_3)_4P]_2SnCl_6$, $[(CH_3)_3NH]_2SnCl_6$, $[(CH_3)_3S]_2PtCl_6$, and $[(CH_3)_3S]_2SnCl_6$, respectively.

Key words: Nuclear Quadrupole Resonance, Spin-Lattice Relaxation, EFG Modulation, Lone-Pair Electrons

1. Introduction

In some cases, the nuclear relaxation in nuclear quadrupole resonance (NQR) is determined by the motion of neighboring atomic groups or counter ions instead of the motion of the resonant nucleus itself. We have found that this relaxation mechanism is effective in Cl NQR of $(pyH)AuCl_4$ [1], $(pyH)ICl_4$ [2], and $(pyH)_2MCl_6$ (M = Sn, Pb, Te) [3, 4]. In these crystals, the motion of the pyridinium ion yields an appreciable fluctuation of the electric field gradient (EFG) at the quadrupolar nuclei of the counter ions. As an extension of these studies, the influence of the motion of another type of counter cation on nuclear relaxation is investigated in the present Cl NQR study of $[(CH_3)_3S]_2MCl_6$ (M = Pt, Sn), $[(CH_3)_3NH]_2SnCl_6$, and $[(CH_3)_4P]_2SnCl_6$. The ^1H NMR study of the cationic motion and the temperature dependences of the ^{35}Cl NQR frequencies in $[(CH_3)_3S]_2MCl_6$ and $[(CH_3)_3NH]_2SnCl_6$ have already been reported [5, 6].

2. Experimental

The spin-lattice relaxation time T_{1Q} was measured with the pulse sequence π-τ-$(\pi/2)$-τ_e-π using a homemade pulsed NQR spectrometer [7, 8], where τ_e was set constant (ca. 100 μs) for observing echo signals. The sample temperature was controlled within ±0.5 K and estimated to be accurate within ±1 K. The error of the T_{1Q} value was less than ca. 20%. Differential thermal analysis (DTA) was performed employing a homemade apparatus which enables measurements down to ca. 45 K using liquid He as a cryogen [9]. The samples were prepared in the similar way as in [5, 6] and were identified, except for $[(CH_3)_4P]_2SnCl_6$, by X-ray powder patterns as well as by observing ^{35}Cl NQR frequencies which were reported earlier [5, 6]. From usual elementary analysis the new compound $[(CH_3)_4P]_2SnCl_6$ was confirmed. Anal. Calcd. for $[(CH_3)_4P]_2SnCl_6$: C, 18.71%; H, 4.71%. Found: C, 18.56%; H, 4.88%.

3. Results

The temperature dependences of the ^{35}Cl NQR frequencies observed for $[(CH_3)_3S]_2MCl_6$ (M = Pt, Sn)

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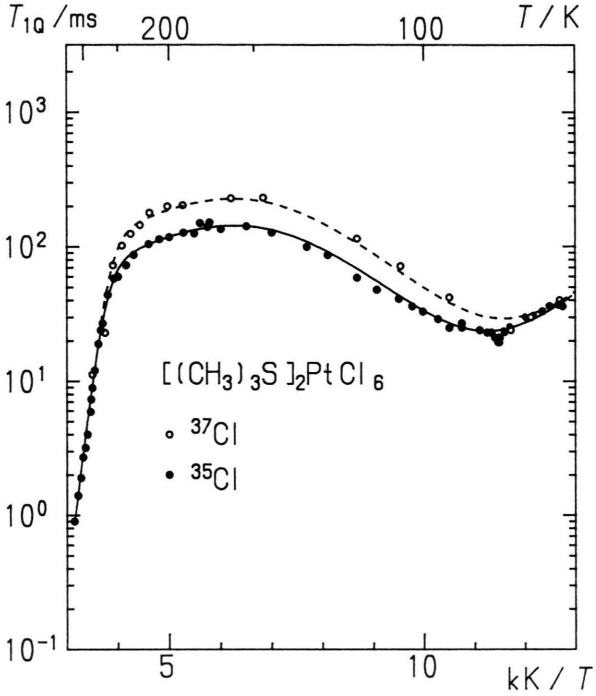

Fig. 1. The temperature dependence of the quadrupole spin-lattice relaxation time T_{1Q} for chlorine nuclei in the crystal of trimethylsulfonium hexachloroplatinate(IV). Solid and dashed lines indicate the theoretical curves calculated for ^{35}Cl and ^{37}Cl, respectively (see text).

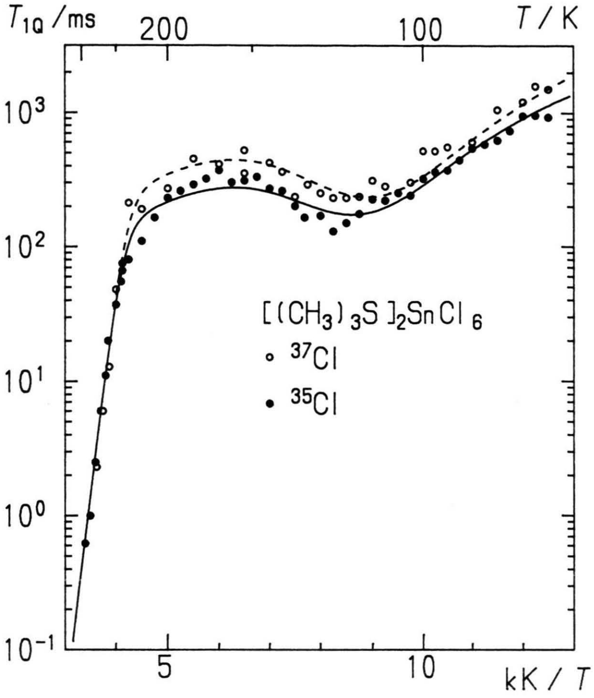

Fig. 2. The temperature dependence of the quadrupole spin-lattice relaxation time T_{1Q} for chlorine nuclei in the crystal of trimethylsulfonium hexachlorostannate(IV). Solid and dashed lines indicate the theoretical curves calculated for ^{35}Cl and ^{37}Cl, respectively (see text).

and $[(CH_3)_3NH]_2SnCl_6$ showed good agreement with those reported earlier [5, 6]. As for the new compound $[(CH_3)_4P]_2SnCl_6$, we found two ^{35}Cl NQR lines at 16.747 ± 0.002 and 16.929 ± 0.002 MHz with the intensity ratio of ca. 1:2 at 80 K. These NQR results and the X-ray powder patterns taken at room temperature indicate a deviation of the crystal symmetry from cubic. The temperature dependence of the ^{35}Cl T_{1Q} relaxation time was determined in the present study only for the lower frequency line.

The temperature dependences of ^{35}Cl, ^{37}Cl T_{1Q} relaxation times in $[(CH_3)_3S]_2PtCl_6$ and $[(CH_3)_3S]_2SnCl_6$ are shown in Figs. 1 and 2, respectively. For both compounds a steep T_{1Q} decrease was observed above ca. 270 K. With decreasing temperature from ca. 160 K, a broad T_{1Q} minimum was located at ca. 90 and 120 K for $[(CH_3)_3S]_2PtCl_6$ and $[(CH_3)_3S]_2SnCl_6$, respectively. The isotope ratios $T_{1Q}(^{37}Cl)/T_{1Q}(^{35}Cl)$ for $[(CH_3)_3S]_2PtCl_6$ have been found to be 1.0 ± 0.2, 1.7 ± 0.2, and 1.0 ± 0.2 in the temperature ranges: above 270 K, 100–200 K, and below 90 K, respectively.

Near the temperature of the T_{1Q} minimum the DTA did not show any heat anomaly for the both compounds. Also no anomalous behavior has been found in the temperature dependences of the ^{35}Cl NQR frequencies, as shown in Figure 3.

The temperature dependences of the ^{35}Cl T_{1Q} relaxation time of $[(CH_3)_3NH]_2SnCl_6$ and $[(CH_3)_4P]_2SnCl_6$ are shown in Figure 4. T_{1Q} showed a steep decrease above ca. 250 and 200 K for $[(CH_3)_3NH]_2SnCl_6$ and $[(CH_3)_4P]_2SnCl_6$, respectively. Below the respective temperature, the T_{1Q} values increased monotonously with decreasing temperature.

4. Discussion

The crystals of $[(CH_3)_3S]_2MCl_6$ (M = Pt, Sn) and $[(CH_3)_3NH]_2SnCl_6$ belong to the space group Pa3 with $Z = 4$ [5, 6, 10–12]. All 24 Cl atoms in the primitive unit cell are crystallographically equivalent. This is in good agreement with the observed single ^{35}Cl NQR line in each compound.

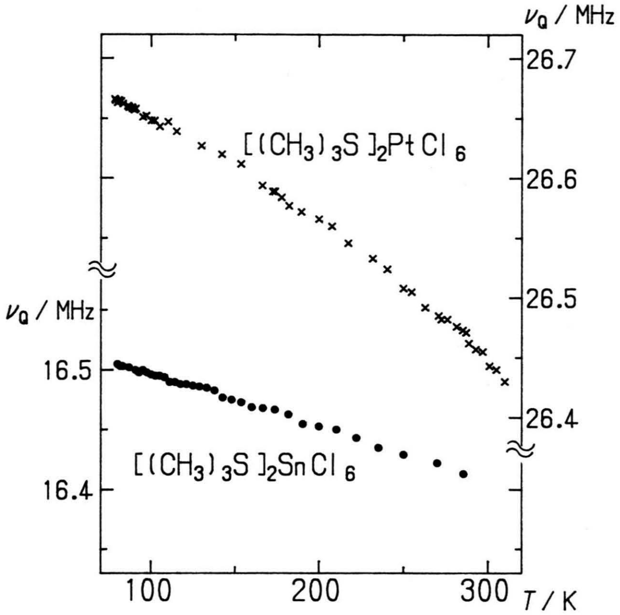

Fig. 3. The temperature dependences of ^{35}Cl NQR frequencies of trimethylsulfonium hexachloroplatinate(IV): × and trimethylsulfonium hexachlorostannate(IV): ●.

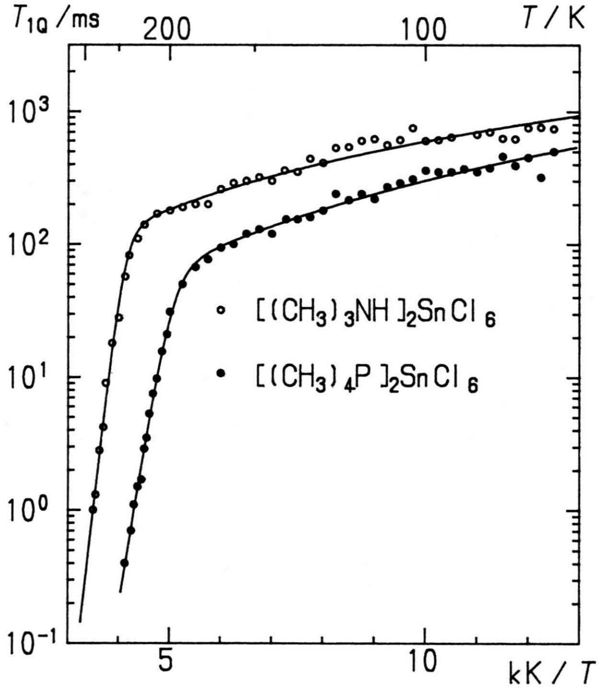

Fig. 4. The temperature dependences of ^{35}Cl NQR spin-lattice relaxation time T_{1Q} of trimethylammonium hexachlorostannate(IV): ○ and tetramethylphosphonium hexachlorostannate(IV): ●.

The steep T_{1Q} decrease at higher temperatures can be assigned to the reorientational motion of complex anions [13], while the relaxation at lower temperatures in $[(CH_3)_3NH]_2SnCl_6$ and $[(CH_3)_4P]_2SnCl_6$ (Fig. 4) is explainable by librational motion [14]. On the other hand, the temperature dependence of T_{1Q}, showing a minimum at ca. 90 and 120 K for $[(CH_3)_3S]_2PtCl_6$ and $[(CH_3)_3S]_2SnCl_6$, respectively, can not be interpreted by the above two mechanisms. The increase of the relaxation rate due to a structural phase transition may account for the anomalous temperature dependence of T_{1Q}. However, no heat anomaly has been detected by DTA, and also no anomalous behavior in the temperature dependence of the ^{35}Cl NQR frequency around the T_{1Q} minimum temperature has been found (Figure 3).

Therefore we interpret this minimum as a result of the EFG modulation due to the motion of the $[(CH_3)_3S]^+$ cations. The isotope ratio $T_{1Q}(^{37}Cl)/T_{1Q}(^{35}Cl)$ of 1.7 and 1.0 above and below the T_{1Q} minimum temperature, respectively, is consistent with the modulation mechanism, while it is expected to be 1.6 on both sides of the T_{1Q} minimum if the softening of the vibrational mode due to a phase transition is responsible for the T_{1Q} minimum [2].

The total relaxation rate T_{1Q}^{-1} of the chlorine nuclei is assumed to be the sum of contributions from (i) the libration of the complex anions as well as the cations, $(T_{1Q}^{-1})_{\text{latt}}$, (ii) the modulation of the EFG due to a motion of the cation, $(T_{1Q}^{-1})_{\text{mod}}$, and (iii) the reorientation of complex anions, $(T_{1Q}^{-1})_{\text{reor}}$. Then, the observed T_{1Q} can be written as

$$T_{1Q}^{-1} = (T_{1Q}^{-1})_{\text{latt}} + (T_{1Q}^{-1})_{\text{mod}} + (T_{1Q}^{-1})_{\text{reor}}, \tag{1}$$

where the motions are assumed to be independent. Assuming a cationic motion among three equal potential wells and an isotropic reorientation of the complex anion, one has the respective contributions [13–15]

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

$$(T_{1Q}^{-1})_{\text{mod}} = (2/3)\,\omega_Q^2 (q'/q)^2 \cdot \tau_m/(1+\omega_Q^2 \tau_m^2), \tag{3}$$

$$(T_{1Q}^{-1})_{\text{reor}} = 6\,\tau_0^{-1} \exp(-E_a/R\,T). \tag{4}$$

In (3), (q'/q), τ_m, and ω_Q denote the modulation fraction of the EFG, the correlation time for the EFG modulation, and the nuclear quadrupole angular resonance frequency of chlorine, respectively. The temperature dependence of τ_m is assumed as

$$\tau_m = \tau_{m0} \exp(E_{am}/R\,T) \tag{5}$$

Table 1. The optimized parameters for the three independent spin-lattice relaxation rate equations (2), (3), and (4) due to libration, the EFG modulation, and the reorientation of complex anion, respectively (see text).

Compounds	Libration			Modulation		Reorientation	
	n	$a/s^{-1}\,K^{-n}$	(q'/q)	τ_{m0}/s	$E_{am}/kJ\,mol^{-1}$	τ_0/s	$E_a/kJ\,mol^{-1}$
$[(CH_3)_3S]_2PtCl_6$	2.0	2.1×10^{-4}	8.8×10^{-4}	9.3×10^{-13}	6.1 ± 0.3	1.7×10^{-12}	59 ± 2
$[(CH_3)_3S]_2SnCl_6$	2.2	3.9×10^{-5}	3.6×10^{-4}	4.2×10^{-12}	7.4 ± 0.7	9.4×10^{-14}	60 ± 2
$[(CH_3)_3NH]_2SnCl_6$	1.7	6.7×10^{-4}	–	–	–	8.1×10^{-15}	65 ± 3
$[(CH_3)_4P]_2SnCl_6$	2.2	1.1×10^{-4}	–	–	–	3.1×10^{-13}	46 ± 1

with the activation energy E_{am} for the cationic motion. In (4), E_a represents the activation energy for the isotropic reorientation of the octahedral complex anions in the crystal, and τ_0 is the correlation time for the motion at infinite temperature.

By use of (1) a fitting calculation to the observed ^{35}Cl T_{1Q} values of $[(CH_3)_3S]_2PtCl_6$ and $[(CH_3)_3S]_2SnCl_6$ was performed, in which $(\omega_Q/2\pi)$ of ^{35}Cl was fixed at the values of 26.6 and 16.5 MHz, respectively. Fitting calculations for $[(CH_3)_3NH]_2SnCl_6$ and $[(CH_3)_4P]_2SnCl_6$ were also done without the modulation term in (1). The calculations were carried out using the least-squares program SALS [16]. The values of the obtained optimized parameters are given in Table 1. The best-fitted curves are shown in Figs. 1, 2, and 4 by solid lines. For $[(CH_3)_3S]_2PtCl_6$ and $[(CH_3)_3S]_2SnCl_6$, the temperature dependence curves of ^{37}Cl T_{1Q} were also calculated using the foregoing best-fitted parameters derived from the ^{35}Cl T_{1Q} data. In these calculations, the values of a and ω_Q^2 were divided by the square of the chlorine nuclear quadrupole moment ratio

$$[eQ(^{35}Cl)/eQ(^{37}Cl)]^2 = 1.61 \tag{6}$$

in order to correct the difference of the quadrupole interaction energies of both chlorine isotopes. The agreement between the theoretical curves indicated by dashed lines in Figs. 1 and 2, and the observed values of ^{37}Cl T_{1Q} is quite good.

Assuming the EFG modulation to be due to the motion of $[(CH_3)_3S]^+$, the present Cl T_{1Q} data can be reasonably well interpreted. However, the question arises about the kind of motion responsible for this modulation. First we considered the CH_3 group reorientation, since it is expected from the ^1H NMR study [5] that the frequency of CH_3 reorientation becomes close to the Cl NQR frequencies of the present compounds at the temperatures around 100–200 K. The ^1H NMR spin-lattice relaxation time T_1 shows a minimum at ca. 150 and 130 K for $[(CH_3)_3S]_2PtCl_6$ and $[(CH_3)_3S]_2SnCl_6$, respectively, using the Larmor frequency 20.0 MHz, and this minimum is attributable to the CH_3 reorientation [5].

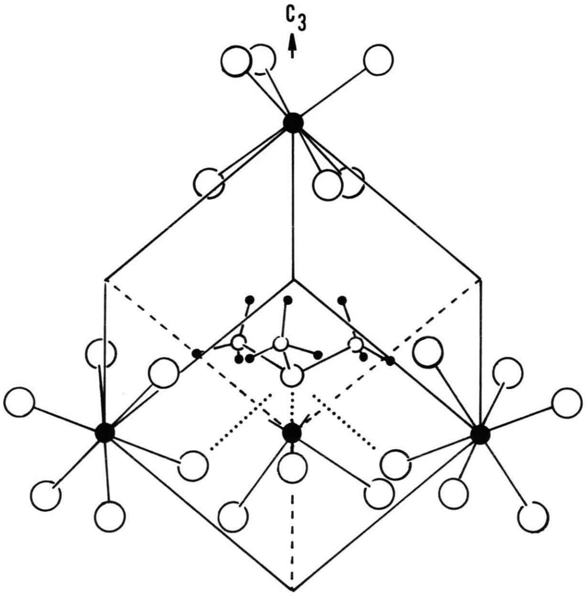

Fig. 5. Atomic arrangement in a 1/8 unit cell of trimethylsulfonium hexachlorostannate(IV) crystal belonging to the space group Pa3 with $Z=4$. The S atom is located on the crystallographic C_3 axis and the site symmetry of the complex anion is C_{3i}. The three shortest S ... Cl distances, 3.50 Å, are indicated by the dotted lines.

The ^{35}Cl T_{1Q} minimum was observed at ca. 90 K for $[(CH_3)_3S]_2PtCl_6$, having a ^{35}Cl NQR frequency of ca. 26.6 MHz. If the T_{1Q} minimum is attributable to the EFG modulation by CH_3 group reorientation, the minimum should occur at temperatures higher than 150 K. Therefore, the CH_3 reorientation can not be responsible for the observed EFG modulation.

Another motional mode detected in the ^1H NMR study is the reorientation of the whole cation about its C_3 axis. However, this mode becomes frequent enough only at higher temperatures, where it is responsible for a 20.0 MHz ^{1}H NMR T_1 minimum at ca. 400 K. Therefore the C_3 reorientation of the whole cation can also not be considered as the origin of the EFG modulation.

The motion of $[(CH_3)_3S]^+$, which in the present case is responsible for the EFG modulation, must involve an only very small jumping angle of protons since it can not be detected by ^{1}H NMR. It should be noted that the EFG modulation is appreciable only in the compounds having $[(CH_3)_3S]^+$ cations. In $[(CH_3)_3NH]_2SnCl_6$ and $[(CH_3)_4P]_2SnCl_6$ the temperature dependence of T_{1Q} can be described by the librational mechanism at lower temperatures and by the reorientation of the complex anion at higher temperatures (Figure 4). We turned our attention to the existence of the lone-pair electrons in $[(CH_3)_3S]^+$, which distinguishes it from $[(CH_3)_3NH]^+$ and $[(CH_3)_4P]^+$.

The time-dependent interaction between lone-pair electrons and the surroundings may directly or indirectly cause the EFG fluctuation at the Cl site. According to a recent X-ray analysis [11], the shortest S ... Cl distance, 3.50 Å, is somewhat smaller than the sum of the van der Waals radii, 3.65 Å. This suggests weak interactions between S and the three nearest Cl atoms indicated by the dotted lines in Figure 5. If the lone-pair electrons of the S atom reorient dynamically among the three equivalent Cl atoms with or without being accompanied by a small angle reorientation of the whole cation, an EFG fluctuation will be produced at the chlorine nuclei in the course of this motion.

At the present stage there exists no direct evidence that the lone-pair axis and the crystallographic C_3 axis do not coincide. However, it is reported that nucleophilic centers (i.e. halogens etc.) tend to approach sulfonium ions along the directions opposite to the C–S primary bonds. This happens also when a single nucleophile approaches a sulfonium ion in the crystal [17]. This is also the case for $[(CH_3)_3S]_2SnCl_6$, in which the three equivalent Cl atoms have contact with the S atom which is lying on the C_3 axis, and the C–S ... Cl angle along the extension of the C–S primary bond is 166.4° [11]. Therefore, it seems acceptable to assume that the lone-pair axis deflects from the crystallographic C_3 axis by a small angle and dynamically jumps among the three equivalent positions due to an interaction with the three Cl atoms.

Acknowledgements

One of us (P. K.) thanks Japan Society for the Promotion of Science for a grant which enabled him to stay 6 months at Nagoya University.

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