Unusual Temperature Dependence of ^{35}Cl NQR Spin-Lattice Relaxation Time in $[(CH_3)_4N]_2[MCl_6]$ (M = Pb, Sn, Te)

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The temperature dependence of the spin-lattice relaxation time (T_{1H}) of ^{1}H NMR measured in tetramethylammonium hexachloroplumbate(IV), $(Me_4N)_2[PbCl_6]$, showed a deep and a shallow minimum near 190 and 115 K, respectively. Since the presence of two kinds of crystallographically nonequivalent cations in the room-temperature Fd3c unit cell has been reported, the deep T_{1H} minimum was assigned to the overall reorientation of three quarters of the Me_4N^+ ions and the shallow minimum to that of the remaining cations. Two different temperature dependences of the chlorine NQR spin-lattice relaxation time (T_{1Q}), attributable to a modulated electric-field-gradient by the protonic motion, were observed in $(Me_4N)_2[MCl_6]$ (M = Pb, Sn, Te). One is found in the Pb complex whose T_{1Q} stems from the cationic motion responsible for the deep T_{1H} minimum, and the other one is determined by the cationic motion giving the shallow T_{1H} minimum. Although all room-temperature phases of these complexes are well described by the Fd3c unit cell, the presence of different temperature dependences of T_{1Q} suggests that the CH_3 groups in the respective complexes take different orientations in the crystals.

Introduction

Tetramethylammonium hexachloro- and hexabromometallates(IV), $(Me_4N)_2[MX_6]$ (M = Pt, Sn, Te; X = Cl, Br) crystallize into the cubic Fd3c lattice ($Z = 32$) at room temperature [1–4]. Above room temperature they have another cubic phase with an Fm3m ($Z = 4$) lattice, and below room temperature several phases with lower symmetries [3–5]. The temperature dependence of the ^{1}H NMR spin-lattice relaxation time (T_{1H}) of these complexes revealed the presence of two minima in the room-temperature Fd3c phase (for example, see Fig. 1) although the low-temperature minimum in $(Me_4N)_2[PtCl_6]$ and $(Me_4N)_2[SnCl_6]$ is masked by the onset of phase transitions [4, 5]. In the majority of complexes, the high-temperature deep minimum has a shoulder on the high temperature side, and this T_{1H} behavior could be assigned to superimposed C_3 rotation of the CH_3 groups and overall reorientation of the whole cation, occurring with almost the same correlation times in this temperature range. Recently, it has been proposed from ^{2}H NMR studies that both minima are due to the overall reorientations of the cations, a quarter of which perform the reorientations at temperatures lower than the rest of the cations [6].

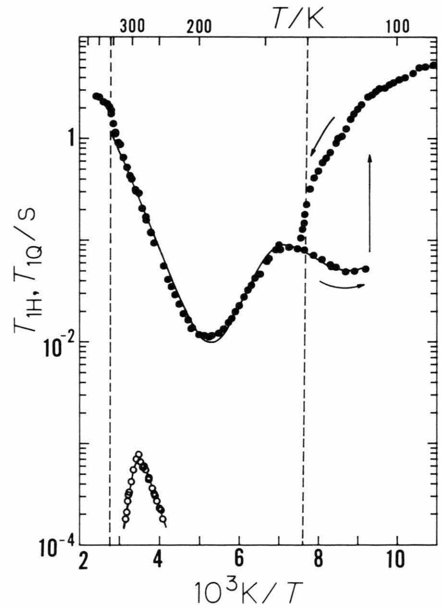

Fig. 1. Temperature dependences of ^{1}H NMR and ^{35}Cl NQR spin-lattice relaxation times (T_{1H} and T_{1Q}, respectively) in $(Me_4N)_2[PbCl_6]$. T_{1H} was measured at 20 MHz. ●: T_{1H}; ○: T_{1Q}. The solid lines for T_{1H} and T_{1Q} are calculated using (1) and (3), respectively. Broken lines indicate the phase transition temperatures determined by DTA.

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In the present study we measured chlorine NQR spin-lattice relaxation times (T_{1Q}) in $(Me_4N)_2[MCl_6]$ (M = Pb, Sn, Te) as functions of temperature in order to obtain further information on the protonic motions. Additionally we measured T_{1H} for $(Me_4N)_2[PbCl_6]$, unavailable so far.

Experimental

All compounds were prepared as in [5, 7]. Differential thermal analysis (DTA) of $(Me_4N)_2[PbCl_6]$ was carried out using a homemade apparatus [8]. ^{1}H NMR and ^{35}Cl NQR T_1 were measured by pulsed spectrometers described elsewhere [5, 9] or a Bruker SXP 4/100 spectrometer. Powder X-ray diffraction patterns of $(Me_4N)_2[PbCl_6]$ were recorded by use of a Rigaku Denki D-3F diffractometer at room temperature. Temperatures were measured by a copper-constantan thermocouple with an accuracy of ± 1 K.

Results and Discussion

DTA and Powder X-ray Diffraction in $(Me_4N)_2[PbCl_6]$

We measured DTA for $(Me_4N)_2[PbCl_6]$ above ca. 80 K. Two heat anomalies were found at 130 and 359 K on heating. The low-temperature one showed a remarkable thermal hysteresis (ca. 20 K), implying that the transition is of first-order. The high-temperature anomaly was accompanied by a long tail on the low temperature side and gave the same peak temperature (359 K) on both cooling and heating. We call, hereafter, the solid phases obtainable above 359 K, below 130 K, and between these two temperatures as high-, low-, and room-temperature phases, respectively. Powder X-ray diffraction patterns recorded at room temperature could be well indexed by assuming a face-centered cubic lattice with $a_0 = 2.578$ nm. This result indicates that the room-temperature phase of $(Me_4N)_2[PbCl_6]$ is isomorphous with the other hexahalometallates(IV) with the Fd3c space group. The high-temperature phase of the Pb complex is analogously expected to have the Fm3m lattice with a lattice constant one half of the Fd3c unit cell, as observed in the other complexes [3, 4].

^1H T_1 in $(Me_4N)_2[PbCl_6]$

Figure 1 shows the temperature dependence of ^{1}H T_1 in $(Me_4N)_2[PbCl_6]$, measured at 20 MHz. In the room-temperature and its supercooled phase, two T_{1H} minima were located at ca. 190 and 115 K. When this phase was cooled, T_{1H} discontinuously lengthened at ca. 110 K and then gradually increased down to 90 K. Since the ^{1}H magnetization recovery curve for T_{1H} became nonexponential below 110 K, the longer component of T_{1H} was plotted in Figure 1. The T_{1H} measurement in the heating process, carried out after keeping the sample at liquid nitrogen temperature for several hours, gave an exponential T_{1H} decay, and the value of T_{1H} decreased smoothly up to the transition point. Just above 130 K, the magnetization recovery became nonexponential, and T_{1H} determined from the initial part of the recovery curve decreased and became close to T_{1H} in the room-temperature phase observed in the cooling run. This behavior of T_{1H} is quite analogous to those in the other complexes already reported, especially $(Me_4N)_2[TeCl_6]$ [4, 5].

The almost symmetric temperature dependence of the deep T_{1H} minimum indicates that the CH_3 rotation has a correlation time approximately equal to or greater than that of the rotation of the whole cation [10]. Here, we assume that these two relaxation processes can be expressed by a single BPP-type equation [10] given by

$$T_{1H}^{-1} = C\{\tau/(1+\omega^2\tau^2) + 4\tau/(1+4\omega^2\tau^2)\}, \quad (1)$$

where C, τ, and ω are a constant determined by the ionic motion in question, its correlation time, and the Larmor frequency, respectively. An Arrhenius-type relationship is assumed for τ:

$$\tau = \tau_0 \exp(E_a/RT). \quad (2)$$

In the analysis it was assumed that the T_{1H} data in the whole room-temperature phase can be expressed by the superposition of two relaxation processes, each obeying (1). The motional parameters determined for the two modes are listed in Table 1.

The shallow T_{1H} minimum yields $E_a = 8.3$ kJ mol^{-1}, being significantly lower than the CH_3 torsion barrier in Me_4N^+ ion, which is usually 17–21 kJ mol^{-1} [11]. Accordingly, it is difficult to assign this minimum to the CH_3 group rotation. In the Fd3c unit cell of the room-temperature phase there exist two kinds of crystallographically nonequivalent Me_4N^+ ions: 48 cations {hereafter denoted by $Me_4N^+(3)$} occupy sites of the point symmetry $\bar{4}$ and the remaining 16 cations {$Me_4N^+(1)$} occupy 23 sites. The crystal structure has been studied in detail on isomorphous $(Me_4N)_2[TeBr_6]$, in which the latter type of

Table 1. Motional parameters determined from the relaxation times in the room-temperature phases of $[(CH_3)_4N]_2[MCl_6]$ (M = Pb, Sn, Te). [a] Ref. [5].

Compound	Nucleus	Ion	$E_a(\Delta E)$ / kJ mol^{-1}	τ_0 / s	q'/q
$[(CH_3)_4N]_2[PbCl_6]$	^{1}H	$Me_4N^+(1)$	8.3	7.8×10^{-13}	
	^{1}H	$Me_4N^+(3)$	19.1	2.8×10^{-14}	
	^{35}Cl		21.7	–	0.032
	^{35}Cl	$[PbCl_6]^{2-}$	72.3	2.4×10^{-16}	
$[(CH_3)_4N]_2[SnCl_6]$	^{35}Cl	$[SnCl_6]^{2-}$	71.0	6.3×10^{-16}	
$[(CH_3)_4N]_2[TeCl_6]$	^{1}H	$Me_4N^+(1)$	12.8[a]	–	
	^{35}Cl		–(4.3)	9.7×10^{-13}	0.021

the cations are placed in a large space surrounded by the bromide ions [1]. It can be supposed, therefore, that the low-temperature T_{1H} minimum is due to the overall reorientation of the $Me_4N^+(1)$ ions and the high-temperature minimum to that of the $Me_4N^+(3)$ ions. This model can well explain the temperature dependence of the ^{2}H NMR spectra observed for CD_3 groups in $[(CD_3)_3CH_3N]_2[MBr_6]$(M = Sn, Te) [6] and also the ratio of the observed two T_{1H} minima. Since the barrier of the whole cation reorientation is governed by intermolecular interactions, the small E_a of 8.3 kJ mol^{-1} for the $Me_4N^+(1)$ ions shows that the interactions between the cation and the chloride ions are quite weak.

^1H T_1 and $T_{1\varrho}$ in $(Me_4N)_2[SnCl_6]$

Figure 2 shows the temperature dependences of ^{1}H T_1 at 60 and 20 MHz and $T_{1\varrho}$ observed at a spin-locking rf field, $H_1 = 10$ G, in $(Me_4N)_2[SnCl_6]$ [12]. The temperature variation of T_{1H} at 20 MHz agrees with that already reported [5]. The low-temperature phase, obtainable below the phase transition point of 166 K, has been reported to have a tetragonal unit cell [12]. In this phase, $T_{1\varrho}$ showed a deep minimum at ca. 135 K. This minimum was assigned to CH_3C_3 reorientation by referring to the analogous temperature dependence of $T_{1\varrho}$ observed for $(Me_4N)X$ (X = Cl, I) [10] and $(Me_4N)ClO_3$ [13]. The E_a of the CH_3 rotation determined from the $T_{1\varrho}$ slope is 14.3 kJ mol^{-1}. This E_a value is acceptable for the CH_3 rotation when comparing with those in a similar type of complexes [4, 5].

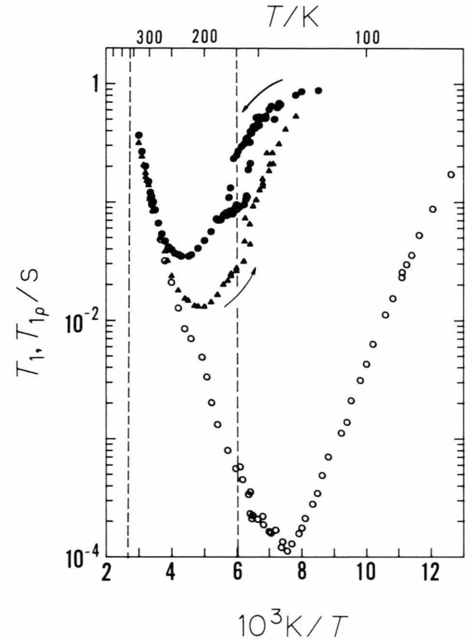

Fig. 2. Temperature dependence of ^{1}H NMR spin-lattice relaxation times in the laboratory (T_{1H}) and rotating frame ($T_{1\varrho}$) in $(Me_4N)_2[SnCl_6]$ [12]. ● and ▲: T_{1H} at 60 and 20MHz, respectively, and ○: $T_{1\varrho}$ at $H_1 = 10$ G. Broken lines show the phase transition temperatures.

^{35}Cl NQR frequency in $(Me_4N)_2[PbCl_6]$

At 299 K, this complex yielded a single ^{35}Cl NQR frequency of 18.539 MHz, in agreement with the previously reported value [7]. The resonance line faded out at ca. 210 K on cooling and around 320 K on heating when the measurements were carried out by a super-regenerative NQR spectrometer. The resonance frequency at 234 and 317 K was 18.660 and 18.494 MHz, respectively.

^{35}Cl NQR T_{1Q} in $(Me_4N)_2[PbCl_6]$

The temperature dependence of the ^{35}Cl T_{1Q} is shown in Figure 1. A maximum of T_{1Q} was located near room temperature. Since T_{1Q} plotted against $1/T$ decreases almost exponentially on both sides of the maximum, T_{1Q} was analyzed by assuming two Arrhenius-type relaxation processes given by

$$T_{1Q}^{-1} = a \exp(-E_{a,\text{reo}}/RT) + b \exp(E_{a,\text{mod}}/RT). \quad (3)$$

By a least-squares fitting calculation the E_a values were determined as listed in Table 1. The best-fitted T_{1Q} curve is shown in Figure 1.

The halogen T_{1Q} in hexahalometallates(IV) having no phase transition is in most cases governed by reorientations of the octahedral $[MX_6]^{2-}$ ions at high temperatures and by lattice vibrations at low temperatures [14]. The T_{1Q} decrease above room temperature is, therefore, assignable to the reorientations of the $[PbCl_6]^{2-}$ anions ($E_{a,\,reo}$ = 72 kJ mol^{-1}). On the other hand, the low temperature behavior of T_{1Q} is unexplainable in terms of lattice vibrations because it lengthens T_{1Q} with decreasing temperature. It is noted that the value of $E_{a,\,mod}$ is almost the same as that for the reorientations of Me_4N^+(3) ions. This suggests that the electric-field-gradient (EFG) at the chlorine sites is strongly modulated by the ionic motion of Me_4N^+(3) ions. This implies, in turn, that this motion takes place between dynamically disordered orientations of the cation; otherwise it gives no marked fluctuation of EFG at the neighboring chlorine sites [15]. Although the atomic positions of the CH_3 groups in this complex are not known, a disordered model of the Me_4N^+(3) ion has been proposed for the $(CD_3)_4N^+$(3) ions in $[(CD_3)_4N]_2[PtCl_6]$ [2]. It is plausible that the orientation of the Me_4N^+(3) ions in $(Me_4N)_2[PbCl_6]$ is disordered and that the cationic reorientations take place among the disordered orientations.

T_{1Q} due to EFG fluctuations by external charges is given by [16]

$$T_{1Q}^{-1} = (1/3)\,\omega_Q^2\,(q'/q)^2\,\tau/(1+\omega_Q^2\,\tau^2), \tag{4}$$

where ω_Q is the angular NQR frequency and q'/q is the fraction of the EFG fluctuation. Since τ was determined from T_{1H}, q'/q was estimated to be 0.032. This q'/q value is much smaller than 0.15 determined from ^{35}Cl T_{1Q} in $(C_5H_6N)_2[MCl_6]$ (M = Sn, Pb) [17], reflecting the spherical and nonpolar structure of the Me_4N^+ ions in comparison with pyridinium cation.

^{35}Cl NQR T_{1Q} in $(Me_4N)_2[SnCl_6]$

The temperature dependence of ^{35}Cl T_{1Q} in $(Me_4N)_2[SnCl_6]$ is shown in Figure 3. In this complex, the NQR signal can be observed even in the low-temperature phase and detected down to 77 K [3]. Above room temperature, T_{1Q} sharply decreased with increasing temperature. Below room temperature, T_{1Q} decreased gradually down to the phase transition temperature of 156 K determined by DTA measured with decreasing temperature [5]. In the low-temperature phase, two ^{35}Cl NQR lines were observed [3]. We determined T_{1Q} of the lower frequency line alone. This T_{1Q} increased to as long as 300 ms at 150 K and gradually increased down to 77 K. The sharp decrease of T_{1Q} observed above room temperature was definitely assigned to the reorientation of the $[SnCl_6]^{2-}$ ions, and its E_a was estimated to be 71 kJ mol^{-1}. The T_{1Q} in the low-temperature phase, showing the T^{-2} dependence, was attributable to lattice vibrations [14, 16]. Since T_{1Q} changes almost exponentially against $1/T$ (with an apparent E_a of ~ 3.5 kJ mol^{-1}) below ca. 250 K in the room-temperature phase, it is unlikely that T_{1Q} is affected by the critical behavior caused by the phase transition. This T_{1Q} variation seems to be related to some kind of cationic motion with a small amplitude. It is possible that the small-angle reorientation of the CH_3 groups [4, 5] or the whole cations taking place in some of the cations in crystals is the origin of this EFG fluctuation.

^{35}Cl NQR T_{1Q} in $(Me_4N)_2[TeCl_6]$

Since the shallow T_{1H} minimum was clearly located in the room-temperature Fd3c phase of this complex [5], we measured the ^{35}Cl T_{1Q} to get information on the assignment of the anomalous T_{1Q} observed in $(Me_4N)_2[SnCl_6]$. The temperature dependence of T_{1Q} in $(Me_4N)_2[TeCl_6]$ (Fig. 4) was similar to that in $(Me_4N)_2[SnCl_6]$, but a shallow T_{1Q} minimum was clearly located at ca. 120 K. At nearly the same temperature (ca. 130 K), the low-temperature T_{1H} minimum is observed. This result strongly suggests that the T_{1Q} decrease below 220 K is governed by the protonic motions contributing to the shallow T_{1H} minimum. However, the apparent E_a value (ca. 4 kJ mol^{-1}) determined from the T_{1Q} data was much smaller than 12.8 kJ mol^{-1} for the Me_4N^+(1) motion derived from T_{1H} [5]. These two kinds of data can be consistently attributed to the same protonic motion if one assume that this motion takes place between unequal potential wells [18]. When this model is adopted, the temperature dependence of T_{1Q} below 220 K in the room-temperature phase of $(Me_4N)_2[TeCl_6]$ is expressed as [17–19]

$$T_{1Q}^{-1} = c\,T^2 + (1/3)\,\{4d/(1+d)^2\}\cdot\omega_Q^2\,(q'/q)^2\,\tau/(1+\omega_Q^2\,\tau^2), \tag{5}$$

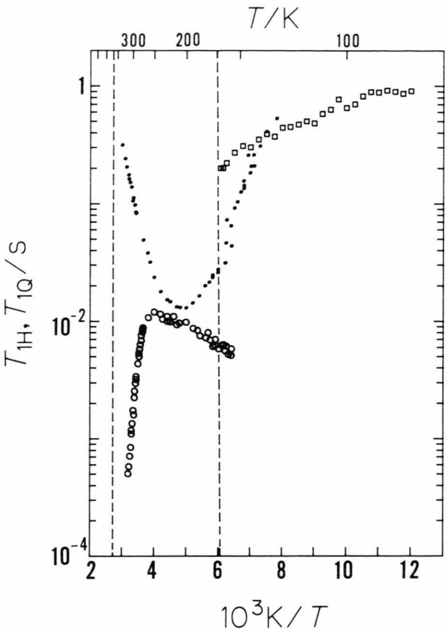

Fig. 3. Temperature dependence of ^{35}Cl NQR T_1 in $(Me_4N)_2[SnCl_6]$. ○: in the room-temperature phase; □: the low-frequency NQR line in the low-temperature phase. ●: T_{1H} at 20 MHz (the same data as given in Figure 2). Broken lines show the phase transition temperatures.

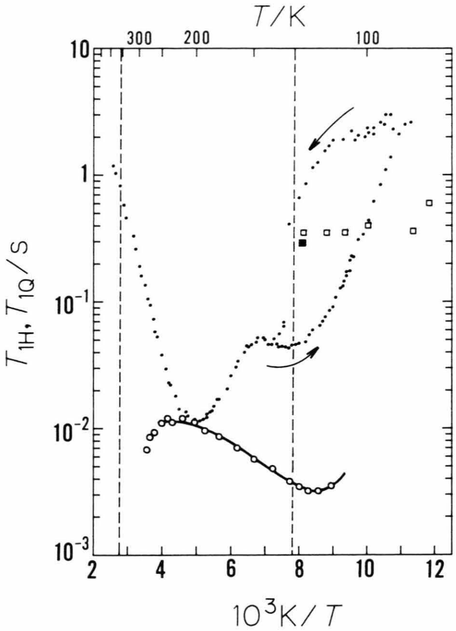

Fig. 4. Temperature dependences of ^{1}H NMR and ^{35}Cl NQR spin-lattice relaxation times (T_{1H} and T_{1Q}, respectively) in $(Me_4N)_2[TeCl_6]$. T_{1H} (●) was measured at 20 MHz [5]. ○: T_{1Q} in the room-temperature phase; □ and ■: T_{1Q} for the low- and high-frequency ^{35}Cl NQR lines in the low-temperature phase, respectively. The solid curve is the calculated T_{1Q} using (5–7). Broken lines show the phase transition temperatures.

where the first term represents the contribution to T_{1Q} from the lattice vibrations and the second from the protonic motion between the unequal potential wells. The parameters d and τ are given by

$$d = \exp(\Delta E/RT), \tag{6}$$

$$\tau = \tau_0 \exp(E_a/RT)/(1+d), \tag{7}$$

where ΔE and E_a are defined in Figure 5.

Equations (5–7) were fitted to the observed T_{1Q} data, where the E_a value was fixed to be 12.8 kJ mol^{-1} as determined from the T_{1H} analysis. The motional parameters thus obtained are given in Table 1. The ΔE and q'/q values are 4.3 kJ mol^{-1} and 0.021, respectively. It has been reported for $(Me_4N)_2[TeBr_6]$ that the thermal parameters of the carbon atoms in the Me_4N^+(1) ions evaluated from the X-ray diffraction data are much larger than those in the Me_4N^+(3) ions [1]. This X-ray result can be explained if the Me_4N^+(1) ions take dynamically disordered two orientations, one of which is stable while the other is metastable. A similar structure is also expectable in the isomorphous hexachloro complex. EFG fluctuation at the chlorine sites can be caused by the jumpings between these two orientations. Small-angle reorientations of the CH_3 groups [4, 5] seem to be another possible origin of this fluctuation.

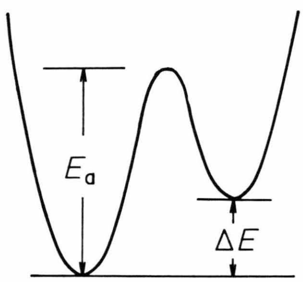

Fig. 5. Unequal potential wells assumed for the protonic motion of Me_4N^+(1) ions.

Conclusion

The temperature dependence of ^{1}H T_1 in $(Me_4N)_2[PbCl_6]$ yields the two minima in the room-temperature phase. These minima are assigned to the overall reorientations of two crystallographically nonequivalent Me_4N^+ ions. The T_{1Q} of ^{35}Cl in the room-temperature phases of $(Me_4N)_2[MCl_6]$ (M = Pb, Sn, Te) is modulated strongly by the protonic motions of the cation, suggesting that these motions take place between disordered orientations. The EFG fluctuation is expected to be produced at the chlorine sites by the protonic motions in the $Me_4N^+(3)$ ions in $(Me_4N)_2[PbCl_6]$ whereas by the $Me_4N^+(1)$ ionic motions in $(Me_4N)_2[MCl_6]$ (M = Sn, Te). Although the crystal structures of the room-temperature phases can be well represented by the same Fd3c lattice for all complexes studied, the microscopic structure of the cation and/or the orientations of the CH_3 groups are expected to be different in the Pb complex from the other two. It is highly desirable to determine CH_3 group orientations in order to thoroughly understand the dynamical behavior of the Me_4N^+ ions in $(Me_4N)_2[MCl_6]$ crystals.

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