Unusual Temperature Dependence of $^{35}$Cl NQR Spin-Lattice Relaxation Time in \([\text{I}(\text{CH}_3)_4\text{N}]_2[\text{MCl}_6]\) (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 hexachloroplatinate(IV), \((\text{Me}_4\text{N})_2[\text{PbCl}_6]\), 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$_4$N$^+$ 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 \((\text{Me}_4\text{N})_2[\text{MCl}_6]\) (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), \((\text{Me}_4\text{N})_2[\text{MX}_6]\) (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 \((\text{Me}_4\text{N})_2[\text{PtCl}_6]\) and \((\text{Me}_4\text{N})_2[\text{SnCl}_6]\) 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 \((\text{Me}_4\text{N})_2[\text{PbCl}_6]\). $T_{1H}$ was measured at 20 MHz.

- $T_{1H}$; o: $T_{1Q}$. 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.
In the present study we measured chlorine NQR spin-lattice relaxation times ($T_1 \rho$) in $(\text{Me}_4\text{N})_2[\text{MCl}_6]$ ($\text{M} = \text{Pb}, \text{Sn}, \text{Te}$) as functions of temperature in order to obtain further information on the protonic motions. Additionally we measured $T_{1\text{H}}$ for $(\text{Me}_4\text{N})_2[\text{PbCl}_6]$, unavailable so far.

**Experimental**

All compounds were prepared as in [5, 7]. Differential thermal analysis (DTA) of $(\text{Me}_4\text{N})_2[\text{PbCl}_6]$ was carried out using a homemade apparatus [8]. $^1\text{H}$ NMR and $^{35}\text{Cl}$ 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 $(\text{Me}_4\text{N})_2[\text{PbCl}_6]$ 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 $\pm 1$ K.

**Results and Discussion**

**DTA and Powder X-ray Diffraction in $(\text{Me}_4\text{N})_2[\text{PbCl}_6]$**

We measured DTA for $(\text{Me}_4\text{N})_2[\text{PbCl}_6]$ 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 $(\text{Me}_4\text{N})_2[\text{PbCl}_6]$ 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].

$^1\text{H} T_1$ in $(\text{Me}_4\text{N})_2[\text{PbCl}_6]$

Figure 1 shows the temperature dependence of $^1\text{H} T_1$ in $(\text{Me}_4\text{N})_2[\text{PbCl}_6]$, measured at 20 MHz. In the room-temperature and its supercooled phase, two $T_{1\text{H}}$ minima were located at ca. 190 and 115 K. When this phase was cooled, $T_{1\text{H}}$ discontinuously lengthened at ca. 110 K and then gradually increased down to 90 K. Since the $^1\text{H}$ magnetization recovery curve for $T_{1\text{H}}$ became nonexponential below 110 K, the longer component of $T_{1\text{H}}$ was plotted in Figure 1. The $T_{1\text{H}}$ measurement in the heating process, carried out after keeping the sample at liquid nitrogen temperature for several hours, gave an exponential $T_{1\text{H}}$ decay, and the value of $T_{1\text{H}}$ decreased smoothly up to the transition point. Just above 130 K, the magnetization recovery became nonexponential, and $T_{1\text{H}}$ determined from the initial part of the recovery curve decreased and became close to $T_{1\text{H}}$ in the room-temperature phase observed in the cooling run. This behavior of $T_{1\text{H}}$ is quite analogous to those in the other complexes already reported, especially $(\text{Me}_4\text{N})_2[\text{TeCl}_6]$ [4, 5].

The almost symmetric temperature dependence of the deep $T_{1\text{H}}$ 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

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

where $C$, $\tau$, and $\omega$ 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 $\tau$:

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

In the analysis it was assumed that the $T_{1\text{H}}$ 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 $T_{1\text{H}}$ minimum yields $E_a = 8.3$ kJ mol$^{-1}$, being significantly lower than the CH$_3$ torsion barrier in Me$_4$N$^+$ 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$_4$N$^+$ ions: 48 cations (hereafter denoted by Me$_4$N$^+$(3)) occupy sites of the point symmetry 4 and the remaining 16 cations (Me$_4$N$^+$(1)) occupy 23 sites. The crystal structure has been studied in detail on isomorphous $(\text{Me}_4\text{N})_2[\text{TeBr}_6]$, in which the latter type of
Table 1. Motional parameters determined from the relaxation times in the room-temperature phases of $[(CH_3)_4N]_2[MC_16]$ (M = Pb, Sn, Te).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Nucleus</th>
<th>Ion</th>
<th>$E_a (\Delta E)$ kJ mol$^{-1}$</th>
<th>$\tau_0$ s</th>
<th>$q'/q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[(CH_3)_4N]_2[SnCl_6]$</td>
<td>$^{35}Cl$</td>
<td>$Sn^{2-}$</td>
<td>71.0</td>
<td>6.3 $\times 10^{-16}$</td>
<td></td>
</tr>
<tr>
<td>$[(CH_3)_4N]_2[TeCl_6]$</td>
<td>$^{35}Cl$</td>
<td>$Te^{2-}$</td>
<td>12.8$^a$</td>
<td>$-$(4.3)</td>
<td>9.7 $\times 10^{-13}$</td>
</tr>
</tbody>
</table>

the cations are placed in a large space surrounded by the bromide ions [1]. It can be supposed, therefore, that the low-temperature $T_{1\text{H}}$ minimum is due to the overall reorientation of the Me$_4^+$ (1) ions and the high-temperature minimum to that of the Me$_4^+$ (3) ions. This model can well explain the temperature dependence of the $^1H$ 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 $T_{1\text{H}}$ 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$_4^+$ (1) ions shows that the interactions between the cation and the chloride ions are quite weak.

$^1H$ $T_1$ and $T_{1\phi}$ in $(Me_4^+N)_2[SnCl_6]$

Figure 2 shows the temperature dependences of $^1H$ $T_1$ at 60 and 20 MHz and $T_{1\phi}$ observed at a spin-locking rf field, $H_l = 10$ G, in $(Me_4^+N)_2[SnCl_6]$ [12]. The temperature variation of $T_{1\text{H}}$ 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, $T_{1\phi}$ showed a deep minimum at ca. 135 K. This minimum was assigned to CH$_3$C$_3$ reorientation by referring to the analogous temperature dependence of $T_{1\phi}$ observed for $(Me_4^+N)X$ (X = Cl, I) [10] and $(Me_4^+N)ClO_3$ [13]. The $E_a$ of the CH$_3$ rotation determined from the $T_{1\phi}$ 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].

$^{35}Cl$ NQR frequency in $(Me_4^+N)_2[PbCl_6]$

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 $T_{1\phi}$ in $(Me_4^+N)_2[PbCl_6]$

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

$$ T_{1\phi}^{-1} = a \exp \left( -E_{\text{a, reco}}/RT \right) + b \exp \left( E_{\text{a, mod}}/RT \right). $$ (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 \([\text{PbCl}_6]^{2-}\) anions (\( E_{a,\text{mod}} = 72 \text{ kJ mol}^{-1} \)). 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 \( E_{a,\text{mod}} \) is almost the same as that for the reorientations of \( \text{Me}_4\text{N}^+ \)(3) ions. This suggests that the electric-field-gradient (EFG) at the chlorine sites is strongly modulated by the ionic motion of \( \text{Me}_4\text{N}^+ \)(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 \( \text{CH}_3 \) groups in this complex are not known, a disordered model of the \( \text{Me}_4\text{N}^+ \)(3) ion has been proposed for the \((\text{CD})_4\text{N}^+ \)(3) ions in \([\text{CD}_3\text{H}_6\text{N}]_2[\text{PtCl}_6] \) [2]. It is plausible that the orientation of the \( \text{Me}_4\text{N}^+ \)(3) ions in \((\text{Me}_4\text{N})_2[\text{PbCl}_6] \) 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]

\[
T_{1Q}^{-1} = (1/3) \omega_0^2 (q'/q)^2 \tau/(1 + \omega_0^2 \tau^2), \tag{4}
\]

where \( \omega_0 \) is the angular NQR frequency and \( q'/q \) is the fraction of the EFG fluctuation. Since \( \tau \) 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 \( ^{35}\text{Cl} T_{1Q} \) in \((\text{C}_2\text{H}_8\text{N})_2[\text{MCl}_6] \) (M = Sn, Pb) [17], reflecting the spherical and nonpolar structure of the \( \text{Me}_4\text{N}^+ \) ions in comparison with pyridinium cation.

\( ^{35}\text{Cl} \) NQR \( T_{1Q} \) in \((\text{Me}_4\text{N})_2[\text{SnCl}_6] \)

The temperature dependence of \( ^{35}\text{Cl} \) \( T_{1Q} \) in \((\text{Me}_4\text{N})_2[\text{SnCl}_6] \) 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 \( ^{35}\text{Cl} \) 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 \([\text{SnCl}_6]^{2-}\) 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 \( \sim 3.5 \text{ kJ mol}^{-1} \)) 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 \( \text{CH}_3 \) groups [4, 5] or the whole cations taking place in some of the cations in crystals is the origin of this EFG fluctuation.

\[ T_{1Q}^{-1} = c T^2 + (1/3) \left( 4d/(1 + d)^2 \right) \cdot \omega_0^2 (q'/q)^2 \tau/(1 + \omega_0^2 \tau^2), \tag{5} \]
where the first term represents the contribution to $T_{1\Omega}$ from the lattice vibrations and the second from the protonic motion between the unequal potential wells. The parameters $d$ and $\tau$ are given by

$$d = \exp(\Delta E/RT),$$

(6)

$$\tau = \tau_0 \exp(E_a/RT)/(1+d),$$

(7)

where $\Delta E$ and $E_a$ are defined in Figure 5.

Equations (5–7) were fitted to the observed $T_{1\Omega}$ data, where the $E_a$ value was fixed to be 12.8 kJ mol$^{-1}$ as determined from the $T_{1\nu}$ analysis. The motional parameters thus obtained are given in Table 1. The $\Delta E$ and $q'/q$ values are 4.3 kJ mol$^{-1}$ and 0.021, respectively. It has been reported for (Me$_4$N)$_2[TeBr_6]$ that the thermal parameters of the carbon atoms in the Me$_4$N$^+$ (1) ions evaluated from the X-ray diffraction data are much larger than those in the Me$_4$N$^+$ (3) ions [1]. This X-ray result can be explained if the Me$_4$N$^+$ (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 fluctuations 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.

**Conclusion**

The temperature dependence of $^1H T_1$ in (Me$_4$N)$_2[PbCl_6]$ yields the two minima in the room-temperature phase. These minima are assigned to the
overall reorientations of two crystallographically nonequivalent Me\textsubscript{4}N\textsuperscript{+} ions. The $T_{10}$ of $^{35}$Cl in the room-temperature phases of (Me\textsubscript{4}N)	extsubscript{2}[MCl\textsubscript{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\textsubscript{4}N\textsuperscript{+}(3) ions in (Me\textsubscript{4}N)	extsubscript{2}[PbCl\textsubscript{6}] whereas by the Me\textsubscript{4}N\textsuperscript{+}(1) ionic motions in (Me\textsubscript{4}N)	extsubscript{2}[MCl\textsubscript{6}] (M = Sn, Te). Although the crystal structures of the room-temperature phases can be well represented by the same Fd\textsubscript{3}c lattice for all complexes studied, the microscopic structure of the cation and/or the orientations of the CH\textsubscript{3} groups are expected to be different in the Pb complex from the other two. It is highly desirable to determine CH\textsubscript{3} group orientations in order to thoroughly understand the dynamical behavior of the Me\textsubscript{4}N\textsuperscript{+} ions in (Me\textsubscript{4}N)	extsubscript{2}[MCl\textsubscript{6}] crystals.

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