Studies on Molecular Motions and Phase Transition in Pyridinium Tetrachloroiodate (III) Crystals by the Measurements of the Temperature Dependences of Chlorine Nuclear Quadrupole. Resonance Frequencies and Relaxation Times

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To elucidate the phase transition of pyridinium tetrachloroiodate(III) at \( T_c = 217 \) K, the temperature dependences of the chlorine NQR frequencies and corresponding NQR spin-lattice and spin-spin relaxation times \( (T_{1Q} \text{ and } T_{2Q}) \) have been measured in the range 77–370 K. Above ca. 370 K and between 206 and 223 K no chlorine NQR frequency could be observed, the chlorine relaxation times becoming extremely short (ca. 100 µs). Except for near \( T_c \), the \( T_{1Q} \) values below ca. 310 K can be explained by fluctuations of the electric field gradient at the chlorine nuclei due to in-plane reorientations of the cations about their pseudohexad axis. The increase of \( T_{1Q} \) in the vicinity of \( T_c \) suggests a critical slowing down of the orientational fluctuations of the cations and a distortion of the complex anions. The decrease of \( T_{1Q} \) above 310 K is considered to be mainly due to the in-plane reorientation of the complex anions. An activation energy of 64 kJ mol\(^{-1}\) is evaluated for that motion.

1. Introduction

Previously, we have studied the motion of pyridinium cations (pyH\(^+\)) in \((\text{pyH})\text{AuCl}_4\) crystals using \(^1\)H NMR [1] and chlorine NQR [2]. In order to elucidate the effect of the motion of pyridinium cations on the quadrupolar relaxation of chlorine nuclei and to clarify the motion of the complex anions themselves, we have extended our NMR-NQR studies to \((\text{pyH})\text{ICl}_4\) crystals. The \((\text{pyH})\text{ICl}_4\) salt, having a square planar anion, is known to undergo a structural phase transition at \( T_c = 215 \) K [3]. It is also one of the important research aims of the present investigation to obtain information about the mechanism of the phase transition.

2. Experimental

We have used a homemade pulsed NQR spectrometer [4, 5]. The pulse sequences \( \pi-\tau-(\pi/2)-\tau-\pi \) and \( (\pi/2)-\tau-\pi \) were employed for the determination of the spin-lattice \( (T_{1Q}) \) and spin-spin \( (T_{2Q}) \) relaxation times, respectively, where \( \tau = \) was set constant (ca. 100 µs) for observing echo signals. The signal amplitude decreased exponentially with \( \tau \) in all measurements. The sample temperatures were controlled within \( \pm 0.5 \) K by means of a temperature controller [4]. The observed temperatures were estimated to be accurate within \( \pm 1 \) K. The same sample was employed in the present investigation as that prepared previously for the study of \(^1\)H NMR experiments [6]. DTA experiments were carried out by means of a homemade apparatus [7].

3. Results

Temperature Dependence of Chlorine NQR Frequencies and Phase Transition

The temperature dependence of the \(^{35}\)Cl NQR frequencies is shown in Figure 1. The resonance frequencies were determined with the spin echo method. Some data are listed in Table 1. Our resonance frequencies agree fairly well with those reported in [3].

In the range 223–370 K a single resonance line, \( v_1 \), and below 206 K two resonance lines, \( v_{1h} \) and \( v_{1l} \) of high and low frequency, respectively, were observed. Above 370 K and between 206 K and 223 K, no echo signal could be detected, \( T_{1Q} \) and \( T_{2Q} \) becoming extremely short (ca. 100 µs).

From our DTA experiments, a phase transition was located at 217 K in the temperature range where no resonance could be observed. When the temperature was increased and decreased in the DTA experiments,
characteristic endo- and exo-thermic heat anomalies with a long tail on the low-temperature side were recorded, as shown in Figure 2. The peak temperatures of both anomalies were the same within experimental errors and have been assigned to \( T_c \) for the reason already reported [7, 8].

The following fact is very interesting. The temperature dependence of the average of \( v_{\text{Ih}} \) and \( v_{\text{III}} \) agrees well with the extrapolated curve of \( v_i \) (cf. Figure 1).

**\( T_{10} \) and \( T_{20} \) of Chlorine Nuclei**

The temperature dependences of \( T_{10} \) and \( T_{20} \) for the \( ^{35}\text{Cl} \) and \( ^{37}\text{Cl} \) nuclei in (pyH)ICl₄ crystals are shown in Figure 3. Some \( T_{10} \) and \( T_{20} \) values are also listed in Table 1.

When the sample was warmed from 84 K to ca. 150 K, the \( ^{35}\text{Cl} \) \( T_{10} \) values of \( v_{\text{Ih}} \) and \( v_{\text{III}} \) decreased with increasing temperature, the curves being slightly convex towards the abscissa around ca. 100 K. In the range 150–190 K, \( T_{10} \) of both lines was almost temperature independent. With increasing the temperature furthermore from 190 to 204 K, both \( T_{10} \) values decreased very rapidly and the \( v_{\text{Ih}} \) and \( v_{\text{III}} \) signals decreased very rapidly and the \( v_{\text{Ih}} \) and \( v_{\text{III}} \) signals

Table 1. Data for the \( ^{35}\text{Cl} \) NQR lines \( v_{\text{Ih}} \) and \( v_{\text{III}} \) in the low-temperature phase and \( v_i \) in the high-temperature phase of (pyH)ICl₄. Data for the \( ^{37}\text{Cl} \) NQR lines corresponding to \( v_{\text{Ih}} \) and \( v_{\text{III}} \) are marked by asterisks. Dashes indicate “no measurements”.

<table>
<thead>
<tr>
<th>T/K</th>
<th>( v )/MHz</th>
<th>( T_{10} )/ms</th>
<th>( T_{20} )/ms</th>
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<tbody>
<tr>
<td>84</td>
<td>25.390</td>
<td>530</td>
<td>–</td>
</tr>
<tr>
<td>84</td>
<td>19.868</td>
<td>130</td>
<td>0.31</td>
</tr>
<tr>
<td>*84</td>
<td>15.658</td>
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<td>0.41</td>
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<tr>
<td>106</td>
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<tr>
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<td>0.24</td>
</tr>
<tr>
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<td>8.2</td>
<td>0.31</td>
</tr>
<tr>
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</tr>
<tr>
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<td>1.4</td>
<td>0.17</td>
</tr>
<tr>
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<tr>
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</tr>
</tbody>
</table>

![Figure 1](image1.png)

**Fig. 1.** The temperature dependence of the \( ^{35}\text{Cl} \) NQR frequencies \( v_{\text{Ih}} \), \( v_{\text{III}} \), and \( v_i \) of (pyH)ICl₄. The averages of \( v_{\text{Ih}} \) and \( v_{\text{III}} \) are indicated by crosses.

![Figure 2](image2.png)

**Fig. 2.** DTA curves for (pyH)ICl₄ crystals across the phase transition temperature \( T_c \).
faded out at 206 K. At 223 K, the ν₁ signal appeared and T₁₀ of ν₁ could be determined above this temperature. When the temperature was increased from 223 K, ³⁵Cl T₁₀ increased with increasing temperature up to ca. 310 K. Above this temperature, T₁₀ of ν₁ showed again a very steep decrease.

The temperature dependence of ³⁵Cl T₁₀ was also determined for the ν₃ and ν₁ lines. The results were very similar to those of the corresponding ³⁵Cl T₁₀ lines. The isotope ratios of T₁₀ (³⁵Cl)/T₁₀ (³⁷Cl) were 1.1, 1.3, 1.0, 1.3, 1.0, and 1.7 for the temperature ranges 84–95 K, 95–125 K, 125–135 K, 135–190 K, 190–204 K, and 223–280 K, respectively.

4. Discussion

NQR Spectra and Molecular Structure

Although the crystal structure of (pyH)ICl₄ has not been determined as yet, X-ray powder patterns taken at room temperature [6] indicate that its crystal structure is similar to that of (pyH)AuCl₄ [9]. The single ³⁵Cl NQR line observed in the high-temperature phase of the present complex indicates that all chlorine atoms in the crystal are crystallographically equivalent. This is consistent with the crystal structure of (pyH)ICl₄ being similar to that of (pyH)AuCl₄, in which [AuCl₄]⁻ forms an approximately square planar complex anion.

The frequency splitting in the low temperature phase (ca. 5 MHz, cf. Fig. 1) is too large to be attributable to a lattice effect of the NQR frequencies or a usual change in the H-bonding scheme of Cl...H-N type. Most probably the [ICl₄]⁻ anions are strongly deformed in the low-temperature phase. This may lead to a large difference in I–Cl bond distances in the anion.

Dillon and Waddington [3] reported that the ³⁵Cl NQR frequencies of various salts containing [ICl₄]⁻ ions are widely spread (over ca. 13 MHz), due probably to a heavy distortion of the complex anion from its D₄h symmetry, leading to expansion and contraction of I–Cl bonds. They showed that the I–Cl bond distance in [ICl₄]⁻ depends linearly on the NQR frequency of ³⁵Cl in question [3]. By applying this relation to the present complex, the I–Cl bond distance can be estimated to be 2.51 Å for the high-temperature phase and 2.54 and 2.47 Å for two different kinds of I–Cl bonds in the low-temperature phase. A structural analysis using a single crystal is now in progress for both high- and low-temperature phases.

Reorientation of Complex Anions

Above ca. 310 K, T₁₀ decreases according to

\[ T_{10} \propto \exp\left(\frac{a}{T}\right). \]  

(1)

This experimental result suggests that sudden 90° reorientations of the complex anion about its pseudotetrad (C₄) axis are the main origin for the quadrupolar spin-lattice relaxation. Introducing an activation energy \( E_a \), (1) can be written in the form [10]

\[ T_{10} = \frac{2}{3} \tau = \frac{2}{3} \tau_0 \exp\left(\frac{E_a}{RT}\right), \]  

(2)

where \( \tau \) denotes the correlation time for the motion.

By use of (2), \( E_a \) could be evaluated from the gradient of the linear portion of the log \( T_{10} \) vs. \( T^{-1} \) plot above 310 K to be 64 kJ mol⁻¹. This is very close to the value of 67 kJ mol⁻¹ already obtained for (pyH)AuCl₄ [2, 11], indicating that the hindering bar-
rier to the $C_4'$ reorientation of the present anion in the crystal is approximately the same as that of $[\text{AuCl}_4^-]$ in the (pyH)$\text{AuCl}_4$ crystal.

**Cationic Motion**

The motion of pyH$^+$ in the present crystals has previously been studied by measuring the $^1$H NMR spin-lattice relaxation time $T_1$ [6] (cf. Figure 3). The temperature coefficients of chlorine $T_{1Q}$ and $^1$H $T_1$ in the range 300–233 K are similar to each other on the log $T_{1Q}$ vs. $T^{-1}$ and log $T_1$ vs. $T^{-1}$ plots, respectively. Accordingly, fluctuations of the electric field gradient (EFG) produced at resonant chlorine nuclei through the motion of the cations can be considered as an effective mechanism for the chlorine nuclear relaxation.

The above explanation is supported by the experimental fact that the ratios $T_{1Q}^{(37\text{Cl})}/T_{1Q}^{(35\text{Cl})}$ were 1.1, 1.3, and 1.7 for the temperature ranges 84–95 K, 135–190 K, and 223–280 K, respectively. When chlorine $T_{1Q}$ is determined mainly through the fluctuation of the chlorine EFG due to the motion of the cations, the theoretically derived isotope ratios are 1.00, 1.27, and 1.61 for the cases that the fluctuation of the EFG is slow, comparable, and fast, respectively, as compared with the NQR frequency [12, 13].

As the most probable mode of the cationic motion, in-plane reorientation of the cation about its $C_6'$ axis can be considered. This is because the excitation of the above motion has been suggested from the temperature dependence study of $^1$H NMR second moments [6]. This motion leads to the fluctuation of the EFG at the chlorine nuclei mainly through the formation and destruction of H-bonds between chlorine and nitrogen atoms.

In the low-temperature phase, the $T_{1Q}$ vs. $T^{-1}$ curves show a shoulder around 100 K (cf. Figure 3). Approximately the same isotope ratio of 1.3 was obtained in two neighboring temperature ranges closely spaced, namely, 95–125 K and 135–190 K. This fact suggests that at least two different correlation times are responsible for the fluctuation of the EFG at the chlorine nuclei. This conforms with our conclusion in the $^1$H NMR study [1, 2] that pyridinium cations perform the $C_6'$ reorientation over unequal potential barriers. On the other hand, the isotope ratio of 1.7 observed in the high-temperature phase indicates that the cationic motion is rapid enough compared with the chlorine NQR frequency.

**Phase Transition**

When the temperature was increased from ca. 190 K, $T_{1Q}$ decreased very rapidly up to near $T_c=217$ K. It has been reported that the log $T_{1Q}$ vs. $T^{-1}$ curves show an anomalous dip near $T_c$ in various crystalline solids [4, 5, 14–19]. In some $R_2\text{MX}_6$ ($R=\text{K, NH}_4$; M = Sn, Os, Re; X = Cl, Br) type complexes, soft mode phase transitions were observed [20–25] and halogen $T_{1Q}$ yielded a dip around $T_c$ because of the softening of the vibrational modes responsible for the fluctuation of the EFG produced at the resonant nuclei [14, 17, 18]. When this mechanism is operative in the phase transition, the isotope ratio $T_{1Q}^{(37\text{Cl})}/T_{1Q}^{(35\text{Cl})}$ is expected to be 1.6 at temperatures nearby $T_c$ on both sides [4, 5].

For the present complex, an isotope ratio of 1.0 was observed at 190–204 K below $T_c$. Therefore, the relaxation mechanism near $T_c$ can not be explained by the softening of a vibrational mode. The present phase transition is assumed to occur through an order-disorder mechanism in the orientation of the pyridinium cations. However, it is strongly suggested that the $[\text{ICl}_4^-]$ anion is heavily distorted below $T_c$, as discussed above. The $v_{\text{in}}$ and $v_{\text{in}}$ lines have positive and negative temperature coefficients, respectively, in the temperature range of 190–204 K. These temperature dependences of the resonance lines are attributable to a gradual distortion of the complex anion below $T_c$. We suggest that the distortion of the complex anion is deeply related to the order parameter of the phase transition, and the orientational disorder of the pyridinium cations might be combined with an anharmonic vibrational mode involving the complex anions.