

# Chlorine Nuclear Quadrupole Relaxation due to the Motion of Pyridinium Cations in Pyridinium Hexachlorometallates(IV): (pyH)<sub>2</sub>MCl<sub>6</sub> (M = Sn, Pb, Te) \*

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The temperature dependence of the chlorine quadrupole spin-lattice relaxation time  $T_{1Q}$  was observed for one of the three  $^{35}\text{Cl}$  NQR lines of (pyH)<sub>2</sub>MCl<sub>6</sub> (M = Sn, Pb, Te). Each  $T_{1Q}$  curve can be divided into three temperature regions. In the low- and high-temperature regions,  $T_{1Q}$  is dominantly determined by the relaxation mechanism due to the libration and reorientation of [MCl<sub>6</sub>]<sup>2-</sup>, respectively. In the intermediate temperature region,  $T_{1Q}$  results from the modulation of the electric field gradient by the motion of the neighboring pyridinium cations. This way the reorientational motion of the cation between potential wells with nonequivalent depths is precisely characterized.

## 1. Introduction

The large amplitude motions of molecular ions in crystals yield appreciable fluctuations of the electric field gradient (EFG) at the quadrupolar nuclei of counter ions. When the former ions have a large electric dipole moment, the motions of these ions provide an effective relaxation mechanism for the quadrupolar nuclei in the latter ions. Since the pyridinium cation (pyH<sup>+</sup>) is such a polar cation, chlorine nuclear quadrupolar relaxation in (pyH)AuCl<sub>4</sub> [1], (pyH)ICl<sub>4</sub> [2], and (pyH)<sub>2</sub>SnCl<sub>6</sub> [3] has been interpreted mainly in terms of the above relaxation mechanism. The present study deals with Cl NQR relaxation in (pyH)<sub>2</sub>MCl<sub>6</sub> (M = Sn, Pb, Te). The results for the middle temperature range are analyzed by the above relaxation mechanism, caused by the cationic motion already reported [4].

## 2. Experimental

We have used a homemade pulsed spectrometer equipped with a transmitter from Matec Inc. [5].  $T_{1Q}$

was determined by the 180°-τ-90° pulse sequence. The sample temperature was controlled to within ±1 K and estimated to be accurate within ±1 K. The samples were the same, except for (pyH)<sub>2</sub>PbCl<sub>6</sub>, as used for the study of  $^1\text{H}$  NMR [4]. (pyH)<sub>2</sub>PbCl<sub>6</sub> was prepared according to the method described in [6]. (pyH)<sub>2</sub>PbCl<sub>6</sub> was identified by usual elementary analysis. Anal. Calcd. for (C<sub>5</sub>H<sub>6</sub>N)<sub>2</sub>PbCl<sub>6</sub>: C, 20.7%; H, 2.1%; N, 4.8%. Found: C, 20.6%; H, 1.9%; N, 4.6%.

## 3. Results and Discussion

Three  $^{35}\text{Cl}$  NQR lines assignable to the three crystallographically nonequivalent chlorines in the complex anion have been reported to exist in the low-temperature phase (LTP), although only one of those lines could be observed up to the transition temperature  $T_c$  while the others faded out rather far below  $T_c$  with increasing temperature [7]. A single line has been reported for the high-temperature phase (HTP). Accordingly, in the present investigation the temperature dependence of  $T_{1Q}$  was observed for the line detectable in the LTP up to  $T_c$  and for the line of the HTP. Hereafter, chlorines showing the NQR line up to  $T_c$  are indicated as a-site chlorines. At 77 K, the  $^{35}\text{Cl}$  NQR frequencies of the a-site chlorines are reported to be 17.580, 19.580, and 16.835 MHz for (pyH)<sub>2</sub>SnCl<sub>6</sub>, (pyH)<sub>2</sub>PbCl<sub>6</sub>, and (pyH)<sub>2</sub>TeCl<sub>6</sub>, respectively [7].

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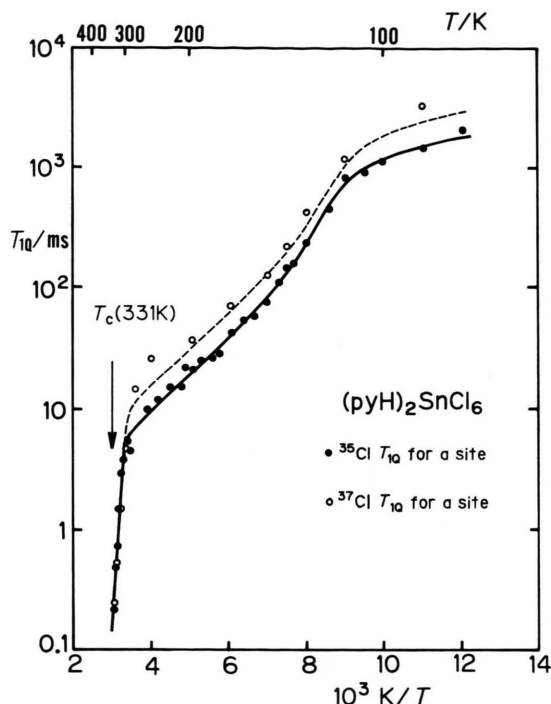


Fig. 1. The temperature dependence of the quadrupole spin-lattice relaxation time  $T_{1Q}$  for chlorine nuclei (located at the site a for the low-temperature phase) in the crystal of pyridinium hexachlorostannate(IV). Solid and dashed lines indicate the theoretical curves calculated for  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ , respectively (see text). The arrow shows the phase transition temperature.

The temperature dependences of the chlorine  $T_{1Q}$  are shown in Figures 1–3. For  $(\text{pyH})_2\text{SnCl}_6$ ,  $T_{1Q}$  could be determined only in the LTP because it became very short close to  $T_c$  and above. In the HTP of  $(\text{pyH})_2\text{TeCl}_6$ , a steep  $T_{1Q}$  decrease was observed near  $T_c$  with decreasing temperature. The marked increase of relaxation rate at  $T_c$  was also observed in the  $^1\text{H}$  spin-lattice relaxation time  $T_1$  of this complex [4]. On the other hand, no anomalous behavior of chlorine  $T_{1Q}$  could be detected at  $T_c$  of  $(\text{pyH})_2\text{PbCl}_6$ .

The  $T_{1Q}$  vs.  $T^{-1}$  curves observed can be divided into the following three portions. In the low- and high-temperature regions, respectively, chlorine  $T_{1Q}$  is explained as determined mainly through the libration and the overall reorientation of the respective complex anions [8, 9]. In the intermediate temperature region, the following relaxation mechanism is considered to be effectively operative.  $T_{1Q}$  of the chlorines is determined by the modulation of the EFG produced by the motion of the neighboring cations.  $T_{1Q}$  of some complexes involving pyridinium cations has already

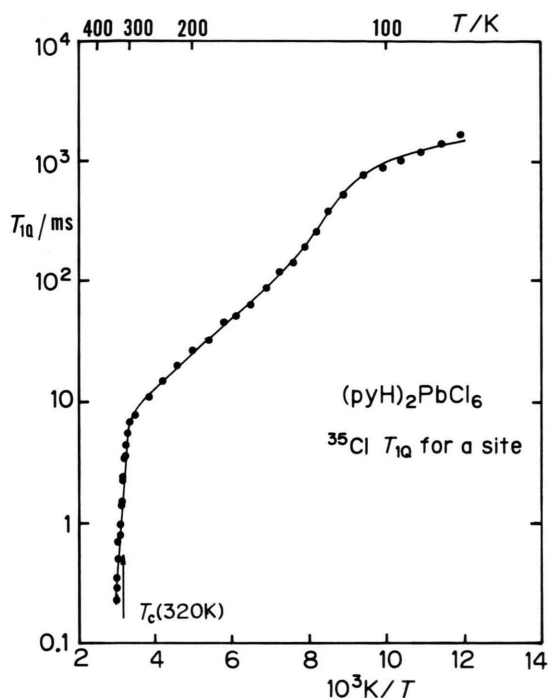


Fig. 2. The temperature dependence of  $T_{1Q}$  for  $^{35}\text{Cl}$  (located at the site a for the low-temperature phase) in the crystals of pyridinium hexachloroplumbate(IV). The solid line is the calculated curve (see text). The arrow shows the phase transition temperature.

been interpreted in terms of this relaxation mechanism [1–3].

In the  $^1\text{H}$  NMR study on the cationic motion in pyridinium hexahalometallates(IV) [4],  $60^\circ$  two-site jumps ( $60^\circ$  flip motion) of the cation around its pseudo  $C_6$  axis have been found. In the LTP, the two orientations of the cation, which are energetically equivalent in the disordered HTP, became inequivalent [7]. The quadrupole spin-lattice relaxation due to reorientations of neighboring atomic groups between unequal potential wells has been precisely investigated by Ainsbinder et al. [10, 11].

When pyridinium cations perform reorientation between potential wells such as shown in Fig. 4, the relaxation rate  $(T_{1Q})_{\text{mod}}^{-1}$  originating from the modulation of the EFG due to the cationic motions can be written for chlorine nuclei with the nuclear spin  $I = 3/2$  as [10]

$$(T_{1Q})_{\text{mod}}^{-1} = (1/12) (e^2 Q q / \hbar)^2 \{ 4a / (1+a)^2 \} \cdot (q'/q)^2 \{ \tau_c / (1 + \omega_Q^2 \tau_c^2) \}. \quad (1)$$

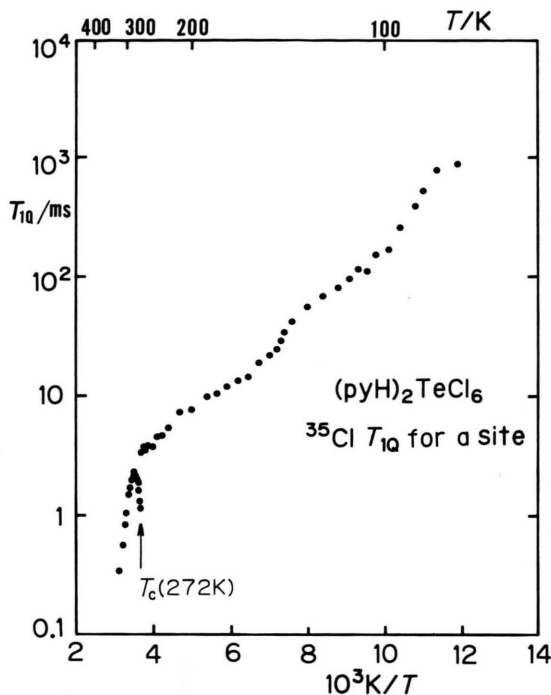


Fig. 3. The temperature dependence of  $T_{1Q}$  for  $^{35}\text{Cl}$  (located at the site a for the low-temperature phase) in the crystal of pyridinium hexachlorotellurate(IV). The arrow indicates the phase transition temperature.

Here,  $(q'/q)$ ,  $\tau_c$ , and  $a$  denote the fluctuation fraction of the EFG, the correlation time for the  $60^\circ$  flip motion of the cation, and the ratio of the steady-state probabilities to find the cation in the orientation  $\alpha$  and  $\beta$  indicated in Fig. 4, respectively. The ratio  $a$  can be expressed as

$$a = \exp\{(E_\alpha - E_\beta)/RT\}, \quad (2)$$

where  $E_\alpha$  and  $E_\beta$  are the respective activation energies. In (1),  $(e^2 Q q/\hbar)$  and  $\omega_Q$  represent the quadrupole coupling constant of chlorine and the nuclear quadrupole angular resonance frequency of chlorine, respectively. By assuming a negligibly small asymmetry parameter  $\eta$  of the EFG, one has

$$(T_{1Q})_{\text{mod}}^{-1} = (1/3) \omega_Q^2 \{4a/(1+a)^2\} \cdot (q'/q)^2 \{\tau_c/(1+\omega_Q^2 \tau_c^2)\}, \quad (3)$$

because  $(e^2 Q q/2)$  is approximately equal to  $\hbar \omega_Q$ .

The correlation time  $\tau_c$  can be written by use of the transition probability rates  $W_{\alpha\beta}$  and  $W_{\beta\alpha}$  for the  $\alpha \rightarrow \beta$  and  $\beta \rightarrow \alpha$  transformations of cationic orientations, respectively, as

$$\tau_c = 1/(W_{\alpha\beta} + W_{\beta\alpha}). \quad (4)$$

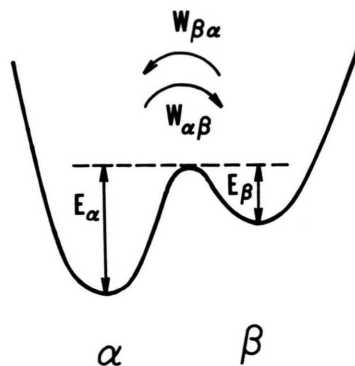


Fig. 4. Unequal potential wells between which the pyridinium cations reorient, for the low-temperature phase of the pyridinium hexachlorostannate(IV) and -plumbate(IV). The two orientations are denoted as  $\alpha$  and  $\beta$ , and the activation energies in the respective wells are as  $E_\alpha$  and  $E_\beta$ .  $W_{\alpha\beta}$  and  $W_{\beta\alpha}$  indicate the transition probability rates for the  $\alpha \rightarrow \beta$  and  $\beta \rightarrow \alpha$  transitions, respectively.

The Arrhenius relationship can be assumed for the transition probability rates as

$$W_{\alpha\beta} = K \exp(-E_\alpha/RT), \quad (5)$$

$$W_{\beta\alpha} = K \exp(-E_\beta/RT). \quad (6)$$

$(T_{1Q})^{-1}$  of chlorine nuclei observed for the present complexes is assumed as the sum of contributions from (i) the libration of the cations as well as the complex anions,  $(T_{1Q})_{\text{latt}}^{-1}$ , (ii) the modulation of the chlorine EFG due to reorientation of the cation,  $(T_{1Q})_{\text{mod}}^{-1}$ , and (iii) the reorientation of complex anions,  $(T_{1Q})_{\text{reorient}}^{-1}$ , involving the resonant nuclei. Then, the observed  $T_{1Q}$  can be written as

$$(T_{1Q})^{-1} = (T_{1Q})_{\text{latt}}^{-1} + (T_{1Q})_{\text{mod}}^{-1} + (T_{1Q})_{\text{reorient}}^{-1}, \quad (7)$$

where each motion is assumed to be independent. For  $(T_{1Q})_{\text{latt}}$  and  $(T_{1Q})_{\text{reorient}}$ , one has [8, 9],

$$(T_{1Q})_{\text{latt}} = b T^{-2}, \quad (8)$$

$$(T_{1Q})_{\text{reorient}} = (1/6) \tau_0 \exp(E_a/RT). \quad (9)$$

Here,  $E_a$  represents the activation energy for the reorientation of the octahedral complex anions in crystals and  $\tau_0$  is the correlation time for the motion in the limit of infinite temperature.

A fitting calculation to the observed  $^{35}\text{Cl}$   $T_{1Q}$  values of  $(\text{pyH})_2\text{SnCl}_6$  and  $(\text{pyH})_2\text{PbCl}_6$  was performed using (7), in which  $(\omega_Q/2\pi)$  of  $^{35}\text{Cl}$  was fixed at the values of 17.5 or 19.5 MHz. The calculation was carried out by use of the least-squares program SALS [12]. The values of the adjustable parameters obtained are

Table 1. The activation energy  $E_a$  and the factor  $\tau_0$  of (9), the factor  $b$  of (8), the preexponential factor  $K$  of (5) and (6), the depths  $E_x$  and  $E_\beta$  of the nonequivalent potential wells for the cationic reorientation, and the fluctuation fraction of the chlorine EFG ( $q'/q$ ).

Complex	$E_a/\text{kJ mol}^{-1}$	$\tau_0/\text{s}$	$b/\text{sK}^2$	$K/\text{s}^{-1}$	$E_x/\text{kJ mol}^{-1}$	$E_\beta/\text{kJ mol}^{-1}$	$(q'/q)$
$(\text{C}_5\text{H}_6\text{N})_2\text{SnCl}_6$	$125 \pm 7$	$2 \times 10^{-23}$	$1 \times 10^4$	$2 \times 10^{11}$	$22 \pm 3$	$8 \pm 1$	$\sim 0.15$
$(\text{C}_5\text{H}_6\text{N})_2\text{PbCl}_6$	$110 \pm 5$	$1 \times 10^{-20}$	$1 \times 10^4$	$5 \times 10^{11}$	$22 \pm 4$	$8 \pm 2$	$\sim 0.15$

shown in Table 1. The best-fitted curves using the above values for the foregoing two complexes are shown in Figs. 1 and 2 by solid lines. The observed temperature dependences of  $^{35}\text{Cl}$   $T_{1Q}$  for the two complexes are well interpreted through the present model.

For  $(\text{pyH})_2\text{SnCl}_6$ , the temperature dependence curve of  $^{37}\text{Cl}$   $T_{1Q}$  was also calculated using the foregoing best-fitted parameters derived from the  $^{35}\text{Cl}$   $T_{1Q}$  data. In the calculation, the values of  $b$  and  $\omega_Q^2$  are multiplied and divided, respectively, by the square of the chlorine nuclear quadrupole moment ratio

$$[eQ(^{35}\text{Cl})/eQ(^{37}\text{Cl})]^2 = 1.61, \quad (10)$$

in order to correct for the difference of the quadrupole interaction energies. The agreement between the theoretical curve indicated by a dashed line in Fig. 1 and the observed values of  $^{37}\text{Cl}$   $T_{1Q}$  is quite good. Accordingly, the  $60^\circ$  flip motion of the pyridinium cation between nonequivalent potential wells, which was found in our previous  $^1\text{H}$  NMR study [4] is confirmed to take place in the LTP's of  $(\text{pyH})_2\text{SnCl}_6$  and  $(\text{pyH})_2\text{PbCl}_6$  by the present analysis of the chlorine  $T_{1Q}$  data.

As for  $(\text{pyH})_2\text{TeCl}_6$ , the temperature dependence of  $^{35}\text{Cl}$   $T_{1Q}$  is more complicated. In the temperature range 90–250 K, chlorine  $T_{1Q}$  is probably governed by the modulation mechanism of the chlorine EFG

due to the motions of the neighboring cations discussed above. In this temperature range, however, there are two shoulders observed in the  $\log T_{1Q}$  vs.  $T^{-1}$  curve. To explain the appearance of the shoulders, the reorientational motions of the cation between more than two nonequivalent potential wells might be considered. Because there are no structural data available for the LTP of this complex, a detailed discussion is not possible at the present stage.

In the HTP of  $(\text{pyH})_2\text{TeCl}_6$ , a maximum of the  $\log T_{1Q}$  vs.  $T^{-1}$  curve was observed. With increasing temperature,  $T_{1Q}$  increased steeply from just above  $T_c$ , reached the maximum and decreased again steeply. The  $\log T_{1Q}$  vs.  $T^{-1}$  curve above the maximum seems to be connected smoothly with the curve observed below  $T_c$ . The temperature dependence of  $^1\text{H}$   $T_1$  for this complex yielded a  $T_1$  dip at  $T_c$  [4]. From these facts, the steep  $T_{1Q}$  decrease below the  $T_{1Q}$  maximum temperature is considered to be due to some effect of the phase transition.

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