A ^{35}Cl NQR Spin-Lattice Relaxation Study on the Motion of D_{4h} Anions in $[C(NH_2)_3]_2PdCl_4$, $[C(NH_2)_3]_2PtCl_4$, and $[C(NH_2)_3]AuCl_4$*

Yoshihiro Furukawa and Daiyu Nakamura

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464, Japan

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The temperature dependence of ^{35}Cl NQR spin-lattice relaxation times $T_{1Cl\varrho}$ was observed for the crystal of the title complexes. For the Pd(II) and Pt(II) complexes, the log $T_{1Cl\varrho}$ vs. $10^3\ T^{-1}$ curves having gentle positive gradients at lower temperatures decreased sharply with increasing temperature from ca. 150 and ca. 130 K, respectively. This sharp decrease of $T_{1Cl\varrho}$ can be explained by the C_4 reorientation of the D_{4h} complex anions with the activation energy E_a of 34 kJ mol^{-1} for the former and 29 kJ mol^{-1} for the latter complex. These values agree well with those estimated from ^{1}H T_1 showing temperature dependent dipolar-quadrupolar cross relaxation. For the Au(III) salt, two of four ^{35}Cl NQR lines showed a sharp decrease in $T_{1Cl\varrho}$ from ca. 270 K, suggesting the onset of the C_4 reorientation of the one kind crystallographically equivalent anions with E_a of 67 kJ mol^{-1}.

Introduction

Previously, we studied the ^{35}Cl NQR, the ^{1}H NMR second moment M_2, and the ^{1}H NMR spin-lattice relaxation time ^{1}H T_1 of $(guH)_2PdCl_4$, $(guH)_2PtCl_4$, and $(guH)AuCl_4$, where guH^+ denotes the guanidinium cation $[C(NH_2)_3]^+$, and found unusual temperature and frequency dependencies of ^{1}H T_1 [1, 2]. This unusual ^{1}H T_1 behavior could be explained by assuming cross relaxations between the ^{1}H Zeeman energy levels and the Zeeman split quadrupolar energy levels of the ^{35}Cl and ^{37}Cl nuclei [2–7], where the latter energy levels were assumed to fluctuate strongly through the C_4 reorientational motion of the complex anions, i.e. random $\pi/2$ reorientation about the symmetry axis of the D_{4h} anion, even far below room temperature for the former two complexes, and at higher temperatures for the Au(III) complex. However, whether or not the occurrence of the C_4 reorientation of the complex anions takes place in these crystals is still a subject of controversy.

Measurements of the temperature variation of the ^{35}Cl quadrupolar spin-lattice relaxation time $T_{1Cl\varrho}$ are expected to provide a clue to clarify this problem [8–10]. Accordingly, we have measured ^{35}Cl $T_{1Cl\varrho}$ of the three complexes at various temperatures to verify the existence of the C_4 reorientation of the anions and to determine its activation energy E_a if it really exists.

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Reprint requests to Prof. Dr. D. Nakamura, Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464, Japan.

Experimental

The same samples as those of our previous experiments of ^{35}Cl NQR and ^{1}H NMR [1, 2] were used for the present investigation.

^{35}Cl $T_{1Cl\varrho}$ was determined at various temperatures above 77 K by means of a frequency variable pulsed NMR spectrometer already described which was operated without external dc magnetic field [1]. The measurements of $T_{1Cl\varrho}$ were performed by plotting the NQR spin-echo amplitude as a function of the delay time τ using a $\pi-\tau-\pi/2-\tau'-\pi$ pulse sequence, where τ' was another constant delay time to obtain appropriate echo signals and was chosen, for the present measurements, around 130 μs at a given temperature. Sample temperatures were determined by use of a copper-constantan thermocouple and were estimated to be accurate within ±1 K. A normal exponential decay of the echo signals was observed at all temperatures. The ^{35}Cl NQR frequencies obtained in the present investigation for the three complexes agree very well with those found in our previous study [1].

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Results and Discussion

$[C(NH_2)_3]_2PdCl_4$ and $[C(NH_2)_3]_2PtCl_4$

From [1], it is known that both complexes yield two ^{35}Cl NQR frequencies having equal intensity in the temperature range of 77−220 K and 77−169 K, respectively. Above each maximum temperature observed, no NQR signal could be detected. The appearance of two equal intensity signals for these complexes agrees well with the results of X-ray analysis [2, 11] showing that both complexes are isomorphous and the anions are crystallographically equivalent in each crystal with two nonequivalent chlorines giving rise to the high- and low-frequency line *a* and *b*, respectively. The ^{35}Cl $T_{1\mathrm{ClQ}}$ values observed for these complexes are shown in Fig. 1 in a log $T_{1\mathrm{ClQ}}$ vs. $10^3\,T^{-1}$ plot.

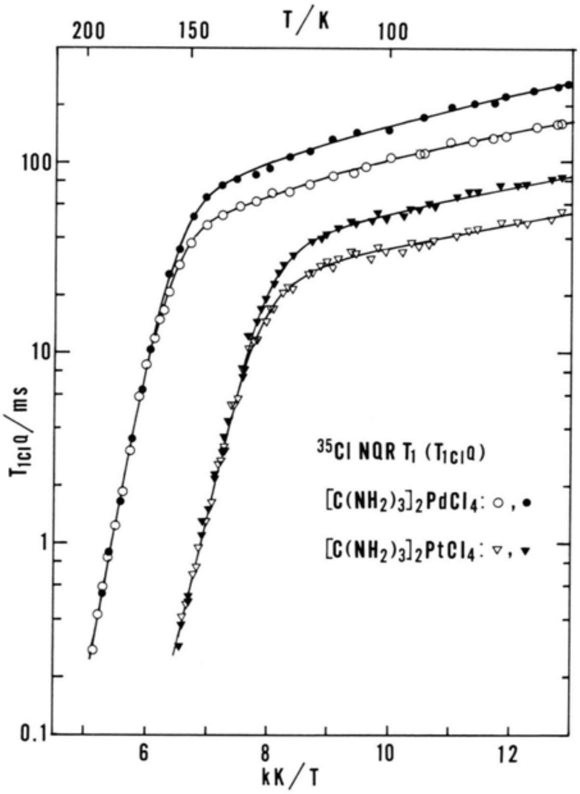

Fig. 1. Temperature dependences of the ^{35}Cl quadrupole spin-lattice relaxation time $T_{1\mathrm{ClQ}}$ for the NQR lines arising from ^{35}Cl nuclei at sites *a* (○) and *b* (●) in $[C(NH_2)_3]_2PdCl_4$ crystals and those at sites *a* (△) and *b* (▲) in $[C(NH_2)_3]_2PtCl_4$ crystals. Solid lines are the best fitted curves.

When the temperature of $(guH)_2PdCl_4$ was raised from 77 K, log $T_{1\mathrm{ClQ}}$ of chlorine (^{35}Cl) at both sites, which has slightly different values at a given temperature, decreased gradually and almost linearly with decreasing $10^3\,T^{-1}$ up to ca. 140 K. In this region, $T_{1\mathrm{ClQ}}$ of chlorine at the site *a* was shorter by a factor of ca. 1.6 than that at *b*. On increasing the temperature further, the two log $T_{1\mathrm{ClQ}}$ values decreased very sharply and almost linearly with $10^3\,T^{-1}$ above ca. 160 K, and the chlorines of both sites gave identical $T_{1\mathrm{ClQ}}$ values at the same temperature. Above 195 K, the intensity of both lines became too weak to determine $T_{1\mathrm{ClQ}}$. This temperature is lower by ca. 25 K than the fade-out temperature determined in the previous cw experiments. The Pt(II) complex yielded a $T_{1\mathrm{ClQ}}$ curve very similar to that of the Pd(II) complex. However, $T_{1\mathrm{ClQ}}$ of the former is significantly shorter than that of the latter. The echo signals for the Pt(II) complex were too weak to determine $T_{1\mathrm{ClQ}}$ above ca. 150 K, which is lower by ca. 20 K than the fade-out temperature of this complex observed by the cw method.

In the low temperature regions of both complexes, where the ^{35}Cl nuclei gave gentle log $T_{1\mathrm{ClQ}}$ vs. $10^3\,T^{-1}$ curves, the dependence of $T_{1\mathrm{ClQ}}$ on the temperature can be interpreted in terms of the quadrupolar mechanism due to the random fluctuations of the electric field gradient (EFG) formed at the resonant nuclei through rotational oscillations or librations of the anions having the librational angular frequency ω_l and the associated moment of inertia I_l. The quadrupolar relaxation due to librations involving oscillations of the principal EFG axes of the resonant nuclei was studied by Bayer [12] and other authors [13−17]. According to Woessner and Gutowsky [14] and to Jones et al. [17], $T_{1\mathrm{ClQ}}^{-1}$ for quadrupolar nuclei, having a nuclear spin equal to 3/2, can be written under the condition of $\hbar\,\omega_l/kT \ll 1$ as

$$T_{1\mathrm{ClQ}}^{-1} = (12 k^2 T^2 \omega_Q^2/\hbar\, I_l\, \omega_l^5\, \tau_g)(1+\gamma). \qquad (1)$$

Here, ω_Q and τ_g are the ^{35}Cl NQR angular frequency and the mean-life time of the anions staying at the librational ground state, respectively, and γ is equal to W_1/W_2, where W_1 and W_2 are the transition probabilities of nuclear quadrupole transitions with the selection rules $\Delta m = \pm 1$ and $\Delta m = \pm 2$, respectively. Equation (1) shows that $T_{1\mathrm{ClQ}}^{-1}$ has an explicit T^2 dependence. This will be confirmed from the later analysis of $T_{1\mathrm{ClQ}}$ obtained

Table 1. Adjusted parameters α and m for the quadrupole spin-lattice relaxation due to librational fluctuations of the electric field gradient at the ^{35}Cl nuclei, and the activation energy E_a for the C_4 reorientation of the complex anions and its correlation time τ_0 at infinite temperature estimated for $(guH)_2PdCl_4$, $(guH)_2PtCl_4$, and $(guH)AuCl_4$.

Compounds	Site	$\alpha/(s^{-1}\,K^{-m})$	m	$E_a/(kJ\,mol^{-1})$	τ_0/s
$[C(NH_2)_3]_2PdCl_4$	a	1.45×10^{-3}	1.9	34.4	2.3×10^{-13}
	b	5.86×10^{-4}	2.0		
$[C(NH_2)_3]_2PtCl$	a	1.55×10^{-2}	1.6	28.5	9.1×10^{-14}
	b	4.90×10^{-3}	1.8		
$[C(NH_2)_3]AuCl_4$	a, c	1.37×10^{-4}	2.2	67.2	1.2×10^{-15}
	b, d	2.24×10^{-4}	2.1	–	–

for both complexes, which indicates that the $T_{1\mathrm{ClQ}}$ values at lower temperatures are governed by the librations of the anions.

In the high temperature region, $T_{1\mathrm{ClQ}}$ of each complex decreased sharply with increasing temperature suggesting the occurrence of some slow motion of the anions such as reorientational motion [8–10]. A small angle reorientation between two stable conformations of the anions formed symmetrically near the single equilibrium conformation at low temperatures can be considered as a conceivable motion for the present complexes. The ^{35}Cl $T_{1\mathrm{ClQ}}$ of CH_2ClCH_2Cl observed below ca. 85 K was explained by a reorientational mechanism similar to this [18]. An analogous motion was proposed for the interpretation of the anomalous temperature variation of the ^{79}Br NQR frequencies detected for $CsAuBr_4$ [19]. However, this motional mode can hardly be employed for the present case because the X-ray analysis of $(guH)_2PdCl_4$ [11] gave fairly well-defined chlorine positions with small anisotropic thermal parameters suggesting the occurrence of in-plane librations of the anions.

Another possible motional mode for the present complexes is the C_4 reorientation of the complex anion as a whole about its symmetry axis. According to Goldman [20], $T_{1\mathrm{ClQ}}$ attributable to the hindered reorientation of the anions under the condition $\omega_Q^2\,\tau_{\mathrm{Cl}}^2 \gg 1$, is expressed as

$$T_{1\mathrm{ClQ}} = (2/3)\,\tau_{\mathrm{Cl}} = (2/3)\,\tau_0 \exp(E_a/kT). \qquad (2)$$

Here, the Arrhenius relationship between the correlation time τ_{Cl} and the activation energy E_a for the motion is assumed, and τ_0 is the correlation time at infinite temperature.

Combining the above two relaxation mechanisms, $T_{1\mathrm{ClQ}}$ observed for the present complexes can be written in a rather general form [10]:

$$T_{1\mathrm{ClQ}}^{-1} = \alpha\, T^m + (3/2)\,\tau_0^{-1} \exp(-E_a/kT). \qquad (3)$$

Here α and m are adjustable parameters. Using (3), fitting calculations to the observed values were performed by changing the α, m, τ_0, and E_a values. The data observed at lower temperatures should mainly determine the values of α and m, while those at higher temperatures the values of τ_0 and E_a. The best fitted parameters are given in Table 1, and the $T_{1\mathrm{ClQ}}$ curves calculated with these are shown by solid curves in Figure 1.

The values of α obtained for the Pd(II) complex are smaller by one order of magnitude than those of the Pt(II) one. However, α contains three unknown parameters, γ, ω_l, and τ_g which may be difficult to evaluate with enough accuracy. Therefore α is not discussed further in the present paper.

Although the Pt(II) complex gives a considerably large E_a value for the C_3 reorientation of the cation than the Pd(II) complex [2], E_a for the C_4 reorientation is smaller for the former than for the latter one. This is a contradictory result in view of the conceivable binding forces operating between complex anions and the cations. The smaller E_a values for the C_4 than for the C_3 reorientations may be understood by considering the smaller reorientational angle for the C_4 reorientations, and the smaller E_a of the C_4 motion for the Pt(II) complex may be explained if it has a shorter metal–ligand bond than the Pd(II) complex, as in the case of K_2PtCl_4 and K_2PdCl_4 [21].

The temperature dependence of τ_{Cl} derived from the present NQR study at lower temperatures and that estimated from the previous ^{1}H NMR one at higher temperatures are given in Figure 2. For each complex, the log τ_{Cl} vs. $10^3\,T^{-1}$ plot is almost linear

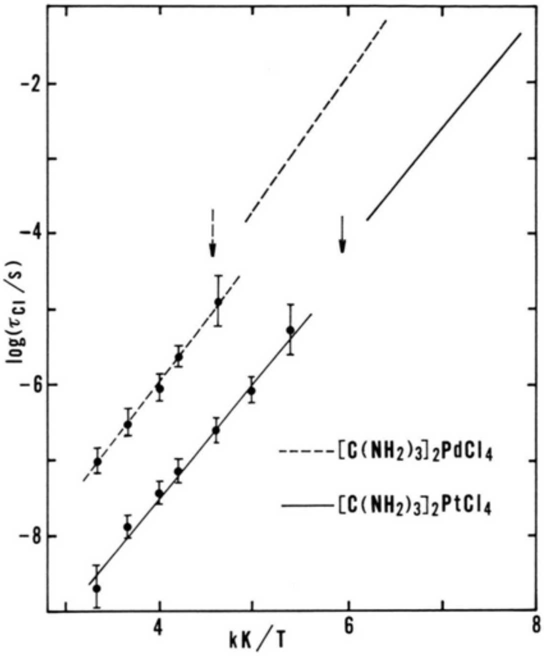

Fig. 2. Temperature variations of the correlation time τ_{Cl} for $[C(NH_2)_3]_2PdCl_4$ and $[C(NH_2)_3]_2PtCl_4$ derived from measurements of T_{1Cl^Q} at low temperatures, where only lines are given, and estimated from ^1H T_1 at higher temperatures, where the values determined at various temperatures are shown with error bars. Arrows indicate the temperatures above which no ^{35}Cl NQR signal was detected.

in both temperature regions with nearly the same gradient and the line extrapolated from the cold side (based on NQR data) for each complex approximately coincides with that estimated from the NMR data [2]. These facts provide a strong support for the analysis of the extraordinary ^{1}H NMR relaxation data of the previous investigation and, then, prove that the chlorine NQR data can be evaluated, in a favorable case, from ^{1}H NMR measurements through quadrupolar-dipolar cross relaxation even in a temperature region where NQR signals are faded out.

$[C(NH_2)_3]AuCl_4$

This complex yields four closely spaced ^{35}Cl NQR frequencies at 77 K, which are named as *a*, *b*, *c*, and *d* in the order of decreasing frequency [1]. The temperature dependence of T_{1Cl^Q} for each line is shown in Figure 3.

Below ca. 240 K, each line gives almost the same T_{1Cl^Q} at a given temperature and also the same $\log T_{1Cl^Q}$ vs. $10^3\,T^{-1}$ curve with a gentle gradient. Above this temperature, T_{1Cl^Q} of the *a* and *c* lines decreases very steeply with increasing temperature and both lines give the same T_{1Cl^Q} curve. The values of T_{1Cl^Q} become ca. 400 μs at 325 K, which explains well the fact that both lines are faded out near 345 K [1]. On the other hand, T_{1Cl^Q} of the remaining lines decreases gradually even above ca. 240 K. However, immediately below the transition temperature T_{tr} (363 K), T_{1Cl^Q} of both lines shows an indication to decrease rapidly with increasing temperature.

The above results are compatible with those of the X-ray analysis [11], revealing the existence of two kinds of anions in the crystal. The data of T_{1Cl^Q} of the NQR lines *a* and *c* attributable to one kind of anions, can be analyzed in the same way as those of the foregoing two complexes. The numerical results

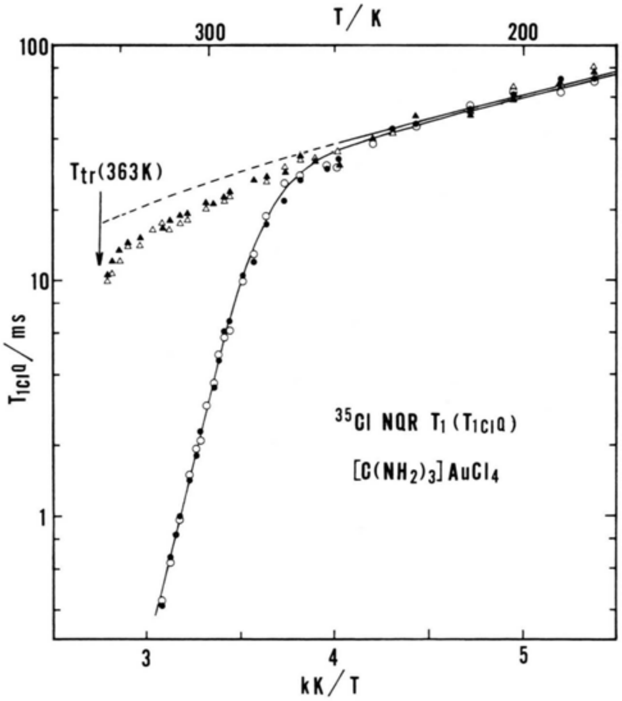

Fig. 3. Temperature dependences of the ^{35}Cl quadrupole spin-lattice relaxation time T_{1Cl^Q} for $[C(NH_2)_3]AuCl_4$. The symbols; ○, ▲, ●, and △ indicate the observed values for the ^{35}Cl NQR lines originating from the chlorine sites *a*, *b*, *c*, and *d*, respectively in the crystal. The solid line is the best fitted curve. The broken line is an extrapolation of the fitted curve at low temperatures.

are given in Table 1, and the curve calculated by using the best fitted values of the parameters is shown in Figure 3. The large E_a of 67.2 kJ mol^{-1} obtained for this kind of anions indicates that the anions are fairly tightly bound in the crystal as compared with the anions in the preceding two complexes. The other kind of the anions does not show an appreciably sharp decrease in T_{1Cl^Q} indicating that T_{1Cl^Q} could be interpreted in terms of librations of the anions. However, the T_{1Cl^Q} values determined deviate gradually with increasing temperature from the curve obtained by extrapolation of the cold-side-fitted one above ca. 250 K, suggesting that a considerable contribution of anharmonicity in the librations of the anions to T_{1Cl^Q} should be taken into account.

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