Chlorine NQR Spin-Lattice Relaxation and Electron Spin Dynamics in Paramagnetic [Co(H₂O)₆][PtCl₆]

Motohiro Mizuno, Tetsuo Asaji, Atsushi Tachikawa, and the late Daiyu Nakamura
Department of Chemistry, Faculty of Science, Nagoya University, Nagoya, Japan

Z. Naturforsch. 46a, 1103–1107 (1991); received September 17, 1991

Chlorine NQR spin-lattice relaxation times \( T_{10} \) were determined for \([\text{Co(H}_2\text{O)}_6][\text{PtCl}_6] \) at 4.2–400 K. Above ca. 350 K, \( T_{10} \) decreased rapidly showing the onset of a reorientation of \([\text{PtCl}_6]^{2-} \). The activation energy \( E_A \) of this reorientation was determined as 125 ± 15 kJ mol⁻¹. With decreasing temperature, \( T_{10} \) showed a maximum at ca. 250 K. Below ca. 200 K, \( T_{10} \) is governed by the magnetic dipolar interaction between chlorines and paramagnetic Co²⁺ ions and is inversely proportional to the electron spin correlation time \( \tau_e \) of Co²⁺. \( \tau_e \) is shown to be determined by the electron spin-lattice relaxation time \( T_1e \) and the temperature independent correlation time \( \tau_s \) for the spin-exchange between neighbouring ions above and below ca. 50 K, respectively. The temperature dependence of \( T_1e \) is explained by assuming the Orbach process with an energy gap \( \Delta/k \) of 530 ± 20 K as \( T_1e = 5 \times 10^{-14} \exp(530/T) \) s. \( \tau_s \) was estimated to be 0.9 \times 10⁻¹⁰ s.

The temperature dependence of the ESR linewidth of Mn²⁺ impurities in single crystal was also measured, intending to study Co²⁺ spin dynamics. The limit of the ESR method is discussed by comparing the obtained results with those of the NQR method.

**Key words:** Spin-lattice relaxation, NQR, ESR, Reorientation, Orbach process.

**Introduction**

The spin-lattice relaxation time \( T_1e \) of Co²⁺ is very short at normal temperatures in an octahedral crystal field [1]. Above 77 K, therefore, even a detection of ESR signals is usually impossible due to the life-time broadening. To investigate such a fast spin dynamics of Co³⁺, ESR of paramagnetic impurity ions doped in the host cobalt salts can be used; the impurity linewidth can reflect the host \( T_1e \), since the linewidth is determined by the host-impurity interaction averaged by the “host spin-lattice relaxation narrowing” mechanism [2–7]. In this method, however, it is not easy to estimate the linewidth in the absence of the narrowing mechanism, because both dipolar and exchange interactions between dissimilar ions, where the latter are generally unknown, contribute to the line broadening. Hence, \( T_1e \) calculated by use of only the dipolar width is just longer limit of the host spin-lattice relaxation time.

Nuclear spin-lattice relaxation times can also give information on the electron spin dynamics in paramagnetic salts [8–10]. For the localized spin system it is easy to estimate the dipolar coupling between para-

---

Reprint requests to Dr. T. Asaji, Department of Chemistry, Faculty of Science, Nagoya University, Nagoya 464-01, Japan.

---

The crystal of \([\text{Co(H}_2\text{O)}_6][\text{PtCl}_6] \) belongs to the space group \( \text{R} 3, a = 7.10 \text{Å}, z = 96.26^\circ, Z = 1 \) [11], and its structure is a slightly distorted CsCl structure composed of the octahedral complexes \([\text{Co(H}_2\text{O)}_6]^{2+} \) and \([\text{PtCl}_6]^{2-} \). Both complex ions are located at 3 sites of the crystal lattice although the atomic positions of chlorines and oxygens are not known. In accord with the crystal structure, a single \(^35\text{Cl}\) NQR frequency has been reported at 4.2–400 K, and no phase transition has been observed [12].

**Experimental**

Equimolar amounts of \( \text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O} \) and \( \text{CoCl}_2 \cdot 6\text{H}_2\text{O} \) were dissolved in a small amount of water [12, 13]. The solution was heated on a water bath until...
dryness without a smell of HCl. The residual was dissolved in water and was filtered off. [Co(H₂O)₆][PtCl₆] crystals were obtained by slow concentration of the solution in a desiccator by P₂O₅ and NaOH. Mn²⁺ doped single crystals of [Co(H₂O)₆][PtCl₆] were prepared from a solution containing a 1/100 molar amount of [Mn(H₂O)₆][PtCl₆], which was synthesized similarly using MnCl₂ • 4H₂O.

A homemade pulsed NQR spectrometer was used for the spin-lattice relaxation time T₁₀ measurements [14, 15]. The 180°-τ-90°-τ-180° pulse sequence was applied, where the spacing time τ was varied while τₑ was set constant (100–500 μs). The error of T₁₀ measurements is estimated to be ca. ±10%. The sample temperature was controlled with temperature controllers, Ohkura EC-61 and Oxford DTC2, equipped with copper-constantan and gold (0.07% Fe)-chromel thermocouples above and below 77 K, respectively. The temperature was estimated to be accurate within ±1 K.

Mn²⁺ ESR spectra of a Mn²⁺ doped single crystal of [Co(H₂O)₆][PtCl₆] were recorded by use of a JEOL SCXA X-band spectrometer with a TE₀₁₁ cylindrical cavity resonator [16, 17]. From the rotation patterns of the ESR spectra, the [1, 1, 1] axis of the crystal was identified. DPPH was used as a marker of the magnetic field. A copper-constantan thermocouple located close to the crystal but outside of the cavity was used for temperature measurements, the accuracy of which was estimated as ±5 K.

Least-squares fitting calculations to the observed data were performed with a theoretical equation by use of SALS reported by Oyanagi and Nakagawa [18] at Nagoya University Computation Center.

Results and Discussion

Spin-Lattice Relaxation of Chlorine Nuclear Quadrupole Resonance

The ³⁵Cl NQR frequencies determined agreed very well with those reported [12]. They and the spin-lattice relaxation times T₁₀ of ³⁵Cl and ³⁷Cl in [Co(H₂O)₆][PtCl₆] are listed in Table 1 for [Co(H₂O)₆][PtCl₆] at several temperatures. Figure 1 shows the temperature dependences of T₁₀ of ³⁵Cl and ³⁷Cl NQR in [Co(H₂O)₆][PtCl₆]. A T₁₀ maximum was observed at ca. 250 K. The rapid decrease above ca. 350 K can be attributed to the onset of a reorientation of [PtCl₆]²⁻, since T₁₀(³⁷Cl)/T₁₀(³⁵Cl)=1 was obtained [19]. On the other hand, the T₁₀ decrease on the lower-temperature side can not be explained by the lattice vibrational relaxation process which is usually operative at low temperatures [19]. T₁₀ showed a constant value of ca. 0.55 ms below ca. 50 K. The ratio T₁₀(³⁷Cl)/T₁₀(³⁵Cl)=1.46 ± 0.1 obtained below ca. 200 K suggests that the relaxation process is dominated by the magnetic dipolar interaction between chlorines and paramagnetic Co²⁺ ions, which gives T₁₀(³⁷Cl)/T₁₀(³⁵Cl)=|γ(³⁷Cl)/γ(³⁵Cl)|² = 1.44 using the square of the ratio of the gyromagnetic ratios γ [19].

The spin-lattice relaxation rate (T₁⁻¹) of chlorine (I = 3/2, gyromagnetic ratio γ) due to the magnetic interaction with paramagnetic Co²⁺ ions (g-value ̃g and fictitious angular momentum ̃J) can be written as

\[
(T₁⁻¹) = 3 \Gamma \gamma^2 \tilde{g}^2 \mu_B^2 \left( \frac{1}{3} \tilde{J}(\tilde{J}+1) \right) (2 \tau_e) A \quad (1)
\]
by assuming a fast isotropic fluctuations of $\bar{J}$ [20]. Here, $\mu_B$, $\tau_s$, and $A$ denote Bohr magneton, the electron spin correlation time of a Co$^{2+}$ ion, and a geometrical factor depend on internuclear vectors between the resonant nucleus and paramagnetic ions. The geometrical factor $A$ is given by

$$A = \sum_{i} \left( |F^{(i)}|^2 + \frac{1}{18} |F^{(0)}|^2 + \frac{1}{2} |F^{(2)}|^2 \right),$$

using the spatial parts of the dipolar Hamiltonian

$$|F^{(i)}|^2 = (1 - 3 \cos^2 \theta_i) \frac{r_i^{-6}}{2},$$
$$|F^{(1)}|^2 = (\sin^2 \theta_i \cos^2 \theta_i) \frac{r_i^{-6}}{2},$$
$$|F^{(2)}|^2 = (\sin^4 \theta_i) \frac{r_i^{-6}}{2},$$
where $r_i$ is the distance between the resonant nucleus and the $i$-th paramagnetic ion, and $\theta_i$ is the angle between the $z$ axis of the electric field gradients (EFG) tensor at chlorine and the distance vector $r_i$.

The electron spin correlation time $\tau_e$ can be written by the temperature-dependent electron spin-lattice relaxation time $T_{1e}$ and the temperature-independent characteristic time $\tau_s$ for the spin flip between neighbouring electrons as [8]

$$\tau_e^{-1} = T_{1e}^{-1} + \tau_s^{-1}.$$  

Hence, by assuming the Orbach process [21]:

$$T_{1e} = a \exp(A/kT)$$

for the electron spin-lattice relaxation process in the instantaneous local magnetic field, where $A$ denotes the energy difference between the ground and the first-excited states of Co$^{2+}$, the temperature dependence of $T_{1O}$ observed below ca. 200 K can be interpreted by (1). Equation (1) can be rewritten as

$$(T_{1O}^{-1})_e = K \{a^{-1} \exp(-A/kT) + \tau_s^{-1} \}^{-1},$$

where $K = 3 (\frac{3}{2})^2 \gamma^2 g^2 \mu_B^2 \frac{1}{2} J (J + 1)(2A)$
$$= 9 \gamma^2 \mu_B^2 A,$$

using the effective Bohr magneton $\mu_{eff} = [g^2 \mu_B^2 J (J + 1)]^{1/2}$ for the Co$^{2+}$ ion. In the following calculations we have assumed that $\mu_{eff}^2 = 24 \mu_B^2$, the value of which was determined for the isomorphous [Co(H$_2$O)$_6$][SiF$_6$] [22], and that $A = 1.63 < 10^{-14}$ cm$^{-6}$, which was estimated from the crystal structure of the isomorphous [Ni(H$_2$O)$_6$][SnCl$_6$] [11, 20].

To explain the $T_{1O}^{-1}$ values in the whole temperature range, the contributions ($T_{1O}^{-1}$)$_h$ and ($T_{1O}^{-1}$)$_c$ from lattice vibrations and a reorientation of the [PtCl$_6$]$^{2-}$ complex anions, respectively, should be considered. These relaxation contributions can be written as

$$(T_{1O}^{-1})_h = b T^2$$

and

$$(T_{1O}^{-1})_c = c \exp(-E_a/RT),$$

where $E_a$ is the activation energy of the reorientation [19]. Using the formula

$$T_{1O}^{-1} = (T_{1O}^{-1})_e + (T_{1O}^{-1})_h + (T_{1O}^{-1})_c,$$

least-squares fitting calculations were performed with $a$, $A$, $\tau_s$, $b$, $c$, and $E_a$ as parameters. The best-fit parameters are listed in Table 2.

<table>
<thead>
<tr>
<th>Contribution</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic interaction with paramagnetic Co$^{2+}$ ions</td>
<td>$a/s$ = $5 \times 10^{-14}$, $\tau_s/s = 0.9 \times 10^{-10}$</td>
</tr>
<tr>
<td>Lattice vibrations</td>
<td>$b/s^{-1}K^{-2}$ = $1 \times 10^{-4}$</td>
</tr>
<tr>
<td>Reorientation of [PtCl$_6$]$^{2-}$</td>
<td>$c/s^{-1}$ = $2 \times 10^{18}$, $E_a/kJ mol^{-1}$ = $125 \pm 15$</td>
</tr>
</tbody>
</table>

The energy difference $A/k = 530 \pm 20$ K (370 ± 15 cm$^{-1}$) obtained for the ground and the first-excited states of the Co$^{2+}$ compares quite well with the experimentally reported values of several compounds [8, 10, 23, 24]. Theoretically, $A$ equals $(3/2) \lambda$ for the Co$^{2+}$ ions in a cubic crystal field, where $\lambda$ is the effective spin-orbit parameter of Co$^{2+}$ [25].

**ESR Spectra of Mn$^{2+}$ in [Co(H$_2$O)$_6$][PtCl$_6$]**

The observed ESR spectra of Mn$^{2+}$ ($S = I = S/2$) consist of 30 lines, as shown in Fig. 2, and are indicating the existence of a single type of [Mn(H$_2$O)$_6$]$^{2+}$ magnetic complexes in the trigonal (R 3) crystal of [Co(H$_2$O)$_6$][PtCl$_6$]. The spectra could be described by an effective spin-Hamiltonian appropriate for trigonal crystal field symmetry:

$$\mathcal{H} = g_\parallel \mu_B H_z S_z + g_\perp \mu_B (H_x S_x + H_y S_y)$$

$$+ D[S_x^2 - \frac{1}{3} S(S + 1)] + A_x S_x I_x + A_y (S_y I_x + S_x I_y)$$

$$+ \frac{d}{6} [S_y^4 + S_x^4 + S_z^4 - \frac{1}{3} S(S + 1)(3S^2 + 3S - 1)],$$
Modulation Narrowing of Mn$^{2+}$ ESR Spectra due to Co$^{2+}$ Spin-Lattice Relaxation

The peak-to-peak linewidth $\Delta H$ of the lowest field hyperfine line was measured as a function of temperature when the magnetic field was applied along the [1, 1, 1] axis. $\Delta H$ decreases from 65 G at ca. 90 K to 15 G at ca. 300 K with increasing temperature as shown in Figure 3. The square of the linewidth can be written approximately as

$$(\Delta H)^2 = (\Delta H_{\text{Mn-Co}})^2 + (\Delta H_{\text{Mn-H}})^2,$$

provided that $\Delta H_{\text{Mn-Co}}$ and $\Delta H_{\text{Mn-H}}$ result from the two independent broadening mechanisms, that is, the magnetic interaction between Mn$^{2+}$ and Co$^{2+}$ ions and the magnetic dipolar interaction between Mn$^{2+}$ and $^1\text{H}$ of water molecule, respectively [2]. Owing to the modulation narrowing due to the rapid electron spin correlation time $\tau_e$ of Co$^{2+}$, the $\Delta H_{\text{Mn-Co}}$ is given by [2]

$$\Delta H_{\text{Mn-Co}} = \frac{2(\Delta H_0^{\text{Mn-Co}})^2}{H_{\text{mod}}}.$$

Here, $\Delta H_0^{\text{Mn-Co}}$ denotes the linewidth in the absence of the modulation, and the modulation field $H_{\text{mod}}$ is defined by use of $\tau_e$ and the $g$-value $\tilde{g}$ of Co$^{2+}$:

$$\tilde{g} \, \mu_B \, H_{\text{mod}} = \hbar / \tau_e.$$  

From (17)–(19) we have

$$(\Delta H)^2 = \left[ \frac{2 \tilde{g} \, \mu_B}{\hbar} (\Delta H_0^{\text{Mn-Co}})^2 \tau_e \right]^2 + (\Delta H_{\text{Mn-H}})^2.$$  

Adopting the relations (6) and (7) for $\tau_e$ and $T_{1e}$, respectively, (20) becomes

$$(\Delta H)^2 = A \exp(-\Delta/kT) + B)^{-2} + (\Delta H_{\text{Mn-H}})^2,$$

where

$$A = \left[ \frac{2 a \, \tilde{g} \, \mu_B}{\hbar} (\Delta H_0^{\text{Mn-Co}})^2 \right]^2,$$

$$B = a \, \tau_e^{-1}.$$  

Least-squares fitting calculations by use of (21) resulted in $A = 0.3 \, \text{G}^2$, $B = 8 \times 10^{-3}$, $\Delta/k = 680 \pm 150 \, \text{K}$, $\Delta H_{\text{Mn-H}} = 15 \pm 2 \, \text{G}$ for the observed temperature dependence of $\Delta H$ shown in Figure 3. The obtained value of $\Delta H_{\text{Mn-Co}}$ is quite reasonable compared with the estimated values of 10–15 G [29]. The energy gap parameter $\Delta$ agrees fairly well with that $(\Delta/k = 530 \, \text{K})$ obtained from the $^{35}\text{Cl} \, T_{1e}$ analysis. These results suggest that the ESR linewidth analysis of impurity paramagnetic ions can be applied to investigate the...
fast electron spin dynamics of host paramagnetic ions. However, to obtain the absolute value of the Co$^{2+}$ spin-lattice relaxation time $T_{1\chi}$, it is necessary to know the value of $\Delta H_{\text{Mn-Co}}^0$, which is very difficult to estimate because the additional contribution from the exchange interaction between dissimilar ions is superimposed on the dipolar width [2].

The dipolar width due to the Mn-Co interaction can be evaluated from the second moment $M_2$ for dipolar broadening. Taking into account of only the adiabatic part of the dipolar Hamiltonian between dissimilar ions (Mn-Co), $M_2$ of Mn$^{2+}$ ESR line is estimated by [30]

$$M_2 = \frac{1}{2} \mu_{\text{eff}}^2 \sum_k r_{jk}^6 (3 \cos^2 \theta_{jk} - 1)^2,$$  

(24)

where $\mu_{\text{eff}}$ is the effective Bohr magneton of the Co$^{2+}$ ion and $\theta_{jk}$ is the angle between the magnetic field direction and the interionic vector $r_{jk}$ connecting the $j$-th Mn$^{2+}$ to the $k$-th Co$^{2+}$. For a Gaussian line-shape, the purely dipolar width $(\Delta H_{\text{Mn-Co}}^0)_{\text{dip}}$ is estimated by

$$(\Delta H_{\text{Mn-Co}}^0)_{\text{dip}} \approx 4 \left( \frac{10}{9} \right) M_2 .$$  

(25)

Here, the relation between the peak-to-peak width and the second moment was employed, and the so-called “10/3 effect” was taken into account in order to include the second moment contribution from the nonadiabatic term of the dipolar Hamiltonian [31]. Based on the crystal structure $R \bar{3}$, $a = 7.10 \, \text{Å}$, $x = 96.26^\circ$ [11], and using $\mu_{\text{eff}}^2 (\parallel [1, 1, 1]) = 33 \mu_B^2$ [32] for $[\text{Co(H}_2\text{O})_6][\text{PtCl}_6]$, $(\Delta H_{\text{Mn-Co}}^0)_{\text{dip}}^2$ was calculated to be $27 \times 10^4 \, \text{G}^2$ when the external field is parallel to the $[1, 1, 1]$ axis.

Putting $(\Delta H_{\text{Mn-Co}}^0)^2 = (\Delta H_{\text{Mn-Co}}^0)_{\text{dip}}^2$ and $\tilde{g}(\parallel [1, 1, 1]) = 6.6$, which was derived from the above $\mu_{\text{eff}}^2$ value by $\mu_{\text{eff}}^2 = \tilde{g}^2 \mu_B^2 J(J + 1)$ assuming $J = 1/2$, the pre-exponential factor $a$ in (7) was calculated as $a = 1 \times 10^{-11} \, \text{s}$ from (22). In spite of a complete disregarding of the exchange contribution to the line broadening, the obtained $a$ value shows a fairly good agreement with that $(0.5 \times 10^{-11} \, \text{s})$ determined by the $^{35}\text{Cl} T_{1\chi}$ analysis, suggesting the minor importance of the exchange contribution in this compound. From the $a$ value, $\tau_a = 1 \times 10^{-11} \, \text{s}$ is calculated by (23). This value is appreciably shorter than that $(9 \times 10^{-11} \, \text{s})$ from the $^{35}\text{Cl} T_{1\chi}$ analysis. In the case of the ESR experiments of impurity Mn$^{2+}$ ions, Mn-Co exchange interaction also affects the electron spin dynamics of Co$^{2+}$ ions adjacent to the probe ions. This may be a possible reason why a shorter value of $\tau_a$ was obtained for Co$^{2+}$ in the Mn$^{2+}$ doped system.

[18] Y. Oyanagi and T. Nakagawa, SALS System Ver. 2.5 for statistical analysis with least-squares fitting, The University of Tokyo, Japan 1981.
[27] Ref. [25], p. 142.
[32] Ref. [25].