$^2$H and $^{195}$Pt NMR Studies of Molecular and Electron Spin Dynamics in Paramagnetic [Cu(H$_2$O)$_6$][PtCl$_6$]*

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Z. Naturforsch. 53 a, 447–452 (1998); received December 31, 1997

The temperature dependences of $^2$H and $^{195}$Pt NMR spectra and the spin-lattice relaxation time $T_1$ were measured for [Cu(H$_2$O)$_6$][PtCl$_6$]. From the simulation of $^2$H NMR spectra, the jump rate of $180^\circ$ flips of the water molecules ($k$), the nuclear quadrupole interaction parameters ($\varepsilon Q_q/h, \eta$) and the electron-nucleon dipolar interaction parameter ($\nu_D$) were obtained. By measuring $^2$H $T_1$, $k$ was estimated in the temperature range where the spectrum is insensitive to the motion of the water molecules. Above the phase transition temperature, the pre-exponential factor $k_0 = 8 \times 10^3$ s$^{-1}$ and the activation energy $E_a = 15$ kJ mol$^{-1}$ for $180^\circ$ flips of the water molecules were obtained from the spectral simulation and $T_1$. $^{195}$Pt NMR spectra showed an axially symmetric and unsymmetric powder pattern of the chemical shift anisotropy at the high and low temperature phase, respectively. For the deuterated compound, the correlation times of the electron spin in Cu$^{2+}$ were estimated from $^{195}$Pt $T_1$ and the activation energy for jumping between the different configurations of Jahn-Teller distortion $\Delta = 200$ K was obtained.

Introduction

[Cu(H$_2$O)$_6$][PtCl$_6$] undergoes a phase transition caused by the cooperative Jahn-Teller effect at 135 K, and the transition temperature shifts to the lower side by 6 K on deuteration [1-3]. [Cu(H$_2$O)$_6$]$^{2+}$ ions, changing between the three Jahn-Teller distorted configurations by thermal excitation in the high temperature phase, distort to one of these configurations in the low temperature phase [1-5]. The lower temperature shift of the phase transition, however, cannot be explained by the change in the motion of [Cu(H$_2$O)$_6$]$^{2+}$ due to the mass difference between $^1$H and $^2$H, and detailed information about the H site is required for clarifying the nature of this phase transition.

Although $^2$H NMR is effective to study the environment of the H site, the analysis of the powder spectra of the paramagnetic compound obtained by the usual quadrupole echo method is very difficult because of the dephasing due to the paramagnetic shift [6]. Recently, $^2$H NMR spectra in paramagnetic compounds, using the shift-compensated pulse sequence which refocuses both the quadrupolar interaction and the paramagnetic shift, have been investigated [6-11]. From the analysis of the powder spectra obtained by this method, the jumping rate of the molecules, static nuclear quadrupolar interaction parameters and the paramagnetic shift parameter have been obtained [7,8]. In the present work, in order to obtain information about the H site and the motion of H$_2$O molecules in [Cu(H$_2$O)$_6$][PtCl$_6$], we measured $^2$H NMR spectra of the powder sample using the shift compensated pulse sequence and performed a simulation. $^2$H $T_1$ was measured to study the motion of H$_2$O in the temperature range where the spectrum is insensitive to the H$_2$O motion and the electron spin dynamics in Cu$^{2+}$. Moreover, the isotope effect on the phase transition is discussed from $^{195}$Pt NMR spectra and $T_1$.

Experimental

The deuterated sample was obtained by repeated recrystallization from heavy water. $^2$H and $^{195}$Pt NMR spectra were measured using a CMX-300 spectrometer with a 5 mmø sample tube at 45.825 and 64.160 MHz, respectively. For $^2$H NMR spectra, the

* Presented at the XIVth International Symposium on Nuclear Quadrupole Interactions, Pisa, Italy, July 20–25, 1997.
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For the $^2\text{H}-\text{Cu}^{2+}$ dipolar interaction, the contribution from the nearest Cu$^{2+}$ ion ($\omega_D = 2\pi\nu_D$) was estimated. On the assumption of the isotropic $g$ tensor, the site frequency $\omega_i$ is written by the second-order Wigner rotation matrix $D_{nm}^{(2)}(\Omega)$ [8, 12, 13] as

$$\omega_i = \mp \omega_Q - \omega_P,$$
$$\omega_Q = \sqrt{\frac{3}{2}} \sum_{n,m=-2}^{2} D_{0n}^{(2)}(\psi, \theta, \phi) D_{n0}^{(2)}(\alpha, \beta, \gamma) T_{mQ}^{(2)},$$
$$\omega_P = \sum_{n=-2}^{2} D_{0n}^{(2)}(\psi, \theta, \phi) D_{n0}^{(2)}(\alpha', \beta', \gamma') \omega_D,$$
$$T_{0Q}^{(2)} = \sqrt{\frac{3}{8}} e^{2} Q q / h, \quad T_{\pm2Q}^{(2)} = (\eta/2) e^{2} Q q / h,$$
$$\omega_D = 2\pi \mu_B g \mu_B (S_z)^{r \text{-} 3},$$

where, $(\alpha, \beta, \gamma), (\psi, \theta, \phi)$ and $(\alpha', \beta', \gamma')$ represent the Euler angles for the transformation from the molecular axes to the principal axes system of the quadrupolar tensor, from the laboratory axes to the molecular axes and from the molecular axes to the principal axes system of the dipolar tensor between the $^2\text{H}$ nuclei and the nearest Cu$^{2+}$, respectively. $(S_z)$ is the expectation value of $S_z$ of the unpaired electron spin in Cu$^{2+}$, $\gamma_D$ is the gyromagnetic ratio of $^2\text{H}$ nucleus, $\mu_B$ the Bohr magneton, $r$ is the distance between the $^2\text{H}$ nucleus and Cu$^{2+}$. The frequencies of $^2\text{H}$ in the two sites $(\omega_1, \omega_2)$ were specified by $\alpha = \alpha' = 0$ and $\pi$. The positions of H atoms are not known, and we assumed $\gamma = 0$. The used angles between the rotation axis and the quadrupole principal axis $\beta = 55^\circ$, and between the rotation axis and the Cu-H vector $\beta = 17^\circ$ were based on the crystal structure of [Ni(H$_2$O)$_6$][SiF$_6$] [14, 15]. The signal which is collected beginning at the top of the resulting echo $G(t, \theta, \phi)$ is written as [8, 12]

$$G(t, \theta, \phi) = P \cdot \text{exp}[\hat{A}t] \text{exp}[\hat{A} \tau] \text{exp}[\hat{A}^\dagger \tau] \cdot 1,$$

$$\hat{A} = \begin{pmatrix} i \omega_1 - k & k \\ k & i \omega_2 - k \end{pmatrix},$$
$$P = (P_1, P_2), \quad 1 = (1, 1).$$

Here, $P$ is a vector of site populations and we assumed $P_1 = P_2 = 1/2$. The signal of the powder sample $G(t)$
The spectrum is obtained by the Fourier transform of $G(t)$. The theoretical spectra are shown in Figure 1(b). Because of the fast motion limit, the spectrum at 293 K was insensitive to the motion of H$_2$O, and $k$ could not be determined accurately. For the quadrupole interaction parameters, though $\eta$ was almost temperature independent, $e^2Qq/h$ which showed 245 kHz at 123 K, decreased with increasing temperature and showed 225 kHz at 293 K. The observed decrease of $e^2Qq/h$ can be considered to reveal the existence of rapid motions, other than the 180° flips of the water molecules, which average the electric field gradient at 2H site.

Figure 2 shows the temperature dependence of 2H $T_1$. The shallow minimum observed at ca. 230 K can be considered to be due to the fluctuation of the EFG at the 2H nucleus caused by the 180° flips of the water molecules. At low temperatures, $T_1$ decreased gradually with decreasing temperature, and the relaxation can be considered to be dominated by the magnetic dipole interaction between 2H nuclei and Cu$^{2+}$ ions. The quadrupole relaxation rate ($T_{1Q}^{-1}$) caused by the 180° flips of the water molecules can be written by assuming $\eta = 0$ as [16, 17]

$$T_{1Q}^{-1} = \frac{1}{10} \left( \frac{3e^2Qq}{4\hbar} \right)^2 \frac{(\sin 2\beta)^2}{\left\{ \frac{\tau_c}{1 + \omega_N^2 \tau_c^2} + \frac{4\tau_c}{1 + \omega_N^2 \tau_c^2} \right\}},$$

where $\beta$ is the angle between the rotation axis and the quadrupole principal axis, $\omega_N$ the angular NMR frequency and $\tau_c$ the correlation time for the 180° flips of the water molecules. Assuming Arrhenius relation, $\tau_c$ is given by

$$\tau_c = \tau_0 \exp(E_a/RT),$$

where $\tau_0$ and $E_a$ are the correlation time at infinite temperature and the activation energy for the 180° flips of the water molecules. If the paramagnetic dipole relaxation is caused by the fluctuation of the electron spin in Cu$^{2+}$, the relaxation rate ($T_{1P}^{-1}$) can be written as [3, 18, 19]

$$T_{1P}^{-1} = \frac{2}{15} \gamma_B^2 g^2 \mu_B^2 \sum_i \tau_i^{-6} S(S+1) \left\{ \frac{3\tau_c}{1 + \omega_N^2 \tau_c^2} + \frac{7\tau_c}{1 + \omega_N^2 \tau_c^2} \right\},$$

Fig. 2. Temperature dependence of $^2$H NMR $T_1$ in [Cu(D$_2$O)$_6$][PtCl$_6$]. The broken lines show the theoretical curves of $T_{1Q}$ and $T_{1P}$. The solid line shows the theoretical curve of $T_1$.

Fig. 3. Temperature dependence of the jumping rate ($k$) for the 180° flip of H$_2$O. The open circle shows $k$ estimated from the spectral simulation and the solid line shows the theoretical curve with the parameters obtained by $T_1$ measurements.
where $\gamma_0$ is the gyromagnetic ratio of the $^2$H nucleus, $\mu_B$ the Bohr magneton, $g$ the $g$-value for Cu$^{2+}$, $\omega_e$ the angular ESR frequency and $\tau_c$ the correlation time of the electron spin. $r_i$ is the distance between the $^2$H nucleus and the $i$-th Cu$^{2+}$ ion. $\omega_N \ll \tau_c^{-1} \ll \omega_e$ can be considered to hold in the 7.0 T magnetic field, and (12) can be rewritten as

$$T_{1P}^{-1} = \frac{2}{15}\gamma_0^2 g^2 \mu_B^2 \sum_i r_i^{-6} S(S+1) 3\tau_c.$$  (13)

When $\tau_c$ is determined by the thermally activated transitions between the three different configurations caused by Jahn-Teller effect, $\tau_c$ can be written as

$$\tau_c = \tau_{eo} \exp(\Delta/kT),$$  (14)

where $\Delta$ is the activation energy for jumping between the different Jahn-Teller states. The least-squares fitting was performed by using equation

$$T_{1P}^{-1} = T_{1Q}^{-1} + T_{1P}^{-1}$$  (15)

with $h^{-1}e^2 Qq \sin(2\beta)/kHz$, $\tau_0/k$, $E_a/k$Jmol$^{-1}$, $\tau_{eo}/s$, and $\Delta$ as parameters. $\sum_i r_i^{-6}$ was obtained from the crystal data of [Ni(H$_2$O)$_6$][SiF$_6$] [14], and the contribution from paramagnetic ions with 11$^3$ primitive cells around the resonant nucleus was calculated. The best-fit parameters are listed in Table 1. The obtained $h^{-1}e^2 Qq \sin(2\beta) = 296$ kHz was slightly larger than $h^{-1}e^2 Qq \sin(2\beta) = 230$ kHz calculated with $\beta = 55^\circ$ and $e^2 Qq/\hbar = 245$ kHz obtained by the lineshape simulation. This discrepancy can be considered to be due to omitting $\eta$ from the calculation of $T_{1Q}$ [20]. Converting $\tau_c$ to the jumping rate $k$ with $k = (2\tau_c)^{-1}$, $k = k_0 \exp(-E_a/RT)$ ($k_0 = 8 \times 10^{11}$ s$^{-1}$, $E_a = 15$ kJmol$^{-1}$) was obtained. Figure 3 shows the temperature dependence of $k$. Above the phase transition temperature, the obtained $k_0$ and $E_a$ values can be considered to describe well the rate of $180^\circ$ flips of the water molecules, since $k$ estimated by these parameters agrees with those obtained from the spectral simulation. From this relatively small $E_a$ value, it is predicted that the torsional oscillation about the bisector of the water molecule contributes largely to the temperature dependence of the $e^2 Qq/\hbar$ value [15].

The $\tau_e$ value showed the order of $10^{-10}$ s from room temperature to the phase transition temperature. This result equals that obtained from $^{195}$Pt NMR and $^{35}$Cl NQR $T_1$ in the protonated compound [2, 3].

$^{195}$Pt NMR

$^{195}$Pt NMR spectra of [Cu(D$_2$O)$_6$][PtCl$_6$] are shown in Figure 4. An H$_2$PtCl$_6$ solution was used for the standard sample of the chemical shift. The spectra showed the axially symmetric and unsymmetric powder pattern of the chemical shift anisotropy in the high and low temperature phase, respectively. The temperature dependences of the principal values of the chemical shift for [Cu(H$_2$O)$_6$][PtCl$_6$] and [Cu(D$_2$O)$_6$][PtCl$_6$] are shown in Figure 5. In the high temperature phase, the principal values decreased gradually with decreasing temperature. The perpendicular component of the principal values in the high temperature phase splitted into two components in the low temperature phase. For the parallel component of the principal values in the high temperature
phase, however, the drastic change around the transition could not be seen. A significant difference in the principal values between [Cu(H\textsubscript{2}O)\textsubscript{6}][PtCl\textsubscript{6}] and [Cu(D\textsubscript{2}O)\textsubscript{6}][PtCl\textsubscript{6}] was not observed. This phase transition, which is known as of first order, can be considered to be nearly second, since the principal values change continuously around the transition temperature \cite{2}.

Figure 6 shows the temperature dependence of $^{195}$Pt NMR $T_1$ of [Cu(D\textsubscript{2}O)\textsubscript{6}][PtCl\textsubscript{6}]. $T_1$ can be considered to be determined by the magnetic dipolar interaction between the $^{195}$Pt nuclei and the Cu\textsuperscript{2+} ions, since the temperature dependence of $T_1$ is similar to that of the result of [Cu(H\textsubscript{2}O)\textsubscript{6}][PtCl\textsubscript{6}] \cite{3}. In this case, $T_1$ can be connected with the electron spin correlation time $\tau_e$ by the equation \cite{3, 18, 19}

$$T_1^{-1} = \frac{2}{15} \gamma_{\text{Pt}}^2 g^2 \mu_B^2 \sum r_i^{-6} S(S+1)3 \tau_e$$  \hspace{1cm} (16)

where, $\gamma_{\text{Pt}}$ is the gyromagnetic ratio of the $^{195}$Pt nucleus, $\mu_B$ is the Bohr magneton, and $g$ is $g$-value for Cu\textsuperscript{2+}. $r_i$ is the distance between the $^{195}$Pt nucleus and $i$-th Cu\textsuperscript{2+} ion.

$c_i^{-6}$ was obtained from the crystal data of [Cu(H\textsubscript{2}O)\textsubscript{6}][PtCl\textsubscript{6}] \cite{21, 22}, and the contribution from paramagnetic ions with 11\textsuperscript{3} primitive cells around the resonant nucleus was calculated \cite{3}. The temperature dependence of $\tau_e$, which was estimated from $T_1$, is shown in Figure 7. $\tau_e$ can be considered to be determined by the thermal jumping rate between the three Jahn-Teller distorted configurations of [Cu(D\textsubscript{2}O)\textsubscript{6}]\textsuperscript{2+} above the transition temperature. By fitting the function $\tau_e = \tau_0 \exp(\Delta/kT)$ to the estimated temperature dependence of $\tau_e$, a pre-exponential factor $\tau_0 = 1.0 \times 10^{-10}$ s and an activation energy $\Delta = 200$ K (140 cm\textsuperscript{-1}) were obtained. The obtained $\Delta$ is smaller than that of the protonated compound \cite{2, 3}. The height of the Jahn-Teller potential is predicted to be lowered by the deuteration, and this is consistent with the lower temperature shift of the phase transition for the deuterated compound.