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## Molecular Motions of $[\text{N}(\text{C}_2\text{H}_5)_4]^+$ and $[\text{N}(\text{CH}_3)_4]^+$ ions by $^1\text{H}$ Nuclear Magnetic Resonance Relaxation in $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{CoCl}_4$ and $[\text{N}(\text{CH}_3)_4]_2\text{CoCl}_4$ Single Crystals

Sua Yoon and Ae Ran Lim\*

Department of Science Education, Jeonju University, Jeonju 560-759, Korea  
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**Abstract:** The line widths and spin–lattice relaxation times of protons in  $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{CoCl}_4$  and  $[\text{N}(\text{CH}_3)_4]_2\text{CoCl}_4$  single crystals were investigated in the temperature range 160–400 K. The temperature dependences of the spin–lattice relaxation times are attributed to the molecular motions of the ethyl and methyl groups in the  $[\text{N}(\text{C}_2\text{H}_5)_4]^+$  and  $[\text{N}(\text{CH}_3)_4]^+$  ions respectively. The NMR line widths indicate that the ethyl groups in  $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{CoCl}_4$  have one more degree of freedom than the methyl groups in  $[\text{N}(\text{CH}_3)_4]_2\text{CoCl}_4$ . The experimental results are interpreted in terms of the reorientations of the methyl and ethyl groups.

Keywords : protaetiamycine analogue, antimicrobial peptide, bacterial cell selectivity, NMR, structure

### INTRODUCTION

$[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{BCl}_4$  and  $[\text{N}(\text{CH}_3)_4]_2\text{BCl}_4$  ( $B=^{59}\text{Co}$ ,  $^{63}\text{Cu}$ , and  $^{67}\text{Zn}$ ) single crystals belong to the group of  $\text{A}_2\text{BX}_4$ -type crystals.<sup>1-5</sup> Crystals of this type have attracted considerable interest due to their multiple phase transitions. Tetraethylammonium tetrachlorocobalt  $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{CoCl}_4$  (hereafter

\* To whom correspondence should be addressed. E-mail : aeranlim@daum.net

denoted  $[\text{TEA}]_2\text{CoCl}_4$ ) crystals exhibit tetragonal symmetry  $P4_2/nmc$  at room temperature.<sup>6</sup> The structure of this crystal can be described approximately as a system of alternating layers oriented perpendicular to the  $[110]$  direction. Each tetraethylammonium  $[\text{N}(\text{C}_2\text{H}_5)_4]^+$  cation is located at the center of a cavity formed by  $\text{CoCl}_4$  ions. The lattice constants of  $[\text{TEA}]_2\text{CoCl}_4$  crystals have been reported to be approximately  $a=b=9 \text{ \AA}$  and  $c=15 \text{ \AA}$ .<sup>6</sup> The organic groups and the anion tetrahedra are disordered at room temperature.  $[\text{N}(\text{CH}_3)_4]_2\text{CoCl}_4$  (hereafter denoted  $[\text{TMA}]_2\text{CoCl}_4$ ) crystals have attracted considerable interest due to their successive phase transitions.<sup>7</sup> The crystal structure of tetramethylammonium tetrachlorocobalt  $[\text{TMA}]_2\text{CoCl}_4$  belongs to the space group  $Pnma$ , in which there are four formula units per cell with the approximate dimensions  $a=12 \text{ \AA}$ ,  $b=9 \text{ \AA}$ , and  $c=15 \text{ \AA}$  [8]. Some disorder has been observed in the orientations of both the  $[\text{CoCl}_4]^{2-}$  and  $[\text{N}(\text{CH}_3)_4]^+$  tetrahedra. The major structural difference between these crystals is the size of the slightly distorted  $[\text{CoCl}_4]^{2-}$  tetrahedra. Only a few studies of  $[\text{TEA}]_2\text{CoCl}_4$  and  $[\text{TMA}]_2\text{CoCl}_4$  crystals have been reported, and the molecular motions of  $[\text{TEA}]_2\text{CoCl}_4$  crystals have not previously been investigated.

The magnetic resonance relaxation times of nuclear spin systems have been widely used to elucidate various types of atomic motions in crystals because these relaxation times are related to the structures and internal motions of solids; in particular, the protons of these solids act as resonant nuclei, so the relaxation times of these nuclei reflect the ionic motions in the solid. Previous studies have established that at temperatures near the phase transition temperatures of  $[\text{N}(\text{CH}_3)_4]_2\text{BCl}_4$  ( $B=\text{Co}$ ,  $\text{Cu}$ ,  $\text{Zn}$ , and  $\text{Cd}$ ) crystals, the magnetic resonance relaxation times and their slopes undergo abrupt

changes; based on this information, it has been concluded that these phase changes are always accompanied by changes in molecular motion.<sup>9-11</sup> This study employed a pulsed nuclear magnetic resonance (NMR) spectrometer to investigate the temperature dependences of the line widths and the spin-lattice relaxation times,  $T_1$ , for  $^1H$  in  $[TEA]_2CoCl_4$  and  $[TMA]_2CoCl_4$  single crystals grown with the slow evaporation method. Although these crystals are type  $A_2BX_4$ , their phase-transition temperatures differ. We attempted to use the  $^1H$  NMR data to determine the role of  $[TEA]^+$  and  $[TMA]^+$  in these crystals' phase transitions. Our experimental results are discussed in terms of the reorientations of the ethyl and methyl groups

$[TEA]_2CoCl_4$  undergoes a phase transition at 227 K.<sup>12-13</sup> The two phases of this crystal are denoted I and II in order of decreasing temperature. According to our X-ray results,  $[TEA]_2CoCl_4$  crystals have a tetragonal structure with lattice constants of  $a=9.041 \text{ \AA}$ ,  $c=14.976 \text{ \AA}$ , and  $\alpha=\beta=\gamma=90^\circ$  at room temperature. These results are consistent with those of Stucky et al. [6] and Kandhaswamy et al.<sup>14</sup> An endothermic peak was found at 229 K ( $T_C$ ) with DSC, which corresponds to the phase transition. And,  $[TMA]_2CoCl_4$  single crystals have been reported to undergo six phase transitions, at 122 K ( $T_{C6}$ ), 192 K ( $T_{C5}$ ), 276 K ( $T_{C4}$ ), 277.6 K ( $T_{C3}$ ), 280.1 K ( $T_{C2}$ ), and 293 K ( $T_{C1}$ )<sup>7</sup>; these phase transition temperatures are consistent with our DSC results. Previous studies have also reported that  $[TMA]_2CoCl_4$  single crystals exhibit seven phases I, II, III, IV, V, VI, and VII in order of decreasing temperature. The highest temperature phase, phase I, has an orthorhombic structure with space group  $Pm\bar{c}n$ . Its orthorhombic lattice constants are  $a=9.001 \text{ \AA}$ ,  $b=15.539 \text{ \AA}$ , and  $c=12.276 \text{ \AA}$  [8], which are

slightly different from those of the hexagonal form. This structure is consistent with our X-ray results. Phases II and IV are incommensurate, with lattice modulation in the *c*-direction. Phases III and V are ferroelectric and ferroelastic respectively.

## EXPERIMENTAL

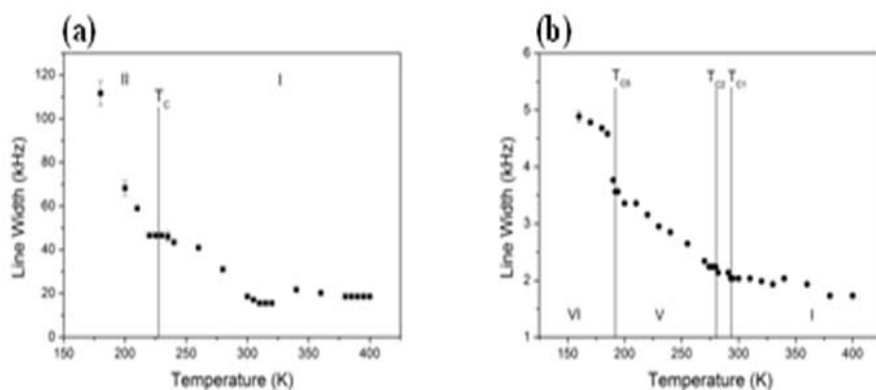
Aqueous solutions of [TEA]<sub>2</sub>CoCl<sub>4</sub> and [TMA]<sub>2</sub>CoCl<sub>4</sub> were prepared with stoichiometric ratios of [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]Cl and CoCl<sub>2</sub>, and [N(CH<sub>3</sub>)<sub>4</sub>]Cl and CoCl<sub>2</sub>, respectively. Single crystals were then grown by slow evaporation of the aqueous solutions at room temperature. The resulting [TEA]<sub>2</sub>CoCl<sub>4</sub> and [TMA]<sub>2</sub>CoCl<sub>4</sub> crystals are bright, transparent, and blue. The orientation of each crystal was identified with an optical polarizing microscope. The external magnetic field for the line width and spin–lattice relaxation measurements was applied along the crystallographic *c*-axis.

The lattice constants of the [TEA]<sub>2</sub>CoCl<sub>4</sub> and [TMA]<sub>2</sub>CoCl<sub>4</sub> crystals at room temperature were determined with an X-ray diffractometer system (Bruker AXS GMBH) at the Korea Basic Science Institute. In addition, in order to determine the phase transition temperatures of [TEA]<sub>2</sub>CoCl<sub>4</sub> and [TMA]<sub>2</sub>CoCl<sub>4</sub>, differential scanning calorimetry (DSC) was carried out on the crystals with a Dupont 2010 DSC instrument; these measurements were performed at a heating rate of 10°C/min. The line widths and spin–lattice relaxation times of <sup>1</sup>H in these two single crystals were measured by using the Varian 200 FT NMR spectrometer at the Korea Basic Science Institute. The static magnetic field was 4.7 T, and the central radio frequency was set at  $\omega_0/2\pi=200.13$  MHz. The spin–lattice relaxation

times were measured using a saturation recovery pulse sequence, sat  $t-\pi/2$ : the nuclear magnetization of the  $^1H$  nucleus at time  $t$  after the sat pulse, a comb of one hundred of  $\pi/2$  pulses applied at a regular interval, were determined following the excitation  $\pi/2$  pulse. The width of the  $\pi/2$  pulse was 2.4  $\mu s$  for  $^1H$ . Temperature-dependent NMR measurements were carried out in the temperature range 150–400 K, with the sample temperature kept constant by controlling the nitrogen gas flow and the heating current, resulting in an accuracy of  $\pm 0.2$  K.

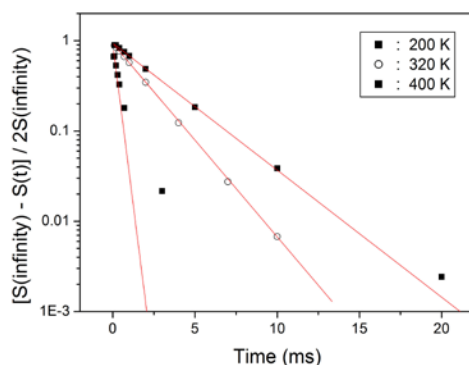
## RESULTS AND DISCUSSION

The variation with temperature of the full width half maximum (FWHM) of the  $^1H$  resonance line of  $[TEA]_2CoCl_4$  and  $[TMA]_2CoCl_4$  single crystals is shown in Fig. 1(a) and (b). In case of  $[TEA]_2CoCl_4$ , the line width below  $T_C$  is approximately 40-100 kHz, and it is narrower than that above  $T_C$ . This abrupt narrowing is attributed to internal motions that have a temperature dependence associated with that observed for the line width. When the temperature increases, the line shape changes from the Gaussian-like shape produced by a rigid lattice to a Lorentzian shape.<sup>15</sup>



**Fig 1.** Temperature dependence of the FWHM of the  $^1\text{H}$  signal for (a)  $[\text{TEA}]_2\text{CoCl}_4$  and (b)  $[\text{TMA}]_2\text{CoCl}_4$  single crystals.

On the other hand, the line width of the  $^1\text{H}$  signal due to the  $[\text{N}(\text{CH}_3)_4]^+$  ions in  $[\text{TMA}]_2\text{CoCl}_4$  single crystals was obtained for the temperature range 160–400 K. The line width for  $[\text{TMA}]_2\text{CoCl}_4$  crystal is more narrower than that of  $[\text{TEA}]_2\text{CoCl}_4$  crystal. The abrupt decreases in the temperature dependence of the line width correspond to phase transitions. As the temperature is increased, the line width of the  $^1\text{H}$  signal decreases. The line width becomes small abruptly at  $T_{c5}$  with increasing temperature, which indicates that the protons in the  $[\text{N}(\text{CH}_3)_4]^+$  ions play an important role in this phase transition. Further, the line widths do not change at other phase transition temperatures, which cannot be identified from changes in the line width.

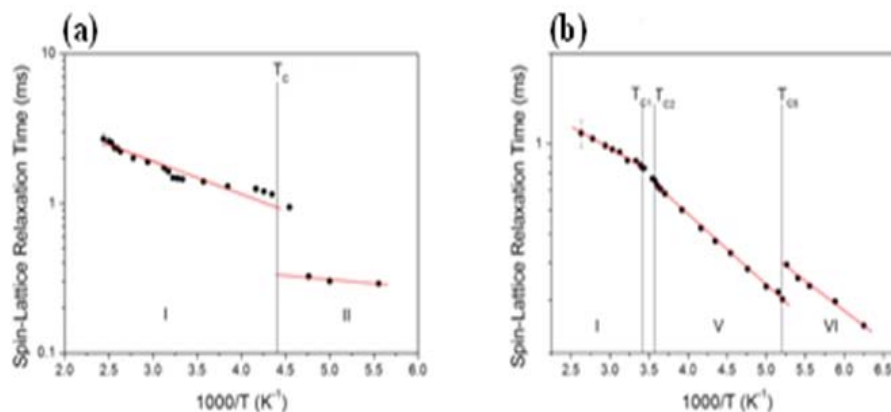


**Fig 2.** Recovery behaviors of  $^1H$  in  $[TEA]_2CoCl_4$  crystals as functions of the delay time.

The nuclear magnetizations of  $^1H$  in  $[TEA]_2CoCl_4$  and  $[TMA]_2CoCl_4$  were determined by using an inversion recovery sequence. The spin-lattice relaxation time,  $T_1$ , was determined directly in each case from the slope of the log  $[(S(\infty) - S(t)) / 2S(\infty)]$  versus time ( $t$ ) curve.<sup>16-17</sup> Figure 2 shows the recovery traces of  $^1H$  at 200 K, 320 K, and 400 K in  $[TEA]_2CoCl_4$  crystals. The slopes of the recovery traces are different at each temperature. The recovery data for the temperatures investigated here can all be fitted with a single exponential function; these fits are shown as solid curves in Fig. 2. The spin-lattice relaxation times,  $T_1$ , for  $[TEA]_2CoCl_4$  and  $[TMA]_2CoCl_4$  above 180 K are shown in Fig. 3(a) and (b) as a function of inverse temperature.  $T_1$  for  $[TEA]_2CoCl_4$  abruptly increases with increasing temperature near  $T_c=227$  K, and the discontinuity at 227 K, as shown in Fig. 3(a), is due to the phase transition: 0.29 ms at 200 K (phase II) and 1.45 ms at 300 K (phase I). The activation energies for the reorientational motion of the  $[TEA]_2CoCl_4$  crystals were determined by fitting the  $T_1$  versus inverse temperature curves, and found to be 4.16 and 1.08 kJ/mol in phases I and II

respectively. The changes in the relaxation time and the line width during the transition between phases I and II are due to structural changes involving the  $[\text{N}(\text{C}_2\text{H}_5)_4]^+$  ions. In case of  $[\text{TMA}]_2\text{CoCl}_4$  crystals, the distinct discontinuity in the relaxation time  $T_1$  at  $T_{C5}$  as shown in Fig. 3(b) can be assigned to a structural phase transition involving the  $[\text{N}(\text{CH}_3)_4]^+$  groups. This result suggests that the transition of the phases VI and V is a first-order type. The significant difference in the  $T_1$  value between phases V and VI indicates that the  $[\text{N}(\text{CH}_3)_4]^+$  groups are significantly affected during this transition. The other phase transitions cannot be identified by examining the  $^1\text{H}$  NMR results, and the  $^1\text{H}$  in the  $[\text{N}(\text{CH}_3)_4]^+$  groups are not susceptible to these transitions. The relaxation time increases with increasing temperature, and is in the fast-motion region. The activation energies obtained from the distinct slopes of the spin-lattice relaxation time versus inverse temperature curves, i.e., the solid lines in Fig. 3(b), have values of 3.16, 4.18, and 3.60 kJ/mol for phases I, V, and VI, respectively. The form of the proton  $T_1$  versus inverse temperature curves for all the phases indicates that their relaxation processes are caused by reorientation motions of  $[\text{N}(\text{CH}_3)_4]^+$ .<sup>9-10</sup>





**Fig 3.** Temperature dependence of the spin–lattice relaxation time,  $T_1$ , for  $^1H$  in (a)  $[TEA]_2CoCl_4$  and (b)  $[TMA]_2CoCl_4$  single crystals.

In simple NMR theory, the general behavior of the spin-lattice relaxation rate,  $T_1^{-1}$ , for random motions of an Arrhenius type can be described in terms of two regions as a function of the correlation time, the fast- and slow-motion regions. The fast-motion region arises for  $\omega_0\tau_c \ll 1$ ,  $T_1^{-1} \sim \exp(E_a/RT)$ , and the slow-motion region for  $\omega_0\tau_c \gg 1$ ,  $T_1^{-1} \sim \omega_0^{-2} \exp(-E_a/RT)$ , where  $\omega_0$  is the Larmor frequency and  $E_a$  is the activation energy.<sup>15</sup>

## CONCLUSION

The  $^1H$  line widths and the spin-lattice relaxation times of  $[TEA]_2CoCl_4$  and  $[TMA]_2CoCl_4$  single crystals have been investigated over a wide temperature range. The changes in the line widths

and relaxation behaviors near the phase-transition temperatures indicate changes in the states of internal motion. The magnetizations of the  $^1\text{H}$  nuclei with nuclear spin  $I=1/2$  in these crystals were determined with inversion recovery sequences and found to follow single exponential functions. The temperature dependences of the spin-lattice relaxation time are due to the molecular reorientational motions of the  $\text{CH}_3$  groups in the  $[\text{N}(\text{CH}_3)]^+$  ions and the  $\text{CH}_2$  plus  $\text{CH}_3$  groups in the  $[\text{N}(\text{C}_2\text{H}_5)]^+$  ions. The temperature dependences of  $T_1$  for the Co-based compounds appear to be very similar, and the influence of the paramagnetic ions is predominant. The spin-lattice relaxation time should be inversely proportional to the square of the magnetic moment of the paramagnetic ion. Therefore, the spin-lattice relaxation of materials containing  $\text{Co}^{2+}$  ions is shorter than those of materials without paramagnetic ions. The  $\text{Co}^{2+}$  spin dynamics clearly dominate the spin-lattice relaxation behaviors of the Co-based crystals. Therefore,  $^1\text{H}$  spin-lattice relaxation is driven in these systems by the fluctuations of the magnetic dipole of the  $\text{Co}^{2+}$  paramagnetic ions. A shorter  $T_1$  indicates that the transfer of energy from the nuclear spin system to the surrounding environment is easier. For both  $[\text{TEA}]_2\text{CoCl}_4$  and  $[\text{TMA}]_2\text{CoCl}_4$  crystals, the line width abruptly decreases with increasing temperature, which is attributed to internal motion. The line width of  $^1\text{H}$  for  $[\text{TEA}]_2\text{CoCl}_4$  crystals is much larger than that for  $[\text{TMA}]_2\text{CoCl}_4$  crystals. The NMR line widths indicate that the ethyl groups in the  $[\text{TEA}]_2\text{CoCl}_4$  compounds have one more degree of freedom than the methyl groups in the  $[\text{TMA}]_2\text{CoCl}_4$  compounds. Thus the phase transitions in these materials are affected by structural changes involving the  $[\text{TEA}]^+$  and  $[\text{TMA}]^+$  cations.

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