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lonic dynamics of the cation in organic–inorganic hybrid compound $(CH_3NH_3)_2MCl_4$ (M = Cu and Zn) by ¹H MAS NMR, ¹³C CP MAS NMR, and ¹⁴N NMR

Ae Ran Lim 🕩 *ab

The ionic dynamics of $(CH_3NH_3)_2MCl_4$ (M = Cu, Zn) by ¹H magic-angle spinning (MAS) nuclear magnetic resonance (NMR), ¹³C cross-polarization (CP) MAS NMR, and ¹⁴N NMR are investigated as a function of temperature with a focus on the role of the $CH_3NH_3^+$ cation. The molecular motions in $(CH_3NH_3)_2MCl_4$ are also discussed based on the ¹H spin–lattice relaxation time in the rotating coordinate frame T_{1p} . From the ¹H T_{1p} results, the activation energies for the tumbling motion of ¹H for CH_3 and NH_3 were similar, and the uniaxial rotations occurred within a large temperature range. The molecular motions for ¹³C and ¹⁴N of the main chain in the $CH_3NH_3^+$ cation were rigid, whereas those for ¹H of the side chain in the $CH_3NH_3^+$ cation reorientation rates induced by heating at high temperatures.

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1. Introduction

Hybrid organic-inorganic compounds have been known since 1976 but recently they have been revisited due to their potential use as substitute materials for perovskites.¹⁻⁶ Metal complexes with the formula $(CH_3NH_3)_2MCl_4$ (M = Mn, Fe, Cu, Zn, Cd) can be classified into two groups from a crystal structure point of view.⁷⁻¹⁴ One group $(CH_3NH_3)_2MCl_4$ (M = Mn, Fe, Cd) has a perovskite-type layer structure consisting of cationic layers and layers of corner-sharing chlorine octahedra with a divalent metal ion at the center.15-18 These compounds are characterized by a two-dimensional metal-chlorine network widely separated from one another by methyl ammonium groups. The metal ions are surrounded by a slightly distorted chlorine octahedron, Cl₆. The other group, to which $(CH_3NH_3)_2MCl_4$ (M = Cu, Zn) belongs, consists of discrete $CH_3NH_3^+$ and MCl_4^{2-} ions packed in an arrangement similar to orthorhombic K₂SO₄-like members.19,20 In these crystals, unassociated Cl4 tetrahedra are presented instead of corner-sharing layers of chlorine octahedra. Hydrogen-bonding takes place between the hydrogens of CH₃NH₃⁺ and Cl⁻, and the several different possible hydrogenbond configurations can give rise to structural phase transitions.

The $(CH_3NH_3)_2CuCl_4$ compound with M = Cu undergoes a structural phase transition at 348 K (= T_C), with the respective phases denoted as orthorhombic structure at high temperature and monoclinic structure at room temperature.²¹ A sharp peak at 230 K from a thermal capacity experiment was also reported by White and Staveley.²² In the case of $(CH_3NH_3)_2ZnCl_4$ with M = Zn, the existence of a phase transition at 483 K (= T_C) was reported by calorimetric, dielectric, thermal expansion, and optical measurements.²³ However, a transition at 426 K (= T'_C) was reported from Raman and IR spectra but not by differential scanning calorimetry (DSC), differential thermal analysis (DTA), and ¹H nuclear magnetic resonance (NMR) measurements. The structure of $(CH_3NH_3)_2ZnCl_4$ is orthorhombic at high temperatures and monoclinic at low temperatures. In addition, it has been reported from low-temperature DSC that a phase transition exists at 265 K during heating.^{24,25}

Following previous NMR investigations, the spin-lattice relaxation time T_1 of ¹H in the CH₃ and NH₃ groups of (CH₃- $NH_3)_2CuCl_4$ at the Larmor frequencies of 12 and 26 MHz was reported. The spectra of the two groups overlap at high temperatures and separate at low temperatures.²⁵ The T_1 at low temperatures exhibits a strong temperature dependence. Moreover, the self-diffusion and reorientation of the methylammonium ions in (CH₃NH₃)₂ZnCl₄ was reported by ¹H NMR.²⁶ In addition, the spin-spin relaxation time T_2 of ⁶³Cu and ³⁵Cl in (CH₃NH₃)₂CuCl₄ has been reported at 1.75 K.^{27,28} In the case of $(CH_3NH_3)_2ZnCl_4$, ¹H T_1 NMR studies at the Larmor frequency of 20 MHz revealed that the cation in the highest-temperature phase performs isotropic rotation and self-diffusion. The cation in the low-temperature phase undergoes reorientation about its C-N bond axis.²⁹ Although the structural phase transitions in (CH₃NH₃)₂CuCl₄ and (CH₃NH₃)₂ZnCl₄ have been performed by several research groups, the corresponding molecular motions and structural geometry changes have not been fully studied by NMR in the rotating frame.

^aAnalytical Laboratory of Advanced Ferroelectric Crystals, Jeonju University, Jeonju 55069, Korea . E-mail: aeranlim@hanmail.net; arlim@jj.ac.kr; Fax: +82-063-220-2053; Tel: +82-063-220-2514

^bDepartment of Science Education, Jeonju University, Jeonju 55069, Korea

In the present study, to clarify the ionic dynamics of CH₃NH₃⁺ cations and to also obtain information of the mechanism of the phase transition in $(CH_3NH_3)_2MCl_4$ (M = Cu, Zn), the chemical shifts and spin-lattice relaxation time in the rotating coordinate frame $T_{1\rho}$ were measured as a function of temperature using ¹H magic-angle spinning (MAS) NMR and ¹³C cross-polarization (CP) MAS NMR. In addition, the ¹⁴N NMR spectra in (CH₃NH₃)₂ZnCl₄ single crystals in the laboratory frame were discussed in order to elucidate the structural geometry. We focus on the structural phase transitions of compounds with the formula (CH₃NH₃)₂MCl₄. We use these results to analyze the behavior of CH₃ and NH₃ near the phase transition temperature from the results of ¹H MAS NMR, ¹³C CP MAS NMR, and ¹⁴N NMR. In addition, we compare the structural geometries of $(CH_3NH_3)_2MCl_4$ (M = Cu, Zn) obtained here and $(CH_3NH_3)_2MCl_4$ (M = Mn, Cd) previously reported.

2. Materials and methods

2.1. Crystal structure

The $(CH_3NH_3)_2CuCl_4$ undergoes a phase transition at 348 K. At temperatures below $T_{\rm C} = 348$ K, the structure is monoclinic, the space group is $P2_1/c$, and the lattice constants are a = 7.155 Å, b =7.424 Å, c = 9.814 Å, and $\beta = 109.18^{\circ}$.⁶ The crystal structure at 363 K is orthorhombic, the space group is Ccmb, and the lattice constants are a = 7.34 Å, b = 18.71 Å, and c = 7.33 Å.^{30,31} The monoclinic structure at room temperature is shown in Fig. 1.3 Here, the methylammonium moieties are located between the

CH₃ b

Fig. 1 The structure of $(CH_3NH_3)_2CuCl_4$ at room temperature.

layers and are connected by hydrogen bonds to the Cl⁻ ions. Further, (CH₃NH₃)₂ZnCl₄ undergoes a phase transition at 483 K. At room temperature, the crystal is monoclinic with the space group $P2_1/c$, and the lattice constants are a = 10.873 Å, b = 12.655Å, c = 7.648 Å, $\beta = 96.71^{\circ}$, and $Z = 4.^{19,23,26,32}$ Here, the two inequivalent sites, CH₃(1) and CH₃(2), and NH₃(1) and NH₃(2), in (CH₃NH₃)₂ZnCl₄ were reported by Morosin et al.¹⁹

2.2. Experimental method

Single crystals of $(CH_3NH_3)_2MCl_4$ (M = Cu, Zn) were prepared by the slow evaporation of an aqueous solution of stoichiometric amounts of CH_3NH_3 ·HCl and MCl_2 (M = Cu, Zn) at room temperature. The color of (CH₃NH₃)₂CuCl₄ single crystals is brown with flat parallelepipeds. In addition, (CH₃NH₃)₂ZnCl₄ single crystals are colorless and transparent with a square shape. The phase transition temperatures were determined using DSC (Dupont, 2010) measurements at a heating rate of 10 $K \min^{-1}$.

¹H MAS NMR and ¹³C CP MAS NMR spectra of (CH₃NH₃)₂- MCl_4 (M = Cu, Zn) in the rotating coordinate frame were obtained at the Larmor frequencies of $\omega_0/2\pi = 400.13$ and 100.61 MHz, respectively, using a Bruker 400 MHz NMR spectrometer at the Korea Basic Science Institute, Western Seoul Center. Powdered samples were placed in a 4 mm CP MAS probe, and the MAS rate was set to 10 kHz for both ¹H MAS and ¹³C CP MAS measurements to minimize the spinning sideband overlap. The chemical shifts were referred with respect to tetramethylsilane (TMS). The spin-lattice relaxation times for ¹H and ¹³C of (CH₃NH₃)₂MCl₄ in the rotating coordinate frame were determined using a $\pi/2 - t$ sequence by varying the duration of the spin-locking pulses. In the case of $(CH_3NH_3)_2CuCl_4$, the width of the $\pi/2$ pulse used for measuring the $T_{1\rho}$ values of ¹H and ¹³C was 3.9 µs, with a spin-locking field of 64.1 kHz. In the case of $(CH_3NH_3)_2ZnCl_4$, the width of the $\pi/2$ pulse used for measuring the T_{10} values of ¹H and ¹³C was 4.5 and 5.6 µs, with the spinlocking field of 55.55 kHz and 44.64 kHz, respectively. The power level for ¹H and ¹³C was 4 db and 6.5 db, respectively. The 13 C $T_{1\rho}$ values were measured by varying the duration of the 13 C spin-locking pulse applied after the CP preparation period.

In addition, the ¹⁴N NMR spectra of the (CH₃NH₃)₂ZnCl₄ single crystals in the laboratory frame were measured using a Unity INOVA 600 NMR spectrometer at the same facility. The static magnetic field was 14.1 T and the Larmor frequency was set to $\omega_0/2\pi = 43.342$ MHz. The ¹⁴N NMR experiments were conducted using a solid-echo pulse sequence.

Temperature-dependent NMR spectra were recorded at 180-430 K as the chemical shift and relaxation time could not be determined outside this temperature range, because of the limitations of the spectrometer used. The sample temperatures were maintained within ± 0.5 K by controlling the nitrogen gas flow and heater current.

3. Results and discussion

The DSC analysis in (CH₃NH₃)₂CuCl₄ revealed two endothermic peaks at 347 K (= $T_{\rm C}$) and 517 K (= $T_{\rm m}$) related to the phase transition and melting point, respectively, as shown in Fig. 2. The enlarged peak near 347 K in Fig. 2 is very small relative to the other endothermic peak. In the case of $(CH_3NH_3)_2ZnCl_4$, two endothermic peaks are obtained at 475 K (= T_C) and 525 K (= T_m), which are due to the phase transition and melting point. In order to understand the additional endothermic peaks at high temperature, we conduct optical polarizing microscopy. The peaks of 517 and 525 K in $(CH_3NH_3)_2CuCl_4$ and $(CH_3NH_3)_2$ - $ZnCl_4$, respectively, are not related to physical changes such as structural phase transitions; they are instead related to the melting point. The phase transition temperatures obtained here are consistent with previous results.^{21,23} This suggests that the differences in the chemical properties of Cu and Zn are responsible for the variations of the phase transition temperatures T_C in the two crystals.

The NMR spectra for ¹H in $(CH_3NH_3)_2MCl_4$ (M = Cu, Zn) were recorded by MAS NMR at a frequency of 400.13 MHz. In the case of the two compounds, the spectrum of the two peaks is assigned to the ¹H in CH₃ and NH₃. One of them, the spectrum of the two peaks at chemical shifts of $\delta = 3.82$ and 12.52 in (CH₃NH₃)₂CuCl₄ at room temperature, is presented in Fig. 3. Here, the unit of the NMR scale is represented according to the IUPAC convention.33,34 The spinning sidebands for CH₃ are marked with open circles and those for NH₃ are marked with crosses. The line component of the lower chemical shift is attributed to the ¹H in CH₃, and that of the higher chemical shift is attributed to the ¹H in NH₃. The protons of CH₃ and NH₃ are distinguished from the ¹H chemical shifts. In the case of $(CH_3NH_3)_2CuCl_4$ across the phase transition temperature of T_C , the chemical shift slowly and monotonously decreases with temperature, indicating that the environments of the surrounding ¹H in the CH₃ and NH₃ groups change continuously (see Fig. 4(a)). However, the proton spectrum of the two peaks in (CH₃NH₃)₂ZnCl₄ at room temperature is recorded at chemical shifts of $\delta = 2.88$ and 6.75. The ¹H chemical shifts in



Fig. 2 Differential scanning calorimetry thermogram of $(CH_3NH_3)_2$ -CuCl₄ and $(CH_3NH_3)_2ZnCl_4$ single crystals.



Fig. 3 1 H MAS NMR spectra of (CH₃NH₃)₂CuCl₄ at 300 K (the spinning sidebands are marked with crosses and open circles).

 $(CH_3NH_3)_2ZnCl_4$ are almost constant with temperature, as shown in Fig. 4(b).

The ¹H spin–lattice relaxation times in the rotating coordinate frame of $(CH_3NH_3)_2MCl_4$ (M = Cu, Zn) were obtained for the CH₃ and NH₃ at several temperatures. The nuclear magnetization decay of ¹H follows a single exponential function. Thus, $T_{1\rho}$ can be determined by fitting the traces with the following equation:³⁵

$$S(t)/S(\infty) = \exp(-t/T_{1\rho}), \qquad (1)$$

where S(t) is the magnetization with the spin-locking pulse duration t and $S(\infty)$ is the total nuclear magnetization of ¹H at thermal equilibrium. The values of ¹H $T_{1\rho}$ for two compounds in the rotating coordinate frame between 180 and 430 K are shown in Fig. 5(a) and (b) as a function of the inverse temperature. The T_{10} values for the methyl protons and ammonium protons in the CH₃NH₃⁺ cations exhibit similar trends with temperature. The T_{10} values of ¹H in the CH₃ and NH₃ groups of (CH₃NH₃)₂CuCl₄ are almost continuous near $T_{\rm C}$, and these values are of the order of milliseconds. Above 400 K, the two $T_{1\rho}$ values abruptly decrease, and the ¹H $T_{1\rho}$ values for CH₃ are longer than those for NH₃. In contrast, the significant change in the ¹³C T_{1p} values of $(CH_3NH_3)_2ZnCl_4$ is strongly affected, which is primarily considered the result of molecular motions. Further, the variation of T_{10} with temperature exhibits a minimum of 16.3 and 12.8 ms for CH_3 and NH_3 near 400 K, respectively. This behavior of T_{10} indicates that distinct molecular motions are present. It is clear that the minimum $T_{1\rho}$ is attributable to the uniaxial rotation of CH_3 and NH_3 ions. The experimental value of T_{10} is expressed in terms of the isotropic correlation time $\tau_{\rm C}$ for molecular motion using the Bloembergen-Purcell-Pound (BPP) theory,36 according to which the $T_{1\rho}$ value for a spin-lattice interaction of molecular motion is given by37-39

$$(nT_{1\rho}^{-1}) = 0.05(\mu_{o}/4\pi)^{2} (\gamma_{H}\gamma_{C}\hbar/r_{H-C}^{-3})^{2} [4a + b + 3c + 6d + 6e],$$
(2)



Fig. 4 (a) ¹H chemical shifts for CH_3 and NH_3 groups in $(CH_3NH_3)_2$ -CuCl₄ as a function of temperature. (b) ¹H chemical shifts for CH_3 and NH_3 groups in $(CH_3NH_3)_2ZnCl_4$ as a function of temperature.

where $a = \tau_{\rm C} / [1 + \omega_1^2 \tau_{\rm C}^2]$, $b = \tau_{\rm C} / [1 + (\omega_{\rm H} - \omega_{\rm C})^2 \tau_{\rm C}^2]$, $c = \tau_{\rm C} / [1 + \omega_{\rm H}^2 - \omega_{\rm C}^2]$ $\omega_{\rm C}^2 \tau_{\rm C}^2$, $d = \tau_{\rm C} / [1 + (\omega_{\rm H} + \omega_{\rm C})^2 \tau_{\rm C}^2]$, and $e = \tau_{\rm C} / [1 + \omega_{\rm H}^2 \tau_{\rm C}^2]$. Here, $\mu_{\rm o}$ is the permeability constant, $\gamma_{\rm H}$ and $\gamma_{\rm C}$ are the gyromagnetic ratios for the ¹H and ¹³C nuclei, respectively, n is the number of directly bound protons, *r* is the H–C internuclear distance, $\hbar = h/k$ 2π (where h is Planck's constant), $\omega_{\rm H}$ and $\omega_{\rm C}$ are the Larmor frequencies of ¹H and ¹³C, respectively, and ω_1 is the spin-lock field of 55.55 kHz. Our data are analyzed assuming $T_{1\rho}$ shows a minimum when $\omega_{\rm C} \tau_{\rm C} = 1$ and the BPP relation between $T_{1\rho}$ and ω_1 is applicable. As the $T_{1\rho}$ curves are found to exhibit minima, it was possible to determine the coefficient, $0.05(\mu_0/4\pi)^2 (\gamma_H \gamma_C \hbar/$ $(r_{\rm H-C})^2$, in the BPP formula. With this coefficient determined, we were then able to calculate the parameter $\tau_{\rm C}$ as a function of temperature. The temperature dependence of $\tau_{\rm C}$ follows a simple Arrhenius expression, $\tau_{\rm C} = \tau_{\rm Co} \exp(-E_{\rm a}/RT)$, where $\tau_{\rm Co}$ is the preexponential factor, T is the temperature, R is the gas constant, and $E_{\rm a}$ is the activation energy. Thus, the slope of the straight-line portion of the semi-log plot can be used to determine $E_{\rm a}$. The activation energy for the uniaxial rotation of CH₃ and NH₃, obtained from the log $\tau_{\rm C}$ vs. 1000/T curve shown in the inset of Fig. 5(b), is 19.72 ± 1.10 and 19.88 ± 0.89 kJ mol⁻¹, respectively,



Fig. 5 (a) ¹H spin-lattice relaxation times in the rotating coordinate frame for CH₃ and NH₃ groups in (CH₃NH₃)₂CuCl₄ as a function of inverse temperature. (b) ¹H spin-lattice relaxation times in the rotating coordinate frame for CH₃ and NH₃ groups in (CH₃NH₃)₂ZnCl₄ as a function of inverse temperature (inset: Arrhenius plots of the natural logarithm of the correlation time for each proton of CH₃ and NH₃ in (CH₃NH₃)₂ZnCl₄ as a function of inverse temperature).

and is the same within the error range. In addition, the $E_{\rm a}$ value for CH₃ and NH₃ at temperatures below 200 K is 6.59 ± 0.51 and 5.92 ± 0.40 kJ mol⁻¹, respectively.

The chemical shifts for ¹³C in $(CH_3NH_3)_2CuCl_4$ were measured as a function of temperature, as shown in Fig. 6. At room temperature, the ¹³C CP MAS NMR spectrum shows a signal at a chemical shift of $\delta = 190.50$ with respect to TMS. The ¹³C chemical shift slowly and monotonously decreases with temperature. In contrast, the chemical shifts for ¹³C in $(CH_3-NH_3)_2ZnCl_4$ were also measured over the temperature range of 180 to 430 K, as shown in the inset of Fig. 6. At room temperature, the ¹³C CP MAS NMR spectrum possesses two signals at chemical shifts of $\delta = 27.82$ and 29.02. These signals are attributed to the methyl carbons of the two inequivalent sites CH_3 (1) and CH_3 (2), and these results are consistent with the Xray result previously reported:¹⁸ there exist two kinds of



Fig. 6 13 C chemical shift in CH₃ groups in (CH₃NH₃)₂CuCl₄ as a function of temperature (inset: that in (CH₃NH₃)₂ZnCl₄ as a function of temperature).

crystallographically inequivalent cations. The ¹³C chemical shifts near 426 K decrease by only one line; the change near 426 K was measured from the ¹³C chemical shift but not by the DSC result. Although the anomaly was not found around 426 K in the present DSC experiment, the existence of the ¹³C chemical shift and ¹³C T_{10} was obtained. This anomaly near 426 K (= T'_{C}) is consistent with that obtained from Raman and IR spectra previously reported. There exist two kinds of inequivalent CH₃ in (CH₃NH₃)₂ZnCl₄, whereas only one kind of equivalent CH₃ in (CH₃NH₃)₂CuCl₄ exists. On the other hand, the chemical shifts of the CH₃ groups in the ¹³C NMR spectra were very different between the two compounds. Generally, the paramagnetic contribution to the NMR shift is responsible for the NMR spectra.⁴⁰ Thus, the ¹³C NMR chemical shift of (CH₃NH₃)₂CuCl₄, which contain paramagnetic ions, was significantly different from that of (CH₃NH₃)₂ZnCl₄, which does not contain paramagnetic ions. The differences in the ¹³C NMR chemical shifts could potentially be due to differences in the electron structures of the metal ions, in particular, the structure of the d electrons, which screen the nuclear charge from the motion of the outer electrons. Zn²⁺ has a filled d shell, whereas Cu²⁺ has one s electron outside the closed d shell.

The $T_{1\rho}$ values were obtained for the carbon of $(CH_3NH_3)_2$ -MCl₄ (M = Cu, Zn) at several temperatures. ¹³C magnetization was generated by CP after spin-locking the protons. All magnetization traces obtained for the methyl carbon were described by a single exponential function $S(t) = S(\infty)\exp(-t/T_{1\rho})$ of eqn (1).³⁵ The recovery curves for various delay times of ¹³C in (CH₃-NH₃)₂CuCl₄ and (CH₃NH₃)₂ZnCl₄ were measured at several temperatures. The saturation recovery traces for ¹³C were measured for delay times ranging from 0.2 to 150 ms at room temperature and are presented in Fig. 7(a) and (b). The recovery traces have different slopes at several temperatures. From these results, the $T_{1\rho}$ values were obtained for the carbon in the two compounds as a function of the inverse temperature. The temperature dependence of the ¹³C $T_{1\rho}$ values in (CH₃NH₃)₂-CuCl₄ is illustrated in Fig. 8, and these values are almost constant with temperature. The $T_{1\rho}$ values around $T_{\rm C}$ are unchanged, in agreement with the conclusion drawn from the ¹³C chemical shifts. In the case of $(\rm CH_3\rm NH_3)_2\rm ZnCl_4$, the phase transition occurring at $T'_{\rm C}$ (= 426 K) reported by Perez-Mato *et al.*²³ is not observed from our DSC results, whereas the changes near $T'_{\rm C}$ are observed by the ¹³C chemical shift and ¹³C $T_{1\rho}$ results. Thus, $T'_{\rm C}$ is denoted by dotted lines in the inset of Fig. 5, 6, and 8. The $T_{1\rho}$ values for the two ¹³C signals of CH₃ (1) and CH₃ (2) in (CH₃-NH₃)₂ZnCl₄ are almost the same within the experimental error range.

In order to obtain information concerning the possible distortion surrounding the ¹⁴N ion, the NMR spectrum of ¹⁴N (I = 1) in the laboratory frame was obtained using static NMR at a Larmor frequency of $\omega_0/2\pi = 43.342$ MHz. Two resonance signals were expected from the quadrupole interactions of the ¹⁴N nucleus. A magnetic field was applied along the crystallographic axis. The *in situ* ¹⁴N NMR spectra and resonance frequency in (CH₃NH₃)₂ZnCl₄ single crystals are plotted



Fig. 7 (a) Recovery spectra for delay times of 13 C CP MAS NMR spectrum in (CH₃NH₃)₂CuCl₄ at room temperature. (b) Recovery spectra for delay times of 13 C CP MAS NMR spectrum in (CH₃NH₃)₂-ZnCl₄ at room temperature.



Fig. 8 13 C spin-lattice relaxation times in the rotating coordinate frame for CH₃ groups in (CH₃NH₃)₂CuCl₄ and (CH₃NH₃)₂ZnCl₄ as a function of temperature.



Fig. 9 The temperature-dependent resonance frequency of ¹⁴N NMR spectra in $(CH_3NH_3)_2ZnCl_4$ single crystal as a function of temperature (inset: ¹⁴N NMR spectra as a function of temperature).

in Fig. 9 as a function of temperature, respectively. The ¹⁴N NMR spectra of the two resonance signals for ¹⁴N are attributed to the NH₃, and this splitting of the ¹⁴N resonance signals slightly decreases with temperature. The small change of the resonance frequency near 300 K is not related to the phase transition. Note that temperature-dependent changes in the ¹⁴N resonance frequency are generally attributed to changes in the structural geometry, indicating a change in the quadrupole parameter of the ¹⁴N nuclei. The electric field gradient tensors at the N sites vary, reflecting the changing atomic configurations around the nitrogen centers.

4. Conclusions

The ionic dynamics of $(CH_3NH_3)_2MCl_4$ (M = Cu, Zn), focusing on the role of the $CH_3NH_3^+$ cation, were investigated by ¹H MAS NMR, ¹³C CP MAS NMR, and ¹⁴N NMR as a function of

temperature. We studied the molecular motions for ¹H and ¹³C in $(CH_3NH_3)_2MCl_4$ (M = Cu, Zn) based on the spin-lattice relaxation time in the rotating coordinate frame. From the ¹H T_{10} results, we found that the molecular motions for ¹H in $(CH_3NH_3)_2CuCl_4$ are very active at high temperatures. In addition, the activation energies for the uniaxial rotation of ¹H for the CH₃ and NH₃ ions in (CH₃NH₃)₂ZnCl₄ have very similar values, and the uniaxial rotation occurs within the hightemperature range. The $T_{1\rho}$ results reveal that the CH₃ and NH_3 cations exhibit high mobility at high temperatures. The T_{10} provides insight into the changes in the cation reorientation rates induced by heating at high temperatures. On the other hand, the minima for (CH₃NH₃)₂ZnCl₄ are attributed to the uniaxial rotation of the CH3NH3 cations. However, minima such as T_{10} for $(CH_3NH_3)_2CuCl_4$ were not reached for that compound. The lack of a minimum T_{10} indicates that this motion is so slow that there was no detectable $T_{1\rho}$ temperature dependence and also that the uniaxial rotation in (CH₃NH₃)₂CuCl₄ was slower than that in (CH₃NH₃)₂ZnCl₄. The motion of the CH₃NH₃ cations is slower than the C₃ internal rotation of CH₃ and NH₃; therefore, it reveals T_{10} minima in the high temperature regime above liquid nitrogen temperature. The minima related to the C_3 rotation will appear in the low temperature regime.

A comparison with other compounds of the $(CH_3NH_3)_2MCl_4$ (M = Cu, Zn) indicates a different phase sequence for $(CH_3-NH_3)_2MCl_4$ (M = Cd, Mn). For M = Cd, Mn, these systems at room temperature reveal orthorhombic symmetry followed by a tetragonal phase below room temperature. A phase with monoclinic symmetry is also reported at low temperatures. It is interesting to compare the results for $(CH_3NH_3)_2MCl_4$ with those for the analogous compounds containing other metals. In the case of $(CH_3NH_3)_2MCl_4$ and $(CH_3NH_3)_2CdCl_4$, there is an intermediate tetragonal phase between the monoclinic and orthorhombic phases.^{16,31} In contrast, the phase transition sequence for $(CH_3NH_3)_2CuCl_4$ and $(CH_3NH_3)_2ZnCl_4$ changes to an orthorhombic to monoclinic structure with decreasing temperature.^{22,31}

The created magnetization decay for each proton in $(CH_3-NH_3)_2MCl_4$ (M = Cu, Zn) was analyzed by a single exponential function $S(t)/S(\infty) = A \exp(-t/T_{1\rho})$, whereas that for each proton in $(CH_3NH_3)_2MCl_4$ (M = Mn, Cd) was analyzed by a double-exponential function $S(t)/S(\infty) = A \exp(-t/T_{1\rho}(s)) + B \exp(-t/T_{1\rho}(L))$. These results are consistent with the interactions between the CH_3NH_3 cations and its surrounding MCl_4^{2-} anions. This difference of $T_{1\rho}$ is possibly due to the difference between the electron structures of metal ions. Cu^{2+} and Zn^{2+} have one and two s electrons, respectively, outside the closed d shell; Mn^{2+} has two s electrons in the unfilled 3d orbital; Cd^{2+} has two electrons outside the closed d shell.

The $T_{1\rho}$ values for ¹H of CH₃ and NH₃ indicate that the protons in the CH₃NH₃ cations that are involved in the hydrogen bonding exhibit large and small $T_{1\rho}$ values corresponding to the long C–H and short N–H bonds, respectively. The molecular motion of the cation is induced by heating at high temperatures. The cation dynamics and interionic interactions through hydrogen bonds are expected to be closely related with the physical properties due to the potential

applications. We will be examined the effect for lengths of alkyl chains as further study.

Conflicts of interest

There are no conflicts to declare.

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