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Thermal property and structural molecular dynamics of organic—inorganic hybrid perovskite 1,4-butanediammonium tetrachlorocuprate †

We investigate the thermal behaviour and physical properties of the crystals of the organic inorganic hybrid perovskite $[(NH_3)(CH_2)_4(NH_3)]CuCl_4$. The compound's thermal stability curve as per thermogravimetric analysis exhibits a stable state up to ~495 K, while the weight loss observed near 538 K corresponds to partial thermal decomposition. The 1H nuclear magnetic resonance (NMR) chemical shifts for NH_3 change more significantly with temperature than those for CH_2 , because the organic cation motion is enhanced at both ends of the organic chain. The ^{13}C NMR chemical shifts for the ' CH_2 -1' units of the chain show an anomalous change, and those for ' CH_2 -2' (units closer to NH_3) are shifted sharply. Additionally, the ^{14}N NMR spectra reflect the changes of local symmetry near T_C (=323 K). Moreover, the ^{13}C T_{1p} values for CH_2 -2 are smaller than those for CH_2 -1, and the ^{13}C T_{1p} data curve for CH_2 -1 exhibits an anomalous behaviour between 260 and 310 K. These smaller T_{1p} values at lower temperatures indicate that ^{14}H and ^{13}C in the organic chains are more flexible at these temperatures. The NH_3 group is attached to both ends of the organic chain, and NH_3 forms a $N-H\cdots Cl$ hydrogen bond with the Cl ion of inorganic $CuCl_4$. When H and C are located close to the paramagnetic Cu^{2+} ion, the T_{1p} value is smaller than when these are located far from the paramagnetic ion.

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Introduction

The search for new and improved functional materials in recent years has resulted in considerable progress in the synthesis of many families of organic-inorganic compounds. The properties and structural phase transition of these compounds are related to their structures and the interaction of the cationic units with complex anionic sublattices. One such group of hybrid compounds, whose structure can be expressed by the general formula $[NH_3(CH_2)_4NH_3]MX_4$ (M = divalent metal ion and X = Cl, Br) is known to crystallise in a 2D perovskite-like structure, and these compounds are usually referred to as organic-inorganic hybrid perovskites or organic-metal-halide composites. 1-6 These perovskites combine the advantages of both organic and inorganic materials in a single molecular scale. 1,7,8 In particular, in the diammonium hybrid perovskite with its formula of [NH₃(CH₂)₄NH₃]MX₄, the NH₃ group is attached to both ends of the organic chain.^{3,7,8} At the end of the

The compound $[(NH_3)(CH_2)_4(NH_3)]CuCl_4$, or 1,4-butanediammonium tetrachlorocuprate, with M = Cu and X = Cl, undergoes a reversible phase transition at 325 K $(=T_C)^{14}$ between the two monoclinic phases II and I. The transition can be explained by order-disorder mechanisms involving a model of twisted conformation chains, which was introduced to explain the decrease in interlayer distance with increasing temperature from X-ray diffraction experiment. From structural considerations, these results can be explained by the conformational change of organic chains from the left-handed conformation in phase II to an all-trans conformation in phase I.14 The structural geometry of [(NH3)(CH2)4(NH3)]CuCl4 in the room-temperature phase II and high-temperature phase I are represented in Fig. 1(a) and (b), respectively. The crystal structure at room temperature is monoclinic, corresponding to space group $P2_1/c$. The unit cell dimensions are a = 9.270 \mathring{A} , $b = 7.600 \, \mathring{A}$, $c = 7.592 \, \mathring{A}$, $\beta = 103.14^{\circ}$, and Z = 2.14,15 Structural

organic part of the chain, the ammonium ion forms a N-H···X hydrogen bond with the halide ion of the metallic inorganic layer. These perovskite hybrids tend to exhibit a number of phase transitions such as order-disorder transitions. Here, we note that the properties of organic–inorganic hybrid perovskites depend on the organic cation, divalent metal, and halogen ion, and thus, it is necessary to investigate the 'structure-directing' properties of these new materials. In general, 2D hybrid perovskites can find use in the fields of energy, optoelectronics, photonics, and catalysis in green chemistry applications. 9-13

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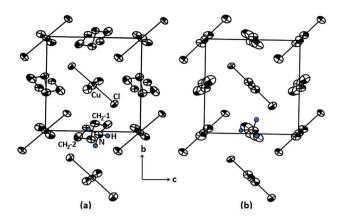


Fig. 1 Crystal arrangement on the bc-plane in $[(NH_3)(CH_2)_4(NH_3)]$ CuCl₄ for (a) room temperature phase II and (b) high temperature phase I. Here, CH₂-1 represents two CH₂ between four CH₂, and CH₂-2 represents two CH₂ close to NH₃.

cohesion is achieved via N-H···Cl hydrogen bonds. [(NH₃) (CH₂)₄(NH₃)]CuCl₄ is composed of alternating inorganic CuCl₄²⁻ layers and organic [NH₃(CH₂)₄NH₃]²⁺ sheets. The CuCl₄²⁻ layers are sandwiched by [NH₃(CH₂)₄NH₃]²⁺ cations, which possess centrosymmetrical chains with left-handed conformations at both ends, thereby forming the organic sheets. Above 325 K, the symmetry changes to that of a monoclinic structure with space group $P2_1/c$, and the corresponding lattice constants are a = 10.420 Å, b = 7.442 Å, c = 7.225 Å, $\beta = 93.46^{\circ}$, and z = 2.15

In the context of the property measurements of such compounds, Snively $et\ al.$ conducted magnetic susceptibility measurements of $[(NH_3)(CH_2)_4(NH_3)]CuCl_4$ powdered and single-crystals in the temperature range of 4 to 200 K.^{16,17} They reported that the interplanar superexchange interaction along the linear Cu–Cl–Cl–Cu path exhibits a significantly stronger Cu–Cu-distance dependence than that along the Cu–Cl–Cu path. This crystal structure has been reported in phases I and II by Garland $et\ al.^{18}$ Subsequently, the phase transitions occurring in the perovskite-type 2D molecular composite $[(NH_3)(-CH_2)_4(NH_3)]$ CuCl $_4$ have been studied by means of differential scanning calorimetry (DSC), X-ray diffraction (XRD), 11 and electron paramagnetic resonance (EPR). 14,19,20

Understanding the structural dynamics of organic–inorganic hybrid perovskite $[(NH_3)(CH_2)_4(NH_3)]CuCl_4$ is essential for their advanced use as new materials. Here, we study the structural dynamics of the organic–inorganic hybrid perovskite $[(NH_3)(CH_2)_4(NH_3)]CuCl_4$ *via* magic angle spinning (MAS) nuclear magnetic resonance (NMR) and static NMR experiments. The chemical shifts and spin–lattice relaxation times in the rotating frame T_{1p} in the low- and high-temperature phases are measured by means of MAS 1 H NMR and cross-polarisation (CP)/MAS 13 C NMR to understand the role of the organic cation in this crystal. The 14 N NMR spectra of the compound in the laboratory frame are also obtained as a function of temperature. We use these results to discuss the structural dynamics of the NH₃–CH₂–CH₂–CH₂–CH₂–NH₃ chain below and above the phase transition temperature T_C . In particular, an

examination of the hydrogen bonding of N-H···Cl between the Cu-Cl layer and the alkylammonium chain within $[(NH_3)(-CH_2)_4(NH_3)]$ CuCl₄ can provide important insights into the operational mechanism as regards potential applications.

II. Experimental method

Crystals of $[(NH_3)(CH_2)_4(NH_3)]CuCl_4$ were prepared by mixing equimolar amounts of $NH_2(CH_2)_4NH_2\cdot 2HCl$ and $CuCl_2$ in aqueous solution and allowing the resulting mixture to slowly evaporate. The light-green-coloured crystals grew as rectangular parallelepipeds with dimensions of 5 mm \times 5 mm \times 1 mm.

The crystal structure of $[(NH_3)(CH_2)_4(NH_3)]CuCl_4$ was determined with a X-ray diffraction system, using a Cu-K α radiation source at the KBSI, Seoul Western Center. DSC (TA, DSC 25) experiments were carried out at a heating rate of 10° C min⁻¹ in the temperature range of 190 to 600 K in a nitrogen-gas atmosphere. Thermogravimetry analysis (TGA) experiments were conducted using a thermogravimetric analyser (TA Instruments) under conditions identical to those of DSC over a temperature range of 300 to 680 K. The DSC and TGA experiments were performed by using crystal sample quantities of 6.23 and 7.53 mg, respectively.

Solid-state MAS NMR investigations of the [(NH₃)(CH₂)₄(-NH₃]CuCl₄ crystals were conducted by using a 400 MHz Avance II+ Bruker NMR spectrometer at the same facility. The MAS ¹H NMR and CP/MAS ¹³C NMR experiments were performed at the Larmor frequencies of $\omega_0/2\pi = 400.13$ and 100.61 MHz, respectively. Solid samples were packed into 4 mm-diameter zirconia rotors and closed off using Vespel caps. The samples were spun at 10 kHz MAS by using dry nitrogen gas. The ¹H and ¹³C NMR chemical shifts were obtained with the use of tetramethylsilane (TMS) as a standard. The T_{1p} data for 1 H and 13 C were obtained by applying a $\pi/2$ pulse, immediately followed by a long spin-locking pulse phase-shifted by $\pi/2$ with respect to the $\pi/2$ pulse. The width of the $\pi/2$ pulse used for T_{10} measurements was 3.3 µs, which yields the frequency of the rotating frame as $\omega_1 = 75.75$ kHz. The T_{10} data were obtained by varying the length of the spin-locking pulse. In addition, the 14N NMR spectra of a $[(NH_3)(CH_2)_4(NH_3)]CuCl_4$ single-crystal were obtained at the Larmor frequency of $\omega_0/2\pi=28.90$ MHz in the laboratory frame. The ¹⁴N resonance frequency was referenced with NH₃NO₃ as the standard sample. The ¹⁴N NMR spectrum was obtained by the application of the following solid-state echo sequence: 8 μs-tau (16 μs)-8 μs-tau (16 μs). The temperature change was maintained within the error range of ± 0.5 K by adjusting the nitrogen gas flow and heater current.

III. Results and discussion

The powder X-ray diffraction pattern of $[(NH_3)(CH_2)_4(NH_3)]$ CuCl₄ at 300 K is described in the ESI,† and this data is consistent with previously reported results. ¹⁴ Fig. 2 shows the DSC curve of the $[(NH_3)(CH_2)_4(NH_3)]$ CuCl₄ crystals obtained with the heating rate of 10° C min⁻¹. An endothermic signal corresponding to the previously reported ¹⁴ II–I phase transition is detected at 323 K. In addition, a very large exothermic peak is

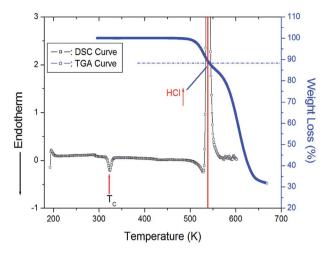


Fig. 2 Differential Scanning Calorimetry (DSC) and thermogravimetric analysis (TGA) curves of [(NH₃)(CH₂)₄(NH₃)]CuCl₄.

observed at 538 K. To understand the origins of this peak, we performed TGA experiments; these results are also shown in Fig. 2. In the TGA curve, a stable state is observed up to ${\sim}495$ K, whereas a weight loss is observed at higher temperatures, which represents partial thermal decomposition. Here, we note that $[(\mathrm{NH_3})(\mathrm{CH_2})_4(\mathrm{NH_3})]\mathrm{CuCl_4}$ crystals show the weight loss with temperature increase. From the TGA experimental results and possible chemical reactions, we compared the weight loss. The weight loss of 12% around 538 K obtained from the DSC experiment is consistent with the calculated decomposition of HCl moieties. From the figure, we note that the weight sharply decreases between 500 and 650 K, with a corresponding weight loss of 67% near 650 K.

Next, we acquired the MAS ¹H NMR spectrum of the [(NH₃)(CH₂)₄(NH₃)]CuCl₄ crystals at various temperatures (Fig. 3). In the figure, we can observe two resonance signals for ¹H. The spinning sidebands corresponding to CH₂ are indicated

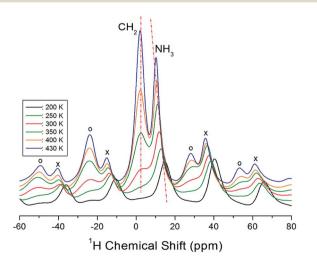


Fig. 3 MAS 1 H NMR spectra for CH₂ and NH₃ of [(NH₃)(CH₂)₄(NH₃)] CuCl₄ at various temperatures (spinning sidebands for CH₂ and NH₃ are indicated by open circles and crosses, respectively).

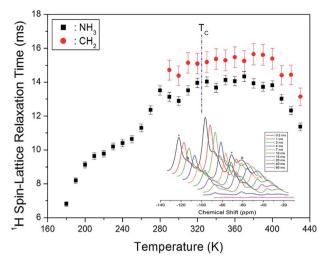


Fig. 4 1 H NMR spin-lattice relaxation times T_{1p} for CH₂ and NH₃ ions of [(NH₃) (CH₂)₄(NH₃)]CuCl₄ as a function of temperature (inset: 1 H NMR spectrum at several delay times at 300 K).

by open circles, and those of NH_3 are indicated by crosses. At 300 K, the 1H NMR chemical shifts for CH_2 and NH_3 are observed at $\delta=2.73$ ppm and $\delta=11.86$ ppm, respectively. Below 300 K, the 1H resonance signal bonded to CH_2 mostly merges with the 1H resonance signal bonded to NH_3 , which makes it difficult to distinguish the two signals. In addition, the 1H resonance signal for CH_2 is related to the number of bonded protons, which means that the signal exhibits a stronger intensity and wider linewidth than the corresponding ones for NH_3 . The 1H NMR chemical shifts according to the temperature exhibit a greater change for NH_3 than CH_2 . These results indicate that NH_3 is temperature-sensitive.

Next, we measured the MAS 1 H NMR spectrum at various temperatures, and the intensity change for the delay time was observed to obtain the spin–lattice relaxation time in the rotating frame $(T_{1\rho})$ for 1 H at each temperature. Normally, the $T_{1\rho}$ data can be obtained as the slope of the intensity or the ratio of the area of the resonance signal to the delay time. The change in the proton magnetisation intensity in terms of $T_{1\rho}$ is expressed as below: $^{21-23}$

$$P(\tau) = P(0) \exp(-\tau/T_{10}),$$
 (1)

where $P(\tau)$ and P(0) denote the signal intensities at time τ and $\tau=0$, respectively. Next, at 300 K, the MAS ¹H NMR signals of CH₂ and NH₃ were plotted for various delay times in the range from 0.2 to 80 ms (Fig. 4); we note that the intensities of the ¹H NMR signal as a function of the delay times exhibit considerable variation. From the slope of the intensity vs. delay time curve, the ¹H $T_{1\rho}$ data of $[(NH_3)(CH_2)_4(NH_3)]$ CuCl₄ were obtained for CH₂ and NH₃ in the low-temperature phase II and high-temperature phase I. From Fig. 4, we note that no changes are observed in the $T_{1\rho}$ value near T_C , and $T_{1\rho}$ slightly increases according to the temperature change. The ¹H $T_{1\rho}$ values for CH₂ and NH₃ at 300 K are 14.37 and 12.88 ms, respectively. Here, the ¹H $T_{1\rho}$ value for NH₃ is smaller than that for CH₂. This is

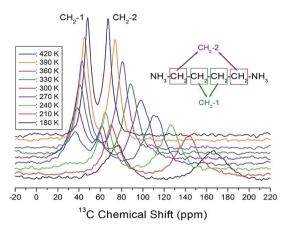


Fig. 5 In situ MAS 13 C NMR spectra for CH₂-1 and CH₂-2 of [(NH₃)(CH₂)₄ (NH₃)]CuCl₄ as a function of temperature.

possibly because NH_3 is closer to the inorganic CuCl_4 layer; the $T_{1\rho}$ value becomes smaller as the distance between H and the paramagnetic Cu^{2+} ion reduces. This is because $T_{1\rho}$ is inversely proportional to the square of the magnetic moment of the paramagnetic ion.²¹

The CP/MAS 13 C NMR chemical shifts measured at various temperatures are shown in Fig. 5. In the study, the MAS 13 C NMR spectrum for TMS was recorded at 38.3 ppm at 300 K, and this value was calibrated to determine the chemical shift in 13 C. Here, the two inner CH $_2$ groups of the four CH $_2$ ones are together designated as CH $_2$ -1, and the two CH $_2$ units close to the NH $_3$ ones are designated as CH $_2$ -2. We note from the figure that the 13 C chemical shifts for CH $_2$ -1 (far from NH $_3$) are different from those for CH $_2$ -2, which is closer to NH $_3$. In the 13 C NMR spectra obtained for CH $_2$ -1 and CH $_2$ -2, two unusual resonance lines are observed between 260 and 310 K. At 300 K, the two resonance signals for CH $_2$ -1 are recorded at chemical shifts of $\delta = 38.44$ and 59.56 ppm. Furthermore, the signal of $\delta = 98.23$ ppm corresponds to CH $_2$ -2. The 13 C chemical shifts

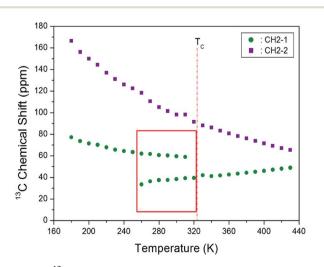


Fig. 6 MAS 13 C chemical shifts for CH₂-1 and CH₂-2 of [(NH₃)(CH₂)₄ (NH₃)]CuCl₄ at low temperature phase II and high temperature phase I.

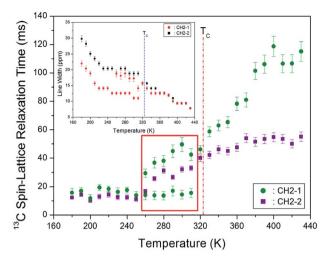


Fig. 7 MAS 13 C NMR spin-lattice relaxation times T_{1p} for CH₂-1 and CH₂-2 of [(NH₃) (CH₂)₄(NH₃)]CuCl₄ as a function of temperature (inset: line widths for CH₂-1 and CH₂-2 according to the temperature).

for CH_2 -1 exhibit an anomalous change with increase in temperature, whereas those for CH_2 -2 shift abruptly with increasing temperature, as shown in Fig. 6. The two resonance lines between 260 and 310 K correspond to CH_2 -1, and hitherto unreported anomalous phenomena are observed in this temperature range.

We next remark that line broadening in the MAS 13 C NMR spectra is influenced by relaxation processes such as the motional modulations of the chemical shift anisotropy and dipolar carbon-proton coupling. Fig. 7 shows the 13 C full-width at half-maximum (FWHM) linewidth of $[(NH_3)(CH_2)_4(NH_3)]$ CuCl $_4$. The 13 C NMR line shapes vary from the Gaussian type at lower temperatures to the Lorentzian shape at higher temperatures. The appearance of these two-component spectra is caused by difference in different molecular motions. The linewidth near the phase transition temperature T_C shows

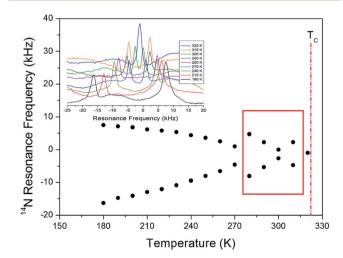


Fig. 8 14 N resonance frequency of [(NH₃) (CH₂)₄(NH₃)]CuCl₄ single crystal as a function of temperature (inset: *in situ* 14 N resonance frequency at several temperatures).

Table 1 Phase transition temperature T_{C} , decomposition temperature T_{d} , structure, space group, lattice constant, spin-lattice relaxation time $T_{1\rho}$ for $[C_2H_5NH_3]_2$ CuCl₄ and $[NH_3(CH_2)_4NH_3]_2$ CuCl₄ crystals

	$[C_2H_5NH_3]_2CuCl_4$	$[\mathrm{NH_3}(\mathrm{CH_2})_4\mathrm{NH_3}]\mathrm{CuCl_4}$
$T_{\mathrm{C}}\left(\mathrm{K}\right)$	236, 330, 357, 371 (ref. 26-31)	325 (ref. 14)
$T_{\rm d}$ (K)	430	495
Structure	Orthorhombic ^{32–34}	Monoclinic ^{14,15}
Space group	Pbca	$P2_1/c$
Lattice constant	a = 7.47	a = 9.270
(Å)	b = 7.35	b = 7.600
	c = 21.18	c = 7.592
		$\beta=103.14^\circ$
1 H $T_{1\rho}$ (ms)	7–20 (ref. 35)	6–16
13 C $T_{1\rho}$ (ms)	2–200	10-120

a monotonic decrease, thereby indicating the presence of motional narrowing at high temperatures.

The spin-lattice relaxation time in the rate of relaxation is due to spin-lattice interactions in the rotating frame. The ¹³C T_{10} relaxations are not influenced by spin diffusion because of the small dipolar coupling which arises from the low natural abundance and large separation of the nuclei. Under these conditions, we next analysed differences in the chain motions. The integration change of the ¹³C NMR spectrum obtained for various delay times was measured, and all the decay curves for CH₂-1 and CH₂-2 were plotted by using a single exponential function. From the slope of their recovery traces, the 13 C T_{10} data were obtained for CH2-1 and CH2-2 as a function of temperature, as shown in Fig. 7. It can be observed that although no change in the $T_{1\rho}$ value is observed near $T_{\rm C}$, $T_{1\rho}$ above $T_{\rm C}$ abruptly increases with increasing temperature. The 13 C T_{1p} values for CH₂-1 and CH₂-2 at lower temperatures (below $T_{\rm C}$) are nearly identical; however, the ¹³C $T_{\rm 1p}$ values for CH₂-2 close to NH3 at high temperatures are smaller than that for CH2-1. At high temperatures, smaller 13 C T_{10} values for CH₂-2 are more flexible than the CH2-1. Just as the 13C resonance lines for CH_2 -1 exhibited anomalies between 260 and 310 K, the 13C T_{10} also exhibits two different sets of values. The relaxation time for Arrhenius-type random motions with correlation time τC is described in term of slow motions; for $\tau C \ll \omega_L$, $T_{10} \sim \tau_C =$ $\tau_0 \exp(-E_a/k_BT)$, where ω_L denotes the Larmor frequency and E_a the activation energy.

The 14 N NMR spectrum in the laboratory frame was next measured in the temperature range from 180 to 430 K by using the solid-state echo method at the Larmor frequency of 28.90 MHz by means of static NMR. The two resonance lines are obtained by spin number $I=1,^{24,25}$ and the resonance frequency around $T_{\rm C}$ (=323 K) changes as shown in Fig. 8. The observed change in the 14 N resonance frequency with temperature is due to structural geometry change, which means a change in the quadrupole coupling constant. The linewidth at 300 K is \sim 44 ppm, and this spectrum is relatively broader than the 1 H and 13 C NMR spectra. The 14 N resonance frequency decreases almost continuously until 270 K, while that of the 14 N signal between 280 and 310 K exhibits an anomalous pattern. Similar to the anomaly of the 13C resonance line observed between 260

and 310 K, an abnormal phenomenon is observed in the 14 N resonance line in this region. At 320 K near $T_{\rm C}$, there is only one $^{14}{\rm N}$ resonance line, and at temperatures >320 K, no resonance lines are observed. At the transition point of 323 K, the $^{14}{\rm N}$ NMR lines merge into one line. This single $^{14}{\rm N}$ resonance line indicates that there is no electric field gradient (EFG) tensor at the N site in phase I because of site symmetry. The EFG tensor changes around the N site, which indicates a change in the structural configuration around the N site near $T_{\rm C}$.

IV. Conclusions

In this study, we investigated the thermal behaviour and physical properties of organic–inorganic hybrid perovskite [(NH₃)(-CH₂)₄(NH₃)]CuCl₄ crystals. The structural dynamics of [(NH₃)(CH₂)₄(NH₃)]CuCl₄ with emphasis on the role of the [(NH₃)(CH₂)₄(NH₃)] cation, were discussed by MAS 1 H NMR, MAS 13 C NMR, and static 14 N NMR as a function of temperature. Firstly, we found that the TGA curve exhibited stability until 495 K, and the observed weight loss of 12% near 538 K was due to the partial thermal decomposition of HCl moieties.

Secondly, the 1 H NMR chemical shift of NH $_{3}$ for crystallographic environments changed more significantly with temperature than that for CH $_{2}$ because the [(NH $_{3}$)(CH $_{2}$) $_{4}$ (NH $_{3}$)] cation motion is enhanced at both ends of the cation of the NH $_{3}$ group. The 13 C NMR chemical shifts for CH $_{2}$ -1 showed an anomalous change, and those for CH $_{2}$ -2 shifted sharply to lower values when compared with that of CH $_{2}$ -1. The 13C chemical shifts of the CH2-2 unit (closer to the N–H····Cl bond) sharply changed relative to those of CH $_{2}$ -1. In addition, the 14 N NMR spectra reflected the changes in the local symmetry of the crystal near T_{C} .

The 1 H $T_{1\rho}$ values for CH₂ and NH₃ slightly increased with temperature increase. Moreover, the 13 C $T_{1\rho}$ value for CH₂-2 was smaller than that of CH₂-1, and the 13 C $T_{1\rho}$ value for CH₂-1 exhibited an anomalous trend between 260 and 310 K. At low temperatures, the 1 H and 13 C $T_{1\rho}$ values were smaller than at high temperatures. Smaller $T_{1\rho}$ values at lower temperatures indicate that 1 H and 13 C in the organic chains are more flexible at these temperatures. Moreover, the 13 C of CH₂-2 close to NH₃ of the organic chain is more flexible than the 13 C of CH₂-1

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between the four CH_2 sites. The NH_3 group is attached to both ends of the organic chain, and it forms a N-H···Cl hydrogen bond with the Cl ion of the inorganic CuCl₄. The T_{10} value is smaller when H and C are located close to the paramagnetic Cu²⁺ ion than when far away. Additionally, the NH₃ groups are coordinated by CuCl₄, and thus, atomic displacements in the environment of the ¹⁴N nuclei with temperature are correlated with CuCl₄. We also note here that detailed studies are required to examine the anomalies observed in the range of 260 to 310 K.

Here, we compared the phase transition temperatures, decomposition temperatures, crystal structures, space groups, lattice constants, and spin-lattice relaxation times of the previously reported [C₂H₅NH₃]₂CuCl₄ (ref. 26-35) and those of [NH₃(CH₂)₄NH₃]CuCl₄ examined in this study; this is summarised in Table 1. The difference between the two crystals is only the presence of organic cation. The two compounds have four and one phase transition temperatures, respectively. The decomposition temperature of [NH₃(CH₂)₄NH₃]CuCl₄ is higher than that of [C₂H₅NH₃]₂CuCl₄, and the [NH₃(CH₂)₄NH₃]CuCl₄ has a high thermal stability. Furthermore, the 1 H and 13 C T_{10} values in [C₂H₅NH₃]₂CuCl₄ are slightly different from those for [NH₃(CH₂)₄NH₃]CuCl₄. Although the two crystals have same anions, the molecular motions according to the 13C bond lengths of the (C₂H₅NH₃) cation in [C₂H₅NH₃]₂CuCl₄ and [NH₃(CH₂)₄NH₃] cation in [NH₃(CH₂)₄NH₃]CuCl₄ are different. The above results suggest that the molecular motions obtained from 1H and 13C $T_{1\rho}$ will be considered as good examples of potential applicability.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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