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Physicochemical properties and structural dynamics of organic–inorganic hybrid $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnX}_4$ ($X = \text{Cl}$ and Br) crystals

Ae Ran Lim^{1,2✉}, Sun Ha Kim^{3,4} & Yong Lak Joo⁵

The physical properties of the organic–inorganic hybrid crystals having the formula $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnX}_4$ ($X = \text{Cl}, \text{Br}$) were investigated. The phase transition temperatures (T_C ; 268 K for Cl and 272 K for Br) of the two crystals bearing different halogen atoms in their skeletons were determined through differential scanning calorimetry. The thermodynamic properties of the two crystals were investigated through thermogravimetric analysis. The structural dynamics, particularly the role of the $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]^+$ cation, were probed through ^1H and ^{13}C magic-angle spinning nuclear magnetic resonance spectroscopy as a function of temperature. The ^1H and ^{13}C NMR chemical shifts did not show any changes near T_C . In addition, the ^1H spin–lattice relaxation time ($T_{1\rho}$) varied with temperature, whereas the ^{13}C $T_{1\rho}$ values remained nearly constant at different temperatures. The $T_{1\rho}$ values of the atoms in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ were higher than those in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$. The observed differences in the structural dynamics obtained from the chemical shifts and $T_{1\rho}$ values of the two compounds can be attributed to the differences in the bond lengths and halogen atoms. These findings can provide important insights or potential applications of these crystals.

Organic–inorganic compounds based on hybrid perovskites, particularly $[(\text{C}_n\text{H}_{2n+1}\text{NH}_3)]_2\text{BX}_4$ ($n = 1, 2, 3, \dots$; $B = \text{Mn}, \text{Co}, \text{Cu}, \text{Zn}, \text{Cd}$; $X = \text{Cl}, \text{Br}$) and $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{BX}_4$ ($n = 2, 3, \dots$) have attracted considerable attention in recent years. Monoammonium series $[(\text{C}_n\text{H}_{2n+1}\text{NH}_3)]_2\text{BX}_4$ ^{1–5} and diammonium series $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{BX}_4$ have been extensively studied because of their relative stability and potential applications^{6–11}. The physical and chemical properties of the organic–inorganic hybrid perovskites depend on the characteristics of the organic cations, geometry of the inorganic anions (metal halide ions; $(\text{BX}_6)^{2-}$ or $(\text{BX}_4)^{2-}$), and reaction stoichiometry^{1–3,12–18}. For $B = \text{Mn}, \text{Cu}$, or Cd , the structure is consists of the corner shared octahedral $(\text{BX}_6)^{2-}$ alternated with organic layers. While for $B = \text{Co}$ or Zn , the structures are tetrahedral $(\text{BX}_4)^{2-}$ sandwiched between layers of organic cations. These compounds have gained research attention because of the multiplicity of their crystal structures, which is correlated to the structural dynamics of the cations and anions. Organic–inorganic hybrid materials based on perovskite structures are of interest due to their potential applications^{19–21}. Recently, solid-state NMR on hybrid perovskite materials has also garnered considerable attention^{22–25}.

The $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ (1,3-propanediammonium tetrachlorozincate (II)) complex ($n = 3$; $B = \text{Zn}$; $X = \text{Cl}$), a member of the diammonium $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{BX}_4$ series, belongs to the monoclinic crystal system (space group: $\text{P}2_1/\text{n}$) at room temperature. Its lattice constants have been reported as $a = 10.692 \text{ \AA}$, $b = 10.611 \text{ \AA}$, $c = 10.786 \text{ \AA}$, $\beta = 118.47^\circ$, and $Z = 4$ ²⁶. Figure 1 shows the structure of the $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ crystal at 300 K (CCDC number : 1227730). The crystal structure of the $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ (1,3-propanediammonium tetrabromozincate (II)) complex ($n = 3$, $B = \text{Zn}$; $X = \text{Br}$) is identical to that of the $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ complex; both belong to the same space group. Its unit cell dimensions were determined as $a = 11.084 \text{ \AA}$, $b = 10.968 \text{ \AA}$, $c = 11.185 \text{ \AA}$, $\beta = 117.07^\circ$, and $Z = 4$ ²⁷. The $[\text{ZnBr}_4]^{2-}$ anion forms a tetrahedron interconnected via the $\text{N} \cdots \text{H} \cdots \text{Br}$

¹Department of Carbon Convergence Engineering, Jeonju University, Jeonju 55069, Korea. ²Department of Science Education, Jeonju University, Jeonju 55069, Korea. ³Korea Basic Science Institute, Seoul Western Center, Seoul 03759, Korea. ⁴Department of Chemistry, Kyungpook National University, Daegu 41566, Korea. ⁵Robert Fredrick Smith School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853, USA. ✉email: arlim@jj.ac.kr

Figure 1. Crystal structure of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ at room temperature.

hydrogen bonds to the $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]$ cation. There is no center of symmetry within the $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]$ cation in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$.

To date, the structures of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnX}_4$ ($\text{X} = \text{Cl}$ and Br) have been reported by Kallel et al.²² and Ishihara et al.²³, who studied the single crystals of the complexes through X-ray diffraction analysis. Although $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnX}_4$ ($\text{X} = \text{Cl}$ and Br) has many applications, the physical properties and structural dynamics of its crystals have not been elucidated.

Herein, the phase transition temperatures and thermodynamic properties of the crystals of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ and $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ complexes are determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The structural dynamics of the crystals of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnX}_4$ (particularly the role of the $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]$ cation) were probed by ^1H magic-angle spinning nuclear magnetic resonance (MAS NMR) and ^{13}C MAS NMR spectroscopy as a function of temperature. The ^1H and ^{13}C NMR spectral profiles were recorded to determine the changes in the chemical shifts. A change in the chemical shift values reflects a change in the structural environment. In addition, the spin–lattice relaxation times ($T_{1\rho}$) in the rotating frame were discussed according to the change of temperature. Based on the MAS NMR results, the effects of different halogen atoms on the hydrogen bond and carbon atoms in the $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ and $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ crystals were investigated. Moreover, comparison of the physical properties of the two crystals revealed important information regarding the basic mechanisms.

Experimental

An aqueous solution containing $\text{NH}_2(\text{CH}_2)_3\text{NH}_2 \cdot 2\text{HCl}$ and ZnCl_2 was slowly evaporated at 300 K to produce the single crystals of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$. Similarly, the slow evaporation at 300 K of an aqueous solution containing $\text{NH}_2(\text{CH}_2)_3\text{NH}_2 \cdot 2\text{HBr}$ and ZnBr_2 , produced the single crystals of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$. Transparent hexagonal crystals of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ and thin-plate-shaped crystals of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ were produced.

The structures of the $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnX}_4$ ($\text{X} = \text{Cl}$ and Br) crystals at 298 K were analysed using an X-ray diffraction system equipped with a Cu-K α radiation source. And, the lattice parameters were determined by single-crystal X-ray diffraction methods at the Western Seoul Center of Korea Basic Science Institute. The crystals were mounted on a Bruker D8 Venture equipped with I μ S micro-focus sealed tube Mo-K α and a PHOTON III M14 detector.

DSC (TA, DSC 25) experiments were carried out at a scanning speed of 10 K/min in the temperature range of 190–620 K under an atmosphere of nitrogen. TGA experiments were performed on a thermogravimetric analyzer (TA Instrument) in the temperature range of 300–870 K. The same heating rate was maintained. The amounts of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ used for the DSC and TGA experiments were 6.04 and 6.72 mg, respectively and the amounts of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ used were 6.40 and 8.96 mg, respectively.

The NMR spectra of the crystals of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ and $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ were recorded on a 400 MHz Avance II + Bruker solid-state NMR spectrometer equipped with 4 mm MAS probes (at KBSI, Western Seoul Center). The MAS ^1H and ^{13}C NMR experiments were conducted at the Larmor frequency of 400.13 and 100.61 MHz, respectively. It was observed that an MAS rate of 10 kHz can minimize the spinning sidebands. Tetramethylsilane (TMS) was used as the standard to record the NMR spectra. As preparation for the MAS NMR experiments, the single crystal was ground into powder. The $T_{1\rho}$ values were obtained using a variable length spin lock pulse. For the two compounds, the width of the $\pi/2$ pulse for ^1H was 3.5 μs and the width of the $\pi/2$ pulse for ^{13}C was 3.96–4.3 μs . The radiofrequency power of the spin-lock pulses was 71.42 kHz for ^1H and 62.50 kHz for ^{13}C . An almost constant temperature (error ± 0.5 K) was maintained even when the rate of flow of nitrogen gas and the heater current were adjusted.

Figure 2. X-ray diffraction patterns of the $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ and $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ at 300 K.

Figure 3. Differential scanning calorimetry (DSC) thermogram of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ and $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$.

Experimental results

X-ray results. The X-ray powder diffraction patterns of the $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnX}_4$ ($X = \text{Cl}$ and Br) crystals at 298 K are displayed in Fig. 2. And, the lattice constants for $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ were determined to be $a = 10.670 \text{ \AA}$, $b = 10.576 \text{ \AA}$, $c = 10.755 \text{ \AA}$, and $\beta = 118.477^\circ$, and those for $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ were determined to be $a = 11.146 \text{ \AA}$, $b = 10.995 \text{ \AA}$, $c = 11.188 \text{ \AA}$, and $\beta = 117.215^\circ$. These results are consistent with those reported previously^{26,27}.

Thermal properties. Two endothermic peaks at 268 and 597 K were observed in the DSC curves of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$, as shown in Fig. 3. The DSC curves of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ revealed the presence of two endothermic peaks at 272 and 589 K, as shown in Fig. 3. The results obtained from the DSC experiments revealed that the peaks that appeared at $\sim 590 \text{ K}$ were significantly larger than the other peaks. An additional TGA and differential thermal analysis (DTA) experiments were performed to determine whether these endothermic peaks are related to the structural phase transitions or melting. The results of the TGA and DTA experiments conducted with the two crystals are presented in Fig. 4a,b. The onset of thermal decomposition temperature ($=T_d$) was observed at temperatures $> 550 \text{ K}$. This was characterized by a loss in the weight of the compounds. It was observed that $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ ($M_w = 283.34 \text{ mg}$) and $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ ($M_w = 461.15 \text{ mg}$) started losing weight at higher temperatures. The amounts of solid residues obtained were calculated from the molecular weights of the compounds and balanced chemical reactions. The amounts were estimated from Eqs. (1), (2), (3), and (4)²⁸.

Figure 4. (a) Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$. (b) Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$.

The amount of residue obtained is determined as follows:

$$[\text{NH}_2(\text{CH}_2)_3\text{NH}_2 \cdot \text{HCl}]\text{ZnCl}_2(\text{s})/[\text{NH}_2(\text{CH}_2)_3\text{NH}_2]\text{ZnCl}_4 = 87.13\%, \quad (1)$$

The amount of residue obtained is determined as follows:

$$[\text{NH}_2(\text{CH}_2)_3\text{NH}_2]\text{ZnCl}_2(\text{s})/[\text{NH}_2(\text{CH}_2)_3\text{NH}_2]\text{ZnCl}_4 = 74.26\%. \quad (2)$$

$[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$.

The amount of residue obtained is determined as follows:

$$[\text{NH}_2(\text{CH}_2)_3\text{NH}_2 \cdot \text{HBr}]\text{ZnBr}_2(\text{s})/[\text{NH}_2(\text{CH}_2)_3\text{NH}_2]\text{ZnBr}_4 = 82.45\%, \quad (3)$$

The amount of residue obtained is determined as follows:

$$[\text{NH}_2(\text{CH}_2)_3\text{NH}_2]\text{ZnBr}_2(\text{s})/[\text{NH}_2(\text{CH}_2)_3\text{NH}_2]\text{ZnBr}_4 = 64.91\%. \quad (4)$$

$[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ was found to lose approximately 13% and 26% of its weight when the temperature was approximately 606 and 621 K, respectively. $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ was found to lose approximately 17% and 35% of its weight when the temperature was approximately 622 and 649 K, respectively. The weight loss can

Figure 5. MAS ^1H NMR line shapes of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ at 300 K.

Figure 6. MAS ^1H NMR spin-lattice relaxation times ($T_{1\rho}$) of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ and $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ as a function of inverse temperature (Inset: recovery curves for delay times of MAS ^1H NMR spectrum in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ at 300 K).

be potentially attributed to the decomposition of HX and 2HX ($X = \text{Cl}$ and Br) moieties, respectively, as shown in Fig. 4a,b. Based on the DSC and TGA results, the phase transition temperatures for $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ and $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ were 268 K and 272 K, respectively. In addition, it was found that the endotherm peaks of 597 K for $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ and 589 K for $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ were related to T_d .

MAS ^1H NMR results. The temperature-induced ^1H NMR chemical shifts for $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ and $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ crystals were recorded through MAS NMR spectroscopy. A single resonance signal was observed in each of the NMR spectra of both the compounds. The ^1H NMR spectrum of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ recorded at 300 K is shown in Fig. 5. The observed resonance signal was asymmetric. The line width represented as symbol 1 and that represented as symbol 2 at the full-width at half-maximum (FWHM) value are not the same as those at 3.54 and 6.11 ppm for 1 and 2, respectively. This asymmetric signal is attributed to the overlapping lines of the two ^1H for CH_2 and NH_3 present in the $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]$ cations. The spinning sidebands were marked with open circles. At 300 K, the ^1H line width of the spectrum recorded for $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ was 10.57 ppm, whereas that of the spectrum recorded for $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ was 9.65 ppm. The ^1H NMR chemical shifts for two ^1H in the $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]$ cations are temperature independent. The chemical shift values remained practically constant over a wide range of temperature, indicating that the structural environment of the protons present in the $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]$ cation does not change when the temperature is increased.

The ^1H $T_{1\rho}$ was measured at each temperature by applying a spin lock of variable duration, t . The relationship between the intensities of the NMR signals and the duration of the spin lock is as follows^{29–31}:

$$I(t) = I(0)\exp(-t/T_{1\rho}), \quad (5)$$

where $I(t)$ and $I(0)$ are the signal intensities at times t and $t = 0$, respectively. The ^1H NMR signals were plotted as a function of the delay times at each temperature. The ^1H NMR signals for $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ at 300 K were

Figure 7. Line widths of ^{13}C for CH_2 -1 and CH_2 -2 in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ and $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ as a function of temperature (Inset: MAS ^{13}C NMR spectra of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ and $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ at 300 K).

recorded by varying the delay times (in the range of 1–150 ms, Fig. 6). The decay curves were fit to an exponential function, as shown in Eq. (5). The $T_{1\rho}$ values of the protons in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ and $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ were obtained as a function of inverse temperature, as shown in Fig. 6. The $T_{1\rho}$ values of the atoms in the two compounds did not change near T_C (268 K for $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ and 272 K for $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$). The $T_{1\rho}$ values initially increased and then decreased when the temperature was increased. In addition, the trend of changes in the ^1H $T_{1\rho}$ values of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ and $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ with temperature was similar. The $T_{1\rho}$ values of the protons in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]$ in both the crystals were 10–1000 ms. The ^1H $T_{1\rho}$ values of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ decreased abruptly at 360 K and that of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ decreased abruptly at 300 K (as represented by lines). The $T_{1\rho}$ value of the protons in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ was higher than that in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ at all studied temperatures. For both the compounds, lower $T_{1\rho}$ values were recorded at higher temperatures. On the slow side of $T_{1\rho}$, a decrease in $T_{1\rho}$ results in smaller value of the correlation time τ_C . The $T_{1\rho}$ values for Arrhenius-type random motions with τ_C are described in terms of slow motions. When $\tau_C < \omega_1$, $T_{1\rho} \propto \tau_C = \tau_0 \exp(-E_a/k_B T)$, where ω_1 denotes the spin-lock frequency and E_a represents the activation energy. The decrease in $T_{1\rho}$ values with temperature indicates an increase in proton mobility at higher temperatures.

MAS ^{13}C NMR results. The MAS ^{13}C NMR chemical shifts in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ and $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ were measured according to the change in temperature. Two resonance signals were observed in the MAS ^{13}C NMR spectra of the compounds. The chemical shift values of the other carbon atoms were determined relative to the TMS signal. Here, the CH_2 group sandwiched between two other CH_2 groups is labeled as CH_2 -1. The CH_2 group close to NH_3 is labeled CH_2 -2. At 300 K, the signals corresponding to the CH_2 -1 and CH_2 -2 carbon atoms in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ appear at $\delta = 26.41$ and $\delta = 38.53$ ppm, respectively. The chemical shift values of the carbon atoms in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ are similar to the chemical shift values of the carbon atoms in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ (Fig. 7, inset). It was observed that for both the crystals, the ^{13}C chemical shift values remained almost constant with changes in temperature (Supplementary Fig. 1).

The change in FWHM for ^{13}C NMR spectra with temperature for both crystals is shown in Fig. 7. In the case of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$, the ^{13}C line widths (CH_2 -1 and CH_2 -2) decreased monotonically with an increase in temperature. Significant anomaly due to phase transition was not observed. The ^{13}C line widths in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ changed with the increase in temperature. A transformation from a Gaussian to Lorentzian shape was observed. The line width reduced because of internal molecular motion. The line width of CH_2 -1 was lower than that of CH_2 -2. The decrease in line width with an increase in temperature can be attributed to the internal molecular motion.

The intensities of the ^{13}C NMR signals were determined by varying the delay times at each temperature. The ^{13}C NMR signals (CH_2 -1 and CH_2 -2) recorded for $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ and $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ were plotted as a function of delay time. The decay curves for CH_2 -1 and CH_2 -2 were fitted to an exponential equation of Eq. (5). From the slopes of the recovery traces, the ^{13}C $T_{1\rho}$ values were obtained (CH_2 -1 and CH_2 -2) as a function of inverse temperature, as shown in Fig. 8. The ^{13}C $T_{1\rho}$ values of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ were higher than those of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$. The ^{13}C $T_{1\rho}$ value of CH_2 -1 was slightly higher than the ^{13}C $T_{1\rho}$ value of CH_2 -2. The $T_{1\rho}$ values of the atoms in both the compounds were temperature independent at > 200 K.

Conclusion

The physical properties of organic–inorganic hybrid crystals $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnX}_4$ ($X = \text{Cl}, \text{Br}$) were investigated through DSC, TGA, and NMR spectroscopy. The TGA results revealed that the $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnX}_4$ ($X = \text{Cl}, \text{Br}$) complex exhibited good thermal stability. When the temperature was increased, the ^1H and ^{13}C chemical shifts

Figure 8. $T_{1\rho}$ for CH_2 -1 and CH_2 -2 of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ and $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ as a function of inverse temperature.

	$[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$	$[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$
Lattice constants	$a = 10.670, b = 10.576, c = 10.755, \beta = 118.477$	$a = 11.146, b = 10.995, c = 11.188, \beta = 117.215^\circ$
T_C	268	272
T_d	597	589
$^1\text{H } T_{1\rho}$	849	234
$^{13}\text{C } T_{1\rho}$ for CH_2 -1	18.78	5.86
$^{13}\text{C } T_{1\rho}$ for CH_2 -2	21.05	6.80

Table 1. The lattice constants ($\text{\AA}$), phase transition temperatures T_C (K), thermal decomposition temperatures T_d (K), and spin–lattice relaxation times $T_{1\rho}$ (ms) in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnX}_4$ ($X = \text{Cl}$ and Br) crystals at 300 K.

remained almost constant. Although the T_C was obtained from the DSC experiments, in particular, changes in the chemical shift values were not observed at temperatures near T_C . This indicated that the chemical environment surrounding the protons and the carbon atoms in the $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]$ cation remained unaltered.

The structural dynamics were discussed in terms of the $^1\text{H } T_{1\rho}$ and $^{13}\text{C } T_{1\rho}$ values. The $^1\text{H } T_{1\rho}$ values changed with the temperature, whereas the $T_{1\rho}$ value of the carbon atom located in the middle of the $\text{N}-\text{C}-\text{C}-\text{N}$ chain did not change significantly with the temperature. The $^1\text{H } T_{1\rho}$ and $^{13}\text{C } T_{1\rho}$ values of the atoms in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ were higher than those in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ (Table 1). The reason why $^{13}\text{C } T_{1\rho}$ values in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnCl}_4$ are longer than $^{13}\text{C } T_{1\rho}$ values in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnBr}_4$ are as follows. The $^{13}\text{C } T_{1\rho}$ is most likely driven by $^1\text{H}-^{13}\text{C}$ interactions, and hence, the $\text{H}-\text{C}$ bond lengths are important.

However, the $\text{H}-\text{C}$ bond lengths of the two materials are unlikely to be different, and also cannot be accurately measured from X-ray results. We assume that the differences in the dynamics between the materials contribute more to the difference in $T_{1\rho}$. Although the structures and lattice constants of two crystals are similar, the differences between the local environments and structural dynamics obtained from the chemical shifts and $T_{1\rho}$ values of the two compounds can be attributed to the different bond lengths and halogen atoms. Thus, the results of this study elucidate the physical properties of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{ZnX}_4$, which will expand the application scope of this organic–inorganic hybrid crystals.

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Author contributions

A.R.L. designed the project and wrote the manuscript. S.H. K. performed NMR experiments. Y.L. J performed TGA experiments and comment.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to A.R.L.

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