Physicochemical Property Investigations of Perovskite-Type Layer Crystals \([\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{MX}_4 \quad (n = 2, 3, \text{ and } 4)\) as a Function of Length \(n\) of \(\text{CH}_2\)

Ae Ran Lim\(^*\) and Sun Ha Kim

ABSTRACT: Hybrid perovskites have potential applications in several electrochemical devices such as supercapacitors, batteries, and fuel cells. Here, the thermal stabilities as a function of the length \(n\) of the \(\text{CH}_2\) groups in \([\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{MX}_4 \quad (n = 2, 3, \text{ and } 4)\) crystals were considered by TGA and DTA. The structural characteristics and molecular dynamics were studied by MAS and static NMR experiments. A comparison of spin--lattice relaxation times indicated that the organic cation containing \(^{1}H\) and \(^{13}C\) was significantly more flexible than the inorganic anion containing \(^{119}Cd\). The flexibility of \(^{1}H\) increased with an increase in the length of \(\text{CH}_2\) in the carbon chain, resulting in a decrease in the activation energy \((E_a)\) of \(^{1}H\). The \(E_a\) of \(^{13}C\) at \(n = 3\) and 4 was more flexible at high temperatures than at low temperatures. In contrast, the \(E_a\) of \(^{13}C\) at \(n = 2\) was more flexible at low temperatures. These results provide insight into the thermal stability and molecular dynamics of these crystals as a function of the length \(n\) of \(\text{CH}_2\) groups in the carbon chain and are expected to facilitate applications.

1. INTRODUCTION

Halide perovskites have been reported as one of the most promising materials for photovoltaic and light-emitting devices.\(^{1,3}\) In recent years, the development of novel functional materials has resulted in considerable progress in the synthesis of several hybrid organic--inorganic perovskites. The organic--inorganic hybrid perovskite crystals \([\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{MX}_4 \quad (n = 2, 3, 4, \ldots; M = \text{Mn, Fe, Co, Cu, Zn, Cd, } \ldots; X = \text{Cl and Br})\) have drawn significant research interest. Their physicochemical properties depend on factors such as the characteristics of the organic cations and geometry of the inorganic metal halide anions constituting the crystal.\(^{4–13}\) The organic cation of the hybrid complex contributes to properties such as structural flexibility and optical properties, whereas the inorganic anion is responsible for the thermal and mechanical properties. In the case of \(M = \text{Mn, Cu, and Cd}\), the crystal structures consist of an alternate octahedron (\(\text{MX}_6\))\(^{2+}\) and organic chains. In the case of \(M = \text{Co and Zn}\), isolated tetrahedral structures are formed, where an inorganic layer of (\(\text{MX}_6\))\(^{2+}\) is sandwiched between the layers of an organic cation.\(^{14–18}\) Perovskite compounds composed of \([\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\) cations and \(\text{MX}_4\) anions are zero-dimensional, whereas those containing \(\text{MX}_6\) anions are two-dimensional. Furthermore, several studies focusing on their molecular structure have reported even--odd effects as the number of carbon atoms in the diammonium chain changes, which affects the structural properties of these materials.\(^{19}\) Structural phase transitions have also been reported for \([\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{MX}_4\) types, in which the link between adjacent octahedral or tetrahedral planes is realized by methylene chains bearing \(\text{NH}_3\) groups on both ends. The \([\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{MX}_4\) organic chains extend along the longest \(c\)-axis. The perovskite \([\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CdCl}_4 \quad (M = \text{Cd, X = } \text{Cl})\) consists of puckered layers of \(\text{CdCl}_6\) separated by nearly perpendicular layers of \([\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\) chains. The distance between the two neighboring inorganic layers depends on the length of the organic chain.\(^{20}\) These compounds have attracted considerable interest owing to the multiplicity of their crystal structures, which governs their thermodynamic properties and structural dynamics. These hybrid perovskites have potential applications in several electrochemical devices such as supercapacitors, batteries, and fuel cells.\(^{21–26}\)

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N–H⋯Cl hydrogen-bonding network. The Cd atom is located on an inversion center, and the coordination environment is described as a highly distorted octahedral.28 1,3-Propylene-diammonium tetrachlorocadmate, [NH3(CH2)4NH3]CdCl4 (n = 3), is known to undergo a structural phase transition at Tc1 = 375 K.29 At room temperature, the crystals are orthorhombic with the space group Pmn1. The unit cell at 299 K has the following parameters: a = 7.373 Å, b = 7.523 Å, c = 19.111 Å, and Z = 4. When the temperature is above Tc1, the crystal is still orthorhombic; however, the space group becomes Imma, and the lattice constants at 403 K become a = 7.38577 Å, b = 7.56974 Å, c = 18.7300 Å, and Z = 4.9 Figure 1 shows the structure of the [NH3(CH2)4NH3]CdCl4 crystal at 300 K. In each formula unit, the six hydrogen atoms in ammonium form hydrogen bonds N–H⋯Cl. The Cd atom is surrounded by six Cl atoms to form nearly regular CdCl6 octahedra. 1,4-Butanediyldiammonium tetrachlorocadmate, [NH3(CH2)4NH3]CdCl4 (n = 4), undergoes two structural phase transitions near 338 K (=Tc2) and 367 K (=Tc3).10 The phases III and II are monoclinic, whereas the high-temperature phase I is orthorhombic. At phases III and II, it is monoclinic, with space group P21/a and Z = 2. The unit cell parameters in phase III (at 293 K) are a = 7.657 Å, b = 7.585 Å, c = 9.541 Å, and β = 101.56°.19 Further, the lattice parameters in phase II (at 350 K) are a = 7.48 Å, b = 7.53 Å, c = 10.18 Å, and β = 97.5°. The high-temperature phase I is orthorhombic, with space group Pmn1 and Z = 2. The unit cell parameters at 373 K are a = 7.377 Å, b = 7.538 Å, and c = 10.600 Å.

The synthesis and characterization of [NH3(CH2)3NH3]CdCl4 by Battaglia et al.28 Subsequently, the X-ray results for this crystal structure at 298 K were reported by Lamhamdi et al.27 The phase transition at 375 K for the [NH3(CH2)4NH3]CdCl4 crystal with n = 3 is reversible and continuous, according to previous dielectric and optical studies.29,30 In addition, the structural, thermal, and vibrational properties as well as molecular motions have been characterized by Staskieqicz et al.31 Recently, the physicochemical properties of this crystal were reported by our group.31 In the case of n = 4, the thermodynamic and crystallographic characters of the phase transitions for NH3(CH2)4NH3CdCl4 were studied, and the crystal structure in each phase was discussed from X-ray diffraction measurements.31,33 However, despite various potential applications, there have been limited studies on compounds containing Cd. In particular, the thermal properties, structural phase transitions, and structural dynamics resulting from differences in the methylene chain length of [NH3(CH2)3NH3]CdCl4 crystals have not been discussed in detail.

This study aims to investigate the thermodynamic properties and molecular dynamics of [NH3(CH2)3NH3]CdCl4 as a function of the length n of CH2 groups in the carbon chain. The crystal structures, phase transition temperatures, and thermodynamic properties of the crystals with n = 2, 3, and 4 are investigated using X-ray diffraction, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and differential thermal analysis (DTA). In addition, the chemical shifts and spin–lattice relaxation time T1p are probed using 1H magic angle spinning nuclear magnetic resonance (MAS NMR), 13C MAS NMR, and static 14N NMR as a function of temperature to elucidate the characteristics of the [NH3(CH2)3NH3] cation. Furthermore, the chemical shifts for 113Cd MAS NMR are recorded as a function of the temperature to understand the geometry of octahedral CdCl6. The results provide insights into the thermodynamic properties and structural dynamics of [NH3(CH2)3NH3]CdCl4 crystals based on the length of CH2 and even–odd effects of the organic chain and are expected to facilitate potential applications in the future.

2. RESULTS

2.1. Crystal Structures. The X-ray powder diffraction patterns of the [NH3(CH2)3NH3]CdCl4 crystals (n = 2, 3, and 4) at 298 K are shown in Figure 2. The lattice constants for the

![Figure 1. Structure of the [NH3(CH2)4NH3]CdCl4 crystal at room temperature.](image1)

![Figure 2. X-ray diffraction patterns of [NH3(CH2)3NH3]CdCl4 (n = 2, 3, and 4) at 298 K.](image2)
was observed at 374 K (=T_C). Finally, in the case of n = 4, two endothermic peaks were observed at 341 K (=T_C2) and 366 K (=T_C1). These phase transition temperatures are consistent with those reported previously.9,19,30

To verify whether the endothermic peaks correspond to phase transition or decomposition, TGA and DTA experiments were performed at the same heating rate. The TGA and DTA curves displayed in Figure 4—6 show that the crystals with n = 2, 3, and 4 are almost stable up to approximately 493, 539, and 536 K, respectively; according to the number n of CH2 groups in the carbon chain, the molecular weight loss near 493, 539, and 536 K marks the onset of partial thermal decomposition (at temperature T_d). [NH3(CH2)_nNH3]CdCl4 undergoes loss in the molecular weight with increasing temperature. The amount remaining as solid residues can be calculated from the molecular weights. When n = 2, the loss of 12 and 23% of its weight at temperatures of about 622 and 804 K was due to the decomposition of HCl and 2HCl, respectively (see Figure 4). The small endothermic peak at 374 K on the DTA curve for [NH3(CH2)_3NH3]CdCl4 is assigned to the phase transition detected in the DSC experiment. Additionally, weight losses of 11% and 22% occurred at temperatures of 613 and 623 K, respectively (see Figure 5). Finally, in the case of [NH3(CH2)_4NH3]CdCl4 crystals with n = 4, the two small endothermic peaks at 341 and 366 K on the DTA curve are attributed to the phase transition seen in the DSC result. At temperatures of 612 and 623 K, 11 and 21% of their weight were lost, respectively (see Figure 6). The molecular weight of the three crystals decreased sharply between 550 and 650 K. In the case of n = 3 and 4 near 800 K, weight losses of 45% occurred, whereas when n = 2, the weight loss was the smallest at 23%.

To support the TGA results, the appearance of single crystals with changing temperature was observed with an optical polarizing microscope (Figure 7). In the case where n = 2, the crystal formed at 300 K was colorless and transparent, while it appeared slightly opaque above 547 K. Upon increasing the temperature to 622 K, HCl was eliminated, and the crystal turned orange. Finally, the surface near 633 K appeared to melt slightly. In the case where n = 3, the crystal had an opaque white color at room temperature. Upon increasing the temperature to 673 K, it remained opaque even though the 2HCl was blown away. For the case where n = 4, the crystal was transparent at 300 K, and it turned opaque white with increasing temperature, likely indicating the elimination of HCl. Finally, it turned bright brown as 2HCl was lost near 670 K.

2.3. 1H MAS NMR. The 1H MAS NMR spectra of [NH3(CH2)_nNH3]CdCl4 crystals according to the length of the carbon chain were recorded as a function of temperature. The results of 1H chemical shifts for n = 2, 3, and 4 are shown in Figure 8. At 300 K, the 1H chemical shifts for NH3 and CH2 were obtained at 7.96 and 4.78 ppm, respectively, in the case of n = 2 and at 7.57 and 3.23 ppm, respectively, in the case of n = 3. Finally, for n = 4, they were obtained at 6.90 and 4.69 ppm,
The chemical shifts for NH$_3$ of all three crystals are nearly exponential function. The decay rate of the spin-locked proton magnetization is characterized by the spin–lattice relaxation time $T_{1p}$ as

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

(1)

where $P(\tau)$ and $P(0)$ are the signal intensities at time $\tau$ and $\tau = 0$, respectively. From the slope of the logarithm of intensities vs delay times plot, the $^1H$ $T_{1p}$ values were determined for NH$_3$ and CH$_2$ at several temperatures. The $^1H$ $T_{1p}$ results are shown in Figure 9 for the three compounds as a function of inverse temperature. In the cases where $n = 2$ and 3, as the temperature increases, the $T_{1p}$ values increase rapidly from 2 to 700 ms and then rapidly reduce at temperatures above 350 K. At 350 K, $^1H$ $T_{1p}$ has maximum values when $n = 2$, and the values for NH$_3$ and CH$_2$ are 352 and 388 ms, respectively. The values for NH$_3$ and CH$_2$ when $n = 3$ are 496 and 683 ms. In the case where $n = 4$, the $^1H$ $T_{1p}$ value tends to increase gradually as the temperature increases. The three compounds show a similar tendency at temperatures below 350 K, but their values at temperatures above 350 K show different trends depending on the length of the carbon chain. It can be seen that the $^1H$ $T_{1p}$ values at high temperatures are different according to the $n$ value. In the case where $n = 3$, there was no significant change in the vicinity of $T_C$ but in the case of $n = 4$, it was found to be slightly discontinuous in the vicinity of $T_{C2}$. The discontinuous changes of $^1H$ chemical shifts and $^1H$ $T_{1p}$ near $T_{C2}$ are thought to be due to the rapid changes in the lattice constants $c$ and $\beta$.

The activation energy ($E_a$) values for $^1H$ in NH$_3$ for the three crystals were evaluated based on the slopes (represented by the solid lines in Figure 9) of their $\rho$ vs $1000/T$ plot. For $n = 2$, $E_a$ was 35.04 ± 4.10 kJ/mol at high temperatures and 12.81 ± 0.42 kJ/mol at low temperatures. For $n = 3$, $E_a$ was 25.36 ± 2.97 kJ/mol above $T_C$ and 8.37 ± 0.34 kJ/mol below $T_C$, and for $n = 4$, $E_a$ was 10.06 ± 2.24 kJ/mol above $T_{C1}$ and 5.18 ± 0.28 kJ/mol below $T_{C2}$. The $E_a$ values for $^1H$ in CH$_2$ for the three crystals were the same as those for $^1H$ in NH$_3$ in the error range.

2.4. $^{13}C$ MAS NMR. The $^{13}C$ MAS NMR chemical shifts for CH$_2$ in [NH$_3$(CH$_2$)$_n$NH$_3$]CdCl$_4$ were recorded at several temperatures. The signal for TMS reference was measured at 38.3 ppm at 300 K, and this value was set to 0 ppm for the $^{13}C$ chemical shift. Here, it is seen that CH$_2$-1 in the
[NH3(CH2)nNH3] cation is far from NH3 and that CH2-2 is located near NH3. The results of 13C chemical shifts according to the methylene chain length at 300 K are shown in the Supplementary Information. In the case where \( n = 2 \), only one 13C resonance line was obtained for CH2-2. In the case where \( n = 3 \) and 4, two 13C resonance lines were obtained for CH2-1 and CH2-2, respectively. At 300 K, the 13C chemical shift for \( n = 2 \) was recorded at 37.36 ppm, and those for \( n = 3 \) were observed at 25.00 and 39.09 ppm for CH2-1 and CH2-2, respectively. The 13C chemical shifts for \( n = 4 \) were observed at 25.30 and 42.85 ppm, respectively. Here, the chemical shifts for CH2-1 are similar for these crystals, but those for CH2-2 are different between \( n = 2, 3, \) and 4. The full width at the half-maximum (FWHM) for 13C NMR at 300 K is relatively narrow, ranging from 1.2 to 1.6 ppm.

Meanwhile, the chemical shifts for the in situ 13C MAS NMR spectra for the three compounds are shown in Figures 10–12 with increasing temperature. In the case where \( n = 2 \) (Figure 10), the 13C chemical shifts for CH2-2 increase slightly as the temperature increases. Some chemical shift changes around 290 K can also be seen. In the case where \( n = 3 \) (Figure 11), the slopes of the chemical shifts marked by red dotted lines are temperature dependent, with more variation for CH2-2 than for CH2-1. In addition, there was no change in chemical shifts near \( T_C \). However, in the case where \( n = 4 \) (Figure 12), the chemical shifts show discontinuity near \( T_{C2} \) whereas they show continuity near \( T_{C1} \). It can be seen that the chemical shifts of CH2-2 near \( T_{C2} \) change more than those of CH2-1. In the three compounds, the chemical shifts of CH2-2 (more so than that of CH2-1) are thought to be affected by the N sites bonded to both ends of CH2-2.

The 13C MAS NMR spectrum showed a change in intensity with increasing delay time at each temperature. All these decay curves could be described by a single exponential function, and from the slope of their recovery traces, the 13C \( T_{1p} \) values for CH2-1 and CH2-2 were obtained for the three compounds and plotted as a function of 1000/\( T \), as shown in Figure 13. In the case where \( n = 2 \), the 13C \( T_{1p} \) value first decreased slightly with increasing temperature and then decreased rapidly at higher temperatures. In the case where \( n = 3 \), it decreased slightly with an increase in temperature, then increased again, and finally decreased more than that of CH2-1. In the three compounds, the chemical shifts of CH2-2 (more so than that of CH2-1) are thought to be affected by the N sites bonded to both ends of CH2-2.
decreased at temperatures above \( T_C \). Meanwhile, the minimum \( T_{1\rho} \) values (34.74 and 28.40 ms for CH2-1 and CH2-2, respectively) occur at 280 K. In the case where \( n = 4 \), \( T_{1\rho} \) decreases slightly as the temperature increases and then increases rapidly near \( T_{C1} \). Similar to that in the case of \( n = 3 \), this tendency results from molecular motion below the phase transition temperature. There are distinct molecular motions, and the minimum \( T_{1\rho} \) is due to the molecular motion of CH2-1 and CH2-2 in the \( [\text{NH}_3(\text{CH}_2)_n\text{NH}_3]^{2+} \) cations in the case where \( n = 3 \) and 4, respectively. These \( T_{1\rho} \) values could be described by the correlation time \( \tau_C \) for the molecular motion, and the \( T_{1\rho} \) value for the molecular motion is given by \( 36,37 \)

\[
T_{1\rho}^{-1} = C(\gamma_H^2t_C^2/\hbar^2)[4f_2 + f_3 + 3f_2 + 6f_3] \tag{2}
\]

where \( f_1 = \tau_C / [1 + \omega_1^2\tau_C^2] \), \( f_2 = \tau_C / [1 + (\omega_H - \omega_C)^2\tau_C^2] \), \( f_3 = \tau_C / [1 + (\omega_H + \omega_C)^2\tau_C^2] \), \( f_4 = \tau_C / [1 + \omega_2\tau_C^2] \), \( f_5 = \tau_C / [1 + \omega_2\tau_C^2] \), \( f_6 = \tau_C / [1 + \omega_2\tau_C^2] \). Here, \( C \) is a coefficient, \( \gamma_H \) and \( \gamma_C \) are the gyromagnetic ratios for \(^1\text{H} \) and \(^{13}\text{C} \), respectively; \( \hbar \) is the reduced Planck constant, \( r \) is the intermolecular distance, \( \omega_H \) and \( \omega_C \) are the Larmor frequencies of \(^1\text{H} \) and \(^{13}\text{C} \), respectively, and \( \omega_1 \) is the frequency of the spin-lock field. Here, the \(^{13}\text{C} \) \( T_{1\rho} \) values were measured using the spin-locking pulse sequence with a locking pulse of \( \omega_1 \) = 75.76 kHz for \( n = 3 \) and \( \omega_1 \) = 70.42 kHz for \( n = 4 \). When \( \omega_1\tau_C = 1 \), \( T_{1\rho} \) has the minimum value. Therefore, a relationship between \( T_{1\rho} \) and \( \omega_1 \) was applied to obtain the coefficient \( C \) in eq 2. Using this coefficient, \( \tau_C \) was calculated as a function of temperature.

According to Bloembergen–Purcell–Pound (BPP) theory, the local field fluctuation is governed by the thermal motion of CH2-1 and CH2-2. The correlation time \( \tau_C \) for molecular motion at several temperatures follows the Arrhenius equation \( 33 \)

\[
\tau_C = T_C \exp(-E_a/k_BT) \tag{3}
\]

where \( E_a \) and \( k_B \) are the activation energy of the motions and Boltzmann constant, respectively. The magnitude of \( E_a \) depends on the molecular dynamics. The plot of \( \log \tau_C \) vs 1000\(^{-1} \) provided the \( E_a \) values for CH2-1 and CH2-2, as shown in Figure 14; in the case where \( n = 3 \), the \( E_a \) values of CH2-1 and CH2-2 below \( T_C \) were 26.96 ± 8.85 and 39.94 ± 10.45 \( \text{kJ/mol} \), respectively. When \( n = 4 \), the \( E_a \) values of CH2-1 and CH2-2 below \( T_{C2} \) were 28.18 ± 2.05 and 23.18 ± 2.51 \( \text{kJ/mol} \), respectively. Additionally, above \( T_C \) when \( n = 3 \), the \( E_a \) values for CH2-1 and CH2-2 were 10.18 ± 2.68 and 8.45 ± 2.04 \( \text{kJ/mol} \), respectively, determined using \( T_{1\rho} = \exp(\pm E_a/k_BT) \) similar to the one expressed in eq 3. Unlike that in the cases of \( n = 2 \) and 3, the trend of \(^{13}\text{C} \) \( T_{1\rho} \) at high temperatures is very different for \( n = 4 \). Above \( T_{C1} \), the values for \( n = 4 \) were 13.42 ± 2.01 and 14.35 ± 1.41 \( \text{kJ/mol} \), respectively. When \( n = 3 \) and 4, the \( E_a \) values at low temperatures are greater than those at high temperatures, whereas when \( n = 2 \), their results are opposite (1.70 ± 0.24 \( \text{kJ/mol} \) below 330 K and 35.19 ± 4.32 \( \text{kJ/mol} \) above 330 K).

### 2.5. Static \(^{14}\text{N} \) NMR

Static \(^{14}\text{N} \) NMR investigations of \( [\text{NH}_3(\text{CH}_2)_n\text{NH}_3]^{2+} \text{CdCl}_4 \) single crystals were conducted over the temperature range of 180–430 K. The \(^{14}\text{N} \) spectra were obtained using the solid-state echo method by static NMR. Two \(^{14}\text{N} \) NMR signals were expected from the quadrupole interactions due to the spin number \( I = 1 \). The static \(^{14}\text{N} \) chemical shifts for \( n = 2, 3, \) and 4 at 300 K are shown in Figure 15. Despite the presence of intense background noise in the spectra due to the extremely low NMR frequency (28.90 MHz) used for the experiment, the \(^{14}\text{N} \) signal was easily discerned.

**Figure 15.** In situ static \(^{14}\text{N} \) chemical shifts of \( [\text{NH}_3(\text{CH}_2)_n\text{NH}_3]^{2+} \text{CdCl}_4 \) \( (n = 2, 3, \) and 4) single crystals at 300 K.

The FWHM of \(^{14}\text{N} \) NMR was similar for the three \( n \) values, which was approximately 33 ppm. The \(^{14}\text{N} \) NMR spectrum for \( n = 2, 3, \) and 4 differed with increasing temperature, as shown in Figure 16. Here, the measurements were performed by keeping the \( c \)-axis of the single crystals parallel to the direction of the magnetic field. In the case of \( n = 2 \), the two resonance lines of one pair decreased with increasing temperature, then decreased to a minimum near 400 K, and then increased again. In the case of \( n = 3 \), the chemical shifts for four resonance lines due to the two pairs caused a large change near \( T_C \). The symbols with the same color below \( T_C \) indicate the same pairs for \(^{14}\text{N} \). Near 374 K (=\( T_C \)), the number of resonance lines and chemical shifts of the NMR spectrum showed abrupt changes; two pairs turned into just one pair. The changes in the \(^{14}\text{N} \) chemical shift as a function of temperature were attributed to the variations in the structural geometry. In addition, the chemical shifts of the \(^{14}\text{N} \) signals below \( T_C \) changed almost continuously, and the chemical shifts for \(^{14}\text{N} \) above \( T_C \) remained constant with temperature. The \(^{14}\text{N} \) NMR spectrum exhibits a reduction in the NMR lines from two to one pair of lines at the phase transition \( T_C \).

Finally, when \( n = 4 \), the two resonance lines showed no change in temperature below \( T_{C2} \) however, it was difficult to detect because the line width suddenly increased above \( T_{C2} \).
the case of \( n = 3 \), the different N spectra were explained as follows. None of the previously reported X-ray results\(^9,19,27,30\) include different N sites; therefore, two different N sites are thought to have a twin domain due to the ferroelastic property in materials with the organic−inorganic perovskite structure reported recently.\(^39,40\)

2.6. \(^{113}\)Cd MAS NMR. \(^{113}\)Cd MAS NMR experiments were performed to examine the structural dynamics in the anions of \([\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CdCl}_4\) single crystals. \(^{113}\)Cd has an isotopic abundance of 12.3% and a spin of \( I = 1/2 \). This information is significant for the deduction of the anion coordination environments around \( \text{Cd}^{2+} \) in \( \text{CdCl}_6 \) with unknown structures.\(^41,42\) The \(^{113}\)Cd MAS NMR spectra for the three crystals were obtained at 300 K, as shown in Figure 17. Spinning sidebands were observed on the three spectra, which have been indicated in the figure by the symbol \(^*\).

Figure 17. In situ \(^{113}\)Cd MAS NMR chemical shifts of \([\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CdCl}_4\) (\( n = 2, 3, \) and 4) at 300 K.

The \(^{113}\)Cd chemical shifts for the three crystals shift slightly in the negative direction as the temperature increases, as shown in Figure 18. However, in the case where \( n = 4 \), it was discontinuous near \( T_{C2} \). This result suggests that in the cases when \( n = 2 \) and 3, there is no significant change in the environment near Cd depending on the temperature, whereas in the case of \( n = 4 \), the environment around Cd changes near the phase transition temperature.

The \(^{113}\)Cd MAS NMR spectrum for three crystals measured the change in intensity with various delay times at 300 K. The decay curves were described by a single exponential function, and the \(^{113}\)Cd \( T_{1P} \) values were obtained from the slope of their recovery traces. In the cases where \( n = 2, 3, \) and 4, the \( T_{1P} \) values were 2058, 1512, and 1101 ms, respectively. All of the \( T_{1P} \) values for \(^1\)H, \(^{13}\)C, and \(^{113}\)Cd of \([\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CdCl}_4\) (\( n = 2, 3, \) and 4) at 300 K are listed in Table 1. \(^{113}\)Cd \( T_{1P} \) was very long compared to \(^1\)H \( T_{1P} \) and \(^{13}\)C \( T_{1P} \). The long \(^{113}\)Cd \( T_{1P} \) values with \( n = 2 \) were considered to be more rigid than the others (\( n = 3 \) and 4); a longer \( T_{1P} \) indicates that the transfer of energy from the nuclear spin system to the surrounding environment is not very easy.

3. DISCUSSION

The structures and phase transition temperatures of the \([\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CdCl}_4\) (\( n = 2, 3, \) and 4) crystals were confirmed using X-ray diffraction and DSC. The thermal stability of the crystal improved as the length of the CH2 groups in the \([\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\) cations increased. Through the NMR analysis of the crystals, we deduced that \( n = 2 \) and 3, and 4, the \( T_{1P} \) values were 2058, 1512, and 1101 ms, respectively. All of the \( T_{1P} \) values for \(^1\)H, \(^{13}\)C, and \(^{113}\)Cd at 300 K are listed in Table 1. \(^{113}\)Cd \( T_{1P} \) was very long compared to \(^1\)H \( T_{1P} \) and \(^{13}\)C \( T_{1P} \). The long \(^{113}\)Cd \( T_{1P} \) values with \( n = 2 \) were considered to be more rigid than the others (\( n = 3 \) and 4); a longer \( T_{1P} \) indicates that the transfer of energy from the nuclear spin system to the surrounding environment is not very easy.
crystallographic environments of $^1$H, $^{13}$C, and $^{14}$N in the cation and $^{113}$Cd in the anion exhibited no significant changes with temperature. For $n = 3$, the results were similar to that of $n = 2$ excluding that of the $^{14}$N NMR, which indicated significant changes in the crystallographic environment of $^{14}$N in the cation. For $n = 4$, crystallographic environments of all atoms of the cation and anion exhibited changes near the phase transition temperature. Through the evaluation of the $T_{1_p}$ values for the various cation lengths, we deduced that the effect of the cation length on the molecular motion was evident only at high temperatures. The $^1$H and $^{13}$C $T_{1_p}$ values for $n = 2$ and 3 decreased rapidly at high temperatures, whereas the values increased for $n = 4$. The Arrhenius-type behavior of $T_{1_p}$ for random motions with a correlation time $\tau_c$ is described by two motion regimes: fast and slow motion regimes. The $^1$H $T_{1_p}$ values at low temperatures for $n = 2$ and 3 were attributed to the fast motion regime, where $\omega_1 \tau_c \ll 1$ and $T_{1_p}^{-1} = \alpha \exp(E_a/k_BT)$, and their values at high temperatures to the slow motion regime, where $\omega_1 \tau_c \gg 1$ and $T_{1_p}^{-1} = \alpha \omega_1^{-2} \exp(E_a/k_BT)$. The $^1$H $T_{1_p}$ for $n = 4$ was associated with fast motion at all temperatures, whereas the $^{13}$C $T_{1_p}$ for $n = 2$ and 3 to slow motion at all temperatures. However, for $n = 4$, the $^{13}$C $T_{1_p}$ was associated to slow motion at low temperatures and fast motion at high temperatures.

### 4. CONCLUSIONS

Even–odd effects were significant on the structural properties of the single crystal but not on its physicochemical properties. In the case of $n = 4$, $^1$H and $^{13}$C $T_{1_p}$ show the opposite nature at high temperatures, unlike the cases of $n = 2$ and 3. Furthermore, $^{113}$Cd $T_{1_p}$ at 300 K was considerably longer than those of $^1$H and $^{13}$C, which indicated that the organic cation containing $^1$H and $^{13}$C was significantly fl exible than the inorganic anion containing $^{113}$Cd. In addition, the fl exibility of $^1$H increased with the length of the $\text{CH}_2$ groups in the cation, which resulted in a decrease in $E_a$ for $^1$H (see Table 2). $E_a$ for $^{13}$C at $n = 3$ and 4 was more fl exible at high temperatures than at low temperatures. On the contrary, $E_a$ for $^{13}$C at $n = 2$ was more fl exible at low temperatures. The effects of the length of $\text{CH}_2$ in the cation on the molecular motion reported in this study will facilitate future research on hybrid perovskites for their potential applications in supercapacitors, batteries, and fuel cells.

### 5. EXPERIMENTAL METHOD

An aqueous solution containing NH$_2$(CH$_2$)$_2$NH$_2$·2HCl (Aldrich, 98%) and CdCl$_2$ (Aldrich, 99.99%) was slowly evaporated in a thermostat at 300 K to produce single crystals of [NH$_3$(CH$_2$)$_2$NH$_3$]CdCl$_4$ ($n = 2, 3,$ and 4). The rectangular transparent single crystals were produced within 3–4 weeks, and these single crystals were stored in a desiccator to avoid moisture. The structures of the [NH$_3$(CH$_2$)$_2$NH$_3$]CdCl$_4$ crystals at 298 K were analyzed using an X-ray diffraction system equipped with a Cu Kα radiation source. The lattice parameters were determined by single-crystal X-ray diffraction at the Seoul Western Center of the Korea Basic Science Institute (KBSI). The crystals were mounted on a Bruker D8 Venture equipped with a 1 μs microfocus sealed tube Mo Kα and a PHOTON III M14 detector.

DSC (DSC 25, TA Instruments) measurements for the three crystals were carried out at a scanning speed of 10 K/min between 190 and 600 K under nitrogen gas. TGA and DTA experiments were performed on a thermogravimetric analyzer (TA Instrument) at the same heating rate between 300 and 873 K under N$_2$ gas. In addition, optical observations were made using an optical polarizing microscope in the temperature range of 300–680 K, where the as-grown single crystals were placed on the heating stage of a Linkam THM-600.

NMR spectra of [NH$_3$(CH$_2$)$_2$NH$_3$]CdCl$_4$ crystals were obtained using a Bruker 400 MHz Avance II+ solid-state NMR spectrometer equipped with 4 mm MAS probes at the Seoul Western Center, KBSI. The Larmor frequencies for $^1$H MAS NMR and $^{13}$C MAS NMR experiments were 400.13 and 100.61 MHz, respectively. The MAS rate to minimize the spinning sideband was 10 kHz, and the NMR chemical shifts were recorded using tetramethylsilane (TMS) as the standard. $T_{1_p}$ values were obtained using a $\pi/2$- pulse, followed by a spin-lock pulse of duration $\tau_s$ and the width of the $\pi/2$ pulse for $^1$H and $^{13}$C was in the range of 3.4–3.62 μs. In addition, static $^{14}$N NMR and $^{113}$Cd MAS NMR spectra were measured with Larmor frequencies of 28.90 and 88.75 MHz, respectively. The $^{14}$N NMR experiments were performed using a solid-state echo sequence: 4 μs-μs-$\pi$-μs; $\tau_s = 5$ μs for $n = 2$, $\tau_s = 8$ μs for $n = 3$ and 4. The $^{113}$Cd MAS NMR experiments were performed using a $\pi/2$-pulse pulse, followed by a spin-lock pulse of duration $\tau_s$ and the width of the $\pi/2$ pulse for $^{113}$Cd was 3.2 μs. The chemical shift measurements referenced NH$_4$NO$_3$ and CdCl$_2$·6H$_2$O as standard samples. The temperature was changed by adjusting the nitrogen gas flow and heater current, and it was maintained within ±0.5 K.

### ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04671.

$^{13}$C NMR spectra for [NH$_3$(CH$_2$)$_2$NH$_3$]CdCl$_4$ ($n = 2, 3,$ and 4) (PDF)

### AUTHOR INFORMATION

**Corresponding Author**

Ae Ran Lim – Department of Carbon Convergence Engineering, Jeonju University, Jeonju 55069, Korea; Department of Science Education, Jeonju University, Jeonju 55069, Korea; orcid.org/0000-0002-5242-9189; Email: arlim@jj.ac.kr, aeranlim@hanmail.net

**Author**

Sun Ha Kim – Korea Basic Science Institute, Seoul Western Center, Seoul 03759, Korea; Department of Chemistry, Kyungpook National University, Daegu 41566, Korea

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Notes
The authors declare no competing financial interest.

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