Advances and Physicochemical Property Investigations by Methylene Chain Length of Perovskite-type Layer Crystals [NH3(CH2)nNH3]CdCl4 (n=2, 3, and 4)

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Research Article

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Advances and physicochemical property investigations by methylene chain length of perovskite-type layer crystals $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CdCl}_4$ ($n=2$, 3, and 4)

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Hybrid perovskites have potential applications in several electrochemical devices such as supercapacitors, batteries, and fuel cells. However, despite various potential applications, there have been limited studies on compounds containing Cd. Therefore, in this study, the structures and phase transition temperatures $T_c$ of organic–inorganic perovskite $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CdCl}_4$ ($n=2$, 3, and 4) were confirmed by X-ray diffraction and DSC experiments. The thermal stabilities obtained by TGA and DTA results were considered as a function of the length $n$ of the CH$_2$ groups in the cation. In addition, structural characteristics and molecular dynamics of the cation and anion near $T_c$ were studied by $^1$H MAS NMR, $^{13}$C MAS NMR, $^{14}$N static NMR, and $^{113}$Cd MAS NMR experiments. From these results, regardless of whether $n$ is even or odd, the differences in thermal and physical properties were minimal. Rather, the difference in molecular motion relative to the length of the cation was seen only at higher temperatures. These results provide insights into the thermal stability and molecular dynamics of $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CdCl}_4$ crystals and are expected to facilitate potential applications.

The organic–inorganic hybrid perovskite crystals $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{MX}_4$ ($n=2$, 3, 4,…; $M=\text{Mn, Fe, Co, Cu, Zn, Cd,}...$; $X=\text{Cl and Br}$) 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.$^{1-10}$ 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 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 ($\text{MX}_4$)$^{2-}$ is sandwiched between the layers of an organic cation.$^{11-15}$ Furthermore, several studies focusing on their molecular structure have reported an even-odd effect as the number of carbon atoms in the diammonium chain changes, which affects the structural properties of these materials.$^{16}$ 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 NH$_3$ groups on both ends. The $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]$ organic chains extend along the longest c-axis. Perovskite, $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CdCl}_4$ ($M=\text{Cd, X=Cl}$), consists of puckered layers of CdCl$_4$ 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.$^{17}$ These compounds have attracted considerable interest owing to the multiplicity of their crystal structures, which govern their thermodynamic properties and structural
dynamics. These hybrid perovskites have potential applications in several electrochemical devices such as supercapacitors, batteries, and fuel cells.\textsuperscript{18-23}

The synthesis and characterization of [NH$_3$(CH$_2$)$_2$NH$_3$]CdCl$_4$ with n=2 were first discussed by Batcaglia et al.\textsuperscript{24} Subsequently, the X-ray results for this crystal structure at 298 K were reported by Lamhamdi et al.\textsuperscript{25} The phase transition at 375 K for the [NH$_3$(CH$_2$)$_3$NH$_3$]CdCl$_4$ crystal with n=3 is reversible and continuous, according to previous dielectric and optical studies.\textsuperscript{26, 27} In addition, the structural, thermal, and vibrational properties as well as molecular motions have been characterized by Staskiewicz et al.\textsuperscript{6} Recently, the physicochemical properties of this crystal were reported by our group.\textsuperscript{28} In the case of n=4, the thermodynamic and crystallographic characters of the phase transitions for NH$_3$(CH$_2$)$_4$NH$_3$CdCl$_4$ were studied, and the crystal structure in each phase was discussed from X-ray diffraction measurements.\textsuperscript{16, 29}

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 [NH$_3$(CH$_2$)$_n$NH$_3$]CdCl$_4$ crystals have not been discussed in detail.

This study aims to investigate the thermodynamic properties and molecular dynamics of [NH$_3$(CH$_2$)$_n$NH$_3$]CdCl$_4$ as a function of the length n of CH$_2$ 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 $T_1$ are probed using $^1$H magic angle spinning nuclear magnetic resonance (MAS NMR), $^{13}$C MAS NMR, and static $^{14}$N NMR as a function of temperature to elucidate the characteristics of the [NH$_3$(CH$_2$)$_n$NH$_3$] cation. Furthermore, the chemical shifts for $^{113}$Cd MAS NMR are recorded as a function of the temperature in order to understand the geometry of octahedral CdCl$_6$. The results provide insights into the thermodynamic properties and structural dynamics of [NH$_3$(CH$_2$)$_n$NH$_3$]CdCl$_4$ crystals based on the length and even–odd effect of the organic chain and are expected to facilitate potential applications in the future.

**Crystal structures**

1,2-Ethylenediammonium tetrachlorocadmate, [NH$_3$(CH$_2$)$_2$NH$_3$]CdCl$_4$ (n=2), crystallizes in the monoclinic form with space group $P2_1/a$, and this crystal does not exhibit any structural phase transitions. The unit cell parameters are $a=7.292$ Å, $b=7.344$ Å, $c=8.609$ Å, $\beta=92.74^\circ$, and $Z=2$.\textsuperscript{24} [NH$_3$(CH$_2$)$_2$NH$_3$] cations are situated between the layers and are linked to the layers via an 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.\textsuperscript{24} 1,3-Propylenediammonium tetrachlorocadmate, [NH$_3$(CH$_2$)$_3$NH$_3$]CdCl$_4$ (n=3), is known to undergo a structural phase transition at $T_c=375$ K.\textsuperscript{6, 24} At room temperature, the crystals are orthorhombic with the space group $Pmna$. The unit cell has the following parameters: $a=7.373$ Å, $b=7.523$ Å.
Å, c=19.111 Å, and Z=4. When the temperature is above T_C, the crystal is still orthorhombic; however, the space group becomes Imma, and the lattice constants become a=7.38577 Å, b=7.56974 Å, c=18.7300 Å, and Z=4. Figure 1 shows the structure of the [NH_3(CH_2)_3NH_3]CdCl_4 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 CdCl_6 octahedra. 1,4-Butanediyldiammonium tetrachlorocadmate, [NH_3(CH_2)_3NH_3]CdCl_4 (n=4), undergoes two structural phase transitions near 338 K (=T_C) and 367 K (=T_C). 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 P2_1/a and Z = 2. The unit cell parameters in phase III are a=7.657 Å, b=7.585 Å, c=9.541 Å, and β=101.56°. Further, the lattice parameters in phase II 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 Pnam and Z=2. The unit cell parameters are a=7.377 Å, b=7.538 Å, and c=10.600 Å. Structural information for the three compounds are summarized in Table 1.

### Table 1. The structures, phase transition temperatures (T_C), lattice constants, and Cd-Cl distances of [NH_3(CH_2)_3NH_3]CdCl_4 (n=2, 3, and 4) crystals.

| Structure          | T_C (K) | Lattice constants (Å) | Cd-Cl (average Å) |
|--------------------|---------|-----------------------|-------------------|
| n=2                |         |                       |                   |
| Monoclinic         | a=7.292, b=7.344, c=8.609, β=92.74° | 2.616 |
| Orthorhombic       | 375 (T_C) | a=7.373, b=7.523, c=19.111 | 2.6288 |
| Orthorhombic       | a=7.38577, b=7.56974, c=18.7300 | 2.6073 |
| n=3                |         |                       |                   |
| Monoclinic         | 338 (T_C) | a=7.657, b=7.585, c=9.541, β=101.56° | 2.646 |
| Orthorhombic       | 367 (T_C) | a=7.48, b=7.53, c=10.18, β=97.5° | 2.6198 |

### Experimental

An aqueous solution containing NH_3(CH_2)_3NH_2·2HCl and CdCl_2 was slowly evaporated at 300 K to produce single crystals of [NH_3(CH_2)_3NH_3]CdCl_4 (n=2, 3, and 4). The structures of the [NH_3(CH_2)_3NH_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 an 1 μS micro-focus 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 °C/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)_3NH_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 ^1H MAS NMR and ^13C 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. The T_{1ρ} values were obtained using a π/2–τ pulse followed by a spin-lock pulse of duration τ, and the width of the π/2 pulse for ^1H and ^13C 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–τ–4 μs–τ; τ=5 μs for $n=2$, τ=8 μs for $n=3$ and 4. The $^{113}$Cd MAS NMR experiments were performed using a π/2−τ pulse followed by a spin-lock pulse of duration τ, and the width of the π/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.

**Experimental results**

**Crystal structures**

The X-ray powder diffraction patterns of the [NH$_3$]($\text{CH}_2$)$_n$NH$_3$]CdCl$_4$ crystals ($n=2$, 3, and 4) at 298 K are shown in Fig. 2. The lattice constants for the [NH$_3$]($\text{CH}_2$)$_2$NH$_3$]CdCl$_4$ crystal with $n=2$ are determined to be $a=7.297 \pm 0.002$ Å, $b=7.336 \pm 0.002$ Å, $c=8.623 \pm 0.002$ Å, and $\beta=92.810 \pm 0.011^\circ$, and those for [NH$_3$]($\text{CH}_2$)$_3$NH$_3$]CdCl$_4$ with $n=3$ are determined to be $a=7.351 \pm 0.006$ Å, $b=7.486 \pm 0.005$ Å, and $c=19.031 \pm 0.014$ Å. In the case of [NH$_3$]($\text{CH}_2$)$_4$NH$_3$]CdCl$_4$ with $n=4$, the lattice parameters are determined to be $a=7.663 \pm 0.003$ Å, $b=7.593 \pm 0.002$ Å, $c=9.514 \pm 0.002$ Å, and $\beta=101.616 \pm 0.016^\circ$. These results are consistent with those reported previously.6, 16, 24-26

**Phase transition temperatures and thermal properties**

The DSC curves of [NH$_3$]($\text{CH}_2$)$_n$NH$_3$]CdCl$_4$ crystals at a heating rate of 10 K/min under a nitrogen atmosphere are shown in Fig. 3. No peak was observed for the case of $n=2$, whereas only one endothermic peak for
Figure 3. Differential scanning calorimetry (DSC) curves of \(\text{[NH}_3\text{(CH}_2\text{)}_n\text{NH}_3\text{]}\text{CdCl}_4\) \((n=2, 3, \text{and 4}).\) 

\(n=3\) was observed at 374 K \((=T_C)\). Finally, for 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.\(^6, 16, 27\)

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 Fig. 4 show that the crystals with \(n = 2, 3, \text{and 4}\) are almost stable up to approximately 493, 539, and 536 K, respectively; according to the number \(n\) of CH\(_2\) groups in the carbon chain, the molecular weight loss near 493, 539, and 536 K marks the onset of partial thermal decomposition (at temperature \(T_d\)). \(\text{[NH}_3\text{(CH}_2\text{)}_n\text{NH}_3\text{]}\text{CdCl}_4\) 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 K and 804 K was due to the decomposition of HCl and 2HCl, respectively (see Fig. 4(a)). The small endothermic peak at 374 K on the DTA curve for \(\text{[NH}_3\text{(CH}_2\text{)}_3\text{NH}_3\text{]}\text{CdCl}_4\) is assigned to the phase transition detected in the DSC experiment. Additionally,
weight losses of 11% and 22% occurred at temperatures of 613 K and 623 K, respectively (see Fig. 4(b)).

Finally, in the case of \([\text{NH}_3(\text{CH}_2)_4\text{NH}_3]\)CdCl$_4$ crystals with $n=4$, the two small endothermic peaks at 341 K and 366 K on the DTA curve are attributed to the phase transition seen in the DSC result. At temperatures of 612 K and 623 K, 11% and 21% of its weight was respectively lost (see Fig. 4(c)). 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 (Fig. 5). For 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. For 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.
[NH₃(CH₂)₃NH₃]CdCl₄ with \( n = 3 \); and (a) 295 K, (b) 353 K, (c) 573 K, (d) 659 K, (e) 670 K for [NH₃(CH₂)₄NH₃]CdCl₄ with \( n = 4 \).

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 Fig. 6. At 300 K, the ¹H chemical shift for NH₃ and CH₃ 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, respectively. It can be seen that the ¹H chemical shifts for NH₃ when \( n = 2 \), 3, and 4 are similar, while the ¹H chemical shifts for CH₃ are very different. In the case where \( n = 3 \), no change was observed near \( T_C \). In particular, in the case where \( n = 4 \), the ¹H chemical shift for CH₃ shows discontinuity near \( T_{C2} \) and continuity near \( T_{C1} \). The chemical shifts for NH₃ of all three crystals are nearly independent of temperature, which means that the surrounding environment of the ¹H in NH₃ does not significantly change with temperature. However, in the case where \( n = 4 \), the surrounding environments of ¹H in CH₃ do significantly change with temperature.

![Figure 6. ¹H NMR chemical shifts for NH₃ and CH₃ in [NH₃(CH₂)ₙNH₃]CdCl₄ (\( n = 2 \), 3, and 4) as a function of temperature.](image)

The ¹H MAS NMR spectra were measured with several delay times at each given temperature, and the plot of spectral intensities vs. delay times were found to follow a single exponential function. The decay rate of the spin-locked proton magnetization is characterized by the spin-lattice relaxation time \( T_{1p} \) as

\[
P(\tau) = P(0)\exp(-\tau/T_{1p}),
\]

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 NH₃ and CH₃ at several temperatures. The ¹H \( T_{1p} \) results are shown in Fig. 7 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 1 to 700 ms, and then rapidly reduces at temperatures above 350 K. At 350 K, ¹H \( T_{1p} \) has maximum values when \( n = 2 \), and the values for NH₃ and CH₃ are 352 and 388 ms, respectively. The values when \( n = 3 \) are 496 and 683 ms. In the case where \( n = 2 \) and 3, as the temperature increases, the \( T_{1p} \) values increase rapidly from 1 to 700 ms, and then rapidly reduces at temperatures above 350 K. At 350 K, ¹H \( T_{1p} \) has maximum values when \( n = 2 \), and the values for NH₃ and CH₃ are 352 and 388 ms, respectively. The values 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 temperature 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 $T_C$. The discontinuous changes of $^1$H chemical shifts and $^1$H $T_1\rho$ near $T_C$ are thought to be due to the rapid changes in the lattice constants $c$ and $\beta$.

![Figure 7](image)

**Figure 7.** $^1$H MAS NMR spin-lattice relaxation times $T_1\rho$ for $\text{CH}_2$ and $\text{NH}_3$ in $[\text{NH}_3\text{(CH}_2)_n\text{NH}_3]\text{CdCl}_4 (n=2, 3, \text{ and } 4)$ as a function of inverse temperature.

$^{13}$C MAS NMR

The $^{13}$C MAS NMR chemical shifts for $\text{CH}_2$ in $[\text{NH}_3\text{(CH}_2)_n\text{NH}_3]\text{CdCl}_4$ 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 $\text{CH}_2$-1 in the $[\text{NH}_3\text{(CH}_2)_n\text{NH}_3]$ cation is far from $\text{NH}_3$, and that $\text{CH}_2$-2 is located near $\text{NH}_3$. The results of $^{13}$C 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 $^{13}$C resonance line was obtained for $\text{CH}_2$-2. In the case where $n=3$ and 4, two $^{13}$C resonance lines were obtained for $\text{CH}_2$-1 and $\text{CH}_2$-2, respectively. At 300 K, the $^{13}$C 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 $\text{CH}_2$-1 and $\text{CH}_2$-2, respectively. The $^{13}$C chemical shifts for $n=4$ were observed at 25.30 and 42.85 ppm, respectively. Here, the chemical shifts for $\text{CH}_2$-1 are similar for these crystals, but those for $\text{CH}_2$-2 are different between $n=2, 3, \text{ and } 4$.

The full width at half maximum (FWHM) for $^{13}$C NMR at 300 K are relatively narrow, ranging from 1.2 to 1.6 ppm.

Meanwhile, the chemical shifts for the in-situ $^{13}$C MAS NMR spectra for the three compounds are shown in Fig. 8 with increasing temperature. In the case where $n=2$ (Fig. 8(a)), the $^{13}$C chemical shifts for $\text{CH}_2$-2 increases slightly as the temperature increases. Some chemical shift changes around 290 K can also be seen. In case where $n=3$ (Fig. 8(b)), the slopes of the chemical shifts marked by red dotted lines are temperature dependent, with more variation for $\text{CH}_2$-2 than for $\text{CH}_2$-1. In addition, there was no
Figure 8(a). In-situ $^{13}$C MAS NMR chemical shifts of $[\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\text{CdCl}_4$, as a function of temperature.

Figure 8(b). In-situ $^{13}$C MAS NMR chemical shifts of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdCl}_4$, as a function of temperature.
change in chemical shifts near Tc. However, in the case where n=4 (Fig. 8(c)), the chemical shifts show discontinuity near Tc2, whereas they show continuity near Tc1. It can be seen that the chemical shifts of CH2-2 near Tc2 changes 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 T1 values for CH2-1 and CH2-2 were obtained for the three compounds and plotted as a function of 1000/T, as shown in Fig. 9. In the case where n=2, the 13C T1 value first decreased slightly with increasing temperature and then decreased rapidly at higher temperatures. In the case where n=3, it decreased slightly with increase in temperature, then increased again, and finally decreased at temperatures above Tc. Meanwhile, the minimum T1 values (34.74 and 28.40 ms for CH2-1 and CH2-2, respectively) occur at 280 K. In the case where n=4, T1 decreases slightly as the temperature increases, and then increases rapidly near Tc2. 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 T1 is due to the molecular motion of CH2-1 and CH2-2 in the [NH3(CH2)nNH3]CdCl4 cations in the case where n=3 and 4, respectively. These T1 values could be described by the correlation time τc for the molecular motion, and the T1 value for the molecular motion is given by

\[ T_1^{-1} = C \left( \gamma^2 / \hbar^2 \right) \left( f_a + f_b + 3f_c + 6f_d + 6f_e \right) \]

where \( f_a = \tau_c / \left( 1 + \omega_1^2 \tau_c^2 \right) \), \( f_b = \tau_c / \left( 1 + (\omega_1 - \omega_2)^2 \tau_c^2 \right) \), \( f_c = \tau_c / \left( 1 + (\omega_1 + \omega_2)^2 \tau_c^2 \right) \), and \( f_d = \tau_c / \left( 1 + \omega_3^2 \tau_c^2 \right) \). Here, C is a coefficient, \( \gamma^2 / \hbar^2 \) are the gyromagnetic ratios for H and 13C, respectively, \( \hbar \) is the reduced Planck constant, \( r \) is the internuclear distance, \( \omega_1 \) and \( \omega_2 \) are the Larmor frequencies of H and 13C, respectively, and \( \omega_3 \) is the frequency of the spin-lock field. Here, the 13C T1 values were measured using the spin-locking pulse sequence with a locking pulse of \( \omega_3=75.76 \) kHz for n=3 and \( \omega_3=70.42 \) kHz for n=4. When \( \omega_3 \tau_c = 1 \), T1 has the minimum value. Therefore, a relationship between T1 and \( \omega_3 \) was applied to obtain the coefficient C in Eq. (2). Using this coefficient, \( \tau_c \) was calculated as a function of temperature. According to the 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

![Figure 8(c). In-situ 13C MAS NMR chemical shifts of [NH3(CH2)nNH3]CdCl4 as a function of temperature.](image)

![Figure 9. 13C MAS NMR spin-lattice relaxation times T1 for CH2-1 and CH2-2 in [NH3(CH2)nNH3]CdCl4 (n=2, 3, and 4) as a function of inverse temperature.](image)
Figure 10. Arrhenius plots of the natural logarithm of the correlation times, $\tau_C$, for $^{13}$C in $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CdCl}_4$ and $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]\text{CdCl}_4$ as a function of inverse temperature.

$$\tau_C = \tau_0 \exp\left(-\frac{E_a}{k_B T}\right)$$  \hspace{1cm} (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. $1000/T$ provided the $E_a$ values for $n=1$ and $n=2$, as shown in Fig. 10; in the case where $n=3$, the $E_a$ values of CH$_2$ and CH$_2$ below $T_C$ were 26.96 ± 8.85 and 39.94 ± 10.45 kJ/mol, respectively. When $n=4$, the $E_a$ values of CH$_2$ and CH$_2$ below $T_C$ were 28.18 ± 2.05 and 23.18 ± 2.51 kJ/mol, respectively. Additionally, above $T_C$ when $n=3$, the $E_a$ values for CH$_2$ and CH$_2$ were 10.18 ± 2.68 and 8.45 ± 2.04 kJ/mol, respectively. Unlike that in the cases of $n=2$ and 3, the trend of $^{13}$C T$_{1p}$ at high temperatures is very different for $n=4$. Above $T_C$, they were 13.42 ± 2.01 and 14.35 ± 1.41 kJ/mol, respectively. When $n=3$ and 4, the $E_a$ values at low temperatures are greater than that at high temperatures, whereas when $n=2$, their results are opposite (1.70 ± 0.24 kJ/mol below 330 K and 35.19 ± 4.32 kJ/mol above 330 K).

Static $^{14}$N NMR
Static $^{14}$N NMR investigations of $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CdCl}_4$ single crystals were conducted over the temperature range of 180–430 K. The $^{14}$N spectra were obtained using the solid-state echo method by static NMR. Two $^{14}$N NMR signals were expected from the quadrupole interactions due to the spin number $I=1$. The $^{14}$N NMR spectra for $n=2$, 3, and 4 differed with increasing temperature, as shown in Fig. 11. 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 six resonance lines due to the three pairs caused a large change near $T_C$. The symbols with the same color below $T_C$ indicate the same pairs for $^{14}$N. Near 374 K ($=T_C$), the number of resonance lines and chemical shifts of the NMR spectrum showed abrupt changes; three pairs turned into just two pairs. The changes in the $^{14}$N chemical shift as a function of temperature were attributed to the variations in the structural geometry. In addition, the chemical shifts of the $^{14}$N signals below $T_C$ changed almost continuously, and the chemical shifts for $^{14}$N above $T_C$ remained constant with temperature. The $^{14}$N NMR spectrum exhibits a reduction in the NMR lines from three to two pairs of lines at the phase transition $T_C$. Finally, when $n=4$, the four resonance lines due to two inequivalent N sites showed no change in temperature below $T_C$; however, it was difficult to detect because the line width suddenly increased above $T_C$. In the cases of $n=3$ and 4, the different N spectra were explained as follows. None of the previously reported X-ray results include different N sites; therefore, two or three 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.
Figure 11. Static $^{14}$N NMR chemical shifts of $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CdCl}_4$ ($n=2$, 3, and 4) as a function of temperature.

$^{113}$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 $I=1/2$. $^{113}$Cd NMR spectroscopy has been used to examine the structure and dynamics of various inorganic and organic materials. The $^{113}$Cd MAS NMR spectra for the three crystals were obtained as a function of temperature, as shown in Fig. 12. The chemical shifts are related to the local field at the position of the resonating nucleus in the crystals. The $^{113}$Cd chemical shifts for the three crystals shift slightly in the negative direction as the temperature increases. However, in the case where $n=4$, it was discontinuous near $T_{C_2}$. 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. In addition, the difference in Cd chemical shifts for the three materials seems to be due to the difference in the Cd–Cl distance as shown in Table 1. In other words, it is consistent that the Cd–Cl distance increases as the $n$ value increases. Similarly, the change in the chemical shift near $T_{C_2}$ is attributed to the shortening of the Cd–Cl distance from the average 2.646 Å to 2.6198 Å.

Figure 12. $^{113}$Cd MAS NMR chemical shifts of $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CdCl}_4$ ($n=2$, 3, and 4) as a function of 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 the $T_{1p}$ values for $^1H$, $^{13}C$, and $^{113}$Cd at 300 K are listed in Table 2. $^{113}$Cd $T_{1p}$ was very long compared to $^1H T_{1p}$ and $^{13}C T_{1p}$. The long $^{113}$Cd $T_{1p}$ values with $n$=2 at 300 K were considered to be more rigid than the others ($n$=3 and 4) because the Cd-Cl length is short as shown in Table 1; a longer $T_{1p}$ indicates that the transfer of energy from the nuclear spin system to the surrounding environment is not very easy.

Table 2. The spin-lattice relaxation times, $T_{1p}$ values for $^1H$, $^{13}C$, and $^{113}$Cd of [NH$_3$(CH$_2$)$_n$NH$_3$]CdCl$_4$ ($n$=2, 3, and 4) at 300 K.

| $n$  | $^1H T_{1p}$ (ms) | $^{13}C T_{1p}$ (ms) | $^{113}$Cd $T_{1p}$ (ms) |
|------|------------------|----------------------|--------------------------|
| 2    | 204.20 (NH$_3$)  | 27.67 (CH$_2$-2)    | 2058                     |
|      | 211.92 (CH$_3$)  |                      |                          |
| 3    | 411.53 (NH$_3$)  | 37.13 (CH$_2$-1)    | 1512                     |
|      | 551.12 (CH$_3$)  | 29.13 (CH$_2$-2)    |                          |
| 4    | 334.98 (NH$_3$)  | 14.06 (CH$_2$-1)    | 1101                     |
|      | 357.83 (CH$_3$)  | 13.90 (CH$_2$-2)    |                          |

Discussion

The structures and phase transition temperatures for [NH$_3$(CH$_2$)$_n$NH$_3$]CdCl$_4$ ($n$=2, 3, and 4) crystals were confirmed by X-ray diffraction and DSC experiments. The thermal stability improved as the length of the carbon chains in the [NH$_3$(CH$_2$)$_n$NH$_3$] cations increased. In addition, based on the information obtained from NMR studies on methylene chain length, the structural dynamics of the [NH$_3$(CH$_2$)$_n$NH$_3$] cation and CdCl$_4$ anion in [NH$_3$(CH$_2$)$_n$NH$_3$]CdCl$_4$ crystals were analyzed. $^1H$, $^{13}C$, $^{14}N$, and $^{113}$Cd NMR were considered by determining the changes in the chemical shifts accompanying a change in the crystallographic environment. When $n$=2, the $^1H$, $^{13}C$, and $^{113}$Cd chemical shifts hardly change with temperature, indicating that there is no phase transition phenomenon. When $n$=3, $^1H$, $^{13}C$, and $^{113}$Cd chemical shifts exhibit a continuous change near $T_c$, indicating that the crystal structure is orthorhombic at both low and high temperatures, and the lattice constant hardly changes. Finally, when $n$=4, the $^1H$, $^{13}C$, and $^{113}$Cd chemical shifts are continuous near $T_{c1}$, but discontinuous around $T_{c2}$. This is attributed to a large change in the lattice parameters $c$ and $\delta$ near $T_{c2}$.

The molecular dynamics near the phase transition temperatures were analyzed in terms of the $T_{1p}$ values for $^1H$ and $^{13}C$. $^1H$ and $^{13}C T_{1p}$ are almost continuous when $n$=2 and 3, but when $n$=4, they show a discontinuity near $T_{c2}$, as with the chemical shifts. Overall, $n$=2 and 3 showed a rapid decrease in $T_{1p}$ of $^1H$ and $^{13}C$ at high temperatures, whereas $n$=4 showed an increase at high temperatures. The short $^{13}C$ $T_{1p}$ values at low temperatures in the case of $n$=4 were considered to be more flexible than the others because the N–C–C–C–C–N lengths are long.

Conclusion

The crystal structures were found to be monoclinic when $n$ was even and orthorhombic when $n$ was odd, but there were little differences in thermal and physical properties. The difference in molecular motion according to the length of the cation was observed only at high temperatures. In the [NH$_3$(CH$_2$)$_n$NH$_3$] cations, $^{13}C T_{1p}$ with $n$=4 at low temperature has shorter values than those with $n$=2 and 3. It was found that as the carbon length increased, it became more flexible. Overall, $^{113}$Cd $T_{1p}$ at 300 K is very long compared to the $^1H$ and $^{13}C$ $T_{1p}$ values. This is thought to be related to the Cd-Cl bond length. These results provide insight into the thermal stability and molecular dynamics of [NH$_3$(CH$_2$)$_n$NH$_3$]CdCl$_4$ ($n$=2, 3, and 4) crystals as a function of the length of CH$_2$ groups in the carbon chain and are expected to facilitate future research as well as potential applications in supercapacitors, batteries, and fuel cells.

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**Author contributions**

A.R.L designed the project, performed NMR experiments, and wrote the manuscript.

**Competing of interests**

The authors declare no competing interests.

**Additional information**

Supplementary information is available for this paper

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Figure 1

The structure of $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdCl}_4$ crystal at room temperature.
Figure 2

X-ray diffraction patterns of [NH3(CH2)nNH3]CdCl4 (n=2, 3, and 4) at 298 K.
Figure 3

Differential scanning calorimetry (DSC) curves of $\text{[NH}_3\text{(CH}_2\text{)}_n\text{NH}_3\text{]}\text{CdCl}_4$ ($n=2$, 3, and 4).
Figure 4

(a). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) results of [NH₃(CH₂)₂NH₃]CdCl₄. (b). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) results of [NH₃(CH₂)₃NH₃]CdCl₄. (c). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) results of [NH₃(CH₂)₄NH₃]CdCl₄.
Figure 5

Changes in crystal by optical polarizing microscopy at (a) 300 K, (b) 547 K, (c) 573 K, (d) 622 K, and (e) 633 K for \([\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\text{CdCl}_4\) with \(n=2\); (a) 296 K, (b) 563 K, (c) 613 K, (d) 653 K, (e) 673 K for \([\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdCl}_4\) with \(n=3\); and (a) 295 K, (b) 353 K, (c) 573 K, (d) 659 K, (e) 670 K for \([\text{NH}_3(\text{CH}_2)_4\text{NH}_3]\text{CdCl}_4\) with \(n=4\).
Figure 6

1H NMR chemical shifts for NH3 and CH2 in [NH3(CH2)nNH3]CdCl4 (n=2, 3, and 4) as a function of temperature.
Figure 7

$^1H$ MAS NMR spin-lattice relaxation times $T_{1p}$ for CH$_2$ and NH$_3$ in [NH$_3$(CH$_2$)$_n$NH$_3$]CdCl$_4$ ($n=2$, 3, and 4) as a function of inverse temperature.
Figure 8

(a). In-situ 13C MAS NMR chemical shifts of [NH3(CH2)2NH3]CdCl4, as a function of temperature. b). In-situ 13C MAS NMR chemical shifts of [NH3(CH2)3NH3]CdCl4, as a function of temperature. (c). In-situ 13C MAS NMR chemical shifts of [NH3(CH2)4NH3]CdCl4, as a function of temperature.
Figure 9

$^{13}$C MAS NMR spin-lattice relaxation times $T_{1p}$ for CH$_2$-1 and CH$_2$-2 in [NH$_3$(CH$_2$)$_n$NH$_3$]CdCl$_4$ ($n=2$, 3, and 4) as a function of inverse temperature.
Figure 10

Arrhenius plots of the natural logarithm of the correlation times, $\tau_C$, for $^{13}$C in $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CdCl}_4$ and $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]\text{CdCl}_4$ as a function of inverse temperature.
Figure 11

Static $^{14}$N NMR chemical shifts of [NH3(CH2)nNH3]CdCl4 (n=2, 3, and 4) as a function of temperature.
Figure 12

$^{113}\text{Cd}$ MAS NMR chemical shifts of $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CdCl}_4$ ($n=2$, 3, and 4) as a function of temperature.

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