Thermodynamic Properties, Structural Characteristics, and Cation Dynamics of Perovskite-Type Layer Crystal \([\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\text{ZnCl}_4\)

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1. INTRODUCTION

Recently, organic–inorganic compounds of two-dimensional (2D) hybrid perovskites have been extensively investigated. Compounds with chemical formulas of \([\text{C}_n\text{H}_{2n+1}\text{NH}_3]\text{BX}_4\) \((n = 1, 2, 3, \ldots); \text{B} = \text{Mn, Co, Cu, Zn, Cd, \ldots}; \text{X} = \text{Cl, Br})\) and \([\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{BX}_4\) \((n = 2, 3, \ldots)\) are examples of organic–inorganic hybrid perovskite-type layer compounds, and they have been attracting considerable attention over recent years. Several studies on the monoammonium series \([\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\text{ZnCl}_4\) have been conducted by researchers worldwide, and the diammonium series \([\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\text{ZnCl}_4\) has an orthorhombic structure with space group \(P2_1_2_1_2_1\) at 298 K. The unit cell dimensions are \(a = 8.832\ \text{Å}, b = 9.811\ \text{Å}, c = 11.089\ \text{Å}\), and \(Z = 4\). The \([\text{ZnCl}_4]^{2-}\) anion forms an isolated tetrahedron, and the tetrahedron is interconnected via \(\text{N}−\text{H⋯Cl}\) hydrogen bonds to the \([\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\) cation. Each \(\text{NH}_3\) group is linked by \(\text{N}−\text{H⋯Cl}\) hydrogen bonds. The \(\text{H}\) atoms were located geometrically with \(\text{N}−\text{H} = 0.86\ \text{Å}\) and \(\text{C}−\text{H} = 0.97\ \text{Å}\). The compounds with \(n = 2\) do not exhibit any structural phase transition up to the decomposition temperature.

In this study, we investigated the structural dynamic features of the \([\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\text{ZnCl}_4\) crystal as a function of temperature through magic angle spinning (MAS) \(^1\text{H}\) nuclear magnetic resonance (NMR), MAS \(^13\text{C}\) NMR, and static \(^{14}\text{N}\) NMR. From the chemical shifts, changes in the structural environments of \(^{13}\text{C}\) and \(^{14}\text{N}\) were evident. The \(^1\text{H}\) spin–lattice relaxation time \((T_1p)\) values at high temperatures undergo molecular motion according to the Bloembergen–Purcell–Pound theory, and the \(^{13}\text{C}\) \(T_1p\) value also varied abruptly with increasing temperature. Although the phase-transition temperature was not detected from the differential scanning calorimetry result, the chemical shifts and \(T_1p\) results showed discontinuities around 300 K. Herein, the activation energies of molecular motion for \(^1\text{H}\) and \(^{13}\text{C}\) obtained from the di

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The physical and chemical properties of the organic–inorganic hybrid perovskite \([\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\text{ZnCl}_4\) type are of significant scientific interest, and they depend on the hybrid perovskite characteristics, such as those of organic cations, inorganic anion geometry of the metal halide ions, \((\text{BX}_6)^{2-}\) or \((\text{BX}_4)^{2-}\), and the reaction stoichiometric ratio. In the cases of \(\text{B} = \text{Mn, Cu, and Cd}\), the crystal structures consist of alternate octahedron \((\text{BX}_6)^{2-}\) and organic chains, whereas for \(\text{B} = \text{Co and Zn}\), isolated tetrahedral structures are formed, where an inorganic layer of \((\text{BX}_4)^{2-}\) is sandwiched between the organic cation layers. The ammonium ions bonded at both ends of the organic chain combine with halide ions in the inorganic layer to stabilize the layered structure by forming \(\text{N}−\text{H⋯Cl}\) hydrogen bonds. This property enables these materials to be used as proton conductors and renders them suitable for potential application in UV detection. These compounds are of notable scientific interest owing to the multiplicity of their crystal structures, which is correlated to the structural dynamics of the cations and anions.

\([\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\text{ZnCl}_4\) \((1,2\text{-ethylenediammonium tetrachlorozincate(II)})\) with \(n = 2\), \(\text{B} = \text{Zn}\), and \(\text{X} = \text{Cl}\) in \([\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\text{ZnCl}_4\) has an orthorhombic structure with space group \(P2_1_2_1_2_1\) at 298 K. The unit cell dimensions are \(a = 8.832\ \text{Å}, b = 9.811\ \text{Å}, c = 11.089\ \text{Å}\), and \(Z = 4\). The \([\text{ZnCl}_4]^{2-}\) anion forms an isolated tetrahedron, and the tetrahedron is interconnected via \(\text{N}−\text{H⋯Cl}\) hydrogen bonds to the \([\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\) cation. Each \(\text{NH}_3\) group is linked by \(\text{N}−\text{H⋯Cl}\) hydrogen bonds. The \(\text{H}\) atoms were located geometrically with \(\text{N}−\text{H} = 0.86\ \text{Å}\) and \(\text{C}−\text{H} = 0.97\ \text{Å}\). The compounds with \(n = 2\) do not exhibit any structural phase transition up to the decomposition temperature. Thus far, the structure of the \([\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\text{ZnCl}_4\) crystal has only been investigated through X-ray diffraction. In addition, although this
compound containing Zn has applications in numerous areas, no study has been reported on it to date. A detailed study on the thermal properties and structural dynamics of the \([\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\text{ZnCl}_4\) crystal has also not been reported.

In this study, the phase transitions and thermodynamic properties of the \([\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\text{ZnCl}_4\) crystal are investigated through differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). \(\text{H}, \text{C},\) and \(\text{N}\) nuclear magnetic resonance (NMR) spectra are used to detect changes in the chemical shifts accompanying changes in the crystallographic environments. The chemical shift by NMR depends on the local field at the site of the resonating nucleus in the crystals. The spin−lattice relaxation times (\(T_1\rho\)) are discussed in terms of the role of the \([\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\) cation on the molecular dynamics as well as by performing magic angle spinning (MAS) \(\text{H}\) NMR and MAS \(\text{C}\) NMR. Based on these results, the thermodynamic properties, crystallographic environments, and structural molecular dynamics of \([\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\text{ZnCl}_4\) crystals are discussed for \([\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\) cations. In addition, we compare the physical properties of diammonium-type \([\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\) compounds obtained in this study and monoammonium-type \((\text{CH}_3\text{NH}_3)_2\text{ZnCl}_4\) with \(n = 2\) previously reported. The results aid in gaining an understanding of the thermodynamic properties and the structural dynamics of \([\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\text{ZnCl}_4\) crystals, which is expected to subsequently facilitate their potential applications.

2. RESULTS AND DISCUSSION

2.1. Thermodynamic Properties. The DSC analysis of the \([\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\) \(\text{ZnCl}_4\) crystal with a heating rate of 10 °C/min under a nitrogen atmosphere exhibits an endothermic peak at 536 K, as shown in Figure 1. To verify whether the endothermic peak at 536 K corresponds to the structural phase transition or melting, TGA was performed with the same heating rate. The TGA result, also displayed in Figure 1, shows the crystal to be almost stable up to approximately 525 K. Above 525 K, the compound \([\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\) \(\text{ZnCl}_4\) (\(M_w = 269.31\) mg) experiences a molecular weight loss with increasing temperature. From the total molecular weights, the amounts of residue were obtained using eqs 1 and 2

\[
\text{Residue:} \\
\left[\text{NH}_3(\text{CH}_2)_2\text{NH}_3\right]\text{ZnCl}_4 \rightarrow \left[\text{NH}_3(\text{CH}_2)_2\text{NH}_3\right]2\text{HCl} + \text{ZnCl}_4 \\
\left[\text{NH}_3(\text{CH}_2)_2\text{NH}_3\right]2\text{HCl} + \text{ZnCl}_4 \rightarrow \left[\text{NH}_3(\text{CH}_2)_2\text{NH}_3\right]2\text{HCl} + \text{ZnCl}_4 (s) + \text{HCl (g)}
\]

\[
\text{Residue:} \\
\left[\text{NH}_3(\text{CH}_2)_2\text{NH}_3\right]2\text{HCl} + \text{ZnCl}_4 \rightarrow \left[\text{NH}_3(\text{CH}_2)_2\text{NH}_3\right]2\text{HCl} + \text{ZnCl}_4 (s) + 2\text{HCl (g)}
\]

Near 536 K, the molecular weight loss begins to mark the onset of partial thermal decomposition (\(T_d\)). Weight losses of approximately 13 and 27% near 589 and 618 K may be attributed to the thermal decomposition accompanied by the partial escape of the HCl and 2HCl moieties, respectively, as shown in Figure 1. The molecular weight sharply decreased between 530 and 650 K with a corresponding weight loss of 44% near 667 K. Therefore, from the DSC and TGA results, the endothermic peak near 536 K is due to the partial thermal decomposition, which caused a sudden weight loss above 536 K corresponding to HCl and 2HCl evaporations.

2.2. MAS \(\text{H}\) NMR. The \(\text{H}\) NMR spectrum in \([\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\) \(\text{ZnCl}_4\) crystals recorded by MAS NMR at different temperatures is shown in Figure 2. The observed resonance lines at 180 K have an asymmetric shape; the line widths at the full-width at half-maximum on the left and right sides are not the same. This asymmetry is due to the overlapping lines of \(\text{H}\) for \(\text{CH}_2\) and \(\text{NH}_3\). The spinning sidebands are marked with “+” in Figure 2. As observed in Figure 2, one overlapping signal begins to separate into two signals at temperatures above 380 K. The resonance lines at 430 K are split into two resonance lines with chemical shifts of 3.83 and 5.83 ppm.
7.31 ppm for CH$_2$ and NH$_3$, respectively. The chemical shifts remain quasi-constant with respect to temperature variation, indicating that the structural environments of $^1$H in the [NH$_3$(CH$_2$)$_2$NH$_3$]$^+$ cation do not change.

The MAS $^1$H NMR spectrum was measured for several delay times at each temperature, and the relation between the intensity of the NMR spectrum and delay time was found to follow a single exponential function. The decay rate of the spin-locked proton magnetization is characterized by $T_{1P}$ as $^{35-37}$

$$P(t) = P(0)\exp(-t/T_{1P})$$  \hspace{1cm} (3)

where $P(t)$ and $P(0)$ are the signal intensities at times $t$ and $t = 0$, respectively. At 300 K, plots of the MAS $^1$H NMR signals in [NH$_3$(CH$_2$)$_2$NH$_3$]ZnCl$_4$ for several delay times in the range of 1–160 ms are shown in Figure 3. All the decay curves were explained by a single exponential function represented by eq 3. From the slope of their recovery traces, the $^1$H $T_{1P}$ values for CH$_2$ and NH$_3$ in [NH$_3$(CH$_2$)$_2$NH$_3$]ZnCl$_4$ were obtained as a function of inverse temperature, as shown in Figure 4. As the temperature rises, $T_{1P}$ gradually increases and then reaches a maximum value of 570 ms at 270 K; however, $T_{1P}$ rapidly decreases above 300 K. Further, the $T_{1P}$ values for CH$_2$ at 410, 420, and 430 K were found to be the same as those for NH$_3$ within the error range. In Figure 4, the $T_{1P}$ versus temperature curve exhibits a minimum of 2.39 ms at 380 K, which is attributed to the molecular motions, and $T_{1P}$ again increases with a further increase in temperature above 380 K. Based on the theory of Bloembergen–Purcell–Pound (BPP), the $T_{1P}$ values are related to the rotational correlation time $\tau_C$. $^{28,29}$

For $^1$H, $T_{1P}$ for the molecular motion is given by

$$1/T_{1P} = C(\gamma_H^2 h/r^3)\{4g_d + g_b + 3g_e + 6g_a + 6g_i\}$$  \hspace{1cm} (4)

where $g_a = \tau_C/[1 + (\omega_H^2 \tau_C^2)]$, $g_b = \tau_C/[1 + (\omega_H^2 + \omega_C^2) \tau_C^2]$,$ g_d = \tau_C/[1 + (\omega_C^2 \tau_C^2)]$, and $g_i = \tau_C/[1 + (\omega_H^2 + \omega_C^2) \tau_C^2]$. Here, $C$ is a coefficient, $\gamma_H$ and $\gamma_C$ are the gyromagnetic ratios for $^1$H and $^{13}$C nuclei, respectively, $r$ is the H–C internuclear distance, $h = h/2\pi$ is the Planck constant, $\omega_H$ and $\omega_C$ are the Larmor frequencies of $^1$H and $^{13}$C, respectively, and finally, $\omega_H$ is a spin–lock field of 59.52 kHz. When $\omega_C \tau_C = 1$, $T_{1P}$ is at its minimum; therefore, this relationship between $T_{1P}$ and $\omega_H$ was applied to obtain the coefficient $C$ in eq 4. Using this coefficient, we calculated the correlation time $\tau_C$ as a function of temperature. According to the BPP theory, the local field fluctuation is governed by the thermal motion of CH$_3$NH$_3^+$, which is activated by thermal energy. In this case, correlation time $\tau_C$ is described by Arrhenius behavior, as follows $^{25,29,30}$

$$\tau_C = \tau_0 \exp(-E_a/k_B T)$$  \hspace{1cm} (5)

where $E_a$ and $k_B$ are the activation energy of the molecular motions and Boltzmann constant, respectively. As the magnitude of $E_a$ depends on the molecular dynamics, we plotted the relation between $\tau_C$ and 1000/temperature on a logarithmic scale. Here, correlation times for the $T_{1P}$ values obtained in the temperature range of 300–430 K are shown in the inset of Figure 4. The $E_a$ values for $^1$H above and below 300 K were estimated to be 78.17 ± 4.39 and 4.91 ± 0.62 kJ/mol, respectively. Here, it should be noted that $T_{1P}$ and $E_a$ for $^1$H are the averaged values for all the hydrogen in the [NH$_3$(CH$_2$)$_2$NH$_3$]$^+$ cation. Furthermore, the molecular motion for $^1$H at the ends of the organic cations was higher at a higher temperature.

### 2.3. MAS $^{13}$C NMR

The MAS $^{13}$C NMR chemical shifts in [NH$_3$(CH$_2$)$_2$NH$_3$]ZnCl$_4$ were recorded as a function of temperature. The MAS $^{13}$C NMR spectrum for TMS was obtained at 38.3 ppm at 300 K, and this value was accurately calibrated to 0 ppm for the $^{13}$C chemical shift measurement of our sample. The MAS $^{13}$C NMR spectra at 180, 220, 260, 300, and 340 K are displayed in the inset in Figure 5. In addition, Figure 5 shows the $^{13}$C NMR chemical shifts with increasing temperature, and the $^{13}$C chemical shifts can be found to have split into two lines; below 300 K, the $^{13}$C NMR chemical shift of CH$_3$ splits into two distinguishable inequivalent lines of a-CH$_3$ and b-CH$_3$ in [NH$_3$(CH$_2$)$_2$NH$_3$]ZnCl$_4$. This splitting indicates the existence of two different a-CH$_3$ and b-CH$_3$ below 300 K in the cation structure, as shown in Figure 5. It is thought that a-CH$_3$ and b-CH$_3$ having different environments exist because the bond lengths of N–H–Cl connected to both ends of NH$_3$ are different. Further, the MAS $^{13}$C NMR spectrum consists of one resonance line for CH$_2$ in the temperature range of 300–370 K. In addition, the $^{13}$C chemical shifts slowly move upward with...
increasing temperature. We will discuss this again in the 14N NMR experiment.

The MAS 13C NMR signals of CH2 in [NH3(CH2)2NH3]2ZnCl4 were obtained for different delay times at each temperature. The decay curves for a-CH2 and b-CH2 were analyzed by a single exponential function represented by eq 3.

From the slope of their recovery traces, the 13C T1ρ values were obtained as a function of 1000/temperature, as shown in Figure 6. Similar to the 1H T1ρ value, the 13C T1ρ value decreases sharply above 300 K with increasing temperature. In addition, the 13C T1ρ values for a-CH2 and b-CH2 are similar, as can be seen in Figure 6. At 300 K, the 13C T1ρ value is 8.35 ms, and it drops significantly to 0.16 ms at 430 K. The activation energies (Ea) obtained from the slopes of the log T1ρ versus 1000/temperature plot (Figure 6) below and above 300 K are estimated to be 2.23 ± 0.45 and 38.88 ± 7.33 kJ/mol, respectively. In addition, the Ea values for b-CH2 below 300 K are the same with those of a-CH2 within the experimental error range. Further, the molecular motion of carbons was higher at a higher temperature.

2.4. Static 14N NMR. The NMR spectra of 14N were measured at a Larmor frequency of 28.90 MHz using the static NMR method. To obtain information concerning possible changes in the surroundings of the 14N ion, static NMR spectra of 14N were obtained. Here, the measurement was performed, keeping the c axis of the single crystal and direction of the magnetic field parallel. Temperature-dependent changes of the 14N chemical shift are attributable to alterations in the structural geometry. Two resonance lines are obtained by the quadrupole interaction of the 14N (I = 1) nucleus. The static 14N NMR spectra at 220, 260, and 300 K are plotted in the inset in Figure 7, and the chemical shifts are referenced with respect to NH3NO3. The four signals, as shown in Figure 7, are attributed to the two inequivalent a′-NH3 and b′-NH3 ions. The two types of 14N resonance lines due to a′-NH3 and b′-NH3 are thought to be related to the two types of 13C resonance lines due to a-CH2 and b-CH2 measured earlier. The 14N chemical shift for a′-NH3 increases with increasing temperature until 300 K, whereas that for b′-NH3 decreases with increasing temperature until 300 K. It should be noted that a′-NH3 and b′-NH3 are arbitrarily determined for NH3. Above 300 K, the 14N chemical shifts for a′-NH3 and b′-NH3 increase sharply with increasing temperature. The temperature-dependent changes in the 14N chemical shifts are attributed to the changes in the structural geometry of N–H...Cl hydrogen bonds, reflecting changes in atomic configurations around the 14N nuclei near 300 K.

3. CONCLUSIONS

To investigate the structural dynamic features of [NH3(CH2)2NH3]2ZnCl4 crystals as a function of temperature, we performed MAS 1H NMR, MAS 13C NMR, and static 14N NMR. From these results, the 1H chemical shifts of the [NH3(CH2)2NH3] cation were found to be nearly temperature-independent. The two inequivalent a-CH2 and b-CH2 were distinguished by 13C NMR experiments, and two inequivalent a′-NH3 and b′-NH3 were distinguished by 14N NMR experiments. NH3 in the structure is correlated to CH2, and the main factor is a change in the surroundings of C–N groups in the [NH3(CH2)2NH3] cation. Remarkably, the changes in the 13C and 14N chemical shifts occurred around 300 K, and 1H and 13C T1ρ exhibited maximum values near 300 K. From the DSC...
results, no phenomenon was observed at 300 K; however, the chemical shifts and $T_{1p}$ results of $^1$H, $^{13}$C, and $^{14}$N nuclei showed discontinuous changes around 300 K. From these results, we can infer that the surrounding environments of $^1$H, $^{13}$C, and $^{14}$N sites change around 300 K.

We compared the phase-transition temperatures, crystal structures, space groups, lattice constants, spin–lattice relaxation times, and activation energies of the previously reported (CH$_3$NH$_3$)$_2$ZnCl$_4$ with those of [NH$_3$(CH$_2$)$_2$NH$_3$]ZnCl$_4$ examined in this study, and the comparison results are summarized in Table 1. The difference between the two crystals lies only in the presence of organic cations. Although $^1$H $T_{1p}$ values are similar for both compounds, $^1$H $E_1$ values at high temperatures are notably different. In addition, for (CH$_3$NH$_3$)$_2$ZnCl$_4$, $^{13}$C $T_{1p}$ has a larger value, whereas $E_1$ values for (CH$_3$NH$_3$)$_2$ZnCl$_4$ and [NH$_3$(CH$_2$)$_2$NH$_3$]ZnCl$_4$ are approximately 3.5 times larger than those for (CH$_3$NH$_3$)$_2$ZnCl$_4$. For both compounds, $E_1$ values for $^1$H and $^{13}$C are relatively similar at low temperatures; however, at high temperatures, the corresponding values for NH$_3$(CH$_2$)$_2$NH$_3$ZnCl$_4$ are approximately 3.5 times larger than those for (CH$_3$NH$_3$)$_2$ZnCl$_4$. A significant difference between the two compounds is thought to be due to the bond lengths of (CH$_3$NH$_3$)$_2$ZnCl$_4$ in monoammonium-type (CH$_3$NH$_3$)$_2$ZnCl$_4$ and the bond lengths of NH$_3$(CH$_2$)$_2$NH$_3$ZnCl$_4$ in di ammonium-type [NH$_3$(CH$_2$)$_2$NH$_3$]ZnCl$_4$. These differences in molecular motions due to the bond lengths will prove to be beneficial for potential applications for the fields of energy and green chemistry.

4. EXPERIMENTAL METHOD

Single crystals of [NH$_3$(CH$_2$)$_2$NH$_3$]ZnCl$_4$ were synthesized by slow evaporation at 300 K from an aqueous solution containing NH$_3$(CH$_2$)$_2$NH$_3$, 2HCl and ZnCl$_2$. Most of the colorless crystals grew in the shape of hexagonal thin plates.

DSC (thermogravimetric analyzer (TA), DSC 25) experimental results with a scanning speed of 10 °C/min were obtained in the temperature range of 190–600 K under nitrogen gas. TGA was performed on a TA (TA Instruments) in a temperature range of 300–680 K with the same heating rate as that in the DSC measurement. The amounts of samples used in DSC and TGA experiments were 5.96 and 7.98 mg, respectively.

NMR spectra of [NH$_3$(CH$_2$)$_2$NH$_3$]ZnCl$_4$ crystal were obtained using a 400 MHz Avance II+ Bruker solid-state NMR spectrometer equipped with 4 mm MAS probes at KBSI, Seoul Western Center. MAS $^1$H NMR and MAS $^{13}$C NMR were measured at Larmor frequencies of 400.13 and 100.61 MHz, respectively. The MAS rate to minimize the spinning sideband was 10 kHz. The NMR chemical shifts were recorded by using tetramethylsilane (TMS) as the standard. The $^1$H and $^{13}$C $T_{1p}$ values were obtained using a $\pi/2$–$\tau$ sequence method by changing the spin-locking pulses, and the widths of the $\pi/2$ pulse for $^1$H and $^{13}$C were approximately 3.75 and 4.2 μs, respectively.

In addition, the static $^{14}$N NMR spectra of the [NH$_3$(CH$_2$)$_2$NH$_3$]ZnCl$_4$ crystals in the laboratory frame were measured using the same abovementioned NMR spectrometer at the same facility. The Larmor frequency for $^{14}$N NMR spectra was set at 28.90 MHz, and the static $^{14}$N NMR experiments were performed using a solid-echo pulse sequence. The temperature change was maintained within an error range of ±0.5 K by adjusting the nitrogen gas flow and heater current.

### Table 1. Phase-Transition Temperature $T_C$, Crystal Structure, Space Group, Lattice Constant, Spin–Lattice Relaxation Time $T_{1p}$, and Activation Energies $E_a$ for (CH$_3$NH$_3$)$_2$ZnCl$_4$ and [NH$_3$(CH$_2$)$_2$NH$_3$]ZnCl$_4$ Crystals

|                  | (CH$_3$NH$_3$)$_2$ZnCl$_4$ | [NH$_3$(CH$_2$)$_2$NH$_3$]ZnCl$_4$ |
|------------------|---------------------------|----------------------------------|
| $T_C$ (K)        | 265                        | 483                              |
| structure        | monoclinic                | orthorhombic                      |
| space group      | $P2_1/c$                   | $P2_12_1$                        |
| lattice constants (Å) | $a = 10.873$             | $a = 8.832$                      |
|                  | $b = 12.655$              | $b = 9.811$                      |
|                  | $c = 7.648$               | $c = 11.089$                     |
| $^1$H $T_{1p}$ (ms) | 10−500                    | 2−600                            |
| $^{13}$C $T_{1p}$ (ms) | 10−200                   | 0.1−20                           |
| $^1$H $E_1$ (kJ/mol) | 19.72 ± 1.10 (CH$_3$ above 250 K) | 78.17 ± 4.39 (above 300 K)       |
|                  | 6.59 ± 0.51 (CH$_3$ below 250 K) | 4.91 ± 0.62 (below 300 K)       |
|                  | 19.88 ± 0.89 (NH$_3$ above 250 K) | 5.92 ± 0.40 (CH$_3$ below 250 K) |
| $^{13}$C $E_1$ (kJ/mol) | 11.19 ± 1.33 (above 250 K) | 38.88 ± 7.33 (above 300 K)      |
|                  | 1.02 ± 0.37 (below 250 K) | 2.23 ± 0.45 (below 300 K)       |

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