Study on Paramagnetic Interactions of (CH$_3$NH$_3$)$_2$CoBr$_4$ Hybrid Perovskites Based on Nuclear Magnetic Resonance (NMR) Relaxation Time

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Abstract: The thermal properties of organic–inorganic (CH$_3$NH$_3$)$_2$CoBr$_4$ crystals were investigated using differential scanning calorimetry and thermogravimetric analysis. The phase transition and partial decomposition temperatures were observed at 460 K and 572 K. Nuclear magnetic resonance (NMR) chemical shifts depend on the local field at the site of the resonating nucleus. In addition, temperature-dependent spin–lattice relaxation times ($T_1$) were measured using $^1$H and $^{13}$C magic angle spinning NMR to elucidate the paramagnetic interactions of the (CH$_3$NH$_3$)$_2^+$ cations. The shortening of $^1$H and $^{13}$C $T_1$ of the (CH$_3$NH$_3$)$_2$CoBr$_4$ crystals are due to the paramagnetic Co$^{2+}$ effect. Moreover, the physical properties of (CH$_3$NH$_3$)$_2$CoBr$_4$ with paramagnetic ions and those of (CH$_3$NH$_3$)$_2$CdBr$_4$ without paramagnetic ions are reported and compared.

Keywords: organic/inorganic hybrid materials; structure; dynamics; (CH$_3$NH$_3$)$_2$CoBr$_4$; MAS/NMR

1. Introduction

Hybrid organic–inorganic compounds based on perovskite structures are currently attracting an increased amount of interest owing to their potential as substitutes for perovskite solar cells [1–10]. However, the toxicity and chemical instability of perovskites continue to be the major problems associated with their use in solar cells. Compounds in the (CH$_3$NH$_3$)$_2$MX$_4$ family (where $M$ is the transition metal and $X$ is halide) exhibit a variety of physical properties [1,11]. Ions of the transition metal $M$ are located in the tetrahedral structure formed by the halogen ions $X$, and lie in the planes bridged by the (CH$_3$NH$_3$)$^+$ cations [12]. These crystals have a layered structure and exhibit quasi-, two-dimensional magnetic properties. Most recently, electrochemical oxygen evolution of (CH$_3$NH$_3$)$_2$CoBr$_4$, a lead-free cobalt-based perovskite, has been reported by Babu et al. [13]. The (CH$_3$NH$_3$)$_2$CoBr$_4$ crystal belongs to the (CH$_3$NH$_3$)$_2$MX$_4$ series and the family of hybrid organic–inorganic compounds in which (CH$_3$NH$_3$)$_2^+$ cations are connected via a bridge structure between the planes that contain the Co$^{2+}$ ions. At room temperature, the (CH$_3$NH$_3$)$_2$CoBr$_4$ crystal structure has monoclinic symmetry and belongs to the space group $P2_1/c$, with lattice constants $a = 7.9782$ Å, $b = 13.1673$ Å, $c = 11.2602$ Å, and $\beta = 96.3260^\circ$ [14]. The unit cell contains four formula units and four magnetic Co$^{2+}$ ions. The (CoBr$_4$)$^{2-}$ units are surrounded by seven (CH$_3$NH$_3$)$^+$ cations, and two different crystallographic (CH$_3$NH$_3$)$^+$ cations exist. Although the tetrahedral anion exhibits only $C_1$ symmetry, the deviation from an idealized tetrahedral symmetry is small. The NH$_3^+$ polar heads of the chains connect the isolated (CoBr$_4$)$^{2-}$ tetrahedral structure with weak N-H···Br hydrogen bonds. On the other hand, (CH$_3$NH$_3$)$_2$CdBr$_4$ crystals at room temperature have a monoclinic structure and belong to the space group $P2_1/c$ with lattice constants $a = 8.1257$ Å, $b = 13.4317$ Å, $c = 11.4182$ Å, $\beta = 96.1840^\circ$, and $Z = 4$ [15,16]. The structure of this crystal is very similar.
to that of the \((\text{CH}_3\text{NH}_3)_2\text{CoBr}_4\). Until now, the phase transition temperature, thermal property, and paramagnetic interactions of \((\text{CH}_3\text{NH}_3)_2\text{CoBr}_4\) have not been studied in full. The paramagnetic ions of the lead-free perovskite are eco-friendly, which is important for application to solar cells.

The present study was conducted to investigate the thermodynamic properties of the \((\text{CH}_3\text{NH}_3)_2\text{CoBr}_4\) crystal using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and optical polarizing microscopy. Additionally, the nuclear magnetic resonance (NMR) chemical shifts and spin–lattice relaxation times \(T_1\) in the rotating frame of \((\text{CH}_3\text{NH}_3)_2\text{CoBr}_4\) were obtained using \(^1\text{H}\) magic angle spinning (MAS NMR) and \(^{13}\text{C}\) cross-polarization (CP)/MAS NMR methods at several temperatures to probe the local environments and study the roles of the \((\text{CH}_3\text{NH}_3)^+\) cations. Moreover, the physical properties of \((\text{CH}_3\text{NH}_3)_2\text{CoBr}_4\) including paramagnetic ions and \((\text{CH}_3\text{NH}_3)_2\text{CdBr}_4\) excluding paramagnetic ions were obtained from previous reports \cite{17}, and used as a comparison to understand the effects of \(\text{Co}^{2+}\) and \(\text{Cd}^{2+}\) ions.

### 2. Results and Discussion

TGA and DSC measurements were obtained to understand the thermal stability, structural phase transitions, and melting temperatures. The TGA and DSC curves of \((\text{CH}_3\text{NH}_3)_2\text{CoBr}_4\) are plotted within the temperature range of 300–770 K, as shown in Figures 1 and 2. The transformation anomaly at 460 K \((=T_C)\) in the DSC curve is related to the phase transition. The mass loss of 3.89\% occurs at approximately 572 K \((=T_d)\), and is ascribed to the onset of partial thermal decomposition. The compound \((\text{CH}_3\text{NH}_3)_2\text{CoBr}_4\) loses its crystallization at increased temperatures. When comparing the experimental TGA results and possible chemical reactions, the solid residue is calculated on the basis of Equations (1) and (2):

\[
(\text{CH}_3\text{NH}_3)_2\text{CoBr}_4\rightarrow(\text{CH}_3\text{NH}_2\cdot\text{HBr})_2\text{CoBr}_2\rightarrow(\text{CH}_3\text{NH}_2)_2\text{CoBr}_2\ (s) + 2\text{HBr}\ (g) \tag{1}
\]

Residue: \([((\text{CH}_3\text{NH}_3)_2\text{CoBr}_2 \ (M = 280.857\ g)]/[((\text{CH}_3\text{NH}_3)_2\text{CoBr}_4 \ (M = 442.681\ g)] = 63.4\% \]

\[
(\text{CH}_3\text{NH}_3)_2\text{CoBr}_4\rightarrow(\text{CH}_3\text{NH}_2\cdot\text{HBr})_2\text{CoBr}_2\rightarrow\text{CoBr}_2\ (s) + 2(\text{CH}_3\text{NH}_2\cdot\text{HBr})\ (g) \tag{2}
\]

Residue: \([\text{CoBr}_2 \ (M = 218.741\ g)]/[((\text{CH}_3\text{NH}_3)_2\text{CoBr}_4 \ (M = 442.681\ g)] = 49.4\% \]

![Figure 1](image-url)  
**Figure 1.** Thermogravimetric analysis (TGA) curve of \((\text{CH}_3\text{NH}_3)_2\text{CoBr}_4\) (inset: states of the crystal at temperatures of (a) 300 K, (b) 400 K, (c) 500 K, (d) 550 K, and (e) 570 K).
They remain quasi-constant with increasing temperature, indicating that the structural environment of the magnetization of the protons at thermal equilibrium. This analysis method is used to obtain the simple mono-exponential function \cite{18–20}.

The T\textsubscript{1} resonance lines are the sidebands. The T\textsubscript{1} values for CH\textsubscript{3} and NH\textsubscript{3} are marked with asterisks. The 1H resonance line has an asymmetric shape, and the full-width at half maximum (FWHM) values on the left and right sides are not equal. The asymmetric line shape is attributed to the overlapping lines of the two 1H in the (CH\textsubscript{3}NH\textsubscript{3})\textsuperscript{+} cations. The 1H-NMR chemical shift of \(\delta = -0.3\) ppm is due to the CH\textsubscript{3}, while the 1H-NMR chemical shift of \(\delta = 4.2\) ppm is due to the NH\textsubscript{3}. The 1H-NMR chemical shifts for the two 1H in the (CH\textsubscript{3}NH\textsubscript{3})\textsuperscript{+} cations are temperature-independent. They remain quasi-constant with increasing temperature, indicating that the structural environment of 1H in the CH\textsubscript{3} and NH\textsubscript{3} groups does not change.

Figure 4 shows the recovery traces for the 1H resonance lines for delay times that range from 1 \(\mu\)s to 20 ms at 300 K. Herein, the arrows mark the resonance lines at each delay time, while the other resonance lines are the sidebands. The T\textsubscript{1p} values are obtained from the intensities of the magnetization recovery curves with respect to the delay time. The recovery traces are described by a simple mono-exponential function \cite{18–20}.

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

where P(\(\tau\)) is the NMR signal intensity measured after recovery time \(\tau\), and P(0) is the total nuclear magnetization of the protons at thermal equilibrium. This analysis method is used to obtain the T\textsubscript{1p} values for the proton in the (CH\textsubscript{3}NH\textsubscript{3})\textsuperscript{+} cations. However, the 1H T\textsubscript{1p} values for CH\textsubscript{3} and NH\textsubscript{3}...
are indistinguishable owing to the overlapping responses of the two protons. The $^{1}$H $T_{1\rho}$ values for (CH$_3$NH$_3$)$_2$CoBr$_4$ obtained herein and the corresponding values for (CH$_3$NH$_3$)$_2$CdBr$_4$ reported previously [17] are shown in Figure 5 as a function of the inverse temperature. In the case of (CH$_3$NH$_3$)$_2$CoBr$_4$, the $^{1}$H $T_{1\rho}$ values increased rapidly near 210 K, and those at high temperatures are almost continuous; the $T_{1\rho}$ value at 180 K is 76 $\mu$s and that at 300 K is 10 times longer than that at 180 K. The $T_{1\rho}$ value is very short at low temperatures, and thus indicates rapid energy transfer from the nuclear spin system to the surrounding environment. On the other hand, the $^{1}$H $T_{1\rho}$ values are obtained for each proton in CH$_3$ and NH$_3$ in the case of (CH$_3$NH$_3$)$_2$CdBr$_4$ as a function of reciprocal temperature. Herein, the $T_{1\rho}$ values for the two protons of the (CH$_3$NH$_3$)$^+$ cations are nearly the same within experimental error. The $T_{1\rho}$ values of $^{1}$H in the CH$_3$ and NH$_3$ ions abruptly decrease at approximately 360 K. The $^{1}$H $T_{1\rho}$ value of (CH$_3$NH$_3$)$_2$CoBr$_4$ including the paramagnetic ions is very short, whereas that of (CH$_3$NH$_3$)$_2$CdBr$_4$ excluding paramagnetic ions is very long.

![Figure 3. $^1$H-NMR spectrum for (CH$_3$NH$_3$)$_2$CoBr$_4$ crystal at 410 K. The open circles are the marked sidebands for CH$_3$ and the asterisks are the marked sidebands for NH$_3$.](image)

![Figure 4. Recovery traces for $^1$H-NMR spectrum in (CH$_3$NH$_3$)$_2$CoBr$_4$ as a function of delay time from 1 $\mu$s to 20 ms.](image)
The 1H T1ρ value of (CH3NH3)2CoBr4 including the paramagnetic ions is very short, whereas that of (CH3NH3)2CdBr4 excluding paramagnetic ions is very long. The local environment of the carbons in (CH3NH3)2CoBr4 was studied by 13C MAS NMR, and the corresponding 13C-NMR chemical shifts are shown in Fig. 6. Attention was paid to 13C-NMR, which should be a sensitive probe of the local environment and of the cation dynamics.

Figure 5. 1H spin–lattice relaxation times in (CH3NH3)2CoBr4 and (CH3NH3)2CdBr4 as a function of inverse temperature.

The local environment of the carbons in (CH3NH3)2CoBr4 was studied by 13C MAS NMR, and the corresponding 13C-NMR chemical shifts are shown in Figure 6. Attention was paid to 13C-NMR, which should be a sensitive probe of the local environment and of the cation dynamics.

Figure 6. 13C-NMR spectrum in (CH3NH3)2CoBr4 at 300 K. The two arrows denote the signals of the two crystallographically different CH3 moieties. The spinning sidebands are marked with open circles and asterisks.

The 13C-NMR spectrum at 300 K in (CH3NH3)2CoBr4 shows two signals at the chemical shifts of δ = 68.3 ppm and δ = 117.9 ppm with respect to TMS [21]. The 13C-NMR spectrum consists of two lines that correspond to a-CH3 and b-CH3. The signals respectively represent the methyl carbons in the two crystallographically different a-CH3 and b-CH3. The 13C-NMR chemical shifts of the two compounds of (CH3NH3)2CoBr4 and (CH3NH3)2CdBr4 are shown in Figure 7 as a function
of temperature. The $^{13}$C-NMR chemical shifts vary significantly with temperature. Specifically, the $^{13}$C-NMR chemical shifts in the case of $(\text{CH}_3\text{NH}_3)_2\text{CoBr}_4$ decrease slowly and monotonically as a function of temperature. Conversely, the $^{13}$C-NMR spectrum at 300 K in $(\text{CH}_3\text{NH}_3)_2\text{CdBr}_4$ shows two signals at chemical shifts of $\delta = 27.9$ ppm and $\delta = 29.3$ ppm. The $^{13}$C-NMR chemical shifts of the crystallographically different a-CH$_3$ and b-CH$_3$ slowly and monotonously increase as a function of temperature. The $^{13}$C chemical shifts of the CH$_3$ groups differ between the two compounds. Generally, the paramagnetic contribution to the NMR shift is responsible for the NMR spectra. The $^{13}$C chemical shift of $(\text{CH}_3\text{NH}_3)_2\text{CoBr}_4$, which contains paramagnetic ions, was significantly different to that of $(\text{CH}_3\text{NH}_3)_2\text{CdBr}_4$, which does not contain paramagnetic ions. The differences in the $^{13}$C chemical shifts could potentially be due to differences in the electron structures of the metal ions.

The signal intensities of the nuclear magnetization recovery curves are fitted by the mono-exponential function of temperature. The $^{13}$C-NMR chemical shifts vary significantly with temperature. Specifically, the $^{13}$C-NMR chemical shifts in the case of $(\text{CH}_3\text{NH}_3)_2\text{CoBr}_4$ decrease slowly and monotonically as a function of temperature. Conversely, the $^{13}$C-NMR spectrum at 300 K in $(\text{CH}_3\text{NH}_3)_2\text{CdBr}_4$ shows two signals at chemical shifts of $\delta = 27.9$ ppm and $\delta = 29.3$ ppm. The $^{13}$C-NMR chemical shifts of the crystallographically different a-CH$_3$ and b-CH$_3$ slowly and monotonously increase as a function of temperature. The $^{13}$C chemical shifts of the CH$_3$ groups differ between the two compounds. Generally, the paramagnetic contribution to the NMR shift is responsible for the NMR spectra. The $^{13}$C chemical shift of $(\text{CH}_3\text{NH}_3)_2\text{CoBr}_4$, which contains paramagnetic ions, was significantly different to that of $(\text{CH}_3\text{NH}_3)_2\text{CdBr}_4$, which does not contain paramagnetic ions. The differences in the $^{13}$C chemical shifts could potentially be due to differences in the electron structures of the metal ions.

To determine the $^{13}$C $T_{1\rho}$, nuclear magnetization was measured as a function of the delay time. The signal intensities of the nuclear magnetization recovery curves are fitted by the mono-exponential function of Equation (3). From these results, $T_{1\rho}$ values were obtained for the carbons in $(\text{CH}_3\text{NH}_3)_2\text{CoBr}_4$ and $(\text{CH}_3\text{NH}_3)_2\text{CdBr}_4$ as a function of the inverse temperature, as shown in Figure 8. In the case of $(\text{CH}_3\text{NH}_3)_2\text{CoBr}_4$, the $T_{1\rho}$ values of $^{13}$C show a minimum value near 330 K, while the $T_{1\rho}$ value abruptly decreases above 410 K. The $T_{1\rho}$ values for a-CH$_3$ and b-CH$_3$ are also very similar and of the order of 10 ms. Conversely, the variation of $T_{1\rho}$ with temperature in the case of $(\text{CH}_3\text{NH}_3)_2\text{CdBr}_4$ exhibits a minimum near 250 K for a-CH$_3$ and b-CH$_3$, respectively, and $T_{1\rho}$ decreases abruptly above 360 K. The presence of these minima are attributed to the effects of the reorientation of $(\text{CH}_3\text{NH}_3)^+$ cations. From the $^{13}$C $T_{1\rho}$ curves, the relaxation processes of $(\text{CH}_3\text{NH}_3)_2\text{CdBr}_4$ are affected by molecular motion described by the Bloembergen–Purcell–Pound (BPP) theory [22]. The experimental values of $T_{1\rho}$ are explained by the correlation time $\tau_C$ for molecular motion based on the BPP theory [22,23],

$$\frac{1}{T_{1\rho}} = 0.05(\mu_c/4\pi)^2[\gamma_H^2\gamma_C^{-2}h^2/r^6][4F_a + F_b + 3F_c + 6F_d + 6F_e]$$

(4)

where

- $F_a = \tau_C/[1 + \omega_1^2\tau_C^{-2}]$,
- $F_b = \tau_C/[1 + (\omega_1 - \omega_2)^2\tau_C^{-2}]$,
- $F_c = \tau_C/[1 + \omega_c^2\tau_C^{-2}]$,
- $F_d = \tau_C/[1 + (\omega_1 + \omega_2)^2\tau_C^{-2}]$,
- $F_e = \tau_C/[1 + \omega_H^2\tau_C^{-2}]$.
where \( \mu_0 \) is the permeability, \( \gamma_H \) and \( \gamma_C \) are the respective gyromagnetic ratios for the \(^1\)H and \(^{13}\)C nuclei, \( r \) is the distance of H–C, \( h = \hbar/2\pi \), and \( \omega_H \) and \( \omega_C \) are the respective Larmor frequencies of \(^1\)H and \(^{13}\)C.

![Figure 8](image_url).

\( \frac{1}{T_{1\rho}} \) spin–lattice relaxation times of \((\text{CH}_3\text{NH}_3)_2\text{CoBr}_4\) and \((\text{CH}_3\text{NH}_3)_2\text{CdBr}_4\) as a function of inverse temperature.

On the other hand, the relaxation processes of \((\text{CH}_3\text{NH}_3)_2\text{CoBr}_4\) with the paramagnetic Co\(^{2+}\) ions are affected by the molecular motion described by the Solomon equation [24]. When paramagnetic ions exist, the \( T_{1\rho} \) are represented by \( \tau_C \), as presented in [24]

\[
\frac{1}{T_{1\rho}} = \left(\frac{1}{15}\right)(\mu_0/4\pi)^2[\gamma_C^2\gamma_e^2\mu_B^2S(S+1)/\hbar^2][4G_a + G_b + 3G_c + 6G_d + 6G_e]
\]

where

\[
\begin{align*}
G_a &= \tau_C/[1 + \omega_1^2\tau_C^2] \\
G_b &= \tau_C/[1 + (\omega_C - \omega_e)^2\tau_C^2] \\
G_c &= \tau_C/[1 + \omega_e^2\tau_C^2] \\
G_d &= \tau_C/[1 + (\omega_C + \omega_e)^2\tau_C^2] \\
G_e &= \tau_C/[1 + \omega_e^2\tau_C^2].
\end{align*}
\]

Here, \( \gamma_e \) is the gyromagnetic ratio of the electron, \( S \) is the total spin quantum number of the paramagnetic ion, and \( \omega_e \) is the Larmor frequency of the electron. Additionally, \( \omega_1 \) is the angular frequency at the spin-lock field; 59.52 kHz for \((\text{CH}_3\text{NH}_3)_2\text{CoBr}_4\) and 67.56 kHz for \((\text{CH}_3\text{NH}_3)_2\text{CdBr}_4\). The \( T_{1\rho} \) exhibits a minimum when \( \omega_1\tau_C = 1 \). Based on this condition, the coefficients of Equations (4) and (5) which are dependent on \( \omega_1, \omega_H, \) and \( \omega_C \), can be obtained. Furthermore, the value of \( \tau_C \) can be calculated, and its temperature dependence follows a simple Arrhenius expression [22] according to,

\[
\tau_C = \tau_0\exp(-E_a/RT)
\]

where \( \tau_0 \) is the preexponential factor, \( T \) is the temperature, \( R \) is the gas constant, and \( E_a \) is the activation energy. The activation energies for the tumbling motion of a-\text{CH}_3 and b-\text{CH}_3 in the case of \((\text{CH}_3\text{NH}_3)_2\text{CoBr}_4\) are obtained from the log \( \tau_C \) vs. 1000/T curve, and are respectively equal to 24.51 ± 0.99 kJ/mol and 23.25 ± 1.30 kJ/mol, whereas the corresponding values in the case of \((\text{CH}_3\text{NH}_3)_2\text{CdBr}_4\) are 8.18 ± 0.37 kJ/mol and 7.65 ± 0.21 kJ/mol (see Figure 9). When paramagnetic Co\(^{2+}\) ions exist, \( 1/\tau_C = \)
1/τᵣ + 1/τᵢ + 1/τₑ, where τᵣ, τᵢ, and τₑ, are the rotational correlation time, exchange correlation time, and electronic relaxation correlation time, respectively. The τᵣ can represent molecular motion. For (CH₃NH₃)₂CoBr₄, there is no chemical exchange or paramagnetic terms, and so τₑ can directly reflect the molecular motion. In the case of (CH₃NH₃)₂CoBr₄, τₑ dominates the total correlation time, and thus, τₑ is not directly related to molecular motion.

\[
\tau = \frac{1}{\tau_0 + \frac{T}{R} + \frac{E_a}{RT}}
\]

where \(\tau_0\) is the preexponential factor, \(T\) is the temperature, \(R\) is the gas constant, and \(E_a\) is the activation energy. The activation energies for the tumbling motion of a-CH₃ and b-CH₃ in the case of (CH₃NH₃)₂CoBr₄ and (CH₃NH₃)₂CdBr₄ are obtained from the log-log plot of the correlation times vs. inverse temperature. For (CH₃NH₃)₂CoBr₄ crystals grown based on the slow evaporation of an aqueous solution with a 2:1 ratio of CH₃NH₂·HBr and CoBr₂ at 300 K. Single crystals have a diamond shape and seagrass color. The thermal properties and phase transition temperature were measured using a TGA (TA, DSC 25) instrument at a heating rate of 10 °C/min. The TGA and DSC curves were measured in an N₂ atmosphere, and the mass of the powder sample used in the experiment was 9.22 mg.

The solid-state MAS NMR spectra and the spin–lattice relaxation time \(T₁\) values were measured based on the variation of the duration of the \(\pi/2\) pulse sequence by varying the duration of the spin-locking pulse. The usual experimental approach assumes the use of cross-polarization from protons to enhance the \(^{13}\)C sensitivity. The widths of the \(\pi/2\) pulses for \(^{1}H\) and \(^{13}\)C were 4.1 µs and 4.2 µs, respectively. The \(T₁\) values were measured in the temperature range of 180–430 K due to limitations of the experimental equipment associated with the measurements of the spectra and \(T₁\) outside of this range. The sample temperatures were held constant by controlling the helium gas flow and the heater current [25,26].

3. Materials and Methods

The (CH₃NH₃)₂CoBr₄ single crystals were grown based on the slow evaporation of an aqueous solution with a 2:1 ratio of CH₃NH₂·HBr and CoBr₂ at 300 K. Single crystals have a diamond shape and seagrass color.

The thermal properties and phase transition temperature were measured using a TGA (TA, DSC 25) instrument at a heating rate of 10 °C/min. The TGA and DSC curves were measured in an N₂ atmosphere, and the mass of the powder sample used in the experiment was 9.22 mg.

The solid-state MAS NMR spectra and the spin–lattice relaxation time \(T₁ρ\) in the rotating frame of (CH₃NH₃)₂CoBr₄ crystals were recorded on a Bruker 400 DSX NMR spectrometer (Bruker, Leipzig, Germany) at the Korean Basic Science Institute at the Western Seoul Center. Solid samples were inserted into 4 mm diameter zirconia rotors. The samples were spun at a sufficient speed to avoid spinning sidebands overlapping. The chemical shifts were defined with respect to tetramethylsilane (TMS). The chemical shifts were defined with respect to tetramethylsilane (TMS). The \(^{1}H\) \(T₁ρ\) values were measured using a \(\pi/2\)-pulse sequence by varying the duration of the spin-locking pulse. The \(^{13}\)C \(T₁ρ\) values were measured based on the variation of the duration of the \(^{13}\)C spin-locking pulse. The usual experimental approach assumes the use of cross-polarization from protons to enhance the \(^{13}\)C sensitivity. The widths of the \(\pi/2\) pulses for \(^{1}H\) and \(^{13}\)C were 4.1 µs and 4.2 µs, respectively. The \(T₁ρ\) values were measured in the temperature range of 180–430 K due to limitations of the experimental equipment associated with the measurements of the spectra and \(T₁ρ\) outside of this range. The sample temperatures were held constant by controlling the helium gas flow and the heater current [25,26].

4. Conclusions

The thermal properties and phase transition temperature of (CH₃NH₃)₂CoBr₄ crystals grown based on the slow evaporation method were investigated with TGA, DSC, and optical polarizing microscopy. The phase transition and partial decomposition temperatures were observed at 460 K and
572 K, respectively. The high-temperature phenomenon above 572 K was not related to a physical change like the structural phase transition. Instead, it was related to a chemical change, such as thermal decomposition.

The paramagnetic interactions of (CH$_3$NH$_3$)$_2$CoBr$_4$, associated with the role of the (CH$_3$NH$_3$)$_2^+$ cations were studied by $^1$H-NMR and $^{13}$C-NMR as a function of temperature. The $^1$H and $^{13}$C MAS NMR were used to probe the dynamics of cations in (CH$_3$NH$_3$)$_2$CoBr$_4$ and (CH$_3$NH$_3$)$_2$CdBr$_4$. The chemical shift by the MAS NMR depended on the local field at the site of the resonating nucleus in crystals. The effect of these crystals on the $^1$H and $^{13}$C-NMR chemical shifts was investigated using temperature-dependent NMR experiments. The contributions to the $^{13}$C-NMR chemical shifts are correlated with the distribution of spin density in the ligand moiety.

The temperature dependence of the $T_{1\rho}$ values for $^1$H reflect the modulation of the inter-NH$_3$ and inter-CH$_3$ dipolar interactions due to the (CH$_3$NH$_3$)$_2^+$ cations. The variation of $T_{1\rho}$ for $^{13}$C yielded a minimum, and it is apparent that the $T_{1\rho}$ values for $^{13}$C are governed by tumbling motions. Moreover, the paramagnetic dopant led to the shortening of their $T_{1\rho}$ values. Accordingly, it has been shown that the $T_{1\rho}$ value is inversely proportional to the square of the magnetic moment of the paramagnetic ion [27]. The $T_{1\rho}$ values of $^1$H and $^{13}$C of the (CH$_3$NH$_3$)$_2$CoBr$_4$ crystals, which contain paramagnetic ions, are much shorter than those of the (CH$_3$NH$_3$)$_2$CdBr$_4$ crystals, which do not contain paramagnetic ions.

The (CH$_3$NH$_3$)$_2$CoBr$_4$ and (CH$_3$NH$_3$)$_2$CdBr$_4$ crystals are of the (CH$_3$NH$_3$)$_2$MX$_4$ type, whereas their individual dynamics differ significantly from the dynamic of the cations. The differences between the $T_{1\rho}$ of the (CH$_3$NH$_3$)$_2$MBr$_4$ crystals ($M=$ Co and Cd) are due to the differences between the electron structures of their Co$^{2+}$ and Cd$^{2+}$ ions. These ions screen the nuclear charge from the motion of the outer electrons. The Co$^{2+}$ has unpaired $d$ electrons, whereas Cd$^{2+}$ has filled $d$ shells. Their NMR properties stem from the differences between the chemical properties of paramagnetic Co$^{2+}$ and non-paramagnetic Cd$^{2+}$ ions. Furthermore, the NMR relaxation of diamagnetic Cd$^{2+}$ ions is mostly probably driven by dipolar interactions, whereas the relaxation of paramagnetic Co$^{2+}$ ions is mostly driven by interactions with the paramagnetic center.

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Sample Availability: Samples of the compounds (CH3NH3)2CoBr4 are available from the authors.