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# A Small Lattice Change Induces Significant Dynamic Changes of CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> Caged in Hybrid Perovskite Crystals: Toward Understanding the Interplay between Host Lattices and Guest **Molecules**

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**S** Supporting Information

**ABSTRACT:** Two perovskite-type compounds, (MA)<sub>2</sub>- $[B'Co(CN)_6]$  (MA = methylammonium, B' = K(I) and Na(I)), have very similar structures, but exhibit marked differences in the phase and dielectric transitions. Solid state <sup>2</sup>H NMR studies reveal the detailed dynamic changes of the caged methylammonium (MA) cations before and after the phase transitions, which are correlated with the different dielectric states of the compounds. Using solid state 59Co NMR, the dynamic changes of the host lattices before and after the transitions, which accompany the changes in the dynamics of the caged MA cations, are unveiled, demonstrating the intriguing interplay between the MA cations and the host lattices. On the basis of these observations, the molecular origins of the dielectric transitions are discussed in detail.



# INTRODUCTION

Molecular motions are a key to understanding the microscopic origins and subsequent evolution of a series of properties and functions of various materials. Design and manipulation of local motions are the core issues regarding molecular machines.<sup>1,2</sup> In particular, the molecular motions often play an essential role in triggering, switching, and driving the system of a molecular machine.<sup>3</sup> In the hybrid perovskite (MA)[PbI<sub>3</sub>] (MA = methylammonium), the local motion of the MA cation caged in the host lattice is closely related to its eye-catching photovoltaic property.<sup>4–9</sup> In responsive dielectric perovskitetype compounds, the motions of the organic polar cations can induce dipolar reorientation, and thus different macroscopic dielectric states of materials.<sup>10-14</sup>

Although challenging, understanding and manipulating the molecular motions and, in turn, establishing a correlation between molecular motions and macroscopic properties of material are becoming the main objectives of crystal engineering. In varied host-guest materials, perovskite-type compounds are good candidates as their structures can be easily tailored by substituting atoms in the host lattice and/or changing the size/shape of the caged cations.<sup>14-17</sup> This high structural flexibility provides material scientists a large imaginary space to design and prepare new perovskite-type

materials with desired properties. Many studies, both theoretical and experimental, have been devoted to correlating molecular structure and motions with macroscopic properties.<sup>8,18-21</sup> However, it becomes apparent that, although the structure of perovskite-type compounds can be precisely adjusted to attain the desired purposes, the molecular motions are not always well controlled.<sup>22-30</sup> In many cases, the strong interplay between the host lattice and the caged molecules makes the motions of the caged molecules become much more complicated than initially thought. Without a deep understanding of the interplay between the host lattice and the caged molecules, to effectively predict and design perovskite-type materials with desired properties is very difficult.

On probing molecular dynamics in varied functional materials, solid state NMR (SSNMR) has been proven to be a particularly powerful technique.<sup>31,32</sup> The main merit of solid state NMR is its capability of monitoring the molecular motions over a wide frequency range from less than Hz to over MHz.<sup>33</sup> Moreover, some NMR methods such as wide line <sup>2</sup>H NMR and chemical shift anisotropy (CSA) analysis can provide not only the information on the motion frequency but

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also the geometry of molecular motion that is often strongly associated with the local environment of the probed molecule or group.<sup>34–36</sup> Analyzing the origin of the characteristic motional geometry thus can offer an opportunity to unveil the delicate interplay between the molecular motion and the local environment, which usually cannot be obtained by the other analytical techniques such as X-ray diffraction or electron microscopy techniques such as scan electronic microscopy (SEM) and transmission electron microscopy (TEM).

Here, an example is presented of how, in well-designed hybrid perovskite crystals, a small change in the host lattices can induce significant dynamic changes of the caged cations and, in turn, different macroscopic dielectric states. The samples two hybrid organic-inorganic perovskite (HOIP) compounds,  $(MA)_2[B'Co(CN)_6]$  (B' = K(I), 1; Na(I), 2), were designed to have the same caged cations (i.e., the MA cations) and very similar host lattices. The only structural difference between the two compounds is the alkali metal ion in the host lattices, that is,  $K^+$  in 1 and Na<sup>+</sup> in 2. Replacing  $K^+$ with Na<sup>+</sup> results in a different lattice size, which is anticipated to cause changes in the motions of the caged MA cations and dielectric transition behaviors. In the previous work,<sup>27</sup> Shi et al. solved the crystal structures of 1 before and after the transition. For 2, only the crystal structure in the high-temperature phase has been solved, while the crystal structures in the intermediate- and low-temperature phases still remain unknown.<sup>27</sup> In this work, first, we tried to solve the crystal structures of 2 in the intermediate- and low-temperature phases. Then, using solid state <sup>2</sup>H NMR, the dynamics of the caged MA cations before and after the transitions were revealed in detail and correlated with the different dielectric states. Using solid state <sup>59</sup>Co NMR, the dynamic changes in the host lattices before and after the transitions that accompany the changes in the caged MA cation dynamics were unveiled, demonstrating the intriguing interplay between the motions of the MA cations and the host lattices. On the basis of these observations, the molecular origins of the different dielectric transitions are discussed in detail.

# EXPERIMENTAL SECTION

Sample Preparation. An aqueous solution (50 mL) containing  $Na_3[Co(CN)_6]$  (2.84 g, 10 mmol) and (MA)Cl (2.03 g, 30 mmol) was evaporated to produce pale-yellow block crystals of 2. Compound 1 was prepared by the same method.

1: Ýield 88% (based on  $K_3[Co(CN)_6]$ ). Theoretical composition calculated (%) for  $C_8H_{12}CoKN_8$  (318.29): C 30.19, H 3.80, N 35.21; measured composition: C 30.38, H 3.80, N 34.90.

2: Yield 82% (based on Na<sub>3</sub>[Co(CN)<sub>6</sub>]). Theoretical composition calculated (%) for  $C_8H_{12}CoN_8Na$  (302.18): C 31.80, H 4.00, N 37.08; measured composition: C 32.18, H 4.19, N 36.18.

For deuterated samples, deuterated (MA)Cl was first prepared by H/D exchange of MA cations in deuterated water (repeated five times via a dissolution–drying process). Then the deuterated (MA)Cl was used with  $D_2O$  (99.8 atom % D, Sigma-Aldrich) to prepare 1-d<sub>3</sub> and 2-d<sub>3</sub>.

**Dielectric Measurements.** Complex dielectric permittivity was measured on crystalline powdered samples in the AglpelletlAg sandwich with an Agilent 4294A impedance analyzer at 1 MHz frequency with an applied electric field of 0.5 V.

**X-ray Diffraction Experiments.** X-ray diffraction experiments were carried out at various temperatures using a Rigaku Saturn 724<sup>+</sup> diffractometer with a Mo–K $\alpha$  radiation source ( $\lambda = 0.71075$  Å) or a Bruker D8 Venture diffractometer with a Cu–K $\alpha$  radiation source ( $\lambda = 1.54178$  Å). Data collection, cell refinement, and data reduction were performed using the CrystalClear software package. The

structures were solved by direct methods and successive Fourier synthesis and then refined by full-matrix least-squares refinements on  $F^2$  using the SHELXTL software package.

**Solid State NMR (SSNMR) Experiments.** The wide line <sup>2</sup>H and <sup>59</sup>Co NMR studies were performed on a Bruker Avance III 300 spectrometer operating at 46.07 MHz for <sup>2</sup>H and 70.84 MHz for <sup>59</sup>Co. A Bruker two-channel static PE probe with a homemade 2.5 mm coil was used to record the <sup>2</sup>H and <sup>59</sup>Co spectra. The <sup>2</sup>H spectra were acquired using the solid echo sequence (90° –  $\tau$  – 90° –  $\tau$  – acquire). The <sup>2</sup>H pulse width was 2  $\mu$ s at an RF field strength of  $\gamma$ B<sub>1</sub>/ $2\pi$  = 125 kHz. The refocusing delays,  $\tau$ , range from 16 to 30  $\mu$ s. The <sup>2</sup>H patterns were simulated using the Weblab software (http://weblab.mpip-mainz.mpg.de/weblab/).<sup>32</sup> The <sup>59</sup>Co spectra were acquired using the EASY<sup>37</sup> pulse sequence. The <sup>59</sup>Co excitation pulse width was 0.5  $\mu$ s at an RF field strength of  $\gamma$ B<sub>1</sub>/ $2\pi$  = 100 kHz.

# RESULTS AND DISCUSSION

**Summary of the Crystal Structures of 1 and 2.** Details of the single-crystal structure study were reported previously.<sup>27</sup> As a background, we would like to summarize the key points of the structures of 1 and 2. Both of the compounds have the same double perovskite structures (Figure 1, Tables S1 and S1)



Figure 1. Schematic illustration of the cage structures of 1 and 2 in different phases. The C atom of the totally disordered MA cation above  $T_{tr1}$  is refined as N atom (a model to show facial reorientations). Hydrogen atoms are omitted for clarity. The temperature scale is arbitrary.

S2), but show strikingly different phase transitions and dielectric transition properties. 1 exhibits only one phase transition at  $T_{tr1} = 423$  K, whereas 2 undergoes two phase transitions at  $T_{tr2} = 200$  K and  $T_{tr1} = 260$  K (see Figures S1 and S2). Above  $T_{tr1}$ , the X-ray data show that both the compounds adopt the cubic space group  $Fm\overline{3}m$ . The anionic cage  $[B'_4Co_4(CN)A_{12}]$  is regular with an edge length (Co- $C\equiv N-B'$ ) of 5.727 Å for 1 at 463 K and 5.502 Å for 2 at 293 K. The MA cation confined in the cage shows a highly orientation disorder and is refined with a face ([100]

orientations) model, similar to the one in the roomtemperature phase of (MA)[PbI<sub>3</sub>]. Below  $T_{trl}$ , 1 undergoes a drastic change in structure to the monoclinic space group C2/ c. The anionic cage is highly distorted due to the tilting of the rigid Co(CN)<sub>6</sub> component, accompanied by the distortion of the relatively labile KN<sub>6</sub> octahedron. In particular, the MA cation becomes totally ordered.

As for 2, it adopts the same cubic system above  $T_{tr1}$  (293 K) as 1. The crystal structure of 2 at above  $T_{tr1}$  was reported in the literature.<sup>27</sup> However, its structures in the intermediate- and low-temperature phases were not resolved previously probably due to crystal quality deterioration. In this study, we solve the tentative structures for the two phases. Between  $T_{tr1}$  and  $T_{tr2}$ at 220 K, 2 adopts the monoclinic space group with C2/c and cell parameters of a = 10.8938(3) Å, b = 11.0012(3) Å, c =10.9958(4) Å, and  $\beta = 89.9970(3)^{\circ}$ , very close to those obtained above  $T_{tr1}$ . Below  $T_{tr2}$ , 2 undergoes another drastic change in structure in the monoclinic space group C2/c with cell parameters of a = 13.1956(19) Å, b = 8.0426(11) Å, c =7.4220(11) Å, and  $\beta = 124.2300^{\circ}$  at 190 K. The distorted structure is the result of tilting of the rigid  $Co(CN)_6$  unit. In both structures, the caged MA cation becomes ordered with certain orientations. Note that the present structures are probably not the final correct ones and they would better be treated as references to the following dynamic SSNMR study.

Motions of MA Cation in  $1 \cdot d_3$ . To obtain a better understanding of the phase transitions and the dielectric transitions of 1 and 2, the molecular dynamics of the caged MA cations were investigated by wide-line <sup>2</sup>H NMR. This NMR method can determine the geometry and frequency of rotational motions on a time-scale ranging from  $10^{-4}$  to  $10^{-8}$ s.<sup>32,38</sup> Two deuterated samples,  $1 \cdot d_3$  and  $2 \cdot d_3$ , in which the  $-NH_3$  group of MA is deuterated, were prepared for the study. Figure 2 demonstrates the temperature dependent <sup>2</sup>H NMR patterns of  $1 \cdot d_3$ . By analyzing the patterns, detailed information on the reorientation processes of MA in  $1 \cdot d_3$ was obtained.

Low-Temperature Phase ( $T < T_{tr1}$ ). At temperatures below  $T_{tr1}$  (e.g., T = 295 K), the static <sup>2</sup>H line shows almost a characteristic Pake pattern shape with a quadrupolar splitting



Figure 2. Simulated (gray line) and experimental (black line) solid state <sup>2</sup>H NMR patterns of  $1-d_3$  from 295 to 425 K. The <sup>2</sup>H patterns were simulated using the NMR Weblab (http://weblab.mpip-mainz.mpg.de/weblab/). The cartoon picture on the left illustrates the motion model of the MA cations. The MA hydrogen atoms are omitted for clarity.

of about 42 kHz. This quadrupolar splitting value indicates that the MA cations undergo an axial rotation along the C-N axis (see Figure S3). The horns of the pattern show a slight bending. This can be attributed to the local wiggling motion along the axis  $C_{n1}$  with an open angle of  $\theta_1$  (see Model I in Figure 2 and Figure S4). With increasing temperature, the patterns gradually develop into a typical Pake line shape with a further reduction in quadrupolar splitting, indicating that the MA cations have gained more motional freedom. Analyzing the line shape of the patterns above 395 K yields asymmetry parameters,  $\eta$ , all equal to 0, indicating that the MA cations have gained some additional motions. In the pattern simulation, a processional motion for MA (i.e., an axial rotation with an open angle,  $\theta_{2}$ , between the C–N bond and the rotation axis  $C_{n2}$ ) (see Model I in Figure 2, and Figures S5 and S6) was introduced. The simulated patterns (the gray lines) fit well with the experimental ones. But note that the processional motion model is not a unique model that can average  $\eta$  to 0, and the value of the angle,  $\theta_{2}$ , in the processional motion model varies with the  $\eta$  value. At 395 K, a small, but clear, sharp signal starts to appear in the middle of the pattern. This signal can be attributed to the fast isotropic tumbling motion of the MA cation. The coexistence of the sharp signal and the wide Pake pattern in the spectrum indicates that a portion of the MA cations in 1 start to undergo a fast isotropic tumbling motion before transition. This can be related to the pretransition phenomenon in the dielectric transition.<sup>12</sup>

High-Temperature Phase  $(T \ge T_{trl})$ . A sudden change is observed in the pattern after the transition (T = 425 K), where the Pake line shape disappears completely and only the sharp signal remains. This indicates that all of the MA cations in 1-d<sub>3</sub> have a fast isotropic tumbling motion.<sup>39,40</sup> This transition temperature is very close to the temperature observed in DSC and dielectric measurements, suggesting the same molecular origin for these transitions.

Motions of MA Cations in 2-d<sub>3</sub>. Figure 3 demonstrates the temperature dependent <sup>2</sup>H NMR patterns of 2-d<sub>3</sub>. Marked changes are observed in the patterns, indicating the significant reorientation of MA cations at different temperatures.

Low-Temperature Phase ( $T \leq T_{tr2}$ ). At 140 K, the patterns of **2-d**<sub>3</sub> show a Pake line shape spanning ca. 42 kHz in width, indicating that the MA cations undergo axial rotation along the C-N axis. A slight bending in the horns of the pattern can be attributed to the wiggling of the MA cations (**Model II**). Analysis of the line shape shows that the asymmetric parameter,  $\eta$ , is not equal to 0, indicating that the processional motion from **Model I** most likely is not present in **2-d**<sub>3</sub>.

Intermediate Phase ( $T_{tr2} < T < T_{tr1}$ ). When the temperature is between  $T_{tr2}$  and  $T_{tr1}$  (e.g., T = 210 K), the pattern shows a clear change in the line shape compared to that before the first transition. The patterns in this temperature range can be simulated with a model considering that the MA cations undergo a 2-site jump about the  $C_n$  axis inclined to the C–N bond at an angle of 48°, with a jump angle of 90° (see **Model III**). On the basis of **Model III**, we have successfully simulated the patterns (the gray lines) as they match very well with the experimental ones. From the simulation, we are able to obtain the jump rates, k. The Arrhenius plot of the jump rates,  $k = k_0$  $\exp(-E_a/RT)$ , yields an activation energy  $E_a = 33.2$  kJ/mol and a pre-exponential factor  $k_0 = 1.66 \times 10^{13}$  s<sup>-1</sup>.

*High-Temperature Phase* ( $T \ge T_{trl}$ ). Above  $T_{trl}$ , the patterns exhibit a sudden change in the line shape. The



**Figure 3.** (a) The three motion models for the MA cations. The MA hydrogen atoms are omitted for clarity. (b) Simulated (gray line) and experimental (black line) solid state <sup>2</sup>H NMR patterns of **2-d**<sub>3</sub> from 140 to 400 K. Below  $T_{tr2}$ , the patterns can be simulated using **Model II**. Between  $T_{tr2}$  and  $T_{tr1}$ , the patterns can be simulated using **Model III**. To obtain the best fit, an additional component based on **Model II** was added into the signal. Above  $T_{tr1}$ , the patterns can be simulated using **Model II** weblab. (c) The Arrhenius plot of the 2-site jump rates, *k*. The jump rates were obtained from the <sup>2</sup>H pattern simulation.

significantly reduced signal width indicates that the MA cations undergo fast dynamics. However, the characteristic splitting in the patterns indicates that the motions of the MA cations are still not isotropic. To fit the patterns, we introduced **Model IV**, where the MA cations perform a 4-site jump motion (or an axial rotation) about the  $C_n$  axis inclined to the C–N bond at an angle,  $\theta$ . By varying  $\theta$ , the patterns acquired above  $T_{tr1}$  can be simulated.

**Correlating the Motions of MA Cations with Dielectric Transitions.** On the basis of the NMR observations, we were able to correlate the motions of MA cations with the dielectric transitions of 1 and 2 (see Figure 4). It is known that dipolar reorientation can contribute



Figure 4. Temperature dependence of the real part of the dielectric constant of powder samples: (a) 1 and (b) 2 in the heating and cooling modes. The frequency is 1 MHz.

significantly to the dielectric response.<sup>36,41</sup> Below  $T_{trl}$ , the polar MA cations of **1** are ordered in the cages. The axial rotation of MA around the C–N bond cannot induce dipolar reorientation and thus makes no contribution to the dielectric response. The gradual, but continuous, increase in the dielectric value below  $T_{trl}$  is likely from the electronic and ionic displacements and the local motions (e.g., the wiggling motion and the processional motion) of MA, which can result in the oscillation of the dipolar moment in the plane perpendicular to the  $C_n$  axis (see Figure 5a). Right below



**Figure 5.** Depictions of (a) the wiggling motion of an MA cation and the resultant oscillation of the dipolar moment; (b) the 2-site jump motion of an MA cation and the resultant oscillation of the dipolar moment; and (c) the 4-site jump motion of an MA cation and the resultant oscillation of the dipolar moment. Left: The red arrows denote the dipolar moment of MA. Right: The red arrows denote the projection of the dipolar moment of MA under each motion.

 $T_{\rm tr1}$ , a portion of the MA cations become disordered by undergoing a fast isotropic tumbling motion. These activated MA cations may also contribute to the increase in the dielectric values before the transition. Above  $T_{\rm tr1}$ , all of the MA cations undergo the fast isotropic tumbling motion. Reflecting this big change in the state of the MA cations, the dielectric value jumps to the high-dielectric state.

Unlike 1, 2 has two phase transitions. The first one has a transition temperature of  $T_{tr2}$  = 200 K. Below  $T_{tr2}$ , the MA cations exhibit the local wiggling and might partially contribute to the slight increase in the dielectric values (see Figure 5a). Above  $T_{tr2}$ , the MA cations start to exhibit the 2-site jump motion. This motion can induce dipolar reorientation and thus may contribute to the increase in the dielectric values (see Figure 5b). With increasing temperature, more and more MA cations start to exhibit this type of jump motion, resulting in a clear increase in the dielectric values between  $T_{tr2}$  and  $T_{tr1}$ . At  $T_{tr1}$ , all of the MA cations start to exhibit 4-site jump motion

(or an axial rotation), resulting in the dipolar reorientation of a large amplitude (see Figure 5c) and consequently the dielectric switching at  $T_{trl}$ .

The origin of different dynamics of MA cations in 1 and 2 during the dielectric transitions can be attributed to the different geometric restrictions on the MA cations caused by the different accessible volume in the host lattice. Take the cubic phase of 1 and 2 above  $T_{tr1}$  for example. The NMR results show that, above  $T_{trl}$ , the MA cations in 2 undergo 4site jump motion, whereas those in 1 immediately experience an isotropic tumbling motion. The different size in the cubic cage between 1 and 2 provides a hint for the origin of this difference. The X-ray results show that, above  $T_{trl}$ , the lattice parameters are a = b = c = 11.454(6) Å for 1 (T = 463 K), and a = b = c = 11.003(4) Å for 2 (T = 293 K). The side length of 1 (see Figure 1) is 0.451 Å longer than that of 2. On one hand, the longer side length indicates that the MA cations residing in the cage of 1 have more space to move, providing a qualitative understanding of the different dynamics of MA cations in the cubic phases of 1 and 2. On the other hand, the relatively small side length of 2 indicates that the caged MA cations in 2 have closer contact with the host lattice, a clue to the interplay between the host lattice and the caged MA cation, which will be discussed in the next section. Reflecting the influence of such an interplay, 1 and 2 have different Goldschmidt tolerance factors and thus different cubic-disordered phase transition temperatures.<sup>27</sup>

Interplay between the Motions of MA Cations and the Host Lattices. Reflecting the interplay between the caged cation and the host lattice, the  $[Co(CN)_6]^{3-}$  anions in the host lattice of the samples show intriguing dynamic changes that accompany the motional changes of MA cations. Figure 6a exhibits the static <sup>59</sup>Co (I = 7/2) NMR spectra of 1-d<sub>3</sub> from



**Figure 6.** Temperature dependent <sup>59</sup>Co NMR powder patterns of (a) **1-d**<sub>3</sub> and (b) **2-d**<sub>3</sub>. These spectra were acquired at a 300 MHz NMR instrument. The chemical shift scale was calibrated using a 1M  $K_3[Co(CN)_6]$  aqueous solution ( $\delta = 0$  ppm). LT phase: Lowtemperature phase. HT phase: High-Temperature phase.

315 to 450 K. Below  $T_{tr1}$  (315–415 K), the signals show the characteristic quadrupole line shape, whereas the signal line shape suddenly changes into a sharp and almost isotropic one when the temperature is above  $T_{tr1}$ . A similar change is also observed in 2-d<sub>3</sub> (see Figure 6b): below  $T_{tr2}$  (LT phase), the signal line shape shows two edges with one horn in the middle, which are typical features of an unsymmetrical tensor. When the temperature is between  $T_{tr2}$  and  $T_{tr1}$  (intermediate phase), the line shape shows the features close to those of an axially symmetric tensor. When the temperature is above  $T_{tr1}$  (HT phase), the signals show a clear narrowing in the width and the line shape approaches an isotropic one.

The <sup>59</sup>Co NMR signal is strongly influenced by the quadrupole coupling and the chemical shift anisotropy, both of which depend on the site symmetry of  $\text{Co.}^{42-44}$  In compounds lacking high symmetry at the Co site, the large electric field gradients (EFGs) may result in large second order quadrupole broadening of the central transition.<sup>45</sup> This explains the origin of the wide signals in the low symmetric phases of the samples (the LT phase for 1-d<sub>3</sub>, and the LT and the intermediate phase for  $2-d_3$ ). In principle, analysis of the line shape can provide the information on the quadrupole interaction and the chemical shift anisotropy, which can be further used to extract detailed dynamic information on the  $[Co(CN)_6]^{3-}$  anions.<sup>46,47</sup> Further experimental study using the <sup>59</sup>Co NMR in different external magnetic fields as well as a simulation study of the pattern line shape is the subject of ongoing studies in our laboratory. In the cubic phases of 1-d<sub>3</sub> and  $2-d_3$ , the high symmetry of the Co sites results in a significant attenuation of both the quadrupole coupling and the chemical shift anisotropy. This explains the origin of the narrow signals of  $1-d_3$  and  $2-d_3$  in the high-temperature phases. Reflecting the symmetry change of the Co sites during the phase transitions, the changes in the <sup>59</sup>Co NMR spectra in Figure 6 clearly indicate that the  $[Co(CN)_6]^{3-}$  anions undergo delicate adjustments during the phase transitions. The  $[Co(CN)_6]^{3-}$  anion is the key linker of the host lattice. The adjustments in  $[Co(CN)_6]^{3-}$  thus clearly evidence the dynamic changes of the host lattice. At the same time, the similar transition temperatures obtained from the <sup>59</sup>Co NMR of  $[Co(CN)_6]^{3-}$  and the <sup>2</sup>H NMR of MA cations indicate the coupling between the caged cation and the host lattice. But so far, we have not been able to tell whether the motions of MA cations initiate the adjustment of the host lattices, or inversely, the adjustment of host lattices initiates the motions of MA cations, or if the motions of MA cations just coincide with the adjustment of the host lattices.

The knowledge of the interplay between the host lattice and the caged MA cation provides a deep understanding of the origin of the dielectric permittivity of 1 and 2. From the point of view of charge distribution, the host lattices of 1 and 2 both have an equivalent negative charge which balances the positive charge of the caged MA cations. If the center of the equivalent negative charge from the host lattice does not completely overlap with the center of the positive charge of the MA cation, an additional dipole moment between the positive charge and the equivalent negative charge may exist. When changing temperature, it is very likely that the interplay between the host lattice and the caged MA cation will induce the change in the additional dipole moment, thus contributing to the dielectric permittivity of the sample. Therefore, the interplay between the host lattice and the caged MA cation indicates that not only the reorientation of the dipole moment of the MA cation but also the accompanying change in the host lattice can contribute to the dielectric permittivity.

# CONCLUSIONS

Dynamic changes of the caged MA cations and the host lattice in two perovskite-type compounds,  $(MA)_2[B'Co(CN)_6](B' =$ K and Na), were investigated in great detail by solid state <sup>2</sup>H and <sup>59</sup>Co NMR. It was found that the two compounds exhibit marked differences in MA dynamics during the phase and dielectric transitions despite having highly similar crystal structures. The MA cation in the K compound undergoes a dynamic change from local wiggling motion to fast isotropic tumbling motion, whereas, in the Na compound, the MA cation undergoes dynamic changes from local wiggling to 2-site jump and then 4-site jump, in addition to the ever-present C-N axial rotation. This is strikingly different from the K compound. Accompanying the motions of MA cations, the host lattices of 1 and 2 show dynamic changes coincidentally occurring at the same transition temperatures, demonstrating the intriguing interplay between the crystal lattice and the motions of caged cations. This information on the interplay between the caged cations and the host lattices of 1 and 2 provides new insights into the dielectric transition behaviors of compounds on a molecular level.

# ASSOCIATED CONTENT

# **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b00497.

DSC curves, temperature dependent dielectric measurements, simulated <sup>2</sup>H NMR patterns, and crystallographic data and structural refinement details (PDF)

## **Accession Codes**

CCDC 1878215 and 1878216 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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