

Supporting Information

A hybrid double perovskite ferroelastic exhibiting the highest number of orientation states

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Experimental

Synthesis

$\text{Ag}_3[\text{Co}(\text{CN})_6]$ was synthesized as a precipitate from $\text{K}_3[\text{Co}(\text{CN})_6]$ reacting with AgNO_3 .^[S1] Trimethylamine N-oxide hydrochloride, $(\text{CH}_3)_3\text{NO}\cdot\text{HCl}$, was obtained by reaction of the trimethylamine N-oxide dehydrate with 36.5% aqueous HCl. Stirring of aqueous solution containing $\text{Ag}_3[\text{Co}(\text{CN})_6]$, ammonium chloride, and trimethylamine N-oxide hydrochloride in a ratio of 1:1:2 at room temperature for one hour. After the AgCl precipitate was filtrated, the pale yellow block crystals of $(\text{Me}_3\text{NOH})_2(\text{NH}_4)[\text{Co}(\text{CN})_6]$ (**1**) were obtained by slow evaporation of solution within several days, in a yield of 87% based on Co.

X-ray Crystallographic Analysis

The *in-situ* variable-temperature single-crystal diffraction intensities data were collected on a Bruker Smart APEX diffractometer (Mo K_{α} , $\lambda = 0.71073 \text{ \AA}$). The APEX3 software package was used for data collection, cell refinement and data reduction. Using Olex2 software,^[S2] the structures were solved by using Intrinsic Phasing with the SHELXT structure solution program and using full-matrix least-squares method with the SHELXL refinement program.^[S3] Non-hydrogen atoms were refined anisotropically and the positions of the hydrogen atoms were generated geometrically. Crystallographic data and structural refinements are summarized in Table S1. Selected bond distances and bond angles are listed in Tables S2-S7. CCDC numbers: 2264543-2264544. Powder X-ray diffraction (PXRD) patterns (Cu K_{α} , $\lambda = 1.54184 \text{ \AA}$) were collected on Panalytical Empyrean with Cu- K_{α} X-ray radiation (40 kV, 45 mA).

Thermal Analysis

Thermogravimetric analysis (TGA) was carried out on a Hitachi NEXTA STA300 with a heating rate of 10 K min^{-1} from 295 to 673 K under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was carried out on a Perkin Elmer Pyris Diamond DSC instrument under a nitrogen atmosphere in aluminium crucibles with heating and cooling rates of 10 K min^{-1} from 298 to 420 K.

Dielectric measurements

The dielectric measurement was carried on a Hewlett-Packard 4284A LCR meter at various frequencies, with an applied voltage of 1.0 V and a temperature sweeping rate of 5 K min⁻¹ approximately in the range of 298–420 K under a programmable cryogenic cooling system. The powder sample of **1** was ground and pressed into tablets. The capacitors were made by painting the two faces of tablet sample with silver conducting paste and using copper wires as the electrodes.

Polarization microscopy

The observations of ferroelastic domain structure were recorded with a polarized microscope Olympus BX53M in transmission mode at room temperature.

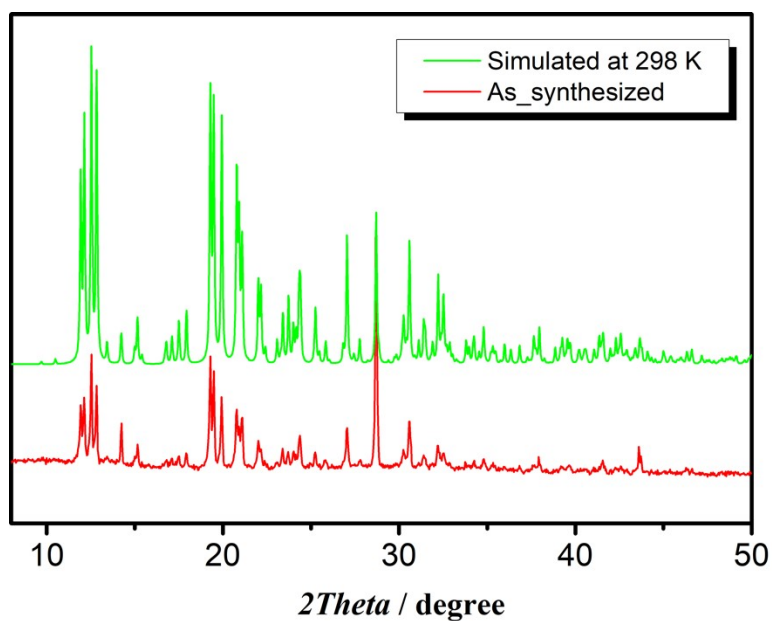


Fig. S1 PXRd patterns confirm the phase purity of the as-synthesized sample of **1** at room temperature.

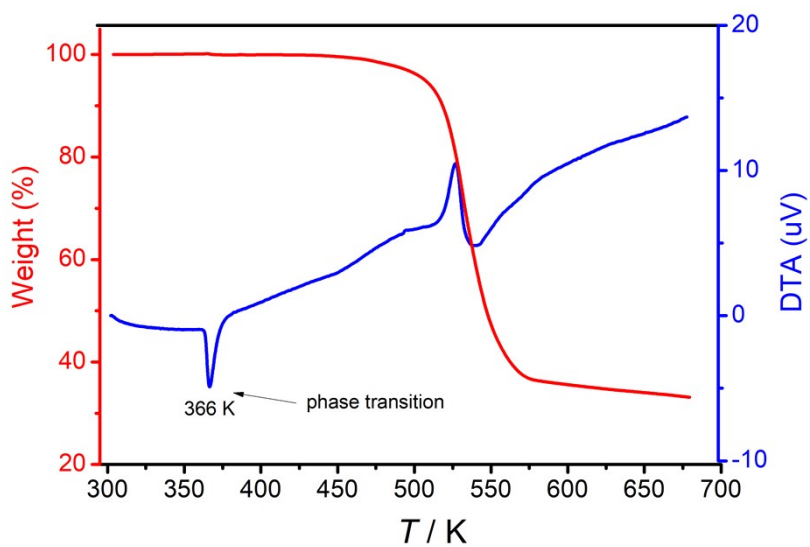


Fig. S2 Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) thermograms of **1**.

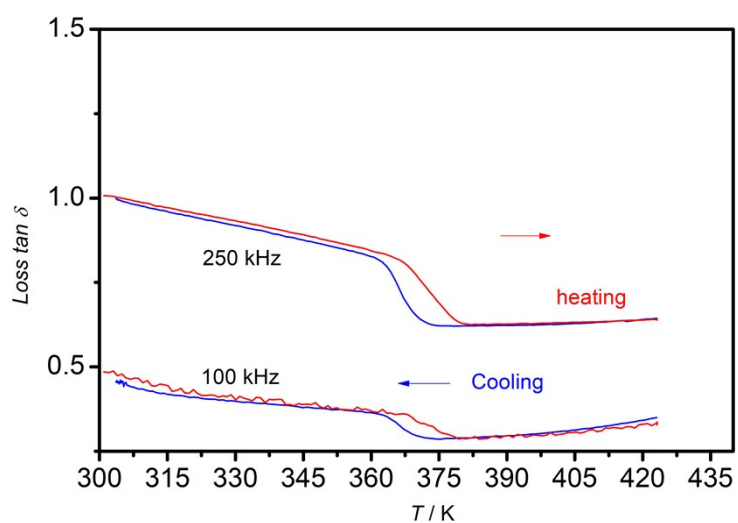


Fig. S3 Temperature dependence of $\tan \delta$ of **1** at 100 kHz and 250 kHz during a heating and cooling cycle, respectively.

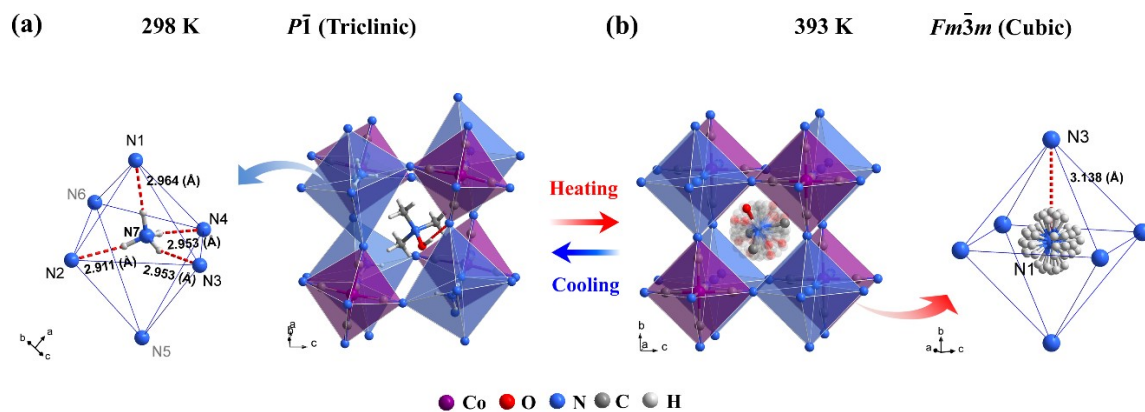


Fig. S4 Structural unit of **1** in (a) the ferroelastic phase at 298 K, and (b) the paraelectric phase at 393 K.

Calculation of spontaneous strain

For the present $m\bar{3}mF\bar{1}$ ferroelastic species, as the cell contents of PP is different from those of FP, a necessary transformation matrix, $(0.5 \ 0.5 \ 0, 0.5 \ 0.5 \ 0, 0 \ 0 \ 1)$, was applied to the cubic cell of PP, giving a transformed cell lattice as, $a_0 = b_0 = 8.802 \text{ \AA}$, $c_0 = 12.4475 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$. As shown in Fig. S4, the unit cell contents of the transformed lattice of PP matches that of FP.

According to a generalized expression of the stain tensor regardless of symmetry,^[S4] the spontaneous strain tensor in FP is expressed as:

$$\varepsilon_{ij} = \begin{bmatrix} \frac{a \sin \gamma}{a_0 \sin \gamma_0} - 1 & \frac{1}{2} \left(\frac{a \cos \gamma}{a_0 \sin \gamma_0} - \frac{b \cos \gamma_0}{b_0 \sin \gamma_0} \right) & \frac{1}{2} \left(\frac{a \sin \gamma \cos \beta_0^*}{a_0 \sin \gamma_0 \sin \beta_0^*} - \frac{c \sin \alpha \cos \beta^*}{c_0 \sin \alpha_0 \sin \beta_0^*} \right) \\ 0 & \frac{b}{b_0} - 1 & \frac{1}{2} \left(\frac{c \cos \alpha}{c_0 \sin \alpha_0 \sin \beta_0^*} - \frac{b \cos \alpha_0}{b_0 \sin \alpha_0 \sin \beta_0^*} + \frac{\cos \beta_0^*}{\sin \beta_0^* \sin \gamma_0} \left(\frac{a \cos \gamma}{a_0} - \frac{b \cos \gamma_0}{b_0} \right) \right) \\ 0 & 0 & \frac{c \sin \alpha \sin \beta^*}{c_0 \sin \alpha_0 \sin \beta_0^*} - 1 \end{bmatrix}$$

In the equation, a , b , c , α , β and γ refer to the cell parameters of the low-symmetry form (FP), and a_0 , b_0 , c_0 , α_0 , β_0 and γ_0 are the transformed cell parameters of the high-symmetry form (PP). β^* and β_0^* are reciprocal lattice angles.

The total spontaneous strain (ε_{ss}) can be calculated with cell parameters measured at 298 K (FP) and 393 K (PP). (Table S1):

$$\varepsilon_{ss} = \sqrt{\sum_{ij} \varepsilon_{ij}^2} = 0.105$$

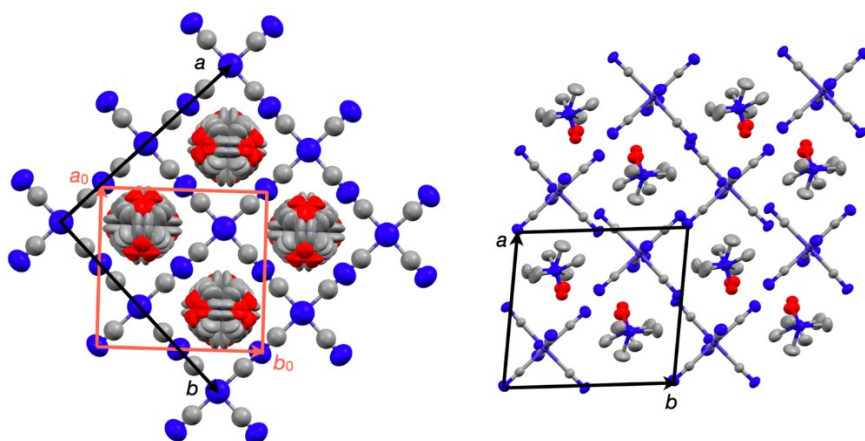


Fig. S5 Transformation of the cubic PP lattice (left) to match the unit cell contents of FP (right).

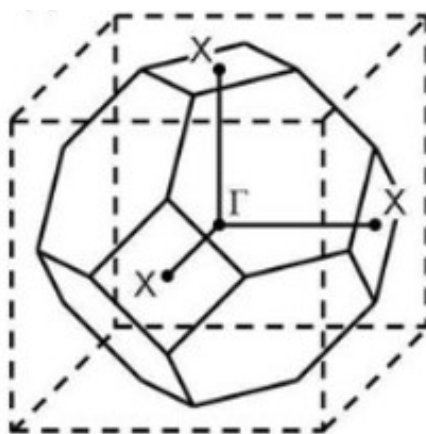


Fig. S6 Brillouin zone of the face-centered cubic structure. Dashed lines outline the Brillouin zone of the simple cubic (perovskite) structure.

Table S1. Crystal data and structure refinement parameters for **1** ferroelastic phase (FP) and paraelastic phase (PP).

Formula	(Me ₃ NOH) ₂ (NH ₄)[Co(CN) ₆]	
<i>T</i> (K)	298(2)	393(2)
Phases	FP	PP
Crystal system	Triclinic	Cubic
Space group	<i>P</i> $\bar{1}$	<i>Fm</i> $\bar{3}m$
<i>a</i> /Å	8.481(2)	12.4475(8)
<i>b</i> /Å	9.175(3)	12.4475(8)
<i>c</i> /Å	12.439(3)	12.4475(8)
α ^o	88.801(7)	90
β ^o	88.422(7)	90
γ ^o	83.065(7)	90
<i>V</i> /Å ³	960.3(4)	1928.6(4)
<i>Z</i>	2	4
<i>D_c</i> /g cm ⁻³	1.333	1.327
μ (mm ⁻¹)	0.917	0.913
reflns coll.	20898	2082
unique reflns	5348	129
<i>R</i> ₁ ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0336	0.0361
<i>wR</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0708	0.1071
<i>R</i> ₁ ^a (all data)	0.0597	0.0590
<i>wR</i> ₂ ^b (all data)	0.0793	0.1288
GOF	1.027	1.291
CCDC number	2264544	2264543

$${}^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|; {}^b wR_2 = [\sum \omega(F_o^2 - F_c^2)^2 / \sum \omega(F_o^2)^2]^{1/2}.$$

Table S2. The parameters of hydrogen-bonding interactions for **1** at 298 K

D	H	A	$d(\mathbf{D}\cdots\mathbf{A})/\text{\AA}$	$\angle\mathbf{D}-\mathbf{H}\cdots\mathbf{A}/^\circ$
O1	H1	N5	2.670(2)	173.3
N7	H7D	N3 ¹	2.953(2)	158.3
N7	H7E	N4 ²	2.953(2)	161.8
N7	H7F	N2 ³	2.911(2)	141.8
N7	H7G	N1 ⁴	2.964(2)	180.0
O2	H2	N6	2.806(2)	166.7

Symmetry codes: ¹1-x,1-y,-z; ²-1+x,+y,+z; ³+x,-1+y,+z; ⁴-1+x,-1+y,+z

Table S3. Bond Lengths for **1** at 298 K.

Atom	Atom	Length/\AA	Atom	Atom	Length/\AA
Co1	C2	1.901(2)	N8	C9	1.480(3)
Co1	C4	1.907(2)	N1	C1	1.145(2)
Co1	C1	1.901(2)	N9	C10	1.483(2)
Co1	C3	1.896(2)	N9	C11	1.481(2)
Co1	C6	1.901(2)	N9	C12	1.486(2)
Co1	C5	1.887(2)	N4	C4	1.145(2)
O1	N9	1.416(2)	N2	C2	1.141(2)
N8	O2	1.418 (2)	N5	C5	1.145(2)
N8	C8	1.480(2)	N3	C3	1.146(2)
N8	C7	1.474(2)	N6	C6	1.148(2)

Table S4. Bond Angles for **1** at 298 K.

\angle Atom	Atom	Atom	Angle/ $^{\circ}$	\angle Atom	Atom	Atom	Angle/ $^{\circ}$
C2	Co1	C4	178.28(7)	O2	N8	C9	104.7(2)
C2	Co1	C1	90.41(7)	C8	N8	C9	111.5(2)
C2	Co1	C6	87.74(6)	C7	N8	C8	111.0(2)
C1	Co1	C4	91.27(7)	C7	N8	C9	110.9(2)
C3	Co1	C2	89.52(7)	O1	N9	C10	109.3(1)
C3	Co1	C4	90.88(7)	O1	N9	C11	109.7(1)
C3	Co1	C1	89.51(7)	O1	N9	C12	104.2(2)
C3	Co1	C6	176.60(6)	C10	N9	C12	111.0(2)
C6	Co1	C4	91.79(7)	C11	N9	C10	111.1(2)
C6	Co1	C1	92.52(7)	C11	N9	C12	111.4(2)
C5	Co1	C2	90.28(7)	N2	C2	Co1	179.0(2)
C5	Co1	C4	88.06(7)	N4	C4	Co1	178.0(2)
C5	Co1	C1	177.09(7)	N1	C1	Co1	177.8(2)
C5	Co1	C3	87.67(7)	N3	C3	Co1	177.8(2)
C5	Co1	C6	90.33(7)	N6	C6	Co1	174.9(1)
O2	N8	C8	108.8(1)	N5	C5	Co1	177.37(2)
O2	N8	C7	109.8(2)				

Table S5. The parameters of hydrogen-bonding interactions for **1** at 393 K

D	H	A	d(D-A)/Å	∠D-H-A/°
N1	H1C	N3	3.138(7)	153.2
N1	H1D	N3 ¹	3.138(7)	180.0

Symmetry codes: ¹-1/2+z,1+x,-1/2+y

Table S6. Bond Lengths for **1** at 393 K.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co1	C1 ¹	1.889(10)	C1	N3	1.197(10)
Co1	C1 ²	1.889(10)	N2	C2	1.494(19)
Co1	C1 ³	1.889(10)	N2	C3	1.494(19)
Co1	C1 ⁴	1.889(10)	N2	C4	1.490(19)
Co1	C1 ⁵	1.889(10)	N2	O1	1.422(2)
Co1	C1	1.889(10)			

Symmetry codes: ¹1-y,2-z,1-x; ²-x,2-y,2-z; ³-1+y,+z,1+x; ⁴1-z,1-x,2-y; ⁵-1+z,1+x,+y

Table S7. Bond Angles for **1** at 393 K.

\angle Atom	Atom	Atom	Angle/ $^{\circ}$	\angle Atom	Atom	Atom	Angle/ $^{\circ}$
C1 ¹	Co1	C1 ²	180.0	C1 ²	Co1	C1 ⁵	90.000(1)
C1 ³	Co1	C1 ⁴	180.0	C1 ¹	Co1	C1	90.000(1)
C1 ¹	Co1	C1 ⁴	90.000(5)	C1 ²	Co1	C1 ⁴	90.000(1)
C1 ⁵	Co1	C1 ⁴	90.000(4)	C1 ⁵	Co1	C1	180.0
C1 ⁵	Co1	C1 ³	90.000(5)	N3	C1	Co1	180.0
C1 ³	Co1	C1	90.000(2)	C3	N2	C2	110.5(17)
C1 ¹	Co1	C1 ³	90.000(3)	C4	N2	C2	111.1(17)
C1 ¹	Co1	C1 ⁵	90.000(1)	C4	N2	C3	110.5(17)
C1 ²	Co1	C1 ³	90.000(5)	O1	N2	C2	108.0(17)
C1 ²	Co1	C1	90.000(1)	O1	N2	C3	108.0(17)
C1 ⁴	Co1	C1	90.000(2)	O1	N2	C4	108.7(17)

Symmetry codes: ¹1-y,2-z,1-x; ²-1+y,+z,1+x; ³-1+z,1+x,+y; ⁴1-z,1-x,2-y; ⁵-x,2-y,2-z

References

- [S1] A. L. Goodwin, M. Calleja, M. J. Conterio, M. T. Dove, J. S. O. Evans, D. A. Keen, L. Peters, M. G. *Science*, 2008, **319**, 794-797.
- [S2] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann. *J. Appl. Cryst.*, 2009, **42**, 339-341.
- [S3] G.M. Sheldrick. *Acta Cryst.*, 2015, **A71**, 3-8.
- [S4] J. L. Schlenker, G. V. Gibbs and M. B. Boisen, Jnr, *Acta Cryst.*, 1978, **A34**, 52-54.