

Ferroic multipolar order and disorder in cyanoelpasolite
molecular perovskites
Supplementary Information

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S1 Refinement details for $[\text{NMe}_4]_2\text{K}[\text{Co}(\text{CN})_6]$

Space group	$I4/m$				
$a/\text{\AA}$	8.87253(6)				
$c/\text{\AA}$	12.06831(13)				
R_{wp}	3.624%				
$\lambda/\text{\AA}$	0.82592				
Atom	x	y	z	occ.	$B_{\text{iso}}/\text{\AA}^2$
K1	0.5	0.5	0.5	1	5.0(3)
Co1	0.5	0.5	1	1	1.35(15)
C1	0.5	0.5	0.8346(13)	1	2.3(4)
C2	0.6716(19)	0.623(2)	1	1	2.3
C3	0.5739(17)	0.1146(13)	0.6777(5)	1	6.0(5)
H3A	0.6503	0.0618	0.6342	1	2.1(15)
H3B	0.6281	0.1849	0.7256	1	2.1
H3C	0.5046	0.1628	0.6344	1	2.1
N1	0.5	0.5	0.7517(15)	1	3.5(4)
N2	0.7732(15)	0.7091(14)	1	1	3.5(4)
N3	0.5	0	0.75	1	3.7(4)

Table S1 Crystallographic refinement details and structural model for $[\text{NMe}_4]_2\text{K}[\text{Co}(\text{CN})_6]$ at 300 K as determined by powder synchrotron X-ray diffraction.

Space group	$Fm\bar{3}m$				
$a/\text{\AA}$	12.48516(10)				
R_{wp}	2.474%				
$\lambda/\text{\AA}$	0.82592				
Atom	x	y	z	occ.	$B_{\text{iso}}/\text{\AA}^2$
Co1	0.5	0	0.5	1	5.4(3)
K1	0.5	0.5	0.5	1	6.6(4)
N1	0.5	0.2381(9)	0.5	1	6.2(5)
C1	0.5	0.1457(14)	0.5	1	11.0(13)
N2	0.75	0.25	0.75	1	3.6(6)
C2	0.7370(18)	0.34(10)	0.66(10)	0.17	6.4(12)
H1	0.6569	0.329	0.6569	0.33	not included
H2	0.7659	0.385	0.6757	0.17	not included
H3	0.7628	0.2945	0.5883	0.17	not included

Table S2 Crystallographic refinement details and structural model for $[\text{NMe}_4]_2\text{K}[\text{Co}(\text{CN})_6]$ at 400 K as determined by powder synchrotron X-ray diffraction.

S2 $[\text{C}_3\text{N}_2\text{H}_5]_2\text{Rb}[\text{Co}(\text{CN})_6]$ hysteresis and beam damage

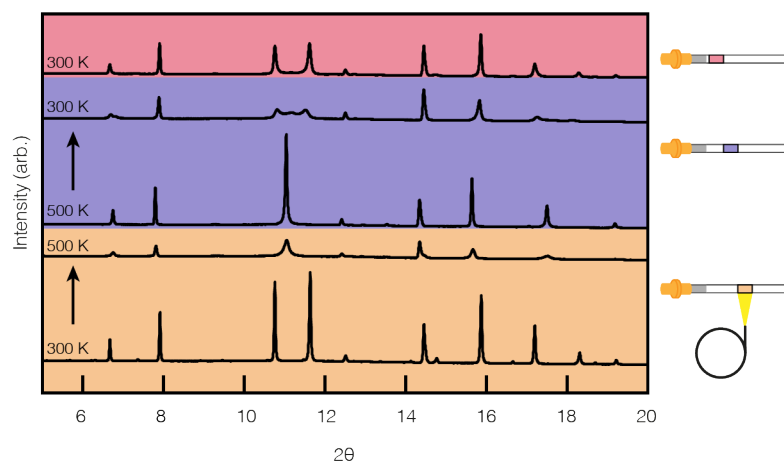


Figure S1 Evidence of X-ray irradiation inhibiting the phase transition on cooling. The cubic phase persists if the sample is cooled in the beam (purple), whilst if the capillary is then translated such that fresh sample is measured, the tetragonal phase is fully recovered (pink). Generic beam damage to the sample is observed in the decrease in intensity between samples prior to, and after, irradiation, as shown in orange.

S3 $[\text{C}_3\text{N}_2\text{H}_5]_2\text{K}[\text{Co}(\text{CN})_6]$

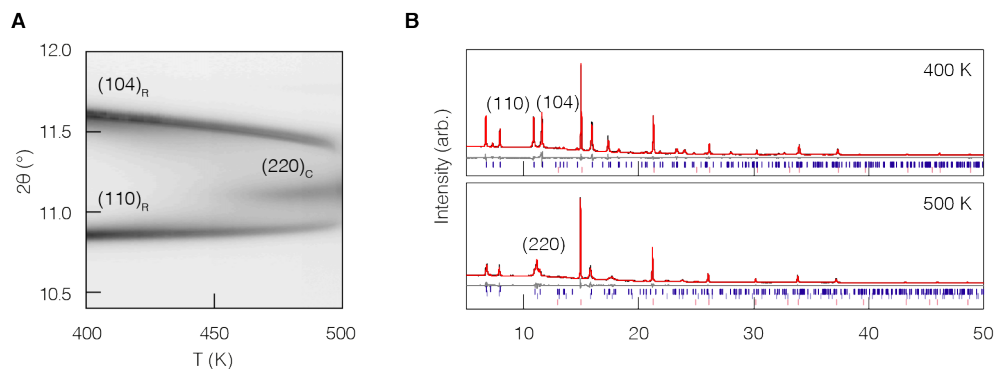


Figure S2 (a) A film plot of variable temperature diffraction data of $[\text{C}_3\text{N}_2\text{H}_5]_2\text{K}[\text{Co}(\text{CN})_6]$ for a small section of 2θ in which the emergence of a cubic peak can be seen. (b) Pawley refinements of synchrotron powder diffraction data at 400 and 500 K. A two-phase refinement was carried out at 500 K containing both the $R\bar{3}m$ and $Fm\bar{3}m$ phases (based on the $Fm\bar{3}m$ structure of $[\text{C}_3\text{N}_2\text{H}_5]_2\text{K}[\text{Co}(\text{CN})_6]$). X-ray diffraction data are shown in red, fit in blue and the difference curve in grey. The estimated peak positions for $[\text{C}_3\text{N}_2\text{H}_5]_2\text{K}[\text{Co}(\text{CN})_6]$ are shown in navy ($R\bar{3}m$) and purple $Fm\bar{3}m$ and those of KCl are shown in pink.

$\lambda/\text{\AA}$	0.82609
R_{wp}	3.836%
Space group	$R\bar{3}m$
$a/\text{\AA}$	8.7055(2)
$c/\text{\AA}$	19.4035(5)

Table S3 Crystallographic refinement details for Pawley fit of $[\text{C}_3\text{N}_2\text{H}_5]_2\text{K}[\text{Co}(\text{CN})_6]$ at 400 K as determined by powder synchrotron X-ray diffraction and shown in figure S3(b).

$\lambda/\text{\AA}$	0.82609
R_{wp}	3.400%
Space group	$R\bar{3}m$
$a/\text{\AA}$	8.6171(6)
$c/\text{\AA}$	19.970(2)
Space group	$Fm\bar{3}m$
$a/\text{\AA}$	11.9922(5)

Table S4 Crystallographic refinement details for Pawley fit $[\text{C}_3\text{N}_2\text{H}_5]_2\text{K}[\text{Co}(\text{CN})_6]$ at 500 K as determined by powder synchrotron X-ray diffraction and shown in figure S3(b).

S4 Variable temperature lattice parameters for $[\text{NMe}_4]_2\text{B}[\text{Co}(\text{CN})_6]$, **B = Rb, Cs**

The product of the Cs-containing synthesis also yielded the desired product $(\text{NMe}_4)_2\text{Cs}[\text{Co}(\text{CN})_6]$ alongside CsCl. $(\text{NMe}_4)_2\text{Cs}[\text{Co}(\text{CN})_6]$ crystallises in the monoclinic space-group $I2/m$ at 200 K as confirmed via Pawley refinement of the diffraction data based on the structure reported in Ref. 1. Lattice parameters and sample dependent Gaussian and Lorentzian strain terms were refined. The resulting lattice parameters were as follows: $a = 8.9142(5) \text{ \AA}$, $b = 8.8597(5) \text{ \AA}$, $c = 12.5183(3) \text{ \AA}$, $\beta = 90.155(4)^\circ$ with $R_{wp} = 8.513\%$. It appears that the strict anisotropy of the rotation axes in the $I4/m$ structures is somewhat relieved by the larger cage size; the absolute rotation axis of the cation now lies close to one of the cubic $\langle 110 \rangle$ axes. Variable temperature data measured from 200–400 K reveal a phase transition at ~ 302 K. The monoclinic angle β is often used both to describe the spontaneous strain and as an order parameter for monoclinic to cubic transitions. However, the resolution of the diffraction data measured for $(\text{NMe}_4)_2\text{Cs}[\text{Co}(\text{CN})_6]$ was too poor to allow accurate refinement of β across the temperature range measured for such a subtle monoclinic distortion. Nonetheless we found it was sufficient to describe the development of the spontaneous strain by setting $\beta = 90^\circ$ and describing the strain evolution of a metrically orthorhombic cell with the spontaneous strain given by:

$$\varepsilon_s = \sqrt{\frac{(\sqrt{2}a - a_0)^2 + (\sqrt{2}b - a_0)^2 + (c - a_0)^2}{a_0^2}}, \quad (\text{S1})$$

with $a_0 = \frac{1}{3}(\sqrt{2}a + \sqrt{2}b + c)$ (*i.e.* the estimated cubic lattice parameter based on the arithmetic mean of all possible strain tensors of an ‘average’ zero-strain structure). We note here that ε_s used for the tetragonal systems is a special case of the above spontaneous strain in which $a = b$.

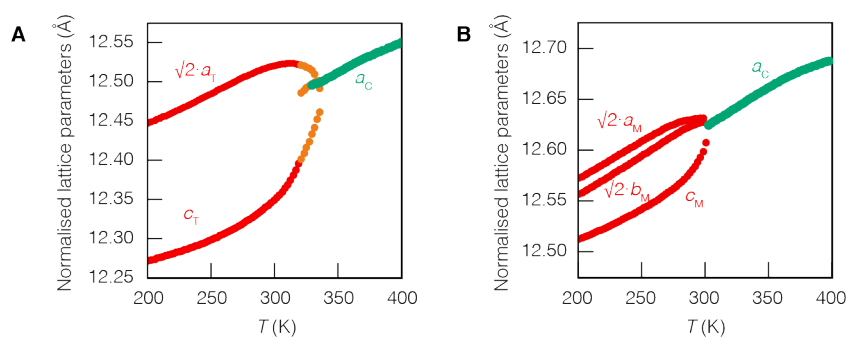


Figure S3 The lattice parameters extracted from batch variable temperature Pawley refinements for $[\text{NMe}_4]_2\text{B}[\text{Co}(\text{CN})_6]$. (a) $\text{B} = \text{Rb}$: The colours represent three different refinement protocols: refinement of $I4/m$ phase only (red), $Fm\bar{3}m$ phase only (green) and both refining (orange). (b) Variable temperature normalised lattice parameters for the second-order transition observed when $\text{B} = \text{Cs}$, for the $I2/m$ phase ($\beta = 90^\circ$) (red) and cubic phase (green).

S5 References

[S1] S. Peschel and D. Babel, *Z. Naturforsch.*, 1994, **49b**, 1373–1380.