Supporting Information

Room-temperature large entropy change in a new hybrid ferroelastic with unconventional bond-switching mechanism

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Experimental

Synthesis

$Na_3[Co(CN)_6]$ was synthesized from $K_3[Co(CN)_6]$ through silver precipitation.[S1] The pale pink block crystals of $(Me_3NNH_2)_2[Co(CN)_6Na(H_2O)]$ (TMC-2) were obtained by slowly evaporating aqueous solution containing $Na_3Co(CN)_6$ and 1,1,1-trimethyl-hydrazoniuiodide in a ratio of 1:2 at room temperature within several days, in a yield of 80% based on Co. Elemental analysis, calcd (%) for TMC-2 ($C_{12}H_{24}ON_{10}CoNa$, 406.33): C, 35.47 ; H, 5.91 ; N, 34.49 . Found, C, 35.79 H, 5.91; N, 34.40.

X-ray Crystallographic Analysis

The *in-situ* variable-temperature single-crystal diffraction intensities data were collected on a RigakuXtaLAB P300DS diffractometer (Mo K_α, λ = 0.71073 Å). The CrystalClear software package (Rigaku) was used for data collection, cell refinement and data reduction. Using Olex^2 program, 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.[S2,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: 2003376-2003377. Powder X-ray diffraction (PXRD) patterns (Cu K_α, λ = 1.54184 Å) were collected on Bruker Advance D8 DA VANCI θ-2θ diffractometer. Pawley refinement of the experimental PXRD patterns were performed using the Reflex module of Material Studio 5.[S4]

Elemental analysis

Elemental (C, H, and N) analyses were performed on a Perkin-Elmer Vario EL elemental analyzer.

Thermal Analysis

Thermogravimetric analysis (TGA) was carried out on a TA Q50 system with a heating rate of 10 K min^{-1} under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was carried out on a TA DSC Q2000 instrument under a nitrogen atmosphere in aluminum crucibles with heating and cooling rates of 10 K min^{-1} from 200 to 373 K.

Dielectric measurements

The dielectric measurement was carried on a Tonghui TH2828A LCR meter at 10 frequencies from 500 Hz to 1 MHz, with an applied voltage of 1.0 V and a temperature sweeping rate of 3 K min^{-1} approximately in the range of 80–350 K in a Mercury iTC cryogenic environment controller of Oxford Instrument. The powder sample of TMC-2 was ground and pressed into tablets under a pressure around 2 GPa. The capacitors were made by painting the two faces of tablet or crystal sample with silver conducting paste and using gold wires as the electrodes.

Variable-temperature polarization microscopy

Variable-temperature polarization microscopy observations were carried out with a polarizing microscope MSHOT MD90 equipped with a Linkam cooling/heating stage THMSE 600. The temperature was stabilized with an accuracy of ±0.1 K.

Deduction of domain orientation

During the phase transition from *Pmmn* (PP) to $P2_1/c$ (FP), a symmetry breaking occurs from 8 (E, C_2, $2C'_2$, i, σ_h, $2\sigma_v$) to 4 (E, i, C_2, σ_h) symmetry elements, classifying TMC-2 to be an *mmm*F2/*m* ferroelastic species with two possible orientation states in the ferroelastic phase. The spontaneous strain within these two states are expressed as

$$\varepsilon_{ij}^{(1)} = \begin{bmatrix} \varepsilon_{11} & 0 & \varepsilon_{13} \\ 0 & \varepsilon_{22} & 0 \\ \varepsilon_{31} & 0 & \varepsilon_{33} \end{bmatrix},\ \varepsilon_{ij}^{(2)} = \begin{bmatrix} \varepsilon_{11} & 0 & -\varepsilon_{13} \\ 0 & \varepsilon_{22} & 0 \\ -\varepsilon_{31} & 0 & \varepsilon_{33} \end{bmatrix}$$

The modified spontaneous strains proposed by Aizu are then [S5]

$$\varepsilon_{sij}^{(i)} = \varepsilon_{ij}^{(i)} - \frac{1}{q}\sum_{k=1}^{q} \varepsilon_{ij}^{(k)}\ \ (i = 1, 2, \ldots, q)$$

In this case,

$$\varepsilon_{sij}^{(1)} = \begin{bmatrix} 0 & 0 & \varepsilon_{13} \\ 0 & 0 & 0 \\ \varepsilon_{31} & 0 & 0 \end{bmatrix}, \varepsilon_{sij}^{(2)} = \begin{bmatrix} 0 & 0 & -\varepsilon_{13} \\ 0 & 0 & 0 \\ -\varepsilon_{31} & 0 & 0 \end{bmatrix}$$

considering the compatibility condition of spontaneous strain

$$[\varepsilon_{sij}^{(1)} - \varepsilon_{sij}^{(2)}]x_i x_j = 0$$

where x_i and x_j are components of unit vector on domain walls, we obtain $2\varepsilon_{13}xz = 0$, which gives the orientation of domain walls $x = 0$ and $z = 0$.

For *mmm*F2/*m* species with monoclinic setting in $P2_1/c$, the spontaneous strain tensor is expressed as:

$$\varepsilon_{ij} = \begin{bmatrix} \frac{a_{\mathrm{FP}}}{a_{\mathrm{PP}}} - 1 & 0 & \frac{c_{\mathrm{FP}}}{2c_{\mathrm{PP}}}\cos\beta \\ 0 & \frac{b_{\mathrm{FP}}}{b_{\mathrm{PP}}} - 1 & 0 \\ \frac{c_{\mathrm{FP}}}{2c_{\mathrm{PP}}}\cos\beta & 0 & \frac{c_{\mathrm{FP}}}{c_{\mathrm{PP}}}\sin\beta - 1 \end{bmatrix}$$

The total spontaneous strain (ε_{ss}) can be calculated with cell parameters measured at 200 K (FP) and 333 K. (Table S1):

$$\varepsilon_{ss} = \sqrt{\sum_{i,j} {\varepsilon_{ij}}^2} = 0.036$$

Table S1. Crystal data and structure refinement parameters for TMC-2 at ferroelastic phase (FP) and paraelastic phase (PP).

Formula	$(Me_3NNH_2)_2[Co(CN)_6Na(H_2O)]$	
T (K)	200(2)	333(2)
Phases	FP	PP
Crystal system	Monoclinic	orthorhombic
Space group	$P2_1/c$	$Pmmn$
a/Å	8.3357(2)	8.4803(3)
b/Å	12.4689(3)	12.4172(9)
c/Å	18.5938(4)	9.5901(6)
β/°	90.564(2)	90
V/Å^3	1932.49(8)	1009.85(10)
Z	4	2
D_c /g cm^{-3}	1.397	1.336
μ (mm^{-1})	0.933	0.893
reflns coll.	17630	4491
unique reflns	3798	1100
R_1 [$I > 2\sigma(I)$]	0.0276	0.0494
wR_2 [$I > 2\sigma(I)$]	0.0700	0.1268
R_1 (all data)	0.0331	0.0627
wR_2 (all data)	0.0751	0.1346
GOF	1.075	1.027
CCDC	2003377	2003376

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = \{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$

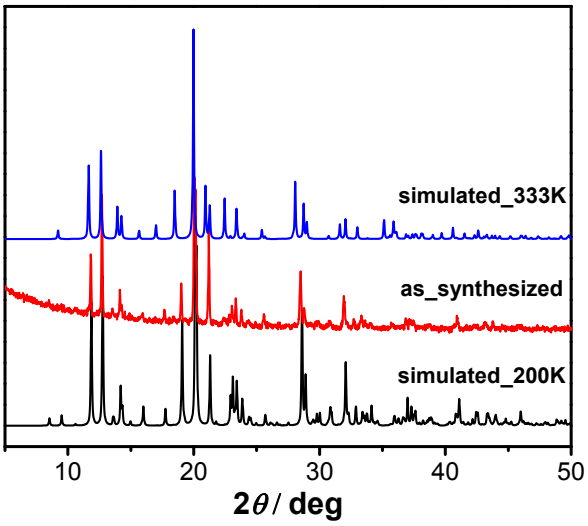

Figure S1. The PXRD patterns confirmed the phase purity of the as-synthesized sample for TMC-2.

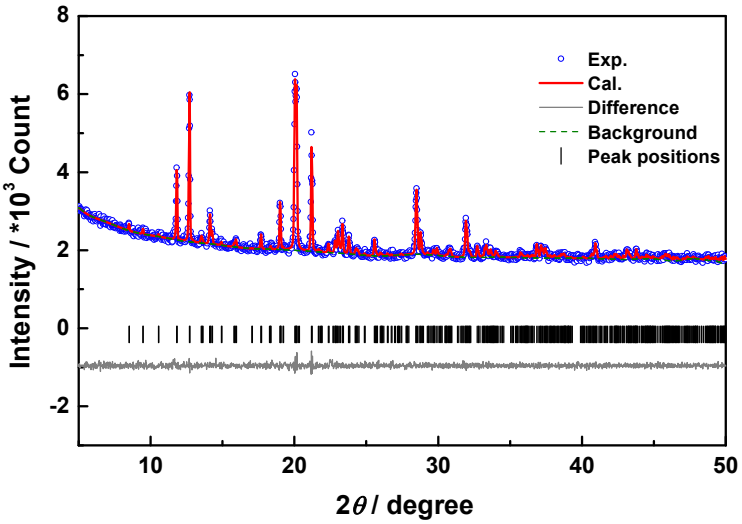

Figure S2. Pawley refinement on the PXRD pattern of **TMC-2** at 295 K reveals the presence of a monoclinic unit cell: a = 8.385(7) Å, b = 12.53(1) Å, c = 18.68(1) Å, β = 90.653(3)°, V = 1962.15(6) Å^3 (residuals R_p = 1.68%, R_{wp}= 2.15%), with $P2_1/c$ as the space group. Experimental pattern (blue circles), calculated pattern (red line), difference profile (grey line) and background profile (dashed line). Stick marks (|) at the bottom of the pattern indicate peak positions allowed by the appointed unit-cell parameters and space group.

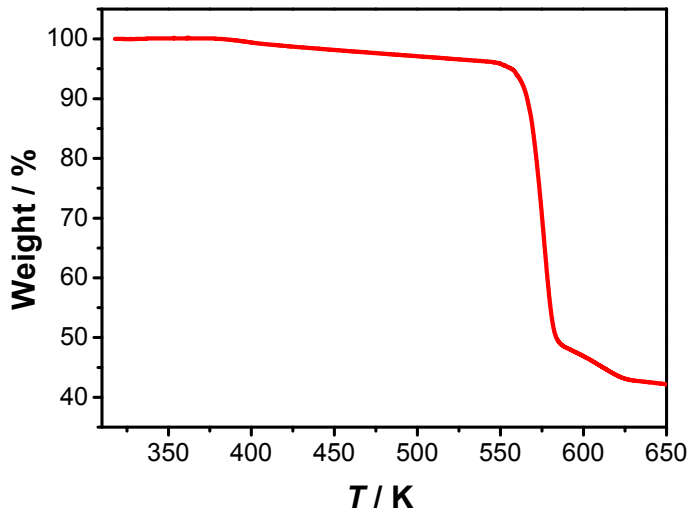

Figure S3. TG profile of TMC-2.

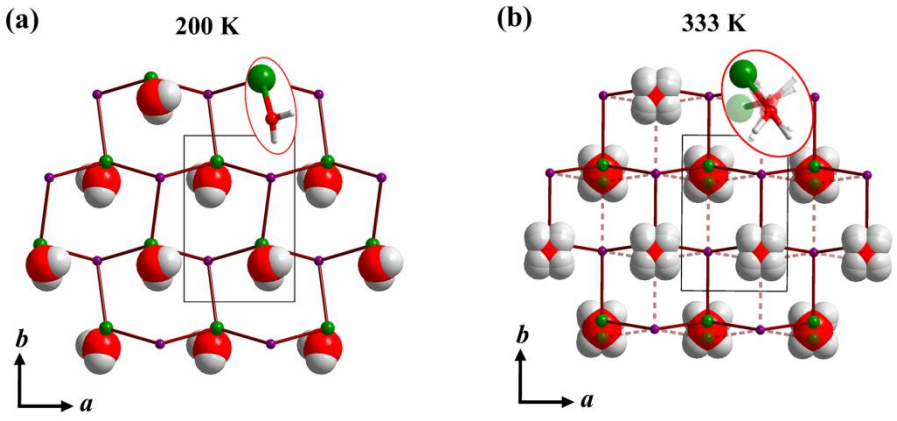

Figure S4. 2D layer structure of TMC-2 in the FP at 200 K (a) and in the PP at 333 K (b). The coordinated H_2O shows four-fold disorder as required by the imposed orthorhombic symmetry.

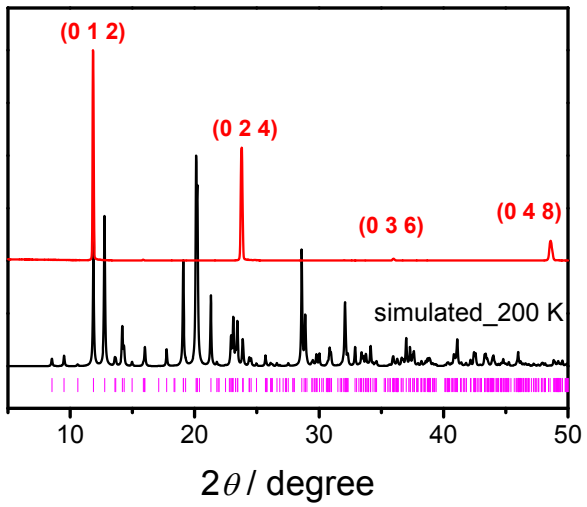

Figure S5. The room temperature PXRD patterns of a single crystal of TMC-2.

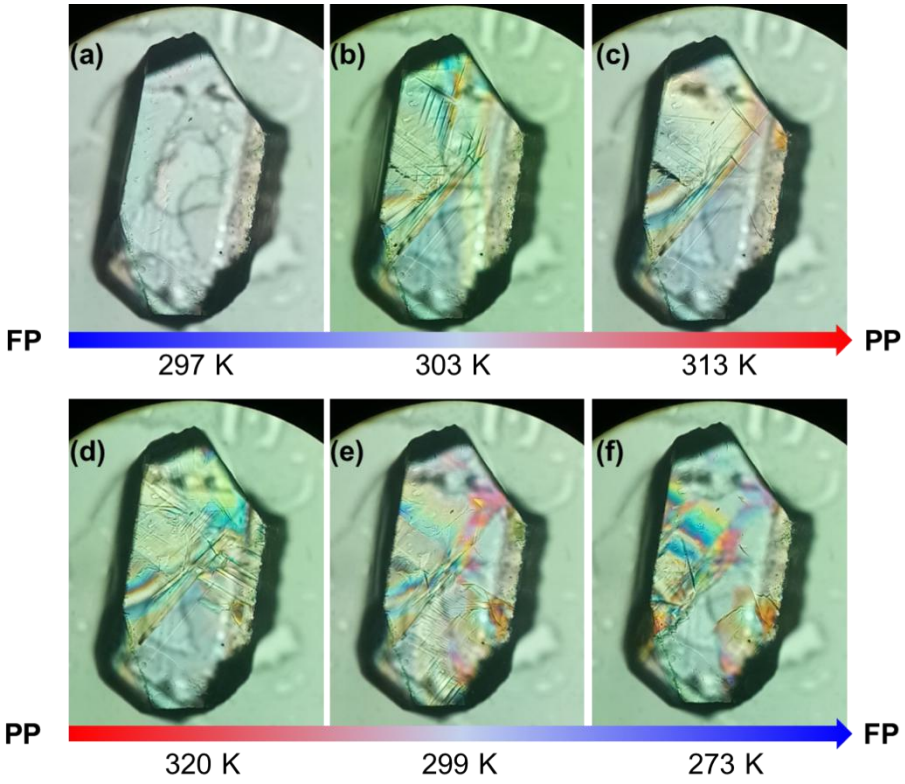

Figure S6. Evolution of the domain structure of TMC-2 in a heating-cooling cycle.

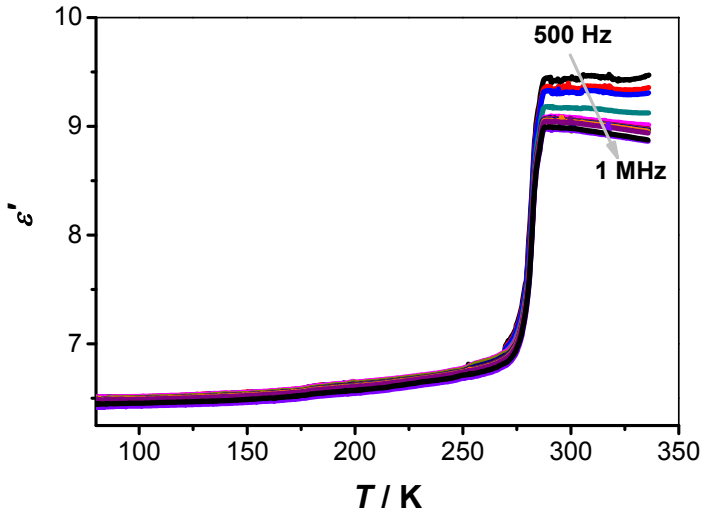

Figure S7. Temperature dependence of the dielectric constant (ε') of TMC-2 measured on a pressed-powder pellet sample at different frequencies in cooling cycle.

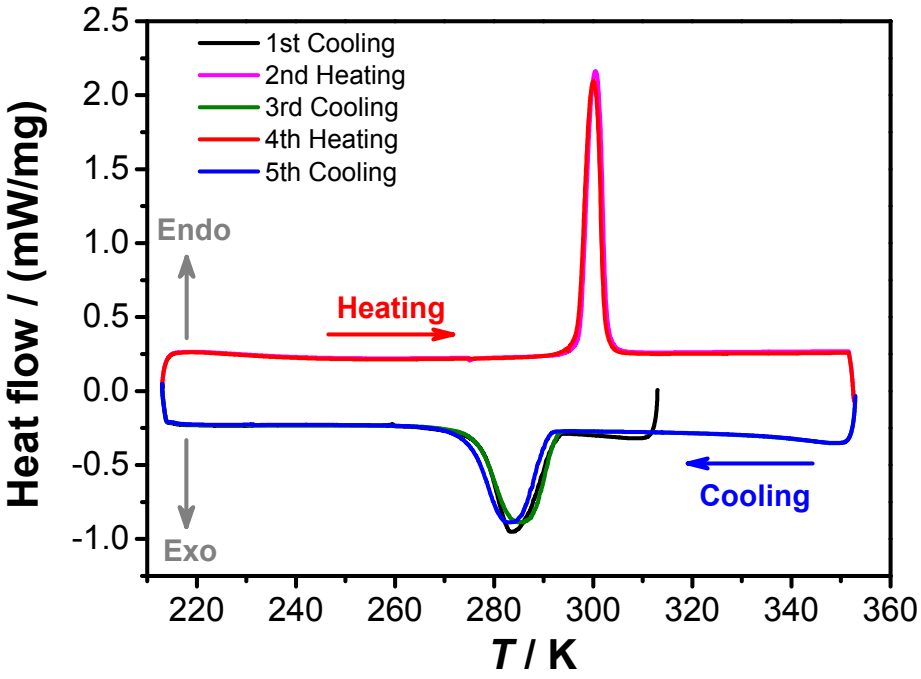

Figure S8. DSC curves of TMC-2 at different heating-cooling cycles with a scanning rate of 10 K min^{-1}.

Table S2. Summary of thermal properties of TMC-2 by DSC measurements at different heating-cooling cycles with a scanning rate of 10 K min^{-1}.

Heating/cooling	T_c	Latent heat (kJ kg^{-1})	ΔS (J mol^{-1} K^{-1})	ΔS (J kg^{-1} K^{-1}) exp
1st cooling	283	40.5	58.1	143
2nd heating	300	44.5	60.3	148
3rd cooling	284	41.5	59.4	146
4th heating	300	43.7	59.2	146
5th cooling	282	41.2	59.4	146

Table S3. The 4th heating DSC data used for calculating dT_c/dP of TMC-2 by the Clausius–Clapeyron equation

T_c (K) exp.	300
M.W. (g mol^{-1})	406.33
ΔS (J mol^{-1} K^{-1}) exp.	146
ΔS (J kg^{-1} K^{-1}) exp.	59.2
$\lvert\Delta V\rvert \times 10^{-5}$ (m^3 kg^{-1}) exp.	3.23
$\lvert dT_c/dP\rvert$ (K $kbar^{-1}$) calc.	22.2

Table S4. The parameters of hydrogen-bonding interactions for TMC-2 at 200 K

D	H	A	*d*(D···A)/Å	∠D–H···A/°
O1	H1A	N4[a]	2.950(2)	146.9
O1	H1B	N3[b]	2.872(2)	153.3
N8	H8A	N6[c]	3.375(2)	165.5
N8	H8B	N4	3.225(2)	158.7
N10	H10B	N2[d]	3.081(2)	169.4

Symmetry codes: (a) 1-*x*, 1/2+*y*, 1/2-*z*; (b) -1+*x*, 3/2-*y*, -1/2+*z*; (c) 1-*x*, -1/2+*y*, 1/2-*z*; (d) +*x*, 3/2-*y*, -1/2+*z*.

Table S5. Bond Lengths for TMC-2 at 200 K.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co1	C1	1.897(1)	N7	C11	1.491(2)
Co1	C4	1.894(2)	N7	C12	1.496(2)
Co1	C2	1.890(1)	N7	C10	1.489(2)
Co1	C5	1.902(1)	N1	Na1[c]	2.460(1)
Co1	C6	1.897(2)	C4	N4	1.148(2)
Co1	C3	1.893(2)	C2	N2	1.151(2)
Na1	O1	2.272(1)	C5	N5	1.149(2)
Na1	N1[a]	2.460(1)	N5	Na1[d]	2.438(1)
Na1	N5[b]	2.438(1)	N6	C6	1.148(2)
Na1	N8	2.825(1)	N10	N9	1.460(2)
Na1	N6	2.480(1)	N9	C8	1.494(2)
Na1	N10	3.023(1)	N9	C9	1.485(2)
C1	N1	1.150(2)	N9	C7	1.479(2)
N7	N8	1.460(2)	N3	C3	1.148(2)

Symmetry codes: (a) 1-*x*, -1/2+*y*, 1/2-*z*; (b) -1+*x*, +*y*, +*z*; (c) 1-*x*, 1/2+*y*, 1/2-*z*; (d) 1+*x*,+*y*,+*z*.

Table S6. Bond Angles for TMC-2 at 200 K.

∠Atom	Atom	Atom	Angle/°	∠Atom	Atom	Atom	Angle/°
C1	Co1	C5	90.78(6)	N8	Na1	N10	83.78(4)
C1	Co1	C6	89.12(5)	N6	Na1	N8	83.11(4)
C4	Co1	C1	178.38(5)	N6	Na1	N10	82.88(4)
C4	Co1	C5	89.86(6)	N1	C1	Co1	176.5(1)
C4	Co1	C6	89.36(6)	N8	N7	C11	106.8(1)
C2	Co1	C1	87.75(6)	N8	N7	C12	112.2(1)
C2	Co1	C4	91.68(6)	N8	N7	C10	106.9(1)
C2	Co1	C5	177.19(6)	C11	N7	C12	110.3(1)
C2	Co1	C6	89.72(6)	C10	N7	C11	110.7(1)
C2	Co1	C3	88.10(6)	C10	N7	C12	109.9(1)
C6	Co1	C5	92.65(6)	C1	N1	Na1[c]	147.5(1)
C3	Co1	C1	92.06(5)	N4	C4	Co1	178.5(1)
C3	Co1	C4	89.44(6)	N2	C2	Co1	176.1(1)
C3	Co1	C5	89.56(6)	N5	C5	Co1	176.9(1)
C3	Co1	C6	177.48(6)	C5	N5	Na1[d]	174.8(1)
O1	Na1	N1[a]	100.15(5)	N7	N8	Na1	126.6(1)
O1	Na1	N5[b]	94.73(5)	C6	N6	Na1	144.2(1)
O1	Na1	N8	174.97(5)	N9	N10	Na1	139.9(1)
O1	Na1	N6	94.73(5)	N10	N9	C8	113.0(1)
O1	Na1	N10	91.45(5)	N10	N9	C9	107.3(1)
N1[a]	Na1	N8	79.86(4)	N10	N9	C7	107.2(1)
N1[a]	Na1	N6	150.13(5)	C9	N9	C8	108.6(1)
N1[a]	Na1	N10	71.07(4)	C7	N9	C8	110.5(2)
N5[b]	Na1	N1[a]	96.66(5)	C7	N9	C9	110.2(2)
N5[b]	Na1	N8	90.26(4)	N6	C6	Co1	177.9(1)
N5[b]	Na1	N6	107.82(5)	N3	C3	Co1	178.1(1)
N5[b]	Na1	N10	167.10(5)				

Symmetry codes: (a) 1-*x*, -1/2+*y*, 1/2-*z*; (b) -1+*x*, +*y*, +*z*; (c) 1-*x*, 1/2+*y*, 1/2-*z*; (d) 1+*x*, +*y*, +*z*.

Table S7. The parameters of hydrogen-bonding interactions for TMC-2 at 333 K

D	H	A	*d*(D···A)/Å	∠D–H···A/°
O1	H1A	N1[a]	2.908(6)	99.9
O1	H1B	N1[b]	3.509(8)	125.8
N5	H5E	N1	3.204(8)	124.8

Symmetry codes: (a) 1/2-*x*, 3/2-*y*, -1+*z*; (b) *x*, *y*, -1+*z*;

Table S8. Bond Lengths for TMC-2 at 333 K.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co1	C3	1.898(3)	Na1	O1	2.259(6)
Co1	C3[a]	1.898(3)	N3	Na1[b]	2.435(3)
Co1	C2	1.900(5)	N3	C3	1.141(5)
Co1	C2[a]	1.900(5)	C2	N2	1.143(7)
Co1	C1	1.890(4)	C1	N1	1.137(5)
Co1	C1[a]	1.890(4)	N2	Na1[c]	2.553(6)
Na1	Na1[b]	1.337(5)	N4	C5	1.473(3)
Na1	N3[b]	2.435(3)	N4	N5	1.482(2)
Na1	N3	2.435(3)	N4	C4	1.484(2)
Na1	N2[c]	2.553(6)	N4	C6	1.484(2)

Symmetry codes: (a) 3/2-*x*, 3/2-*y*, +*z*; (b)1/2-*x*, 3/2-*y*, +*z*; (c) 1-x, 1-*y*, 1-*z*.

Table S9. Bond Angles for TMC-2 at 333 K.

∠Atom	Atom	Atom	Angle/°	∠Atom	Atom	Atom	Angle/°
C3	Co1	C3[a]	93.14(18)	N3	Na1	N3[b]	110.5(2)
C3[a]	Co1	C2[a]	89.49(7)	N3	Na1	N2[c]	111.8(1)
C3[a]	Co1	C2	89.49(7)	N3[b]	Na1	N2[c]	111.8(1)
C3	Co1	C2[a]	89.49(7)	O1	Na1	N3[b]	108.3(5)
C3	Co1	C2	89.49(7)	O1	Na1	N3	113.0(4)
C2	Co1	C2[a]	178.5(2)	O1	Na1	N2[c]	101.3(4)
C1	Co1	C3[a]	177.7(1)	Na1[b]	N3	Na1	31.9(1)
C1	Co1	C3	89.1(2)	C3	N3	Na1	161.5(1)
C1[a]	Co1	C3[a]	89.1(2)	C3	N3	Na1[b]	161.5(1)
C1[a]	Co1	C3	177.7(1)	N3	C3	Co1	177.5(3)
C1	Co1	C2	90.5(1)	N2	C2	Co1	177.3(3)
C1	Co1	C2[a]	90.5(1)	N1	C1	Co1	178.9(4)
C1[a]	Co1	C2[a]	90.5(1)	C2	N2	Na1[c]	171.7(3)
C1[a]	Co1	C2	90.5(1)	C5	N4	N5	105.5(2)
C1	Co1	C1[a]	88.6(2)	C5	N4	C4	105.3(2)
Na1[b]	Na1	N3[b]	74.1(1)	C5	N4	C6	112.2(2)
Na1[b]	Na1	N3	74.1(1)	N5	N4	C4	111.2(2)
Na1[b]	Na1	N2[c]	168.2(1)	N5	N4	C6	111.3(2)
Na1[b]	Na1	O1	67.0(4)	C6	N4	C4	111.1(1)

Symmetry codes: (a) 3/2-*x*, 3/2-*y*, +*z*; (b) 1/2-*x*, 3/2-*y*, +*z*; (c) 1-*x*, 1-*y*, 1-*z*.

.

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