

ESI

Slider-crank Mechanism in a Molecular Crystal: Conversion of Linear Thermal Expansion of Lattice to Circular Rotation of Coordination Chain

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1. Experimental Procedures

1-1. Spectroscopic studies.

Single crystals of **1** was obtained by slow diffusion. Solution A was slowly layered on solution B. After 1-2 weeks of slow diffusion, blueish columnar single crystals were obtained (Figure S1); yield 19.3% based on Co.

Solution A; 0.1 M of dabco in MeOH

Solution B; 0.1 M of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.2 M of KOCN om $\text{H}_2\text{O}:\text{MeOH}=1:1$ mixed solution

Elemental analysis; found: C 32.001, H 3.715, N 20.834 and calc C 32.15, H 3.60, N 20.83 for $\text{KCo}(\text{C}_6\text{H}_{12}\text{N}_2)(\text{OCN})_3$

FTIR (cm^{-1}): 2231 (s), 1323 (m), 1057(m), 997(w), 918(w), 843(w), 793(m), 611(m)

Uv-vis-NIR (cm^{-1}): 19474, 17873, 16821, 11834

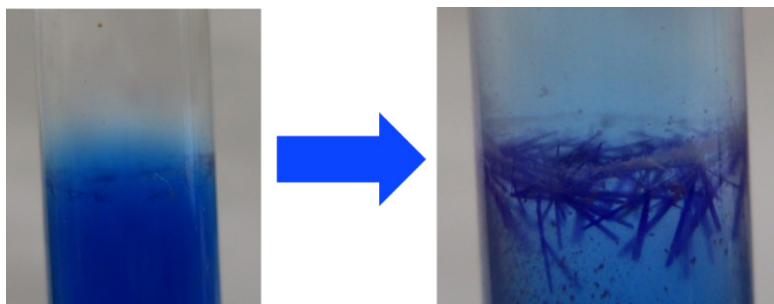


Figure S1. Photos before and after crystallization.

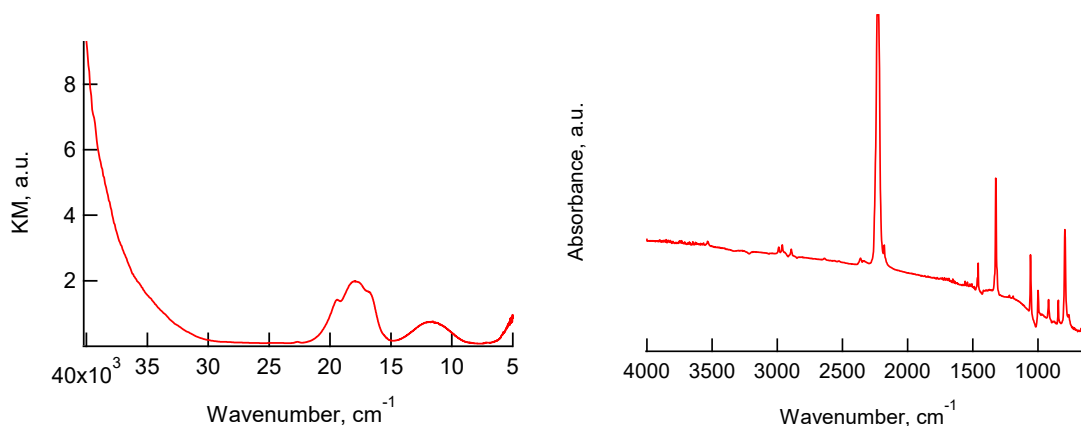


Figure S2. UV-vis-NIR (left) and IR (right) spectra of crystal **1**.

1-2. Single-crystal X-ray diffraction analysis

Single-crystal analysis of **1**;

135 K, CCDC 2159526

187 K, CCDC 2159527

239 K, CCDC 2159525

303 K, CCDC 2159523

342 K, CCDC 2159522

390 K, CCDC 2159528

446 K, CCDC 2159524

A suitable crystal $0.29 \times 0.27 \times 0.22$ mm³ was selected and mounted on a suitable support on an XtaLAB Synergy R, HyPix diffractometer. The crystal was kept at a steady temperature during data collection. The structure was solved with the ShelXT 2018/2 structure solution program using the Intrinsic Phasing solution method and by using Olex2 as the graphical interface. The model was refined with version 2018/3 of ShelXL 2018/3 using Least Squares minimisation. Further details of the crystallographic analysis are summarised in the CIF file deposited at the CCDC. Crystallographic parameters were summarized in Table S1.

Table S1. Summary of crystallographic data.

CCDC#	2159526	2159527	2159525	2159523	2159522	2159528	2159524
Formula	C ₉ H ₁₂ CoKN ₅ O ₃						
$D_{calc}/g\text{ cm}^{-3}$	1.687	1.674	1.660	1.642	1.629	1.602	1.584
m/mm^{-1}	1.622	1.609	1.595	1.578	1.566	1.540	1.522
Formula Weight	336.27						
Colour	violet						
Shape	block						
Size/ mm^3	0.29×0.27×0.22						
T/K	135	187	239	303	242	390	446
Crystal System	hexagonal						
Flack Parameter	0.01(2)	0.02(3)	0.000(17)	0.04(3)	0.01(2)	0.00(4)	-
Hoof Parameter	0.004(15)	-0.00(2)	-0.014(14)	0.04(2)	0.01(2)	0.03(3)	-
Space Group	<i>P</i> -62 <i>c</i>	<i>P</i> -62 <i>c</i>	<i>P</i> -62 <i>c</i>	<i>P</i> -62 <i>c</i>	<i>P</i> -62 <i>c</i>	<i>P</i> -62 <i>c</i>	<i>P</i> 6 ₃ / <i>mmc</i>
$a/\text{Å}$	10.3499(5)	10.3782(6)	10.4110(7)	10.4530(5)	10.4730(10)	10.5556(6)	10.6103(12)
$c/\text{Å}$	7.1351(4)	7.1530(4)	7.1669(4)	7.1875(3)	7.2162(6)	7.2239(3)	7.2328(6)
$V/\text{Å}^3$	661.92(7)	667.21(9)	672.75(10)	680.13(7)	685.46(14)	697.06(8)	705.17(17)
Z	2						
Wavelength/Å	0.71073						
Radiation type	Mo K_{α}						
Measured Refl.	5956	6158	6166	4236	3914	4706	1136
Independent Refl.	643	670	670	605	603	618	340
Reflections with $I > 2(I)$	603	593	598	503	520	495	292
R_{int}	0.0711	0.1259	0.0470	0.0558	0.0468	0.1077	0.0442
Parameters	35	36	36	36	36	35	30
Restraints	0	0	0	0	0	0	0
Largest Peak	0.217	0.311	0.346	0.188	0.215	0.402	0.20
Deepest Hole	-0.312	-0.296	-0.445	-0.233	-0.182	-0.405	-0.27
GooF	0.710	1.086	1.138	1.097	1.072	1.005	1.092
wR_2 (all data)	0.0834	0.0747	0.0680	0.0682	0.0743	0.1259	0.0873
wR_2	0.0814	0.0725	0.0665	0.0648	0.0715	0.1161	0.0839
R_1 (all data)	0.0282	0.0352	0.0317	0.0374	0.0350	0.0574	0.0321
R_1	0.0261	0.0300	0.0274	0.0279	0.0288	0.0452	0.0284

2. DSC

DSC was shown in Figure S1 measured at different scan rate and cycle measurement at 15 K min⁻¹. Transition temperature, differential enthalpy and entropy were summarized in table S1. Differential entropy 5.5 J K⁻¹ mol⁻¹ was well agree with 5.76 J K⁻¹ mol⁻¹ (=Rln2) for order disorder type transition.

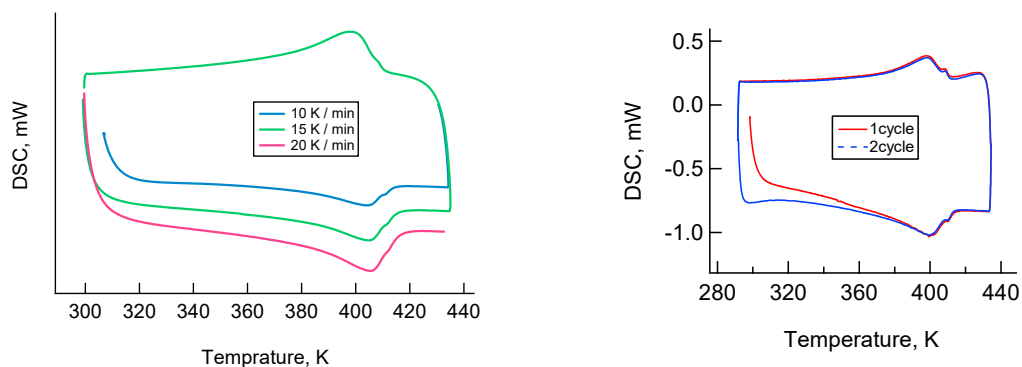


Figure S3. DSC (left) of compound **1**.

Table S2. Transition temperature (T_c), differential enthalpy (ΔH) and entropy (ΔS)^[a]

	T_c , K	ΔH , kJ mol ⁻¹	ΔS , J K ⁻¹ mol ⁻¹
Heating run	400	-2.2	5.5
Cooling run	398	-1.7	4.3

[a] differential entropy was estimated using equation of $\Delta S = -\Delta H/T_c$.

3. Crystallographic analysis

Figure S4 is plots of unit cell parameters and volume against temperature. Structural evolution is continuous against increases in temperature. From the temperature dependence of the lattice parameter a and c as well as distance between K^+ and Co^{2+} , thermal expansion coefficients α_a , α_c , and α_x were determined, respectively (Table S3).

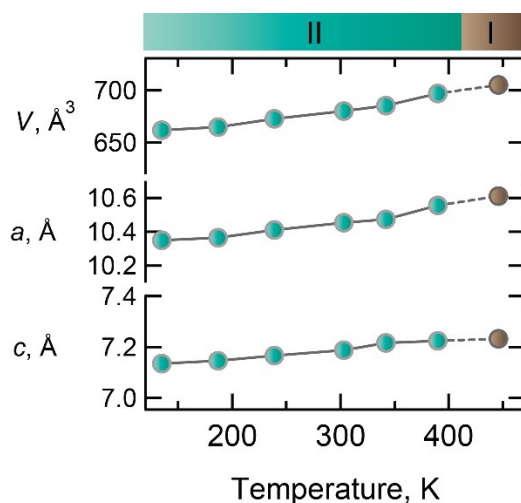


Figure S4. Plots of unit cell parameters and volume against temperature.

Table S3. Thermal expansion coefficient estimated for lattice parameter a (α_a) and c (α_c) as well as distance between K^+ and Co^{2+} (α_x).

	135 K	187 K	239 K	303 K	342 K	390 K	446 K
x , \AA	5.975	5.992	6.011	6.035	6.047	6.094	6.126
α_x , 10^{-5} K^{-1}	-	5.78	6.17	5.79	11.2	12.5	-
a , \AA	10.3499	10.3652	10.411	10.453	10.473	10.5556	10.6103
α_a , 10^{-5} K^{-1}	-	5.67	7.27	5.76	11.3	12.5	-
c , \AA	7.1351	7.1467	7.1669	7.1875	7.2162	7.2239	7.2328
α_c , 10^{-5} K^{-1}	-	7.28	7.91	6.66	5.80	2.21	-

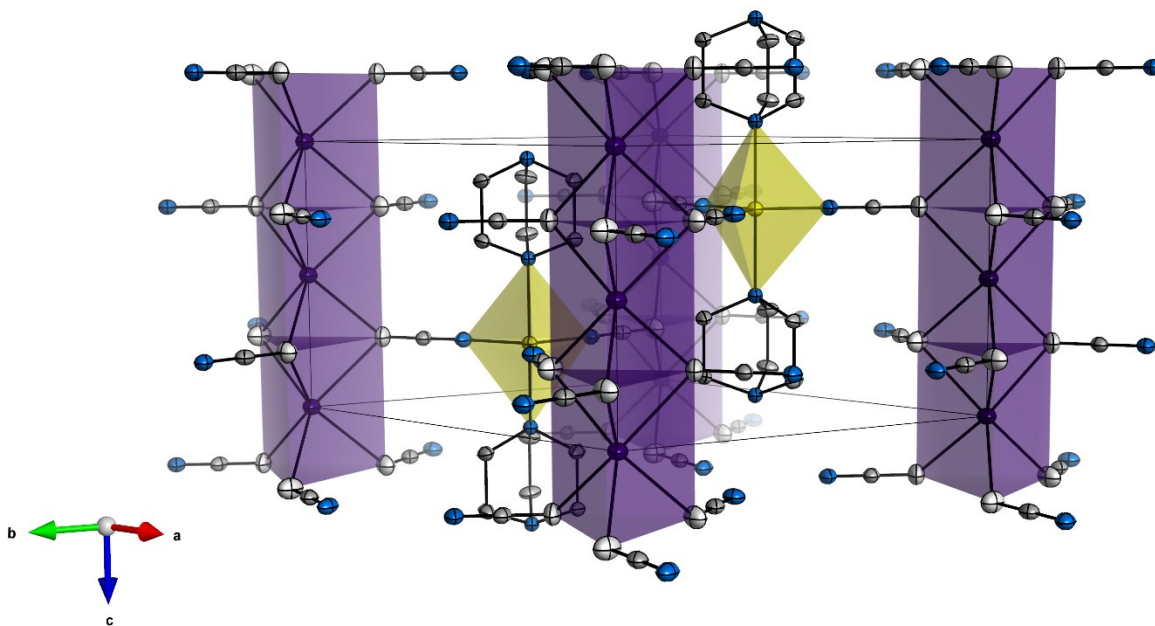


Figure S5. Packing structure at 135 K (thermal ellipsoid: 50 % of probability).

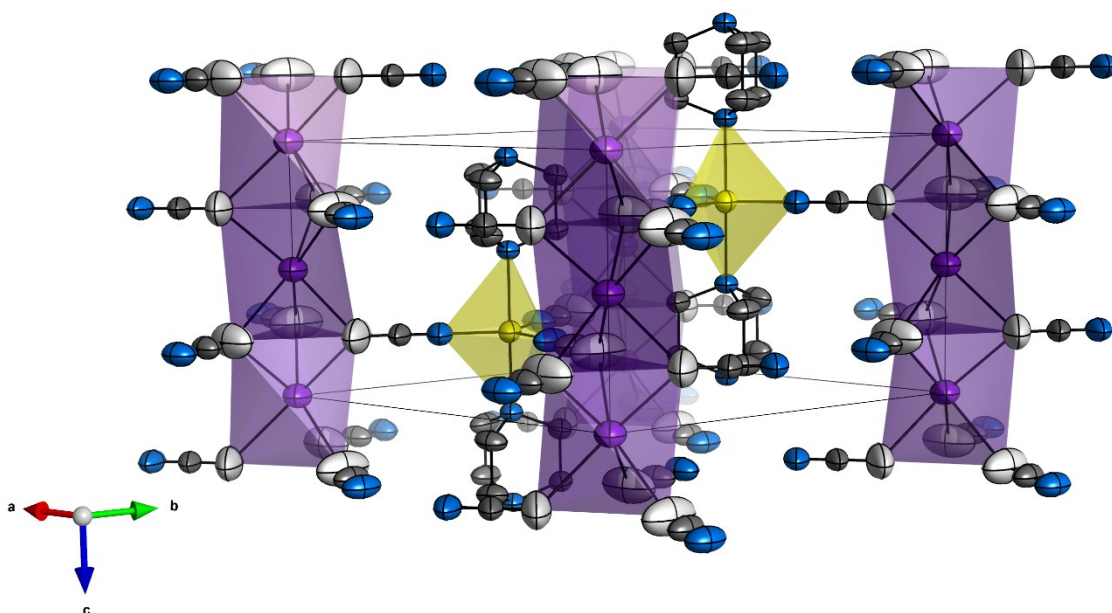


Figure S6. Packing structure at 390 K (thermal ellipsoid: 50 % of probability).

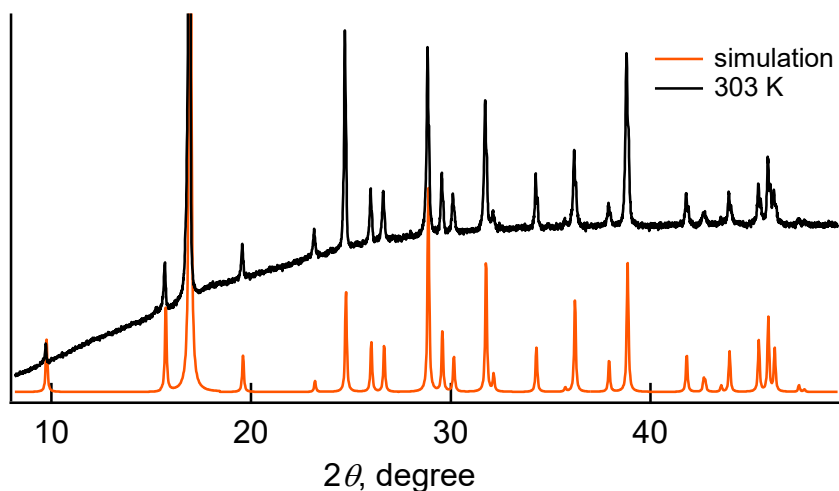


Figure S7. Powder X-ray diffraction pattern at 303 K.

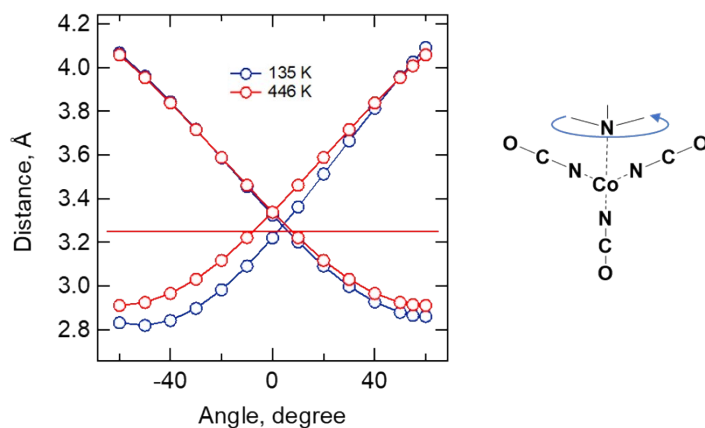


Figure S8. Plot of distances between C of dabco and N of OCN^- against angle by which dabco molecule was rotated with coordination bonds constant (data at 135 K (blue) and 446 K (red)). At both temperature, distances were lowered below the sum of vdW radii 3.25 Å (red line) when orientational angle of dabco and cyanate triangle differed above $\sim 10^\circ$, indicating correlated rotational motion is originated from steric hindrance. This is probably an origin for why N atoms are not thermally disordered at the phase-I.

Table S4. Summary of interatomic distances in cyanate. In the crystal **1**, bond length of N-C and C-O of cyanate differs. This type of structure suggests $\text{N}\equiv\text{C}-\text{O}^-$ rather than $^-\text{N}=\text{C}=\text{O}$. Coordination Co-N-C is almost linear, which is compatible with approximate sp hybridization of the N atom in $\text{N}\equiv\text{C}-\text{O}^-$. Negative charge is considered to be located on O atom.

Compound	$d(\text{N}-\text{C}), \text{\AA}$	$d(\text{C}-\text{O}), \text{\AA}$	Method	ref
NCO^-	1.17(1)	1.26(1)	Photoelectron spectra at gas phase	1
$(\text{NH}_4)\text{NCO}$	1.191(5)	1.215(5)	Neutron powder diffraction experiment at 14 K	2
AgNCO	1.195(11)	1.180(11)	Single crystal X-ray diffraction	3
1	1.163(4)	1.216(4)	Single crystal X-ray diffraction	This work

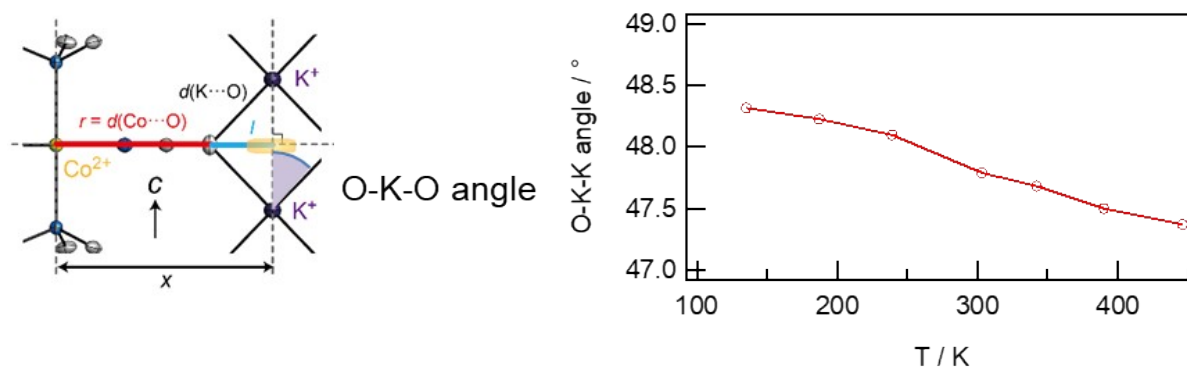


Figure S9. Definition and temperature dependence of O-K-O angle.

References

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- [3] D. Britton, J. D. Dunitz, *Acta Crystallogr.* **1965**, 18, 424–428.