

## Supporting information

### **Order-disorder phase transition in the first thiocyanate-bridged double perovskite-type coordination polymer: $[\text{NH}_4]_2[\text{NiCd}(\text{SCN})_6]$**

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## Experimental details

**Materials and instrumentations.** All chemicals were obtained from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) patterns (Cu  $K\alpha$ ,  $\lambda = 1.54056 \text{ \AA}$ ) were collected on a Bruker Advance D8 DA VANCE  $\theta$ - $2\theta$  diffractometer. Thermogravimetric analyses (TGA) were carried out on a TA Q50 system at a heating rate of 10 K/min under a nitrogen atmosphere. Differential scanning calorimeter (DSC) measurements were performed by heating and cooling the powder samples at a rate of 10 K/min on a TA DSC Q2000 instrument. The complex permittivity was measured using a Tonghui TH2828A LCR meter in a Mercury iTC cryogenic environment controller of Oxford Instrument.

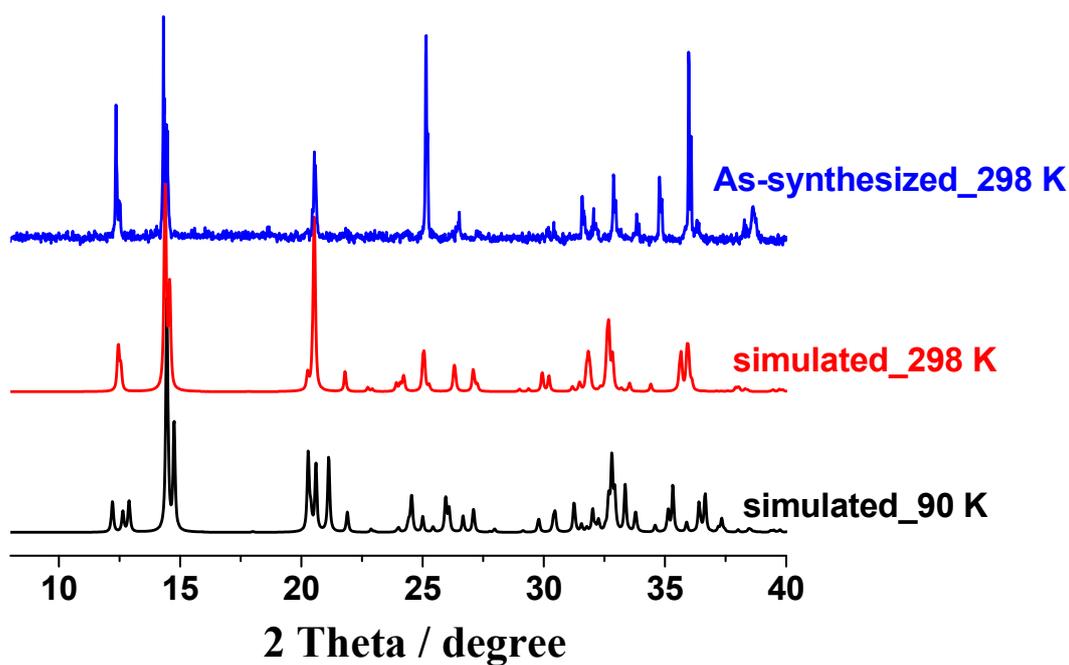
**Synthesis of  $[\text{NH}_4]_2[\text{NiCd}(\text{SCN})_6]$  (**1**).**  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (291 mg, 1 mmol),  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (308 mg, 1 mmol) and KSCN (583 mg, 6 mmol) was added into 12 mL methanol. The mixture was stirred for 30 minutes, and then filtered. The resultant light green solution was allowed to stand at room temperature. After three days, blue block-shaped crystals of **1** were deposited from the filtrates, in ca. 70% yield based on Cd.

**Single-crystal X-ray crystallography.** Diffraction intensities for a single-crystal at 90 K, and 298 K were collected on an Oxford Gemini S Ultra CCD diffractometer with graphite-monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The sample temperature was controlled by a dry nitrogen open flow using a Cryojet controller of Oxford Instrument, and corrected by a thermal couple at the crystal position. Absorption corrections were applied by using multi-scan program SADABS.<sup>S1</sup> Using Olex2,<sup>S2</sup> the structure was solved with the ShelXS<sup>S3</sup> structure solution program using Direct Methods and refined with the ShelXL<sup>S4</sup> refinement package using least-squares minimisation. Anisotropic thermal parameters were applied to all non-hydrogen atoms. All the hydrogen atoms were generated geometrically.

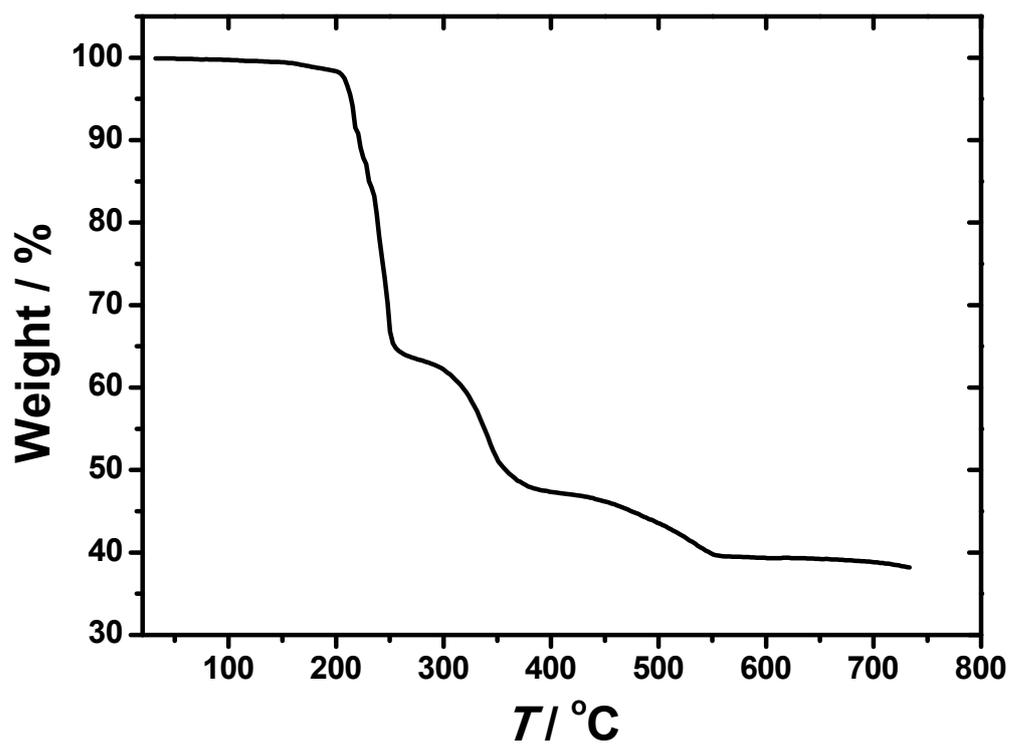
**Table 1** The geometric data (Å, °) of hydrogen-bonding interactions in **1**.

Temperature	D–H···A	D···A	D–H–A
90 K	N4–H4A···S1	3.248(4)	172.5
	N4–H4B···S1a	3.312(4)	148.6
	N4–H4D···S2c	3.315(4)	145.2
298 K	N4–H4A···S2a	3.44(2)	140.3
	N4–H4B···S1	3.42(2)	154.6
	N4–H4C···S3b	3.28(2)	140.4
	N4–H4D···S2c	3.29(2)	167.0
	N4'–H4'A···S1	3.23(1)	170.5
	N4'–H4'D···S2c	3.32(1)	171.5

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



**Fig. S1** Powder XRD patterns of **1**.



**Fig. S2** TGA curve for **1**.

#### References

- S1. APEX2, SADABS and SAINT. Bruker AXS Inc.: Madison, Wisconsin, USA. 2008.
- S2. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst.* 42, 339-341.
- S3. Sheldrick, G.M. (2008). *Acta Cryst.* A64, 112-122.
- S4. Sheldrick, G.M. (2015). *Acta Cryst.* C71, 3-8.