

## Supporting Information

### **A pentanuclear {Co<sub>5</sub>} cluster motif forming a capped breathing kagomé lattice**

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**Fig. S1** Co 2p XPS spectrum of compound **1**.

**Fig. S2** ac susceptibilities of compound **1** measured with different frequencies from 100 to 10000 Hz.

**Fig. S3** Magnetization plateau under applied field at 2K for **1**.

**Fig. S4** The PXRD patterns of compound **1**.

**Fig. S5** The TGA profile of compound **1**.

**Fig. S6** The IR spectrum of compound **1**.

**Table S1** Crystal data and structure refinements for compound **1**

**Table S2** Bond lengths [Å] and angles [°] for compound **1**

### **Experimental details:**

#### **1. Materials and Instrumentation**

All chemicals for the synthesis were used as supplied without further purification. Powder X-ray diffraction (PXRD) pattern was obtained on crushed single crystals in the 2θ range of 5-50° using Cu Kα radiation on a Mini Flex 600 X-Ray Diffractometer. Thermogravimetric experiment was carried out

using a GA/NETZSCH STA449C instrument heated from 30-1000 °C (heating rate of 10 °C min<sup>-1</sup>, nitrogen stream). FT-IR spectra were recorded on a PerkinElmer Spectrum One Spectrometer using KBr as pellets in the range 4000-400 cm<sup>-1</sup>. X-ray photoelectron spectrum (XPS) was recorded by using a Thermo Scientific ESCALAB 250Xi Spectrometer. Magnetic property measurements were performed with a Quantum Design PPMS-9T system. Diamagnetic corrections were made using Pascal's constants.

## 2. Synthesis of Compound 1

A mixture of CoCl<sub>2</sub>·6H<sub>2</sub>O (59.46 mg, 0.25 mmol), 2-mercaptoisonicotinic acid (77.50 mg, 0.5 mmol), distilled water (3.0 mL) and acetonitrile (4.0 mL) were sealed in a 25 mL Teflon-lined stainless-steel vessel (25 mL), and heated at 160 °C for 3 days. The reactor was then cooled to room temperature for 2 days. Orange block crystals of **1** were isolated (40 mg, 36% yield, based on the ligand). Anal. Calc. (%) for C<sub>36</sub>H<sub>46</sub>N<sub>6</sub>O<sub>28</sub>S<sub>3</sub>Co<sub>5</sub>: C, 30.83, H, 3.28, N, 5.99. Found: C, 30.94, H, 3.28, N, 6.08. IR (cm<sup>-1</sup>): 3390 (w), 1633 (s), 1598 (s), 1540 (s), 1368 (vs), 1400 (vs), 781 (m), 752 (m), 688 (m), 680 (w), 574(w).

## 3. Crystal Structure Analysis

Single-crystal X-ray diffraction data was collected on a Rigaku diffractometer with a Saturn 724 CCD area detector (Mo K $\alpha$ ;  $\lambda$  = 0.71073 Å). The structures were solved by SHELXT methods with the Olex2 program,<sup>1,2</sup> and refined by the full-matrix least squares methods based on  $F^2$  with anisotropic thermal parameters for all non-H atoms using the SHELXL-2016 program.<sup>1</sup> The hydrogen atoms of the organic ligands and the coordinated water molecules were generated geometrically and refined as riding. Because the lattice water molecules are highly disordered, their hydrogen atoms, together with those of the hydronium ions have not been determined. A summary of the crystallographic details is tabulated in Table S1 and the selected bond lengths and angles are listed in Table S2. Crystallographic data for **1** have been deposited at the Cambridge Crystallographic Data Centre.

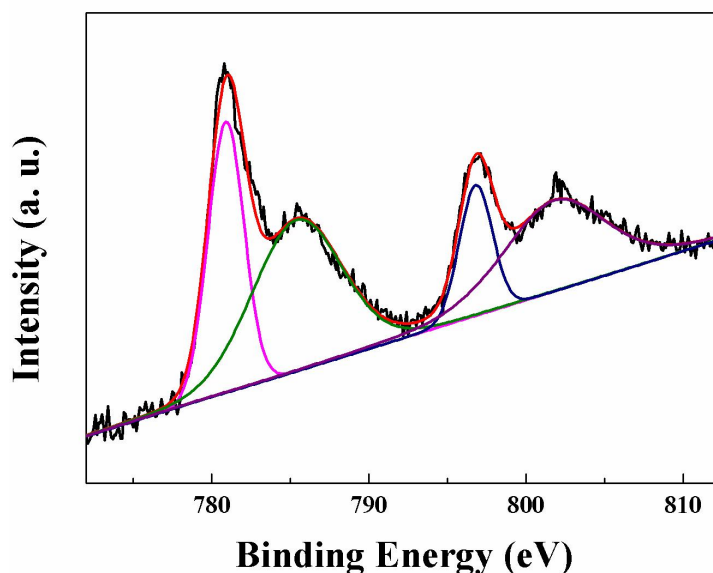
## 4. Characterization of compound 1

The Co2p XPS spectrum is shown in Fig. S1, in which the peaks corresponding to Co 2p<sup>3/2</sup> and Co 2p<sup>1/2</sup> are at around 780.9 and 796.8 eV, respectively, with a  $\Delta E_{3/2-1/2}$  of -15.9 eV, suggesting that in **1** the state of cobalt must be Co<sup>2+</sup>. The phase purity

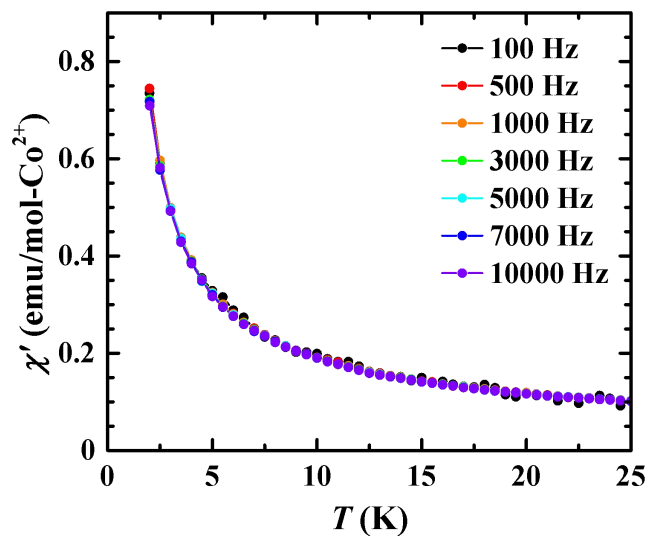
of **1** was confirmed by recording its X-ray powder diffraction data. As shown in Fig. S4), similar diffraction patterns between the simulated data (calculated from the single-crystal X-ray diffraction) and the experimental data ensured the bulk homogeneity of **1**. TGA curve of **1** (Fig. S5) displays a weight loss of 12.44% at about 138 °C corresponding to the loss of the lattice water molecules in **1** (calculated: 12.84%). The water-free framework remains stable up to 320 °C, at which it starts to decompose. In FT-IR spectrum of **1** (Fig. S6), the characteristic bands in the region 1632-1400  $\text{cm}^{-1}$  can be assigned to the carboxylate moiety of the  $\text{L}^{2-}$  ligand. The broad band at 3390  $\text{cm}^{-1}$  is attributed to the characteristic stretching of O–H groups.

## 5. Reference

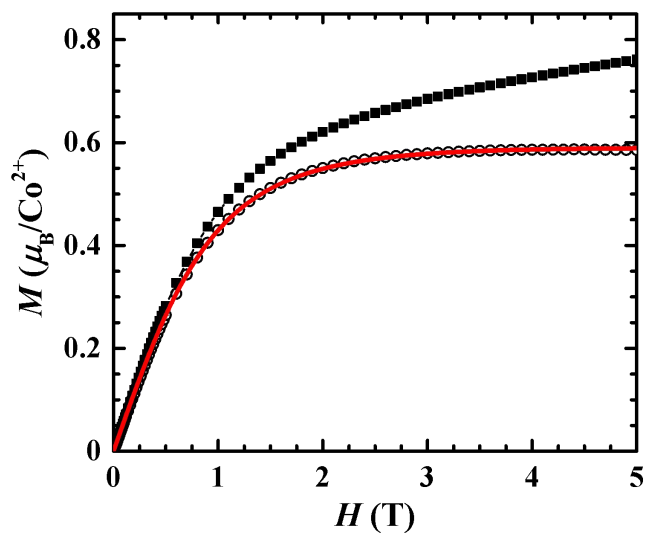
1. G. M. Sheldrick, *Acta Crystallogr., C: Struct. Chem.*, 2015, **A71**, 3–8.
2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.



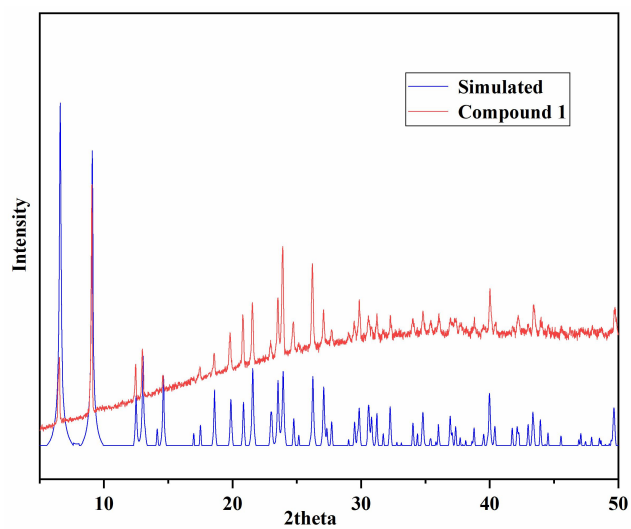
**Fig. S1** Co 2p XPS spectrum of compound **1**.



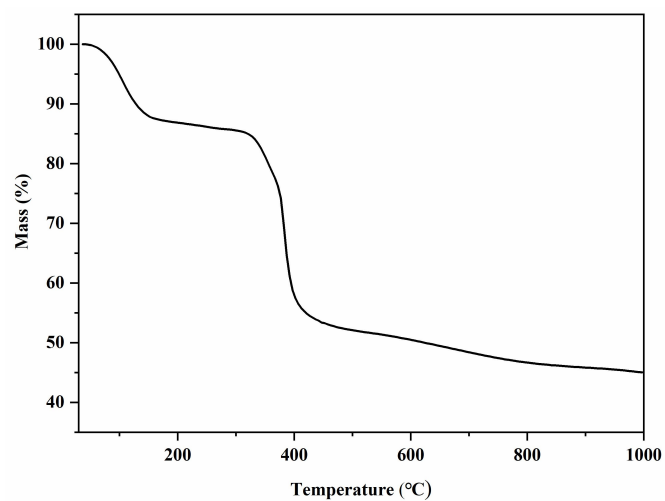
**Fig. S2** ac susceptibilities of compound **1** measured with different frequencies from 100 to 10000 Hz.



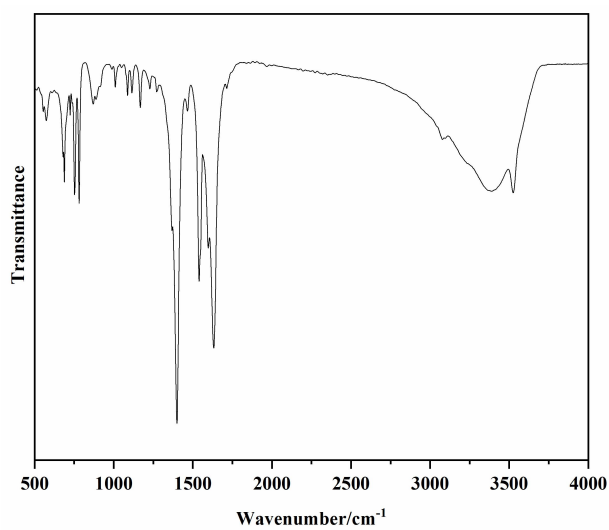
**Fig. S3** Magnetization plateau under applied field at 2K for **1**. Here the open circles are raw data (solid) subtracting the Van Vleck paramagnetic contribution with linear component and the red line is the fit using the spin-3/2 Brillouin function.



**Fig. S4** The PXRD patterns of compound **1**.



**Fig. S5** The TGA profile of compound **1**.



**Fig. S6** The IR spectrum of compound **1**.

**Table S1** Crystal data and structure refinements for compound **1**

Empirical formula	C <sub>36</sub> H <sub>46</sub> Co <sub>5</sub> N <sub>6</sub> O <sub>28</sub> S <sub>3</sub>
Formula weight	1401.45
<i>T</i> , K	Room temperature
$\lambda$ , Å	0.71073
Space group	<i>P</i> 6 <sub>3</sub> / <i>m</i>
<i>a</i> , Å	15.469(4)
<i>c</i> , Å	14.150(6)
<i>V</i> , Å <sup>3</sup>	2932(2)
<i>Z</i>	6
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.588
$\mu$ , mm <sup>-1</sup>	1.576
GOF on <i>F</i> <sup>2</sup>	1.248
<i>F</i> (000)	1378
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>a</sup>	0.0507, 0.1265
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0511, 0.1268

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

**Table S2** Bond lengths [Å] and angles [°] for compound **1**

Co1–O1	2.121(3)	O3–Co1–O3A	86.83(14)
Co1–O3	2.082(3)	O1–Co2–O2	96.08(12)
Co2–O1	2.000(4)	O1–Co2–O4	178.7(2)
Co2–O2	2.097(3)	O2–Co2–O2C	86.96(15)
Co2–O4	2.143(6)	O2–Co2–O4	82.96(15)
Co2–N1	2.182(4)	O1–Co2–N1	93.99(13)
O1–Co1–O1A	79.93(11)	O2–Co2–N1	92.35(13)
O3–Co1–O1	100.52(13)	O2–Co2–N1C	169.92(14)
O3–Co1–O1A	172.61(14)	O4–Co2–N1	86.97(16)
O3–Co1–O1B	92.86(13)	N1–Co2–N1C	86.69(19)

Symmetry codes: A: 1 - *x* + *y*, -*x*, *z*; B: -*y*, -1 + *x* - *y*, *z*; C: *x*, *y*, 0.5 - *z*.