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Electronic Supplementary Information

A Bilayer Triangular Lattice with Crown–like Co_7 Spin Cluster SBUs Exhibiting High Spin Frustration

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Experimental Section

Materials and Physical Measurements

All materials were commercially available and used as received. Infrared spectrum was recorded on a Nicolet magna 750 FT-IR spectrophotometer using KBr pellets in the range of 400~4000 cm^{-1}. Elemental analyses were performed *via* Vario EL III Etro Elemental Analyzer. Thermogravimetric analysis (TGA) was performed under atmosphere with a heating rate of 10 °C/min^{-1} using TGA/SDTA851e. Powder X-ray diffraction (PXRD) pattern was recorded on a Philips X′PertPro instrument with Cu *Kα* radiation (λ = 1.54056 Å) in the range 2 θ = 5–50° at room temperature. Magnetic measurements were carried out on a Quantum Design MPMS-XL SQUID magnetometer, and diamagnetic corrections were estimated from Pascal's constants.

Synthesis of $\{[Co_7(OH)_6(1,4\text{-npa})_4(H_2O)_3](dmt)_{0.5}\cdot 4H_2O\}_n$ (1)

A mixture of $CoCl_2\cdot 6H_2O$ (0.476 g, 2 mmol), 1,4-npa (0.216 g, 1 mmol) and dmt (0.125 g, 1 mmol), and H_2O (10 mL) was placed in a Teflon–lined stainless steel vessel, heated to 150 °C for 3 days, then cooled to room temperature. Red crystals of **1** were obtained, washed by H_2O (Yield: 0.086 g, 22.3 % based on 1,4-npa). Elemental analysis (%): calcd for C 38.50, H 3.07, N 2.24; found C 38.47, H 3.46, N 2.35.

Crystallographical Section

X–ray single crystal data were collected at 113.15 K on a MERCURY–CCD areadetector diffractometer with Mo *Kα* radiation (λ = 0.71073 Å). Data reduction and absorption correction were made with multi–scan methods. These structures were solved by direct methods using SHELXS–97[1] and refined by full matrix least–squares methods using SHELXL–97[2]. Anisotropic displacement parameters were refined for non–hydrogen atoms except O8, O9, O8A, O9A, C12A, C13A, C31 and C31A. Crystal data for $Co_7C_{50}H_{47.5}N_{2.5}O_{29}$, M_r = 1559.92, trigonal, space group *R*–3, *a* = 14.997(3) Å, *b* = 14.997(3) Å, *c* = 52.244(16) Å, γ = 120 °, *V* = 10176 $Å^3$, *T* = 113.15 K, *Z* = 6, μ = 1.749 mm^{-1}, ρ = 1.527 *g*/cm^{-3}, *S* = 1.048, *R* = 0.0650, and *wR* = 0.1912 for independent reflections 3694 [$I > 2\sigma(I)$]. Due to high symmetry, two 1,4-naphthalic acid ligands are disordered and treated as two parts. The disordered guest molecule (2,4-diamine-6-methyl-triazine) or solvents in the lattice pores could not be modeled in terms of atomic sites and were treated using the SQUEEZE routine[3] in the PLATON software package[4]. However, due to the addition of the guest and solvent molecules to the SFAC and UNIT list, the cell content didn't agree, accordingly, Alert level A “CHEMW03_ALERT_2_A ALERT: The ratio of given/expected molecular weight

as calculated…" appeared. Crystal data and refinement details are presented in Table S1. Selected bond distances and bond angles are listed in Table S2.

Table S1 Crystallographic data for compound **1**.

	1
Empirical formula	$C_{50}H_{47.5}Co_7N_{2.5}O_{29}$
Formula weight	1559.92
Crystal system	trigonal
Space group	*R*–3
Unit cell dimensions	
a (Å)	14.997(3)
b (Å)	14.997(3)
c (Å)	52.244(16)
γ (º)	120
V (Å^3)	10176(4)
Z	6
ρ calcd.(Mg/m^3)	1.527
μ (mm^{-1})	1.749
F(000)	4716
θ limits (º)	2.96 to 25
h, *k*, *l* limits	–17 to 17, –17 to 17, –58 to 62
Reflections collected / unique	22014 / 3694 [*R*(int) = 0.0232]
Data / restraints / parameters	3952 / 655 / 432
GOOF	1.084
R index [$I>2\sigma(I)$]	$R_1 = 0.0650$, $wR_2 = 0.1912$
R (all data)	$R_1 = 0.0672$, $wR_2 = 0.1941$
Largest and mean delta/sigma	0.001/0.000

$R = \sum(||F_o|-|F_c||)/\sum|F_o|$, $wR = \{\sum w[(F_o^2-F_c^2)^2]/\sum w[(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$, $P = (F_o^2+2F_c^2)/3]$, $a = 0.1275$, $b = 107.5097$.

Table S2 Selected bond lengths [Å] and angles [°] for compound **1**.

Bond length [Å]			
Co(1)–O(6)	2.048(4)	Co(2)–O(7)	2.090(4)
Co(1)–O(4)	2.049(4)	Co(2)–O(5)	2.092(4)
Co(1)–O(9)	2.049(4)	Co(2)–O(3)	2.109(4)
Co(1)–O(1)	2.077(4)	Co(2)–O(2)	2.261(3)
Co(1)–O(2)	2.155(3)	Co(3)–O(8A)	1.983(13)
Co(1)–O(8)#1	2.161(12)	Co(3)–O(8A)#1	2.396(12)
Co(1)–Co(3)	2.9143(9)	Co(3)–O(2)	2.168(3)
Co(2)–O(1)	2.054(3)		
Bond angles [°]			
O(6)–Co(1)–O(4)	86.3(2)	O(7)–Co(2)–O(2)	98.29(14)
O(6)–Co(1)–O(9)	80.3(2)	O(5)–Co(2)–O(2)	98.11(14)
O(4)–Co(1)–O(9)	80.4(2)	O(3)–Co(2)–O(2)	174.02(13)
O(6)–Co(1)–O(1)	97.81(16)	O(2)–Co(3)–O(8)	100.7(4)
O(9)–Co(1)–O(1)	177.2(2)	O(8)#3–Co(3)–O(8)#2	71.6(6)
O(6)–Co(1)–O(2)	177.67(18)	O(8)#3–Co(3)–O(2)#2	103.4(4)
O(4)–Co(1)–O(2)	94.69(18)	O(8)#2Co(3)–O(2)#2	100.7(4)
O(9)–Co(1)–O(2)	97.8(2)	O(8)–Co(3)–O(2)#2	171.7(4)
O(1)–Co(1)–O(2)	84.15(11)	O(8–Co(3)–O(2)#3	103.4(4)
O(1)–Co(2)–O(1)#2	98.79(15)	O(2)#2o(3)–O(2)#3	83.89(12)
O(1)–Co(2)–O(7)	171.38(16)	O(8)#3–Co(3)–O(2)	171.4(4)
O(1)–Co(2)–O(5)	90.29(16)	O(8)#3–Co(3)–O(8A)#4	35.0(5)
O(7)–Co(2)–O(5)	81.1(2)	O(8)#2–Co(3)–O(8A)#4	98.2(5)
O(1)–Co(2)–O(3)	94.04(13)	O(2)#2–Co(3)–O(8A)#4	76.4(4)
O(7)–Co(2)–O(3)	86.27(15)	O(2)#3–Co(3)–O(8A)#4	76.0(3)
O(5)–Co(2)–O(3)	86.37(15)	O(2)–Co(3)–O(8A)#4	153.1(3)
O(1)–Co(2)–O(2)	82.03(11)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+y+1$, $-x-1$, z; #2 $2-x$, $y-2$, $1+z$; #3 $3+x$, $2+y$, $2+z$; #4 $-x+y$, $-x$, $2+z$.

Table 3 BVS analyses of Co, μ_3–O and μ_4–O atoms for compound **1**.

Atoms	Co(1)	Co(2)	Co(3)	μ_3–O(1)	μ_4–O(2)
BVS	1.970	1.969	2.148	1.104	1.134
Assignment	Co^{2+}	Co^{2+}	Co^{2+}	OH^-	OH^-

The oxidation state of a particular atom can be taken as the nearest integer to the value.[5]

Physical Characterization Section

From IR spectra (Fig. S1), the sharp peak at 3605 cm^{-1} of **1** should be attributed to the stretching vibration of OH groups, demonstrating the existence of OH group in compound **1**. The antisymmetric stretching vibration of carboxylic group is assigned to the 1573 cm^{-1}, while the symmetric stretching vibration at 1371 cm^{-1}, which show the bridging mode of carboxylic group.[6]

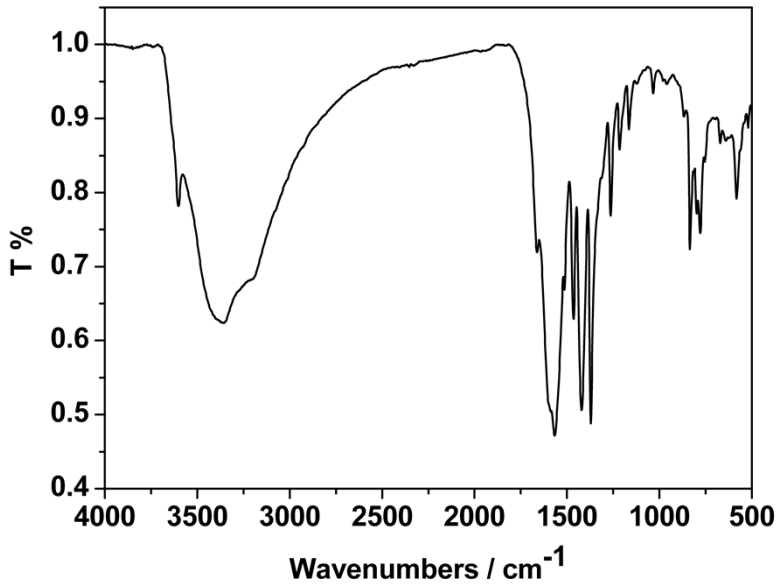

Fig. S1 IR spectra for the compound **1**.

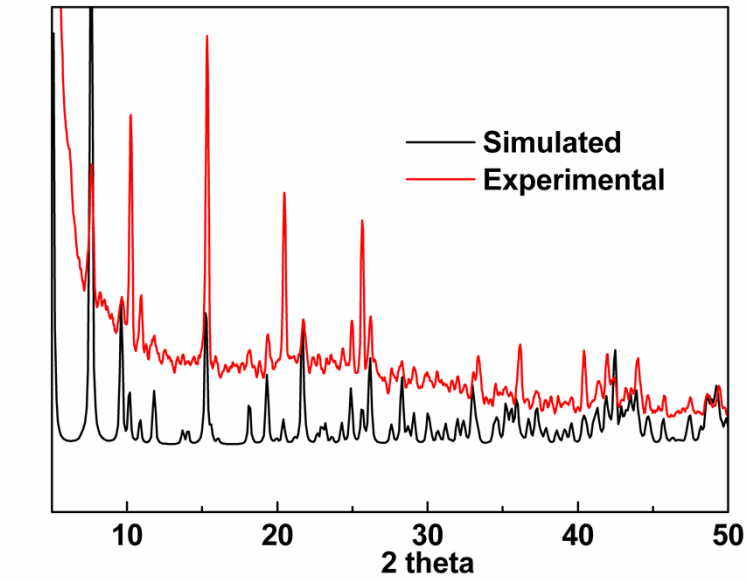

Fig. S2 PXRD curves for the cmpound **1.**

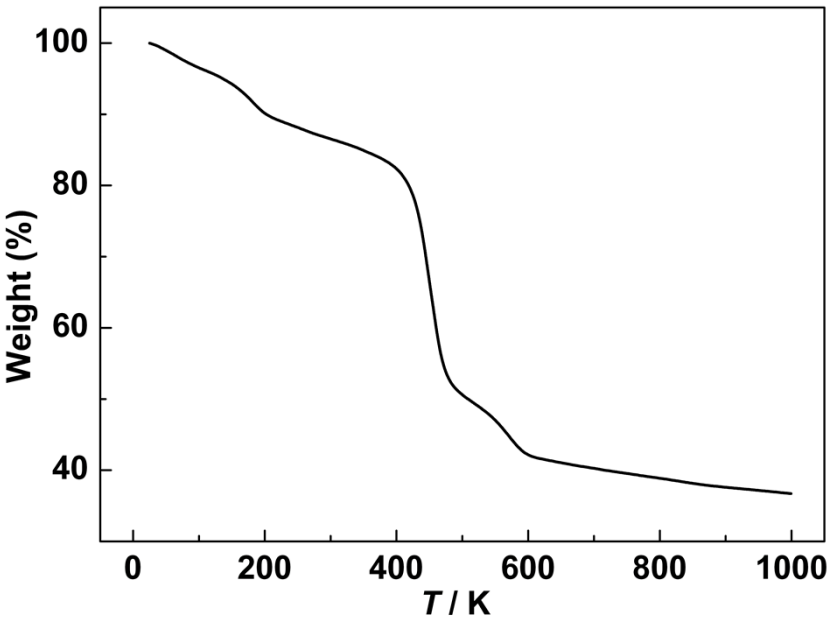

Fig. S3 TGA curve for the compound **1**.

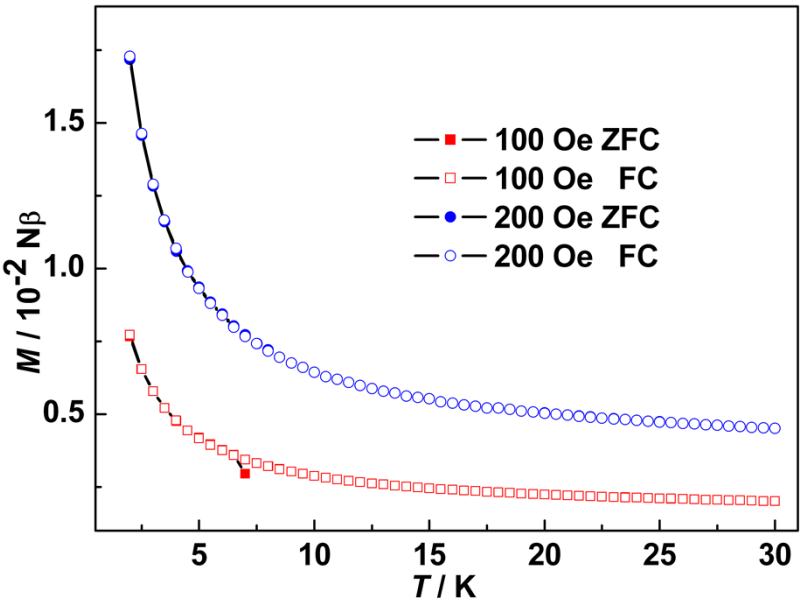

Fig. S4 FCM and ZFCM curves at 100 Oe and 200 Oe for **1**.

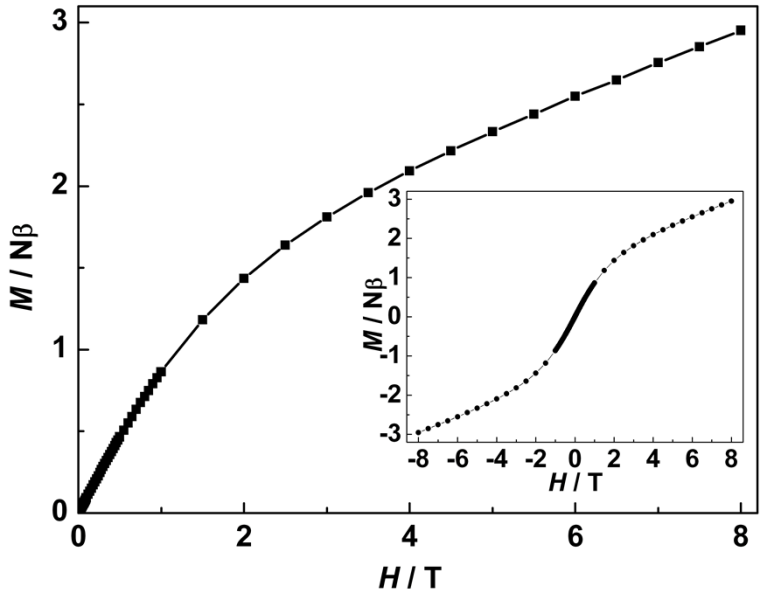

Fig. S5 The curves of magnetization *vs.* applied fields at 2 K in **1**.

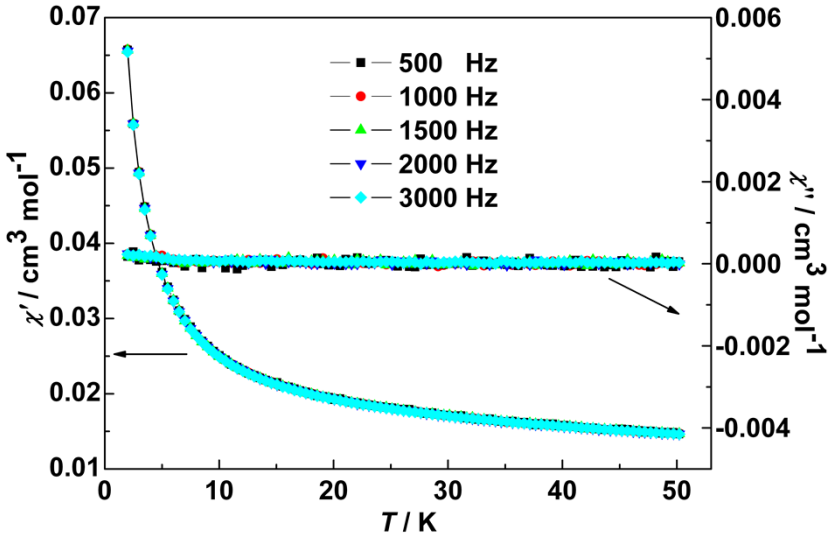

Fig. S6 Plots of the temperature dependence of the ac susceptibility χ' and χ'' obtained at 3 Oe field for **1**.

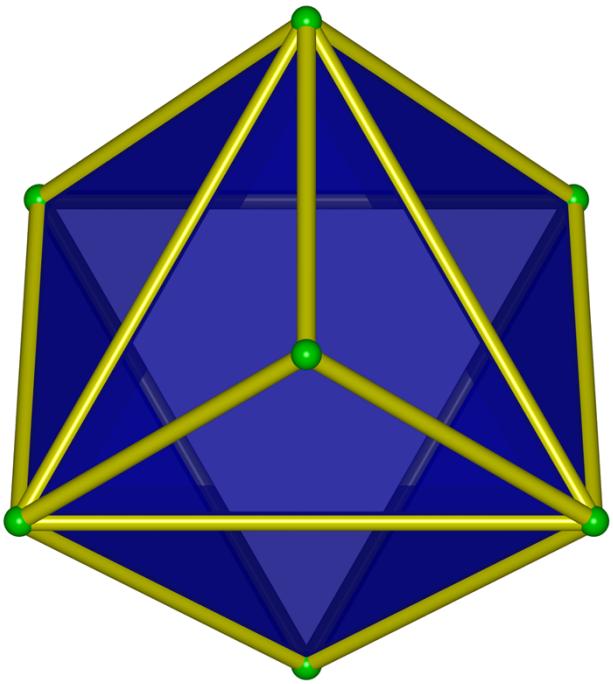

Fig. S7 The cobalt skeleton highlighting the polyhedron with eleven triangular faces shaded in blue for **1**.

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