

Electronic Supplementary Information

A Homospin Cobalt(II) Topological Ferrimagnet

Ji-Yong Zou,^{a,b} Wei Shi,^{*a} Na Xu,^a Lei-Lei Li,^a Jin-Kui Tang,^c Hong-Ling Gao,^b Jian-Zhong Cui^b and Peng Cheng^{*a}

^a Department of Chemistry, Key Laboratory of Advanced Energy Material Chemistry (MOE), and Tianjin Co-Innovation Center of Chemical Science and Engineering, Nankai University, Tianjin 300071, P. R. China.

^b Department of Chemistry, Tianjin University, Tianjin 300072, P. R. China.

^c State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China.

1. Synthesis.....	2
2. Crystallographic Studies.....	4
3. Thermogravimetric Analysis.....	5
4. Power X-Ray Diffraction.....	5
5. X-ray Photoelectron Spectroscopy.....	6
6. Magnetic Data.....	6
7. BVS Calculation.....	8

1. Synthesis

Materials and General Characterization. H₃TDA (H₃TDA = 1*H*-1,2,3-triazole-4,5-dicarboxylic acid) was prepared according to literature.¹ All other reagents and solvents employed were commercially available and used as received without further purification. Elemental analyses for C, H and N were carried out on a Perkin–Elmer analyzer. Powder X-ray diffraction measurements were recorded on a D/Max-2500 X-ray diffractometer using Cu-K α radiation. FT-IR spectra were measured with a Bruker Tensor 27 Spectrometer on KBr disks. Thermogravimetric analysis (TGA) was carried out on a Delta Series TA-SDTQ600 analyzer in nitrogen atmosphere from room temperature to 800 °C (10 °C min⁻¹) using aluminum crucibles. Magnetic susceptibility measurements were performed on a Quantum Design SQUID MPMS XL-7 magnetometer. Diamagnetic corrections were made for all the constituent atoms with Pascal's constants and the sample holders. X-ray Photoelectron Spectroscopy (XPS) was carried out on Axis Ultra DLD.

Synthesis of {[H₂N(CH₃)₂][Co₃(TDA)₂(TZ)(H₂O)]·3.5H₂O}_n (1): A mixture of Co(OAc)₂·4H₂O (0.0252 g, 0.1 mmol), H₃TDA (0.0319 g, 0.2 mmol) and HTZ (0.0070 g, 0.1 mmol) (HTZ = 1*H*-1,2,4-triazole) was dissolved in H₂O (3 mL) and DMF (3 mL). The pH of the solution was adjusted to 6.46 with 0.2 mol dm⁻³ NaHCO₃ aqueous solution. The mixture was sealed in a 25 mL Teflon-lined stainless steel reactor heated at 90 °C for 72 h, and then cooled to room temperature at a speed of 1 °C h⁻¹. Pink rhombic crystals of **1** in *ca.* 43% yield (based on Co) were obtained. Anal. calcd. Calcd for C₁₂H₁₉N₁₀O_{12.5}Co₃ (%): C, 21.19; H, 2.82; N,

20.59. Found (%): C, 21.36; H, 2.75; N, 20.64. IR (KBr, cm^{-1}): 3436s, 3192s, 1680m, 1599vs, 1513m, 1412vs, 1372m, 1291s, 1225s, 1146s, 1070m, 991w, 831m, 703m, 661m.

2. Crystallographic Studies

Single-crystal X-ray diffraction measurement of **1** was recorded on an Oxford Supernova diffractometer with a graphite monochromatic *Mo-K α* radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct method and refined by full-matrix least-squares techniques on F^2 using the *SHELXS-97* and *SHELXS-97* programs.² Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were placed in idealized positions and located in the difference Fourier map. The formula was identified by combining single-crystal structure, element analysis and thermogravimetric analysis (Figure S1). The crystallographic data for **1** are listed in Table S1. Selected bond lengths and bond angles are listed in Table S2. CCDC 909522 for **1** contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/data_request/cif).

Scheme S1. Representation of H₃TDA and HTZ and their coordination modes in **1**.

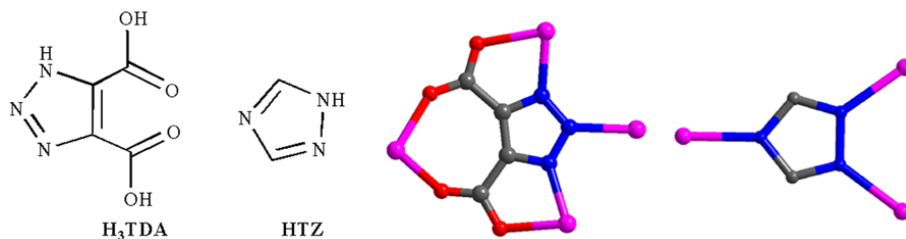


Table S1. Crystal data and structure refinements for **1**.

compound	1
formula	C ₁₂ H ₁₉ N ₁₀ O _{12.5} Co ₃
formula weight	680.14
crystal system	orthorhombic
space group	<i>Fddd</i>
<i>a</i> (Å)	15.6139(8)
<i>b</i> (Å)	18.3439(11)
<i>c</i> (Å)	34.336(3)
α (°)	90
β (°)	90
γ (°)	90
<i>V</i> (Å ³)	9834.5(11)
<i>Z</i>	16
<i>D_c</i> , g cm ⁻³	1.829
μ , mm ⁻¹	2.079
F(000)	5424
GOF on <i>F</i> ²	1.127
<i>R</i> _{int}	0.0486
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > σ (<i>I</i>)]	0.0490, 0.1473
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0694, 0.1574
Residues (e Å ⁻³)	1.263/-0.410

Table S2. Selected bonds lengths (Å) and angles (°) for **1**.

1			
Co1—N1 ^{#1}	2.048(5)	N2—Co1—O4 ^{#3}	114.23(19)
Co1—N4 ^{#2}	2.079(5)	N1 ^{#1} —Co1—O2 ^{#1}	75.40(17)
Co1—N3 ^{#3}	2.091(5)	N4 ^{#2} —Co1—O2 ^{#1}	85.68(18)
Co1—N2	2.156(5)	N3 ^{#3} —Co1—O2 ^{#1}	110.28(17)
Co1—O4 ^{#3}	2.230(4)	N2—Co1—O2 ^{#1}	161.51(18)
Co1—O2 ^{#1}	2.247(4)	O4 ^{#3} —Co1—O2 ^{#1}	77.93(17)
Co2—N5	2.063(7)	N5—Co2—O5	180.0
Co2—O5	2.063(7)	N5—Co2—O3 ^{#4}	90.98(13)
Co2—O3	2.085(4)	O5—Co2—O3 ^{#4}	89.02(13)
Co2—O3 ^{#4}	2.085(4)	N5—Co2—O3	90.98(13)
Co2—O1	2.155(4)	O5—Co2—O3	89.02(13)
Co2—O1 ^{#4}	2.155(4)	O3 ^{#4} —Co2—O3	178.0(3)
N1 ^{#1} —Co1—N4 ^{#2}	115.3(2)	N5—Co2—O1	88.72(12)
N1 ^{#1} —Co1—N3 ^{#3}	154.9(2)	O5—Co2—O1	91.28(12)
N4 ^{#2} —Co1—N3 ^{#3}	89.7(2)	O3 ^{#4} —Co2—O1	85.74(16)
N1 ^{#1} —Co1—N2	91.41(17)	O3—Co2—O1	94.25(16)
N4 ^{#2} —Co1—N2	88.5(2)	N5—Co2—O1 ^{#4}	88.72(12)
N3 ^{#3} —Co1—N2	87.14(18)	O5—Co2—O1 ^{#4}	91.28(12)
N1 ^{#1} —Co1—O4 ^{#3}	84.56(17)	O3 ^{#4} —Co2—O1 ^{#4}	94.24(16)
N4 ^{#2} —Co1—O4 ^{#3}	150.20(18)	O3—Co2—O1 ^{#4}	85.80(16)
N3 ^{#3} —Co1—O4 ^{#3}	73.26(17)	O1—Co2—O1 ^{#4}	177.4(2)

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1,-y+1,-z+1$ #2 $x-1/4,-y+1,z-1/4$ #3 $-x+5/4,-y+5/4,z$ #4 $-x+7/4,-y+3/4,z$

3. Thermogravimetric Analysis

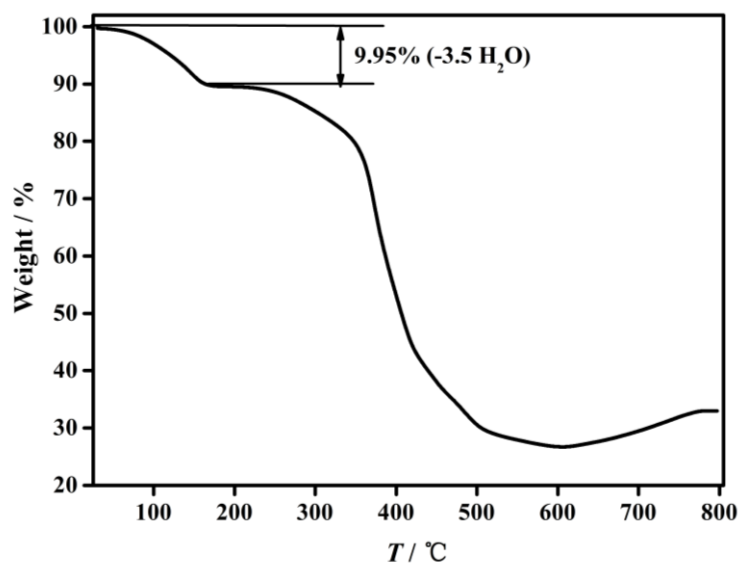


Fig. S1. The thermal gravimetric analysis (TGA) of **1**.

4. Power X-Ray Diffraction

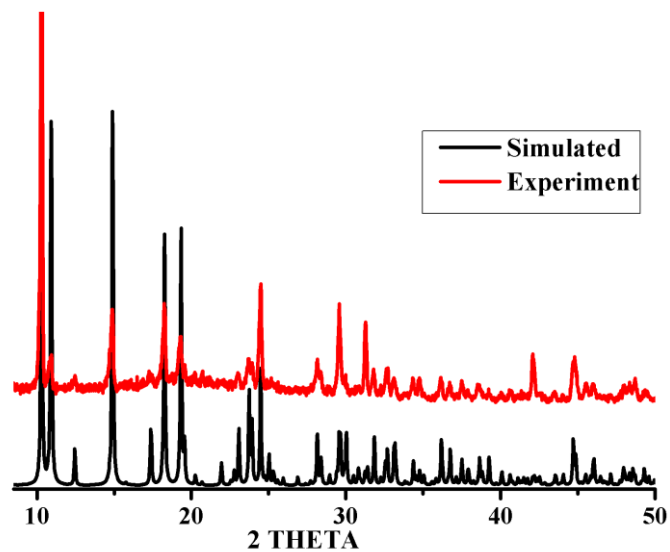


Fig. S2. Comparison of the experimental PXRD pattern of the as-synthesized **1** with the one simulated from its single crystal data.

5. X-ray Photoelectron Spectroscopy

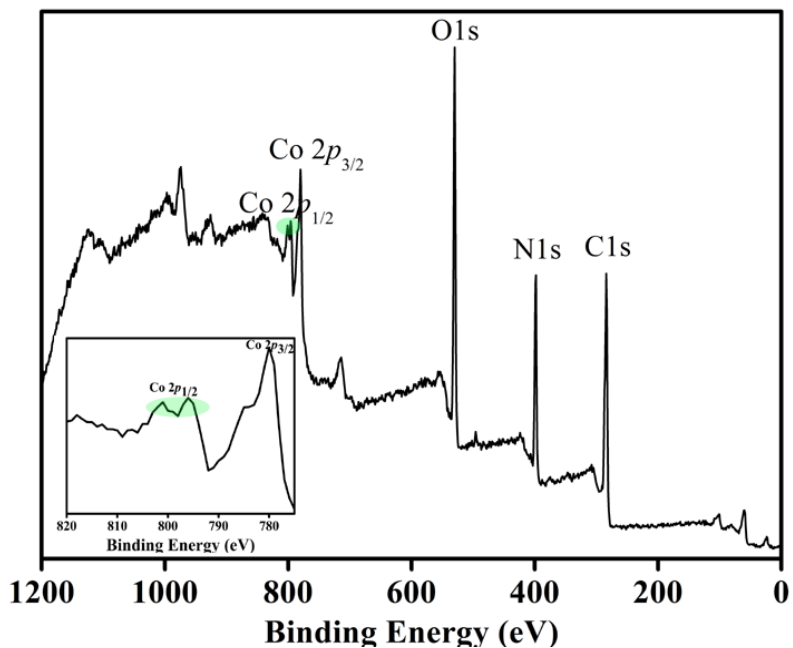


Fig. S3. X-ray photoelectron spectroscopy (XPS) of 1. Inset: XPS of the Co 2p level in 1.

6. Magnetic Data

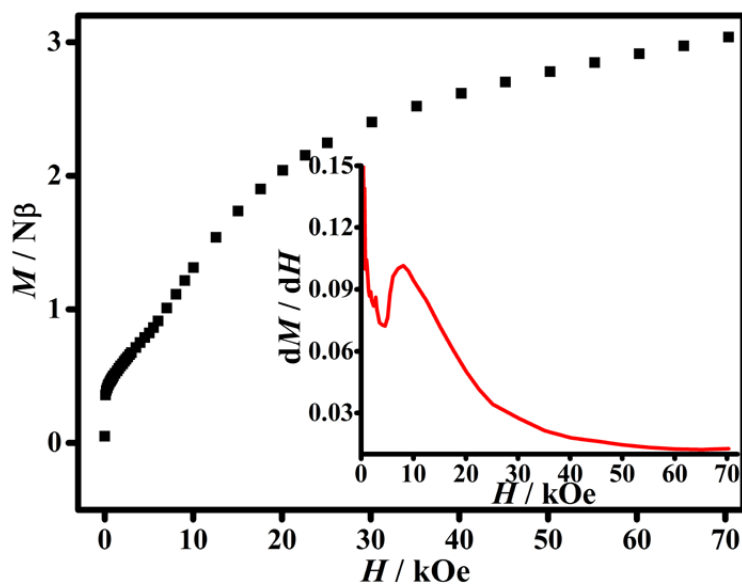


Fig. S4. Field dependence of magnetizations for 1 at 2 K. Inset: The plots of the dM / dH vs H at 2 K for 1.

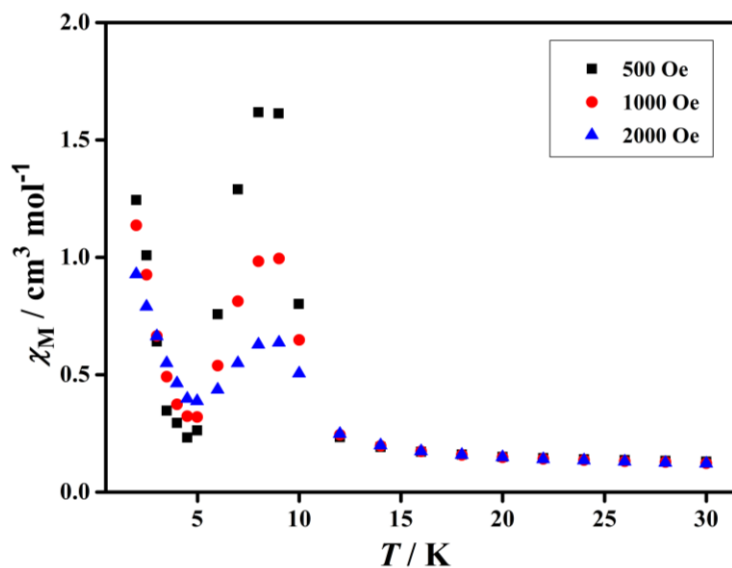


Fig. S5. Temperature dependence of magnetic susceptibilities of **1** in different applied dc field.

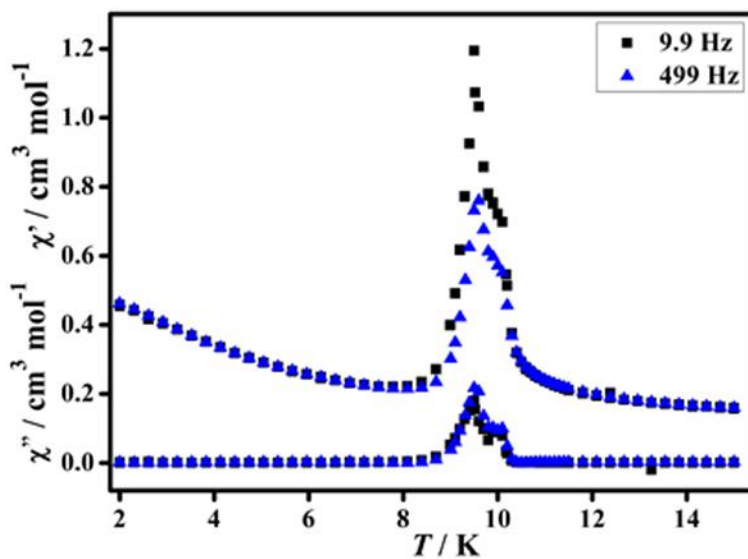


Fig. S6. The *ac* susceptibilities of **1** measured at 9.9 and 499 Hz under zero *dc* field.

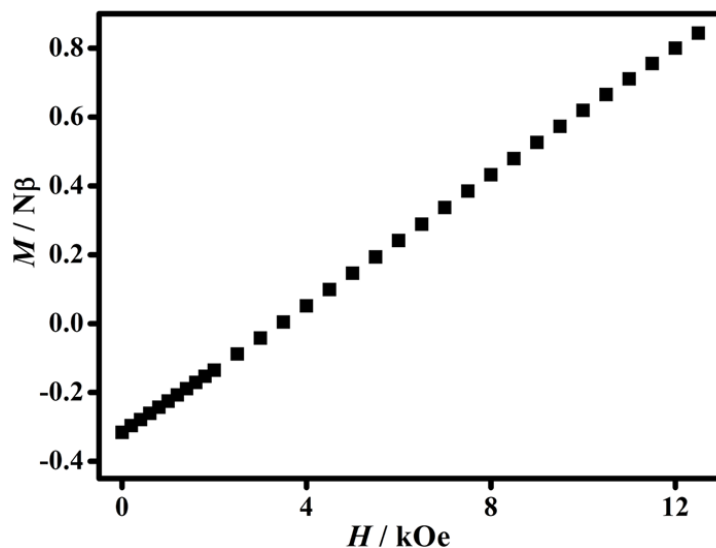


Fig. S7. Field dependence of magnetizations for **1** at 2 K after FC measurement in cooling mode.

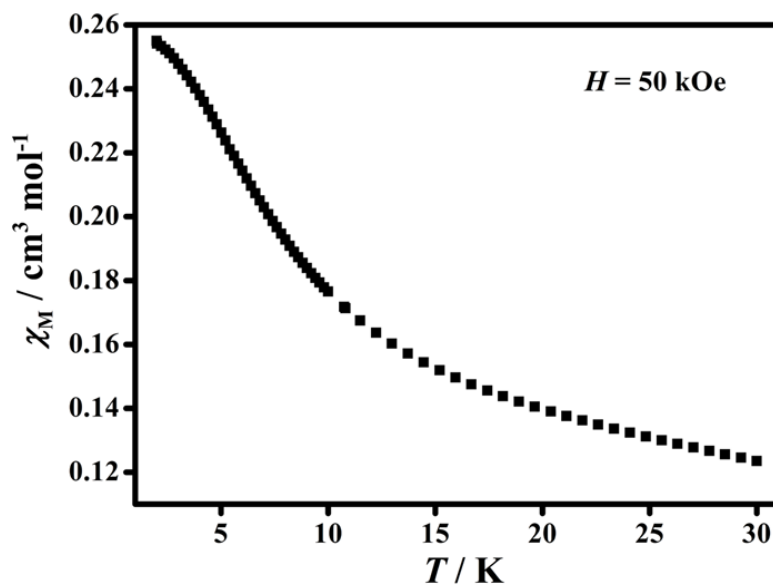


Fig. S8. Temperature dependence of magnetic susceptibilities of **1** at 50 kOe.

7. BVS Calculations

The bond valence sum (BVS) calculations have been carried out based on BVS model.³ In this method, the valence ν_{ij} of a bond between two atoms i and j can be expressed by an empirical expression (eqn (1)) where R_{ij} is the length of the bond and R_0 is a parameter characteristic of the bond.

$$v_{ij} = \exp[(R_0 - R_{ij})/0.37] \quad (1)$$

The sum of all valences from a given atom i with *valence* V_i obey an empirical expression (eqn (2)).

$$V_i = \sum v_i \quad (2)$$

Table S3. Bond valence values for cobalt centers in **1**.

Bond type ^a	Bond distance / Å	Bond valence ^b	Bond valence sum
Co1—N1 ^{#1}	2.048(5)	0.499	2.226 for Co1
Co1—N4 ^{#2}	2.079(5)	0.456	
Co1—N3 ^{#3}	2.091(5)	0.443	
Co1—N2	2.156(5)	0.370	
Co1—O4 ^{#3}	2.230(4)	0.235	
Co1—O2 ^{#1}	2.247(4)	0.223	
Co2—N5	2.063(7)	0.480	2.104 for Co2
Co2—O5	2.063(7)	0.362	
Co2—O3	2.085(4)	0.346	
Co2—O3 ^{#4}	2.085(4)	0.346	
Co2—O1	2.155 (4)	0.285	
Co2—O1 ^{#4}	2.155(4)	0.285	

^a #1 -x+1,-y+1,-z+1 #2 x-1/4,-y+1,z-1/4 #3 -x+5/4,-y+5/4,z #4 -x+7/4,-y+3/4,z
^b $R_0(\text{Co-N}) = 1.790 \text{ \AA}$; $R_0(\text{Co-O}) = 1.692 \text{ \AA}$

1. L. E. Hinlel, G. O. Richards and O. Thomas, *J. Chem. Soc.*, 1937. 1432.
2. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.
3. I. D. Brown, *Chem. Rev.*, 2009, **109**, 6858.