Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers

Electronic Supplementary Information

Spin canting and metamagnetism in 3D pillared-layer homospin cobalt(II) molecular magnetic materials constructed via a mixed ligands approach

Ji-Yong Zou,[a,b] Wei Shi,*[a] 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 Synergetic Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, P. R. China

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

1. Thermogravimetric Analysis

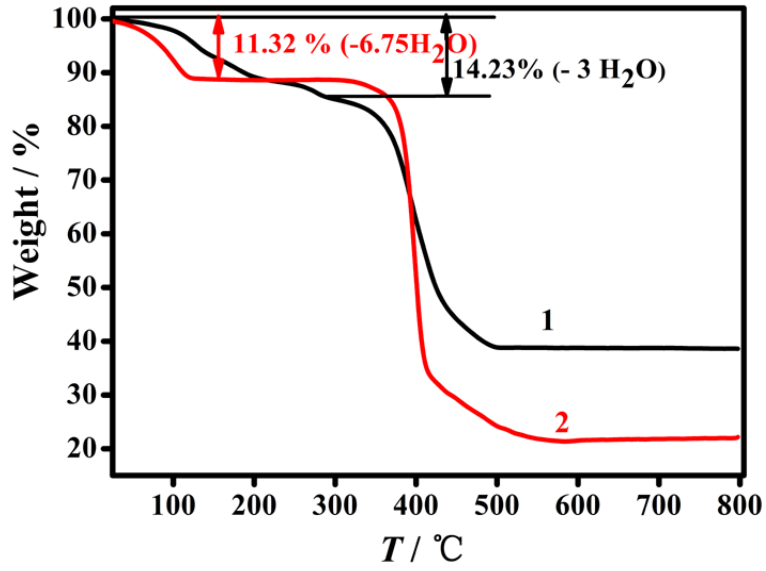

Fig. S1. The thermal gravimetric analysis (TGA) of **1** and **2**.

2. Power X-Ray Diffraction

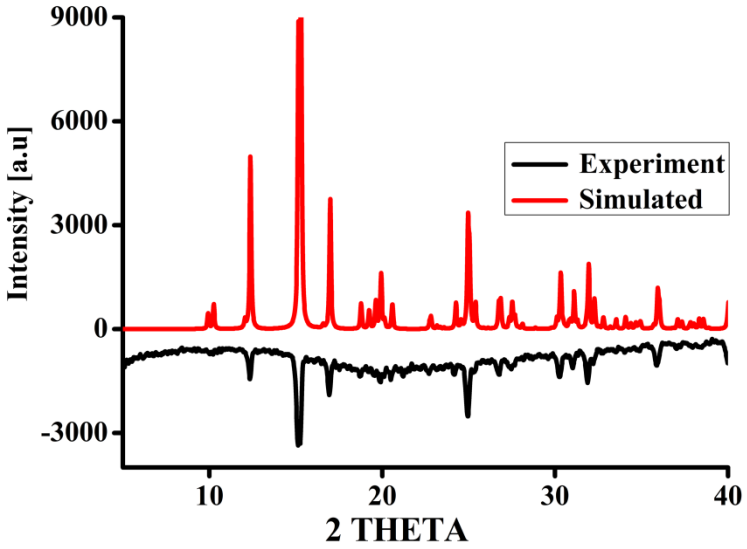

Fig. S2. Comparison of the experimental PXRD pattern of as-synthesized **1** with the one simulated from its single crystal structure.

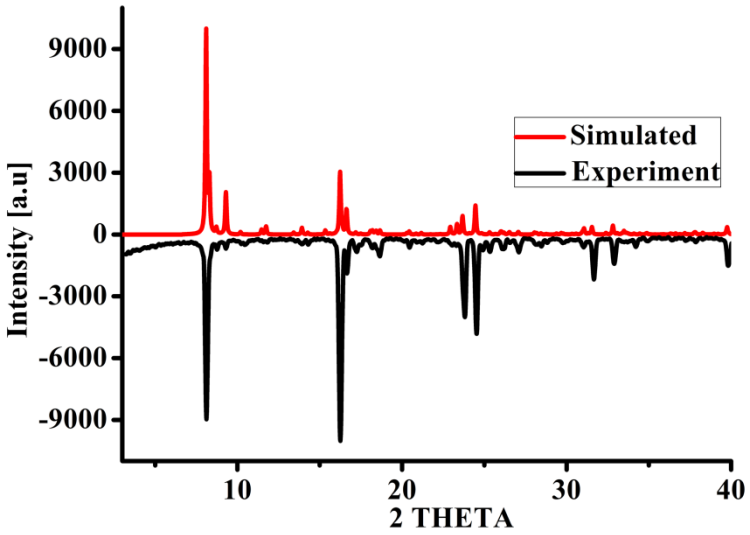

Fig. S3. Comparison of the experimental PXRD pattern of as-synthesized **2** with the one simulated from its single crystal structure.

3. Magnetism Measurements

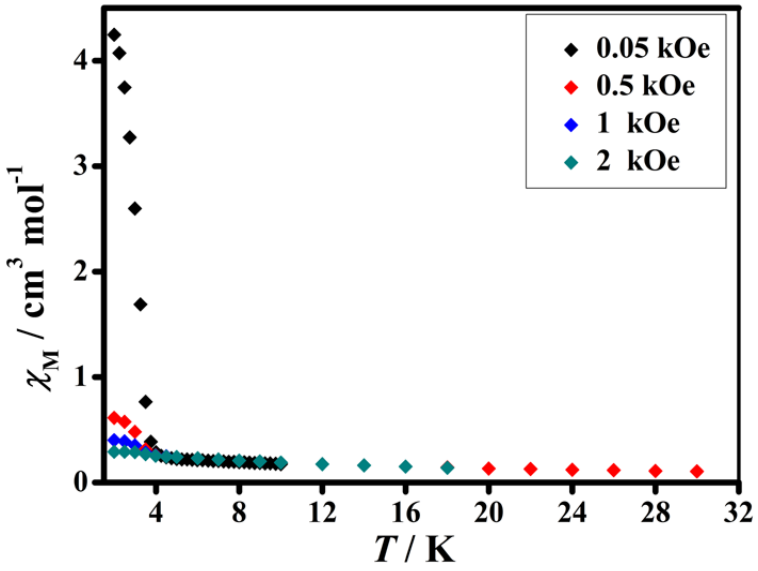

Fig. S4. The temperature dependence of magnetizations for **1** in various applied fields.

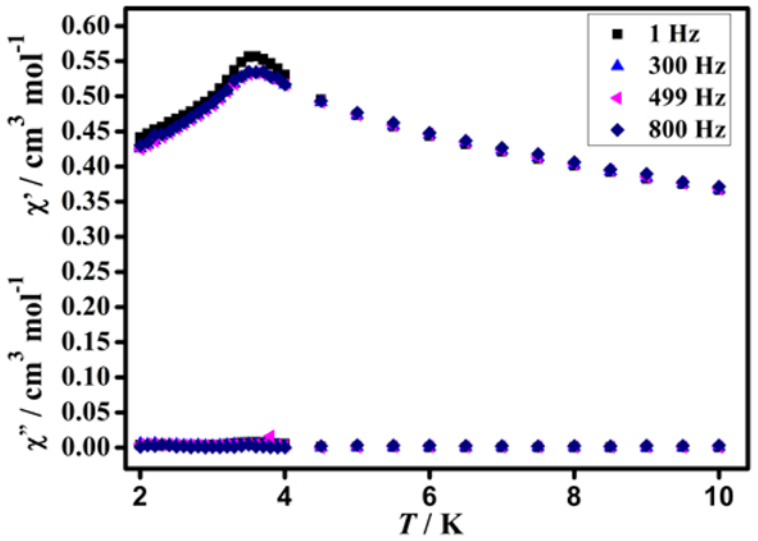

Fig. S5. The *ac* susceptibilities of **1** measured at different oscillating frequencies under a zero *dc* field.

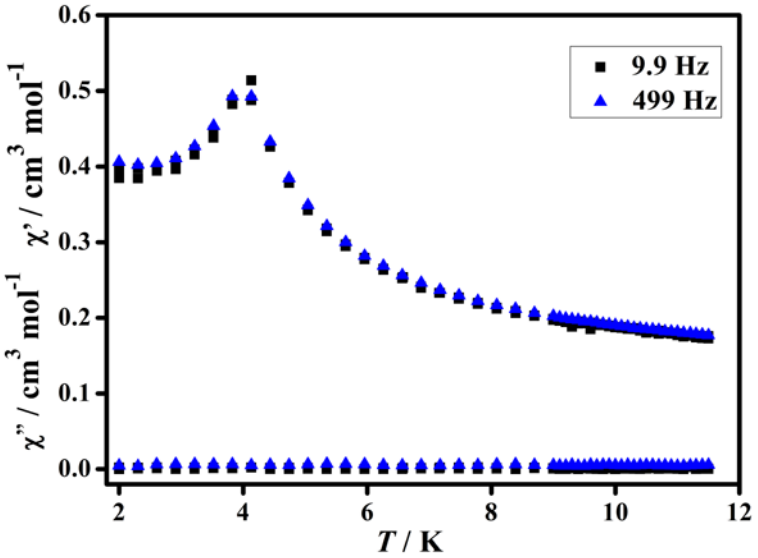

Fig. S6. The *ac* susceptibilities of **2** measured at 9.9 and 499 Hz under a zero *dc* field.

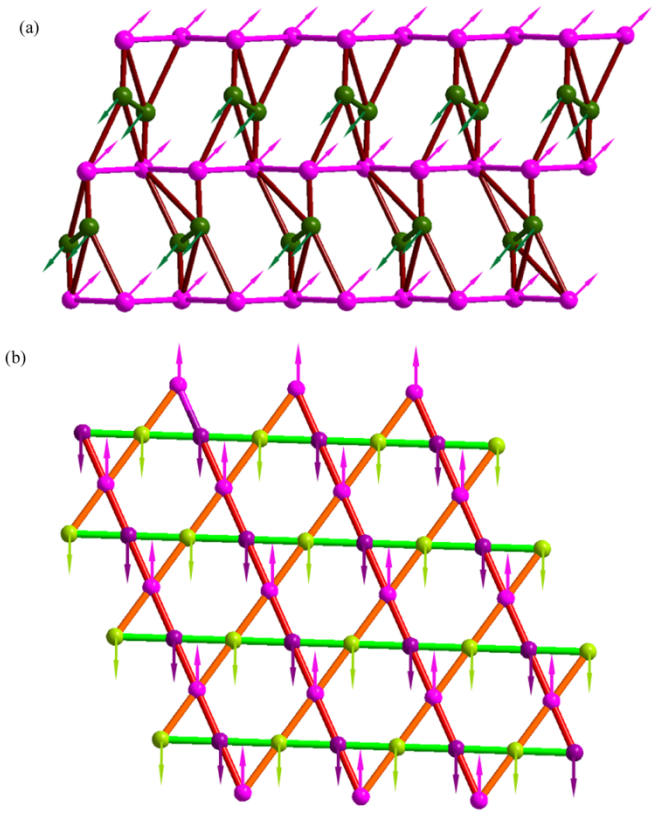

Fig. S7. (a) Representation of the possible spin alignments in **1**. Pink: Co1; cyan: Co2; (b) Representation of the possible spin alignments (Kagomé lattice) in **2**. Green: Co1; purple: Co2; pink: Co3.

Table S1. Selected bonds lengths and angles for **1** and **2**.

1			
Co1—N5	2.070(7)	N6$^{\#2}$—Co1—O4	89.7(3)
Co1—O2$^{\#1}$	2.079(6)	N5—Co1—O3$^{\#1}$	84.1(3)
Co1—N3	2.081(6)	O2$^{\#1}$—Co1—O3$^{\#1}$	88.4(2)
Co1—N6$^{\#2}$	2.101(7)	N3—Co1—O3$^{\#1}$	81.5(3)
Co1—O4	2.144(6)	N6$^{\#2}$—Co1—O3$^{\#1}$	174.6(2)
Co1—O3$^{\#1}$	2.183(6)	O4—Co1—O3$^{\#1}$	94.8(2)
Co2—O5	2.083(7)	O5—Co2—O1$^{\#3}$	88.4(3)
Co2—O1$^{\#3}$	2.105(6)	O5—Co2—N4	95.5(3)
Co2—N4	2.121(7)	O1$^{\#3}$—Co2—N4	87.0(2)
Co2—N2	2.123(7)	O5—Co2—N2	90.4(3)
Co2—N1$^{\#3}$	2.156(7)	O1$^{\#3}$—Co2—N2	168.1(2)
Co2—O6	2.156(7)	N4—Co2—N2	104.9(3)
N5—Co1—O2$^{\#1}$	94.0(3)	O5—Co2—N1$^{\#3}$	95.7(3)
N5—Co1—N3	100.8(3)	O1$^{\#3}$—Co2—N1$^{\#3}$	77.1(2)

O2$^{\#1}$—Co1—N3	161.1(2)	N4—Co2—N1$^{\#3}$	160.3(3)
N5—Co1—N6$^{\#2}$	91.3(3)	N2—Co2—N1$^{\#3}$	91.2(2)
O2$^{\#1}$—Co1—N6$^{\#2}$	94.8(3)	O5—Co2—O6	175.4(3)
N3—Co1—N6$^{\#2}$	96.6(3)	O1$^{\#3}$—Co2—O6	94.4(3)
N5—Co1—O4	177.9(2)	N4—Co2—O6	81.1(3)
O2$^{\#1}$—Co1—O4	87.7(2)	N2—Co2—O6	87.6(3)
N3—Co1—O4	77.3(2)	N1$^{\#3}$—Co2—O6	88.5(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x-1/2,y-1/2,-z+1/2 #2 -x+1/2,y+1/2,-z+1/2 #3 -x,-y+2,-z+1

2

Co1—N3	2.071(5)	N4-Co1-N4$^{\#1}$	179.999(2)
Co1—O3	2.106(4)	N1$^{\#2}$-Co-N1	179.999(2)
Co1—N3$^{\#1}$	2.071(5)	N1$^{\#2}$-Co2-O2	100.95(18)
Co1—N4$^{\#1}$	2.178(6)	N1-Co2-O2	79.05(18)
Co1—N4	2.178(6)	N1$^{\#2}$-Co2-O2$^{\#2}$	79.05(18)
Co1—O3$^{\#1}$	2.106(4)	N1-Co)-O2$^{\#2}$	100.95(18)
Co2—O2	2.105(5)	O2-Co2-O2$^{\#2}$	180.0
Co2—O2$^{\#2}$	2.105(6)	N1$^{\#2}$-Co)-N5$^{\#2}$	91.0(2)
Co2—N5	2.174(6)	N1-Co2-N5$^{\#2}$	89.0(2)
Co2—N1	2.070(5)	O2-Co2-N5$^{\#2}$	92.1(2)
Co2—N1$^{\#2}$	2.070(5)	O2$^{\#2}$-Co2-N5$^{\#2}$	87.9(2)
Co2—N5$^{\#2}$	2.156(7)	N1$^{\#2}$-Co2-N5	89.0(2)
Co3-O1	2.077(5)	N1-Co2-N5	91.0(2)
Co3-O1$^{\#3}$	2.077(5)	O2-Co2-N5	87.9(2)
Co3-O4	2.084(5)	O2$^{\#2}$-Co2-N5	92.1(2)
Co3-O1$^{\#4}$	2.084(5)	N5$^{\#2}$-Co2-N5	180.0
Co3-N6	2.142(6)	O1$^{\#3}$-Co3-O1	179.999(1)
Co3-N6 $^{\#4}$	2.142(6)	O1$^{\#3}$-Co3-O4	86.53(19)
N3$^{\#1}$-Co1-N3	180.0(2)	O1-Co3-O4	93.47(19)
N3$^{\#1}$-Co1-O3$^{\#1}$	78.41(19)	O1$^{\#3}$-Co3-O4$^{\#3}$	93.47(19)
N3-Co1-O3$^{\#1}$	101.59(19)	O1-Co3-O4$^{\#3}$	86.53(19)
N3$^{\#1}$-Co1-O3	101.59(19)	O4-Co3-O4$^{\#3}$	179.999(1)
N3-Co1-O3	78.41(19)	O1$^{\#3}$-Co3-N6$^{\#3}$	93.2(2)
O3$^{\#1}$-Co1-O3	180.0(3)	O1-Co3-N6$^{\#3}$	86.8(2)
N3$^{\#1}$-Co1-N4	90.0(2)	O4-Co3-N6$^{\#3}$	90.0(2)
N3-Co1-N4	90.0(2)	O4$^{\#3}$-Co3-N6$^{\#3}$	90.0(2)
O3$^{\#1}$-Co1-N4	93.7(2)	O1$^{\#3}$-Co3-N6	86.8(2)

O3-Co1-N4	86.3(2)	O1-Co3-N6	93.2(2)
$N3^{\#1}$-Co1-$N4^{\#1}$	90.0(2)	O4-Co3-N6	90.0(2)
N3-Co1-$N4^{\#1}$	90.0(2)	$O4^{\#3}$-Co3-N6	90.0(2)
$O3^{\#1}$-Co1-$N4^{\#1}$	86.3(2)	$N6^{\#3}$-Co3-N6	179.999(1)
O3-Co1-$N4^{\#1}$	93.7(2)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1 #2 -x,-y+2,-z #3 -x,-y+2,-z+1

Table S2. Summary of some typical 3D Co(II) metamagnets with spin canting.

compounds[a]	T_N (K)	M_r (Nβ)[b]	H_c (Oe)[c]	α (°)[d]	Ref.
$\{[Co_4(pico)_4(4,4'\text{-bpy})(H_2O)_2]\cdot H_2O\}_n$	3.5	unknow	160	unknow	22a
$\{[Co_2(tzc)_2(bpea)]\}_n$	9	0.13	700	3.9-4.6	22b
$\{[Co_4(\mu\text{-}H_2O)_2(3\text{-pyca})_8]_{0.94}[Co_5(\mu_3\text{-}OH)_2(3\text{-pyca})_8]_{0.06}\}_n$	9.5	0.075	500	0.54	22c
$\{[W(CN)_6(2,2'\text{-bpy})]\ [Co(H_2O)_2]\cdot 4H_2O\}_n$	8	0.01	10	0.6	22d
$\{[Co_2(TDA)(TZ)(H_2O)_2]\cdot H_2O\}_n$ **(1)**	3.5	0.04	500	1.07	this work
$\{[Co_3(TDA)_2(4,4'\text{-bpy})_3]\cdot 6.75H_2O\}_n$ **(2)**	4	0.002	15	0.053	this work

[a] Abbreviations: pico = 3-hydroxypicolinate, bpy = bipyridine, tzc = tetrazolate-5-carboxylate, bpea = 1,2-bis(4-pyridyl)ethane, H_3TDA = 1*H*-1,2,3-triazole-4,5-dicarboxylic acid, HTZ = 1*H*-1,2,4-triazole. [b] Remnant magnetization at 2 K. [c] Coercive field at 2 K. [d] Canting angle.