Supplementary materials for

Field-Induced Slow Relaxation of the Magnetization in a Distorted Octahedral Mononuclear High-Spin Co(II) Complex

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Table S1. Crystallographic data for compounds **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{28}H_{26}N_6CoO_8$	$C_{28}H_{26}FeN_6O_8$
Formula weight	633.48	630.40
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	15.286(3)	15.276(3)
b/Å	9.921(2)	9.993(2)
c/Å	19.852(4)	19.942(4)
β/（º）	108.46(3)	108.46(3)
V/（Å^3）	2855.8(11)	2887.6(11)
Z	4	4
Dc/g·cm^{-3}	1.473	1.450
Reflections	39014	66619
Unique reflections	6549	6615
R_{int}	0.0493	0.0907
Gof	1.038	1.083
Final *R* indices [I>2σ(I)]	R1 = 0.0511, *w*R2 = 0.1051	R1 = 0.0547, *w*R2 = 0.1124

Table S2. Selected bond lengths /Å and angles /° for compounds **1** and **2**.

1		**2**	
Co1–O1	2.1104(19)	Fe1–O1	2.109(2)
Co1–O5	2.0894(18)	Fe1–O5	2.090(2)
Co1–N1	2.155(2)	Fe1–N1	2.206(3)
Co1–N2	2.096(2)	Fe1–N2	2.153(3)
Co1–N3	2.149(2)	Fe1–N3	2.206(3)
Co1–N5	2.143(2)	Fe1–N5	2.198(3)
O5–Co1–O1	178.82(7)	O5–Fe1–O1	177.21(9)
O5–Co1–N5	99.96(8)	O5–Fe1–N2	94.53(9)
O5–Co1–N3	78.72(7)	O5–Fe1–N5	99.88(9)
O5–Co1–N2	93.34(8)	O5–Fe1–N3	77.49(9)
O5–Co1–N1	93.68(8)	O5–Fe1–N1	94.60(10)
O1–Co1–N5	78.88(7)	O1–Fe1–N2	88.13(9)
O1–Co1–N3	101.49(8)	O1–Fe1–N5	77.65(9)
O1–Co1–N1	86.16(8)	O1–Fe1–N3	101.22(10)
N5–Co1–N3	92.22(8)	O1–Fe1–N1	86.83(10)
N5–Co1–N1	91.81(8)	N2–Fe1–N5	162.69(10)
N3–Co1–N1	171.92(8)	N2–Fe1–N3	99.91(10)
N2–Co1–O1	87.77(8)	N2–Fe1–N1	76.90(10)
N2–Co1–N5	164.12(8)	N5–Fe1–N3	92.57(10)
N2–Co1–N3	98.91(8)	N5–Fe1–N1	92.34(10)
N2–Co1–N1	78.61(8)	N3–Fe1–N1	171.31(10)

Table S3. Hydrogen-bonded parameters /Å, ° for compounds **1** and **2**.

Compound	D–H···A	D–H	H···A	D···A	DHA
1	N6#1–H6#1···O6	0.86	1.98	2.807(3)	160
	N4#2–H4#2···O8	0.86	2.00	2.825(3)	160
2	N6#1–H6#1···O6	0.86	1.99	2.811(3)	160
	N4#2–H4#2···O8	0.86	1.99	2.816(3)	159

Symmetry code: #1: 0.5-x, 0.5+y, 0.5-z; #2: 1-x, -y, 1-z.

Table S4. Relaxation fitting parameters from least-squares fitting of $\chi(f)$ data under 2000 Oe dc field of **1**.

T(K)	χ_T	χ_S	α
4.5	0.614	0.019	0.060
5	0.562	0.018	0.047
5.5	0.509	0.019	0.023
6	0.471	0.018	0.024
6.5	0.439	0.013	0.031
7	0.409	0.016	0.035
7.5	0.383	0.014	0.030
8	0.359	0.015	0.026

Table S5. ZFS parameters and relaxation parameters with easy-plane anisotropy of Co(II) ions in mononuclear complexes.

Molecular Formula	Chromophore	D/cm^{-1}				DC field /Oe	τ_0/s	U_{eff} / cm^{-1}	Ref.
		D^a	D^b	D^c	E/D^d				
cis-[Co^{II}(dmphen)$_2$(NCS)$_2$]·0.25EtOH (**3**)	{CoN$_4$N'$_2$ }	98	-	-	146	1000	(3.0-4.4)×10^{-7}	16-18	38
[(3G)CoCl](CF$_3$SO$_3$) (**4**)	{CoN$_3$Cl }	12.7	-	-	-	1500	1.9×10^{-10}	24	36
{Co(N[CH$_2$C(O)NC(CH$_3$)$_3$]$_3$)} (**5**)	{CoN$_4$ }	16	-	-	-	1500	8×10^{-6}	8.7	41
dmphCoBr(**6**)	{CoN$_2$Br$_2$}	10.62	-	-	0.22	1000	3.5 × 10^{-9}	20.3	40
[Co^{II}(H$_2$dapb)(H$_2$O)(NO$_3$)](NO$_3$) (**7**)	{CoN$_3$O$_2$O'O''}	32.4	-	-	-	1000	6×10^{-10}	56.3	39
[Co^{II}L$_{N5}$(H$_2$O)$_2$]Cl$_2$·4H$_2$O (**8**)	{CoN$_4$O$_2$}	24.6	-	-	-	1000	1.2×10^{-6}	20.7	39
[Co^{II}(dapb)(im)$_2$]H$_2$O (**9**)	{CoN$_3$N$_2$O$_2$ }	24.8	-	-	-	1000	8.7×10^{-11}	62.3	39
[Co(abpt)$_2$(tcm)$_2$] (**10**)	{CoN$_4$N'$_2$ }	48		53.7	0.27	3000	1.37×10^{-9}	60.1	43
CoL^{1}Cl$_2$ (**11**)	{CoN$_3$Cl$_2$ }	-	150	-	-	2	1.4×10^{-7}	18.6	42
[Co(acac)$_2$(H$_2$O)$_2$] (**12**)	{CoO$_4$O'$_2$}	-	-	91.2	0.31	>600	-	14-17	34
Co(L^2)$_3$(NO$_3$)$_2$] (**13**)	{CoN$_3$O$_4$}	35.8	35.8	-	0.002	1000	7.5×10^{-10}	41.7	35
[Co(L^3)$_3$(NO$_3$)$_2$] (**14**)	{CoN$_3$O$_4$}	35.7	35.7	-	0.051	1200	8.5×10^{-8}	24.5	35
[Co(9Accm)$_2$(py)$_2$] (**15**)	{CoN$_2$O$_4$}	74.1	-	167.1	-	1500	-	-	37
[Co(9Accm)$_2$(2,2'-bpy)] (**16**)	{CoN$_2$O$_4$}	24.1	-	71.6	-	700	-	-	37
[Co(L^4)$_2$](ClO$_4$)$_2$ (**17**)	{CoN$_6$ }	61.1	-	68.9	-	2000	7.18×10^{-7}	10.7	22
[Co(L^5)$_2$](ClO$_4$)$_2$ (**18**)	{CoN$_6$ }	68.1	-	67.3	-	2000	2.06×10^{-8}	19.78	22
[Co(L^5)$_2$](ClO$_4$)$_2$·MeCN (**19**)	{CoN$_6$ }	56.4	-	71.5	-	2000	3.44×10^{-7}	16.38	22
[Co(L^6)$_2$](ClO$_4$)$_2$ (**20**)	{CoN$_6$ }	62.9	-	85.0	-	2000	4.95×10^{-7}	14.78	22
[Co(L^7)$_2$](ClO$_4$)$_2$ (**21**)	{CoN$_6$ }	74.9	-	72.1	-	2000	1.67×10^{-6}	5.8	22

a) Axial magnetic anisotropy obtained from the fit of the experimental field dependence of magnetization data; b) Axial magnetic anisotropy obtained from the fit of the magnetic susceptibility data ; c) Axial magnetic anisotropy obtained from theory calculations. d) Axial magnetic anisotropy obtained from HF-EPR.

Abbreviations: Dmphen = 2,9-dimethyl-1,10-phenanthroline; 3G = 1,1,1-tris-[2N-(1,1,3,3-tetramethylguanidino)methyl]ethane; dmph = 2,9-dimethyl-1,10-phenanthroline; H$_2$dapb = 2,6-diacetylpyridine bis(benzoylhydrazine); L$_{N5}$ = 2,13-dimethyl-3,6,9,12-tetraaza-1(2,6)-pyridinacyclotridecaphane-2,12-diene; im = imidazole; abpt = 4-amino-3,5-bis(2-pyridyl)-1,2,4-triazole; tcm = tricyanomethanide Anion; L^1 = 4-hept-1-ynyl-2,6-dipyrazol-1-ylpyridine; acac = acetylacetonate; btm = bis(1H-1,2,4-triazol-1-yl)methane; L^2 = 4-tert-butylpyridine, L^3 = isoquinoline; 9Accm = curcuminoid; py = pyridyl; 2,2'-bpy = 2,2'-bipyridyl; L^4 = Pyridine-2,6-bis(oxazoline)；L^5 = Pyridine-2,6-bis(5,5'-dimethyloxazoline)；L^6 = 4-(4-methyl)-phenyl-pyridine-2,6-bis(5,5'-dimethyloxazoline)；L^7 = 4,4'-bipyridine-2,6-bis(5,5'-dimethyloxazoline).

Table S6 Energy levels (cm^{-1}) of ligand field multiplets in zero field derived from CASSCF/NEVPT2/def2-TZVP(f) CASSCF(7,5) (ORCA) calculations for the complex **1**.

0	0.0	30	19098.4	60	24807.4	90	38642.0
1	0.0	31	19098.4	61	24807.4	91	38642.0
2	184.7	32	19485.8	62	26994.8	92	38760.9
3	184.7	33	19485.8	63	26994.8	93	38760.9
4	697.5	34	19841.5	64	29098.3	94	39184.6
5	697.5	35	19841.5	65	29098.3	95	39184.6
6	947.7	36	20240.3	66	29769.9	96	42979.2
7	947.7	37	20240.3	67	29769.9	97	42979.2
8	1650.9	38	20274.9	68	30016.3	98	43554.4
9	1650.9	39	20274.9	69	30016.3	99	43554.4
10	1695.5	40	20463.1	70	30516.7	100	43857.3
11	1695.5	41	20463.1	71	30516.7	101	43857.3
12	9521.7	42	20519.9	72	31149.4	102	45728.2
13	9521.7	43	20519.9	73	31149.4	103	45728.2
14	9561.8	44	22014.6	74	31400.9	104	46293.2
15	9561.8	45	22014.6	75	31400.9	105	46293.2
16	10065.0	46	22244.6	76	32572.1	106	46622.6
17	10065.0	47	22244.6	77	32572.1	107	46622.6
18	10119.2	48	22814.1	78	33546.2	108	46713.5
19	10119.2	49	22814.1	79	33546.2	109	46713.5
20	10454.5	50	23141.4	80	35765.6	110	66257.8
21	10454.5	51	23141.4	81	35765.6	111	66257.8
22	10517.6	52	23308.9	82	36138.3	112	66892.3
23	10517.6	53	23308.9	83	36138.3	113	66892.3
24	10683.9	54	23814.8	84	36599.7	114	67512.4
25	10683.9	55	23814.8	85	36599.7	115	67512.4
26	11338.5	56	24058.8	86	37479.4	116	67964.9
27	11338.5	57	24058.8	87	37479.4	117	67964.9
28	18843.1	58	24544.5	88	38099.7	118	68269.0
29	18843.1	59	24544.5	89	38099.7	119	68269.0

Table S7 Individual contributions to *D*-tonsor for complex **1** by CASSCF/NEVPT2/def2-TZVP(f) CASSCF(7,5) (ORCA).

2*S*+1	Root	*D*	*E*
4	0	0	0
4	1	46.205	46.268
4	2	23.679	-23.680
4	3	-7.558	-0.567
4	4	0.441	0.887
4	5	1.642	3.103
4	6	0.001	0.000
4	7	0.073	-0.073
4	8	0.077	0.075
4	9	0.007	0.006
2	0	-0.234	2.594
2	1	-0.262	0.559
2	2	-0.086	-0.047
2	3	-1.076	-1.082
2	4	-0.109	-0.105
2	5	-0.205	0.174
2	6	-0.350	0.338
2	7	-0.774	0.777
2	8	3.221	0.004
2	9	-0.123	-0.117
2	10	-0.004	0.003
2	11	-0.078	0.080
2	12	0.450	0.005
2	13	-0.173	-0.115
2	14	-0.190	-0.088
2	15	-0.198	0.186
2	16	-0.133	-0.141
2	17	-0.119	-0.124
2	18	-0.550	0.878
2	19	0.192	-0.110
2	20	1.037	0.068
2	21	-0.260	-0.165
2	22	-0.041	-0.013
2	23	0.004	0.006
2	24	-0.114	-0.042
2	25	-0.077	0.077
2	26	-0.202	-0.139
2	27	0.002	0.000
2	28	0.043	-0.047
2	29	0.004	-0.008

2	30	0.065	-0.022
2	31	-0.049	0.048
2	32	-0.053	-0.026
2	33	-0.050	-0.025
2	34	-0.002	0.002
2	35	0.015	-0.001
2	36	-0.003	0.007
2	37	0.011	0.002
2	38	-0.002	0.022
2	39	-0.022	0.023

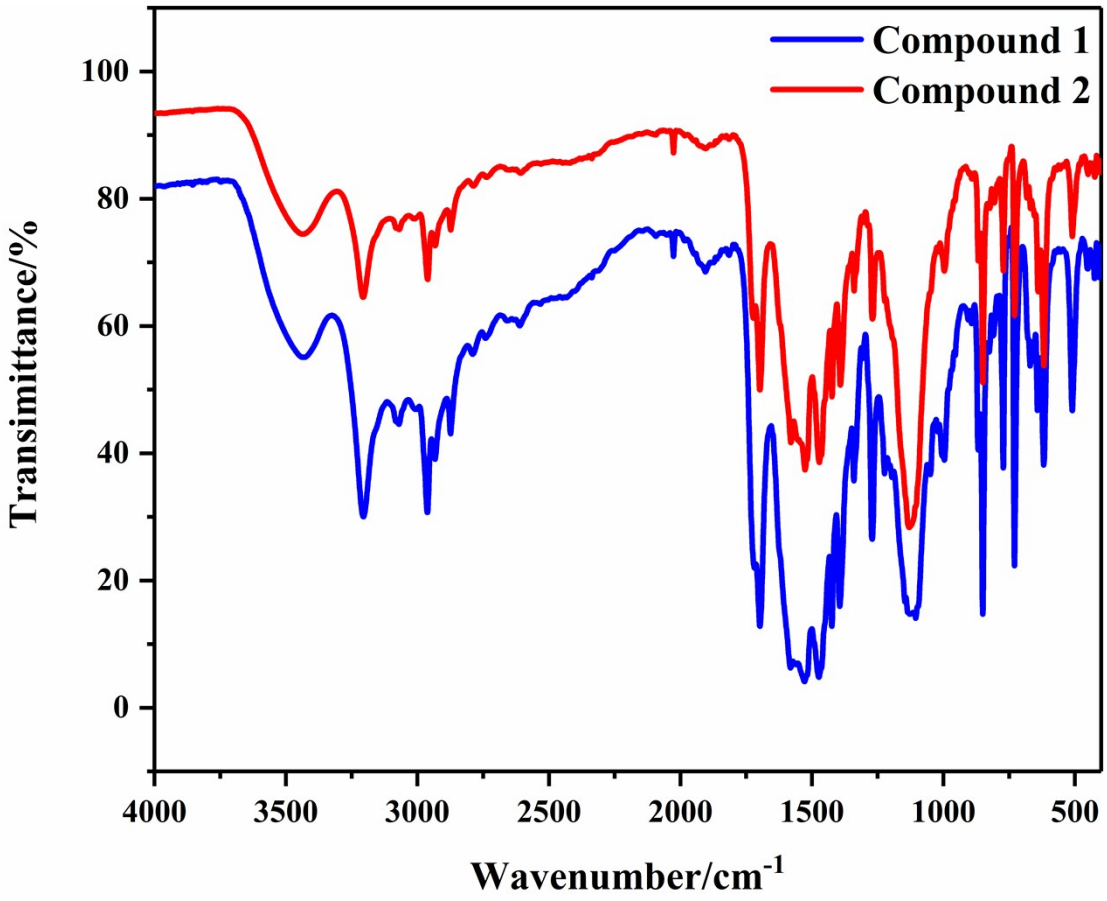

Fig. S1 IR spectrum for **1** (blue) and **2** (red).

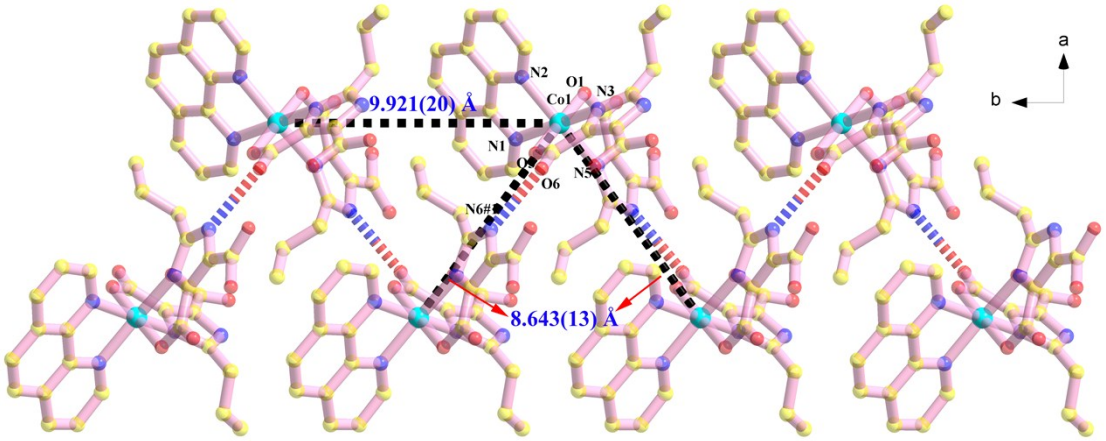

Fig. S2 The 1D chain of **1** along *b* axis formed *via* intermolecular N6#1–H6#1···O6 hydrogen bonds. Symmetry code: #1: 0.5-x, 0.5+y, 0.5-z.

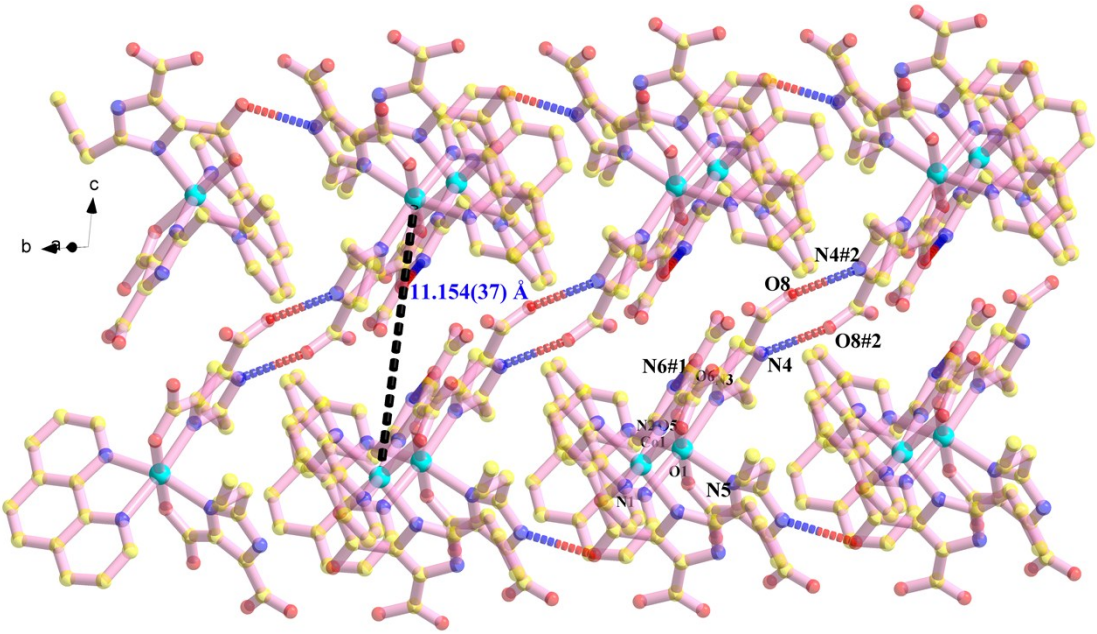

Fig. S3 The 2D supramolecular layer of **1** parallel *bc* plane formed *via* intermolecular N4#2–H4#2···O8 hydrogen bonds. Symmetry code: #2: 1-x, -y, 1-z.

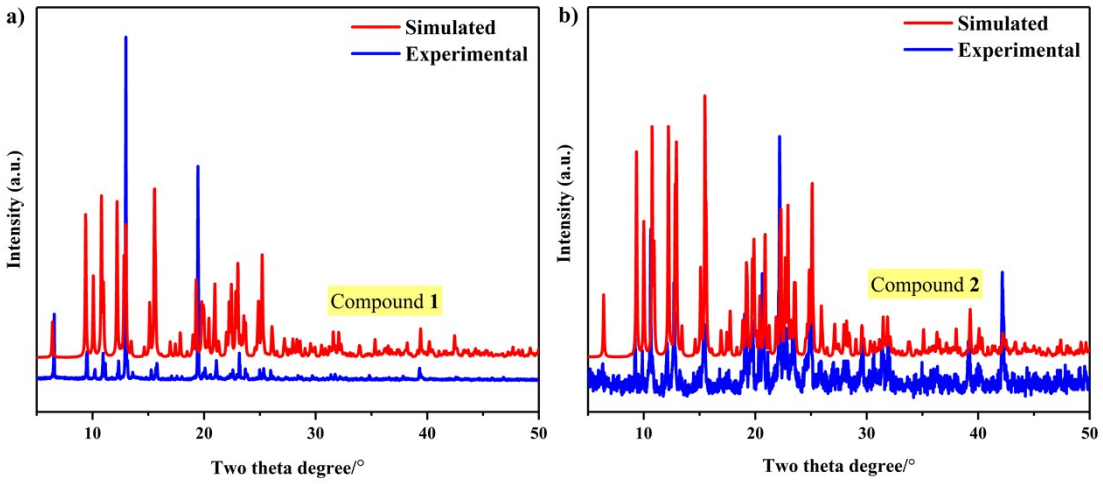

Fig. S4 PXRD patterns for complexes **1** and **2**.

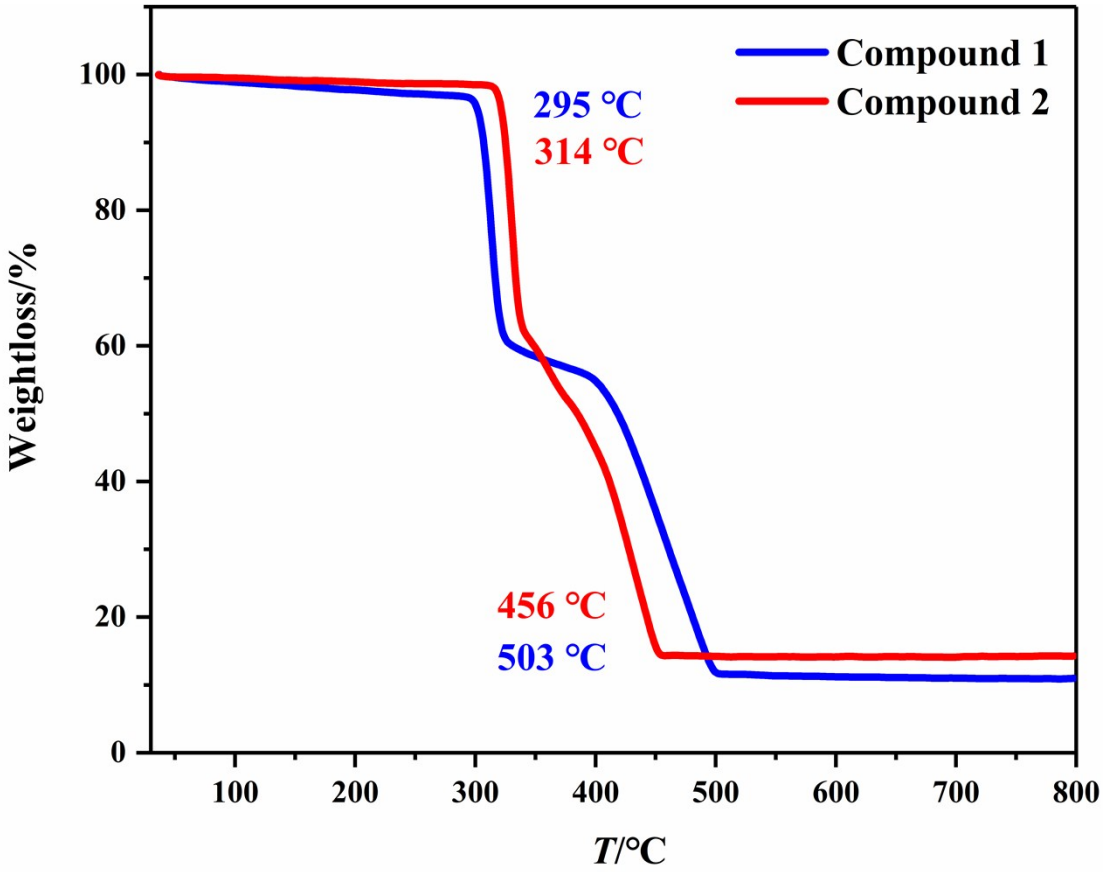

Fig. S5 TGA curves of **1** (blue) and **2** (red) under air atmosphere.

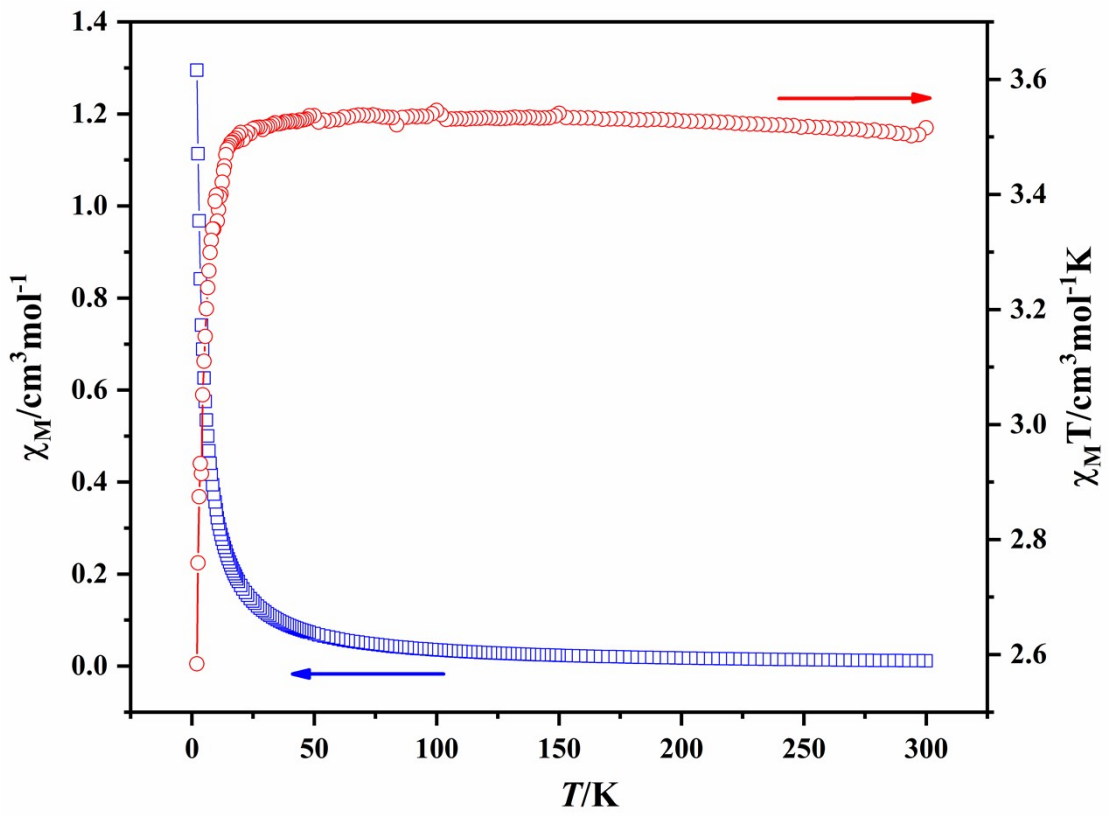

Fig. S6 Temperature dependence of the $\chi_M T$ and χ_M product for **2**.

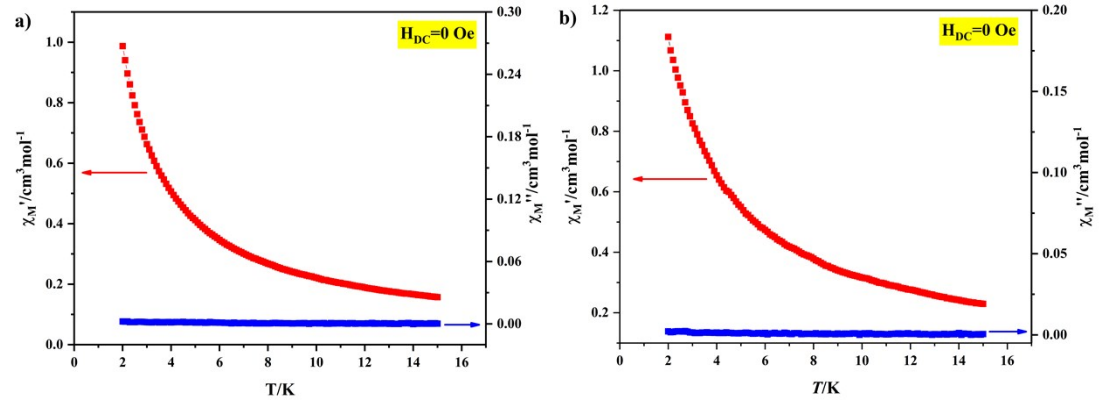

Fig. S7 The ac magnetic susceptibility measurements for **1** and **2** in 0 Oe static field showing no out-of-phase signals.

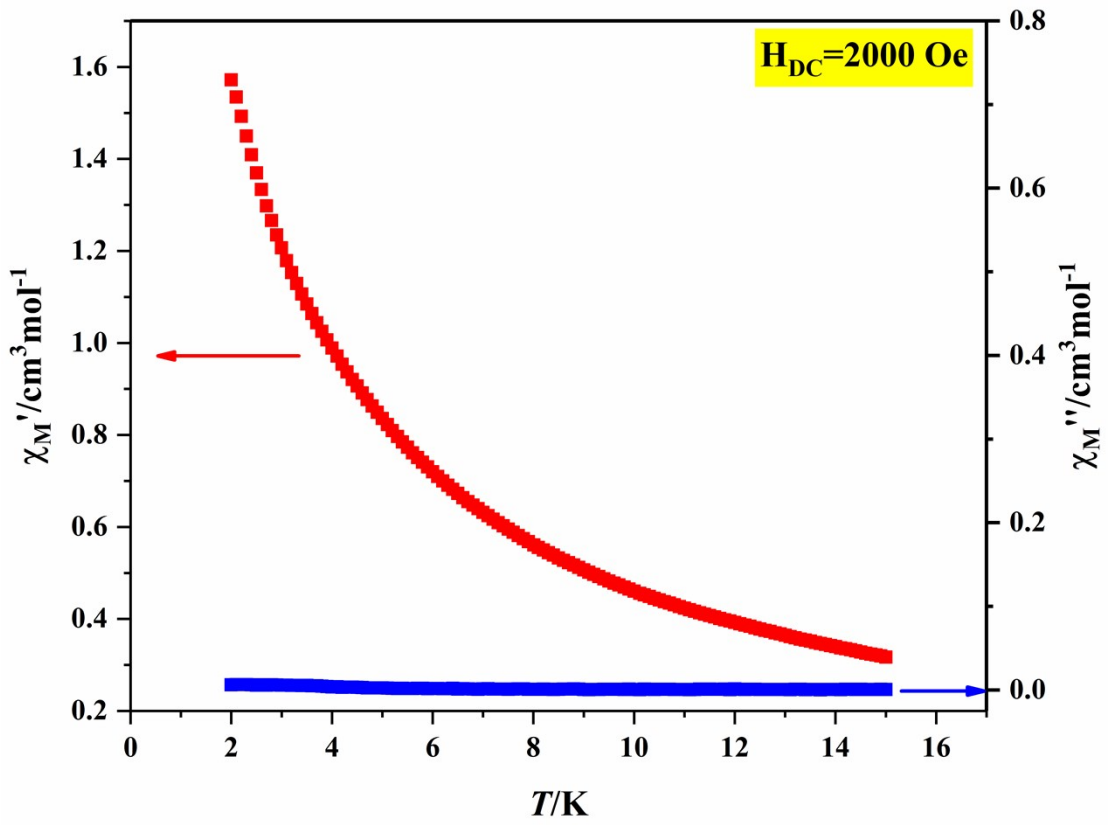

Fig. S8 The ac magnetic susceptibility measurements for **2** in 2000 Oe static field showing no out-of-phase signals.