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Syntheses and Magnetic Properties of a Pyrimidyl-Substituted Nitronyl Nitroxide Radical and its Cobalt (II) Complexes

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Supporting Information

Table of contents:

1. Physical Measurements

IR data were measured on KBr pellets using a Bruker Vector 22 FT-IR spectrometer in the 4000-400 cm^{-1} range. Elemental analyses for C, H, and N were performed at Elementar Vario MICRO analyzer. Magnetic susceptibility measurements were performed using a Quantum Design SQUID VSM magnetometer on micro crystalline samples for all compounds. Direct current (dc) measurements were conducted from 300 to 2 K under an external magnetic field of 1000 Oe. The field dependences of the magnetization were measured at 2 K with dc magnetic field between 0 and 7 T. All magnetic data were corrected for the sample holder, the eicosane and for the diamagnetic contribution of the sample.

2. Synthesis

All preparations and manipulations were performed under aerobic conditions. All starting material and solvents were obtained from commercial sources and used as received. The solvents were commercially purchased and used as received. The starting material $Co(hfac)_2 \cdot 2H_2O$ (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonato) were used as purchased from Sigma-Aldrich. The pyrimidine-2-carbaldehyde was synthesized following a published method. [S1]

NIT-2-Pm (1). This new radical was synthesized by the reported method using pyrimidine-2-carbaldehyde as the starting aldehyde. [S2] Yield: 45%. Color: purple. Anal. Calcd (%) for $C_{11}H_{15}N_4O_2$: C, 56.16; H, 6.43; N, 23.81. Found: C

56.21; H, 6.26; N, 23.72. IR (KBr pellet, cm^{-1}): 3140(m), 23141(m), 1638(s), 1448(s), 1222(s), 1261(s), 1186(s), 826(m), 635(m), 584(m).

(NIT-2-Pm)Co(hfac)$_2$ (2). A solution of Co(hfac)$_2$ 2H$_2$O (51.1 mg, 0.1 mmol, 1.0 eq) in 25 mL of dry boiling n-heptane was heated to reflux for 4 h and then cooled to 80 ℃. Then 10 mL of $CHCl_3$ solution of NIT-2-Pm (23.5 mg, 0.1 mmol, 1.0 eq) was added with stirred for 30 min. The final solution was cooled to room temperature and filtered. After 3 days, black crystals of **2**, suitable for X-ray diffraction, were obtained. Yield: 21.4 mg (30%). Anal. Calcd (%) for $CoC_{21}H_{15}N_4O_6F_6$: C, 42.58; H, 2.55; N, 9.46. Found: C, 42.45; H, 2.51; N, 9.49. IR (KBr pellet, cm^{-1}): 3136(m), 2345(m), 1676(s), 1457(s), 1234(s), 1207(s), 1150(s), 823(m), 644(m), 596(m).

(μ-NIT-2-Pm)Co$_2$(hfac)$_4$ (3). Complex **3** was synthesized in a way similar to that of complex **2**. When the equivalence ratio of Co(hfac)$_2$ 2H$_2$O and NIT-2-Pm was changed from 1:1 to 1:2, complex **3** was obtained. Yield: 22.8 mg (38%). Anal. Calcd (%) for $Co_2C_{31}H_{15}N_4O_{10}F_{12}$: C, 39.22; H, 1.59; N, 5.90. Found: C, 39.18; H, 1.62; N, 5.88. IR (KBr pellet, cm^{-1}): 3124(m), 2347(m), 1658(s), 1498(s), 1267(s), 1213(s), 1142(s), 801(m), 660(m), 584(m).

3. EPR Spectrum for 1

The EPR spectrum of compound **1** at 300 K in CH_2Cl_2 solution shows five similar major lines in the ratio of 1:2:3:2:1, as expected for coupling with two identical nitrogen atoms of N-O groups in the radicals. The *g* value is estimated as 2.01, and the nitrogen hyperfine coupling constants α^N is 7.34 G.

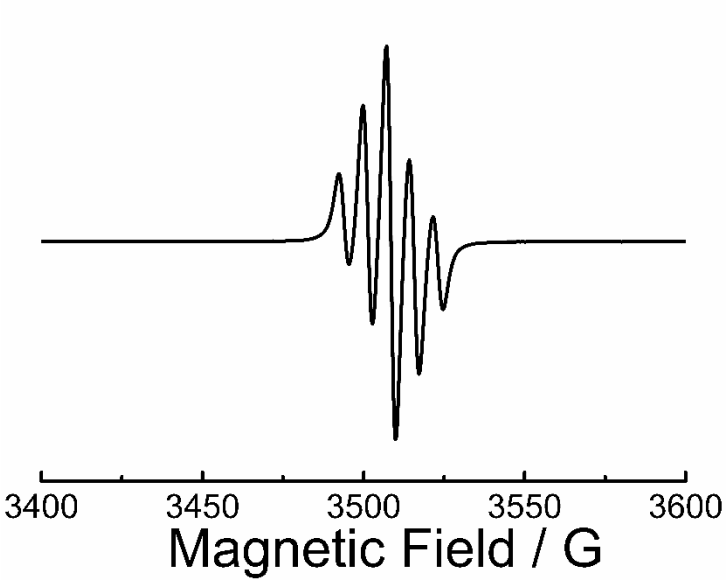

Fig. S1 EPR spectrum of the radical ligand **1**.

4. X-ray crystallography

Single crystal x-ray crystallographic data were collected on a Bruker APEX II or APEX Duo diffractometer with a CCD area detector (Mo-Kα radiation, λ = 0.71073 Å). The APEX[II] program was used to determine the unit cell parameters and for data collection. The data were integrated and corrected for Lorentz and polarization effects using SAINT.[S3] Absorption corrections were applied with SADABS.[S4] The structures were solved by direct method and refined by full-matrix least-squares method on F^2 using the SHELXTL crystallographic software package.[S5] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the organic ligands were refined as riding on the corresponding non-hydrogen atoms. Additional details of the data collections and structural refinement parameters are provided in Table **1**. Selected bond lengths of **1**-**3** are listed in Table **2**-**4**. CCDC-1449528 (**1**), CCDC-1449529 (**2**) and CCDC-1449530 (**3**) contain the supplementary crystallographic data for this

paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic Data and Structure Refinement Parameters for **1-3**

complex	**1**	**2**	**3**
Formula	$C_{11}H_{15}N_4O_2$	$CoC_{21}H_{19}N_4O_6F_{12}$	$Co_2C_{31}H_{23}N_4O_{10}F_{24}$
Mr ($gmol^{-1}$)	235.27	710.33	1185.39
Crystal size(mm^3)	0.45×0.41×0.27	0.33×0.20 ×0.12	0.35×0.21×0.18
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a (Å)	6.211(3)	14.967(3)	12.6019(7)
b (Å)	40.769(17)	15.106(3)	20.7451(12)
c (Å)	9.646(4)	15.938(3)	17.6713(11)
α (˚)	90.000	69.812(2)	90.000
β (˚)	96.104(7)	62.763(2)	104.6650(10)
γ (˚)	90.000	66.380(2)	90.000
V ($Å^3$)	2428.6(18)	2877.0(9)	4469.3(5)
Z	8	4	4
T , K	296(2)	296(2)	296(2)
ρ_{calcd}($g\ cm^{-3}$)	1.287	1.640	1.762
μ(Mo–$K\alpha$) (mm^{-1})	0.092	0.717	0.898
F (000)	1000	1424	2348
θ range (˚)	2.00 – 27.84	2.30 – 26.37	1.54 – 27.54
Refl.collected/unique	16524 / 5746	16946 / 11587	30366 / 10295
R(int)	0.0787	0.0283	0.0227
T_{max}/T_{min}	0.9756 / 0.9598	0.8699 / 0.7979	0.8551 / 0.8134
R_1^a/wR_2^b ($I > 2\sigma(I)$)	0.0703 / 0.1373	0.0753 / 0.2321	0.0666 / 0.2103

R_1/wR_2 (all data)	0.1748 / 0.1695	0.1043 / 0.2627	0.0855 / 0.2296
GOF on F^2	1.008	1.057	1.069
Max/min (e Å^{-3})	0.168 / -0.232	2.465/ -0.732	1.444 / -0.771

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

Table S2 Selected bond lengths (Å) for **1**.

O1-N1	1.279(3)	O2-N2	1.281(3)
O3-N7	1.278(3)	O4-N8	1.282(3)

Table S3 Selected bond lengths (Å) for **2**.

O1-N4	1.267(7)	O2-N3	1.289(6)
O7-N8	1.271(9)	O8-N7	1.288(6)
Co1-O2	2.043(4)	Co2-O8	2.033(4)
Co1-O3	2.056(5)	Co2-O9	2.056(3)
Co1-O4	2.042(3)	Co2-O10	2.037(4)
Co1-O5	2.053(3)	Co2-O11	2.060(5)
Co1-O6	2.044(4)	Co2-O12	2.067(4)
Co1-N1	2.169(5)	Co2-N5	2.151(5)

Table S4 Selected bond lengths (Å) for **3**.

O1-N1	1.283(5)	O2-N2	1.274(5)
Co1-O1	2.075(3)	Co1-O3	2.049(3)
Co1-O4	2.034(3)	Co1-O5	2.034(3)
Co1-O6	2.032(3)	Co1-N1	2.152(3)
Co2-O2	2.048(3)	Co 2-O7	2.039(3)
Co 2-O8	2.046(3)	Co 2-O9	2.030(3)
Co 2-O10	2.061(4)	Co 2-N2	2.178(3)

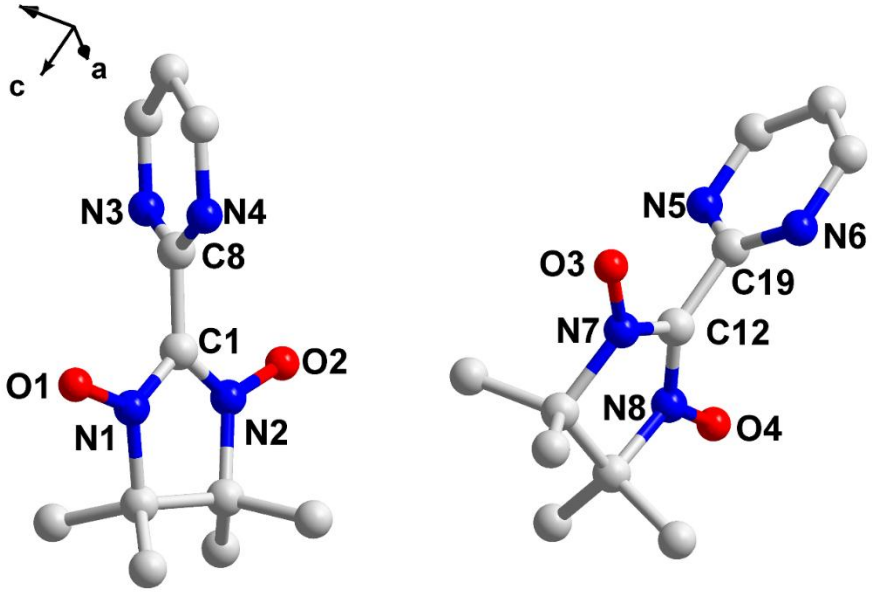

Fig. S2 The asymmetric unit of compound **1**. Atoms: carbon (gray), nitrogen (blue) and oxygen (red). All hydrogen atoms were omitted for clarity.

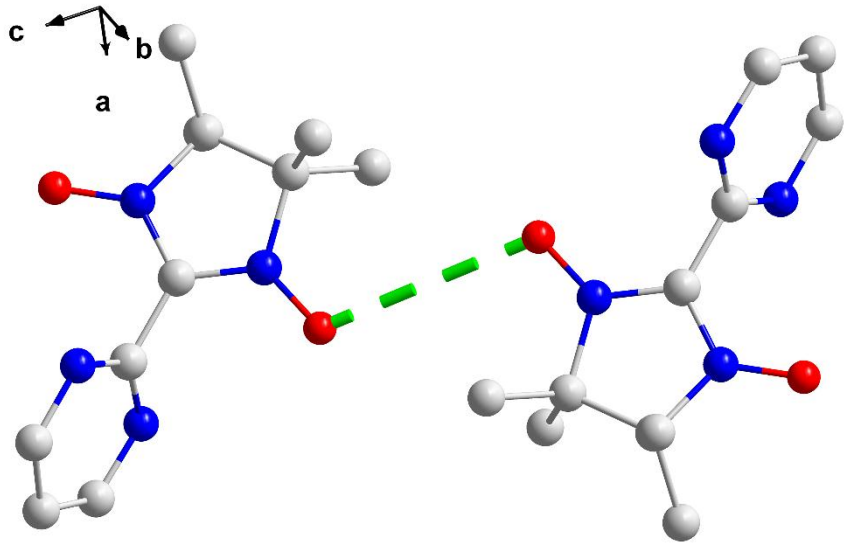

Fig. S3 The shortest O…O distance in **1**. Atoms: carbon (gray), nitrogen (blue) and oxygen (red). All hydrogen and fluorine atoms are omitted for clarity.

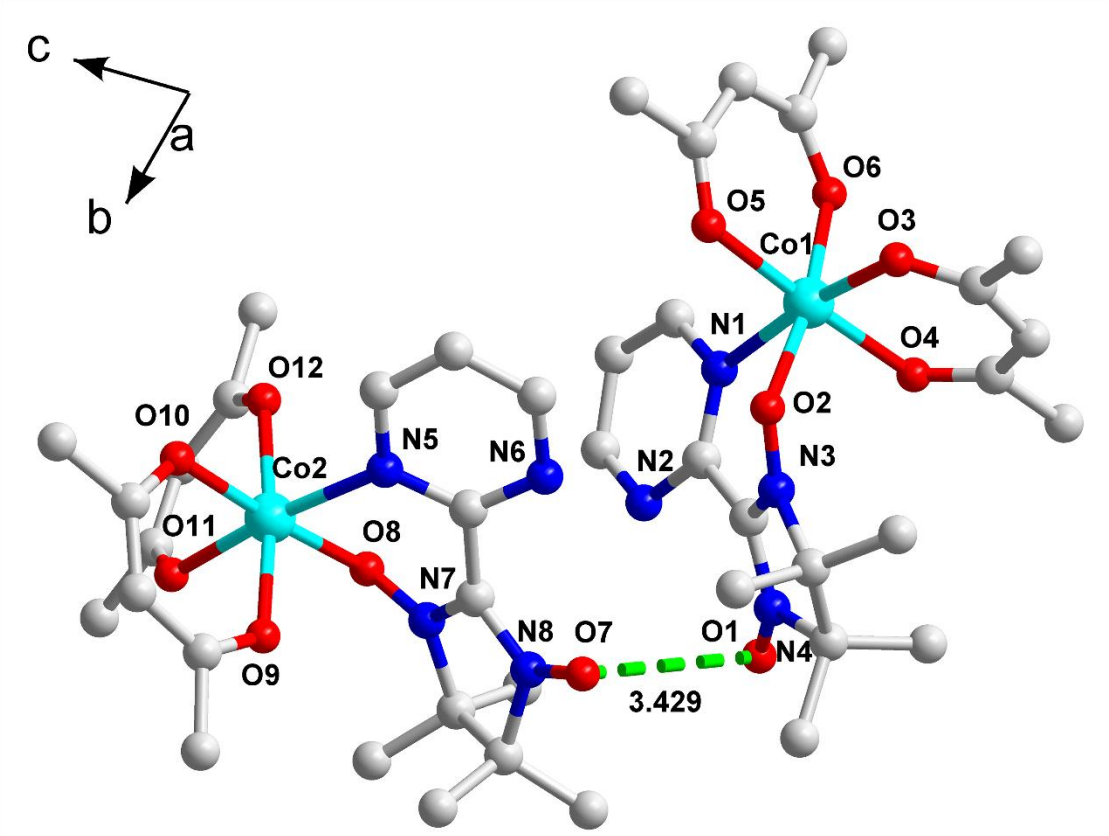

Fig. S4 Crystal structure of compound **2**. Atoms: carbon (gray), nitrogen (blue) oxygen (red) and cobalt (II) (cyan). All hydrogen and fluorine atoms are omitted for clarity.

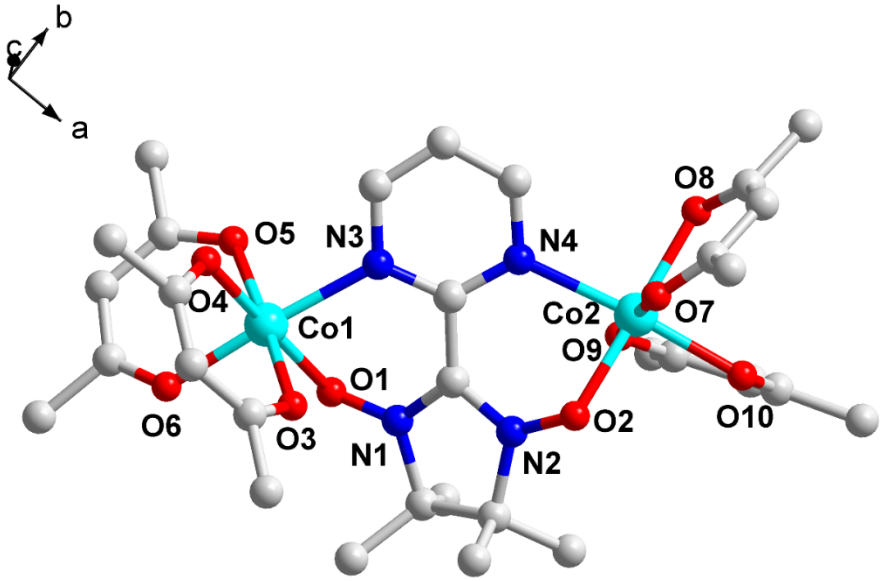

Fig. S5 The asymmetric unit of compound **3**. Atoms: carbon (gray), nitrogen (blue) oxygen (red) and cobalt (II) (cyan). All hydrogen and fluorine atoms are omitted for clarity.

5. Powder X-ray diffraction (PXRD) spectra of 1, 2 and 3

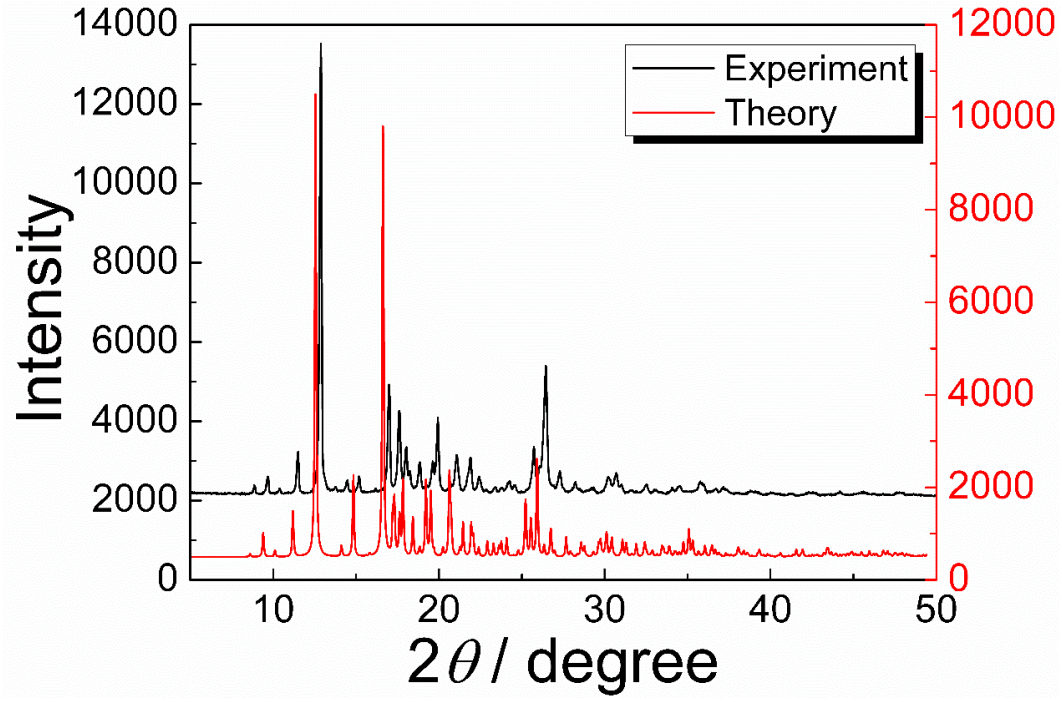

Fig. S6 Powder X-ray diffraction pattern of radical ligand **1** at room temperature, together with the calculated pattern from the single crystal data.

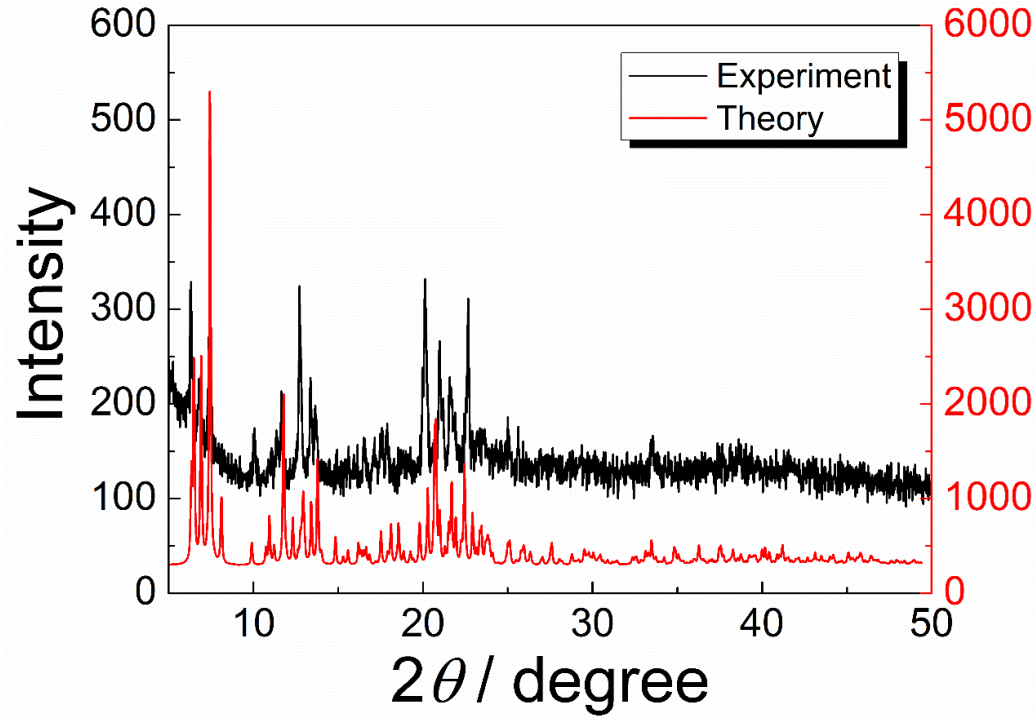

Fig. S7 Powder X-ray diffraction pattern of compound **2** at room temperature, together with the calculated pattern from the single crystal data.

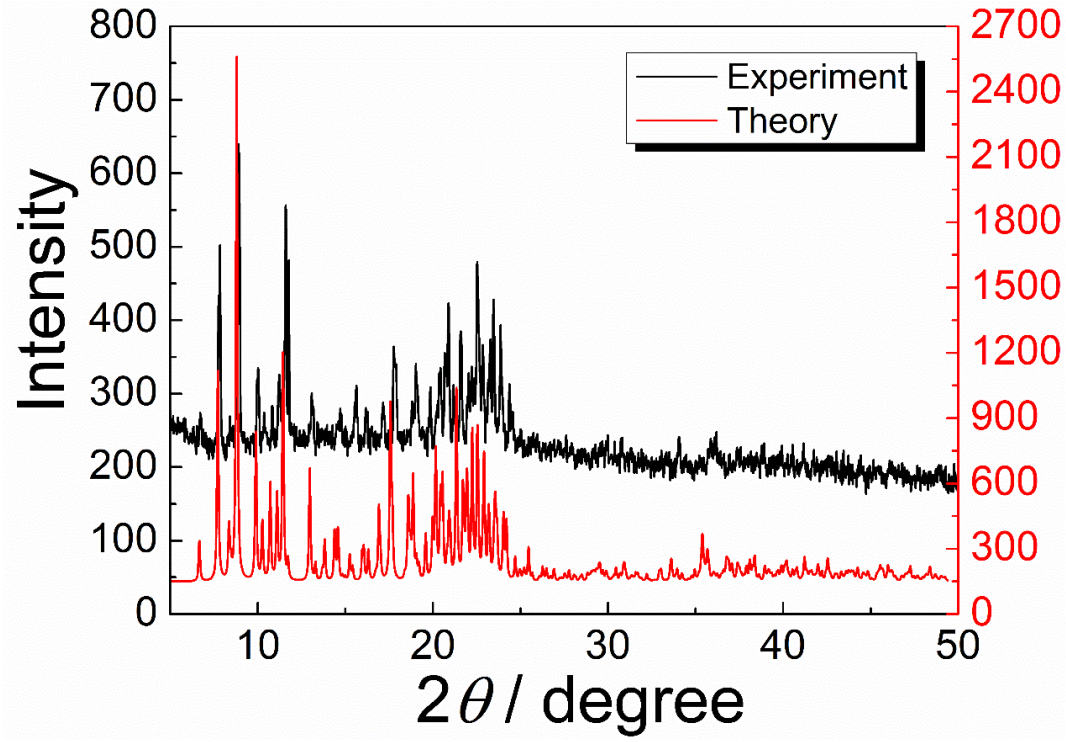

Fig. S8 Powder X-ray diffraction pattern of compound **3** at room temperature, together with the calculated pattern from the single crystal data.

6. Magnetic measurements

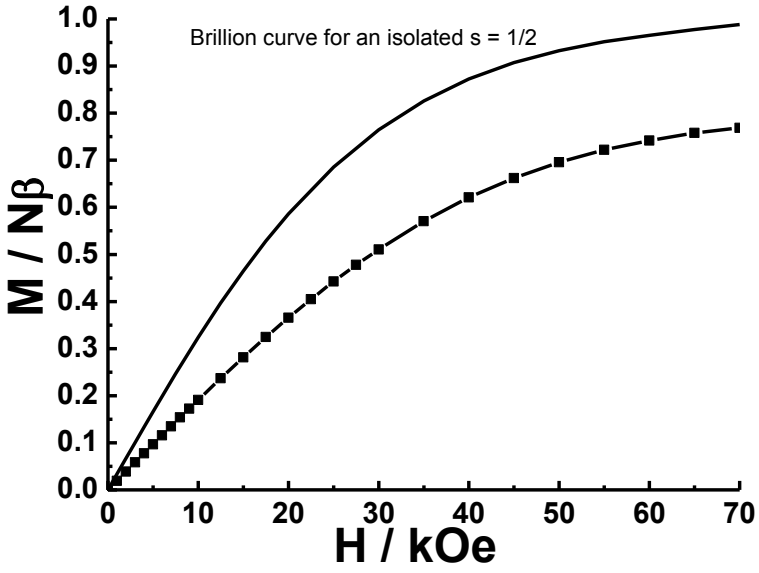

Fig. S9 The field dependent magnetization curve of **1** at 2 K. The solid line represents the calculated Brillion curve for an isolated s = 1/2.

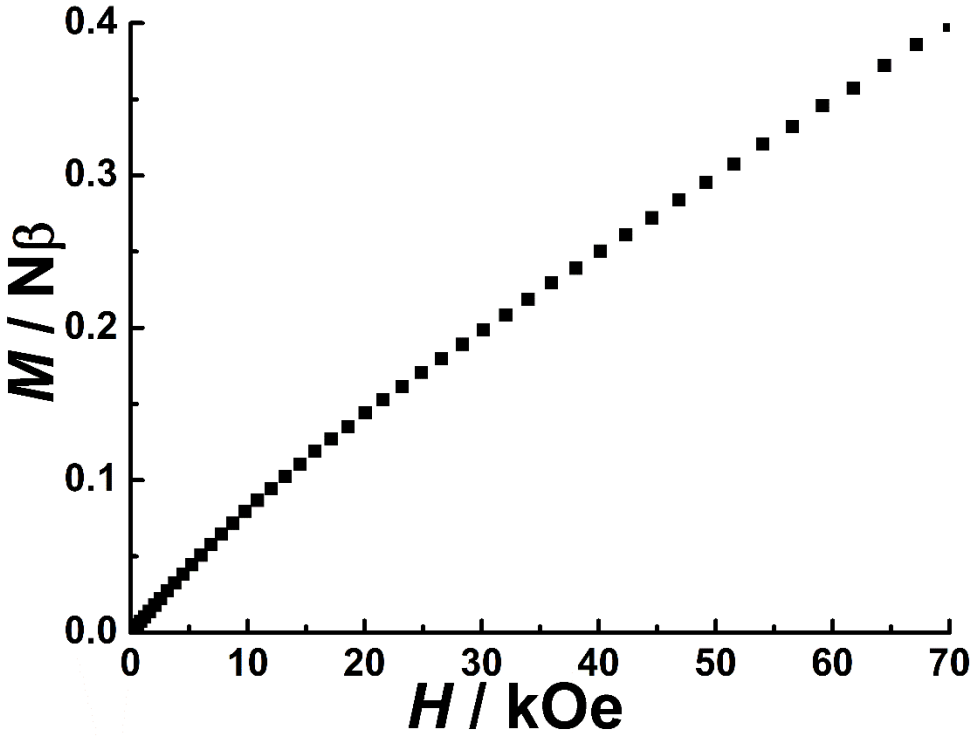

Fig. S10 The field dependent magnetization curve of **2** at 2 K.

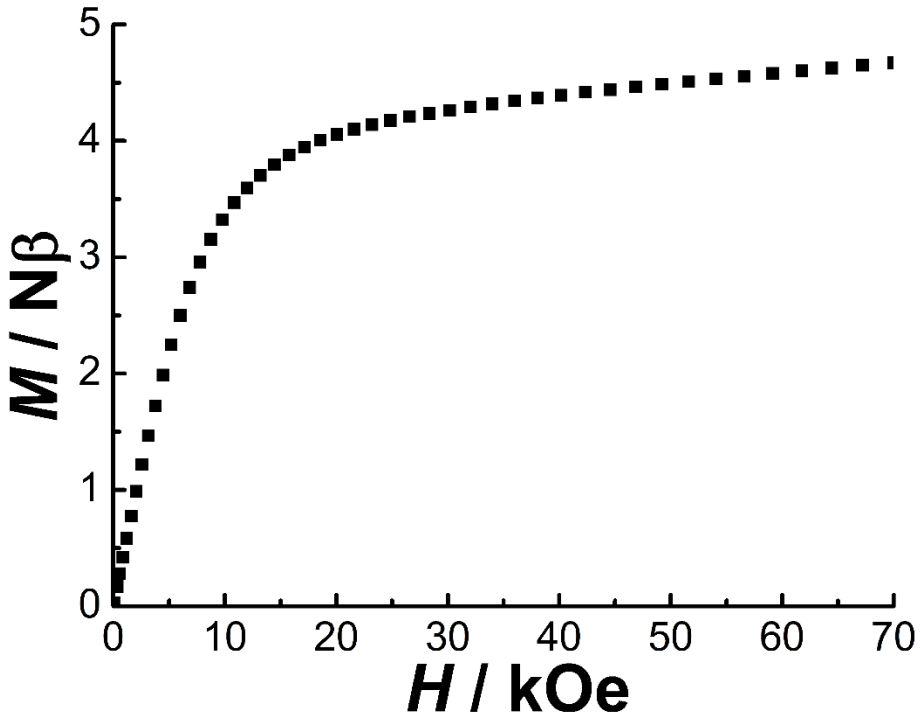

Fig. S11 The field dependent magnetization curve of **3** at 2 K.

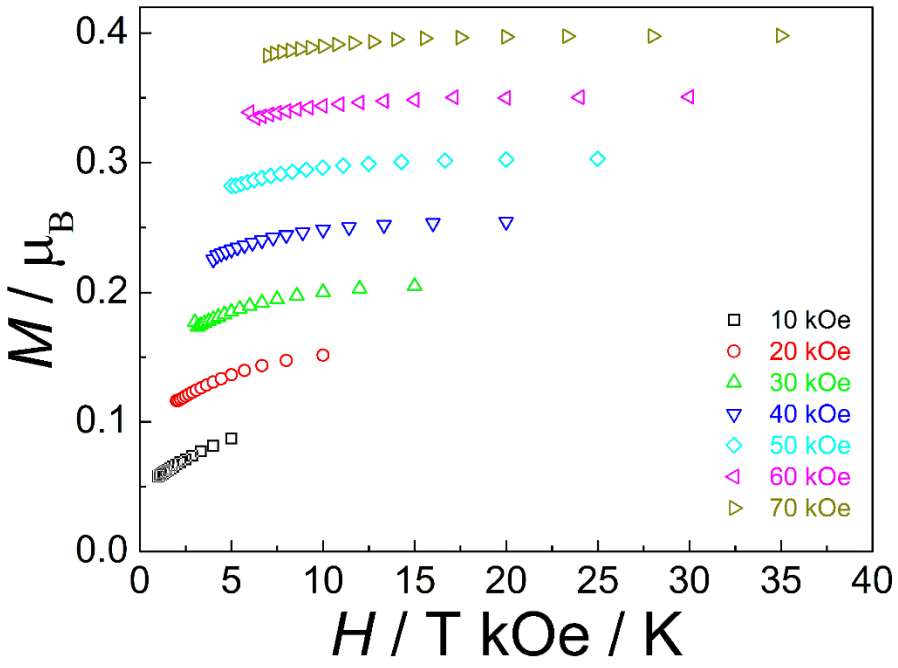

Fig. S12 The reduced magnetization data of **2** collected under various applied dc fields.

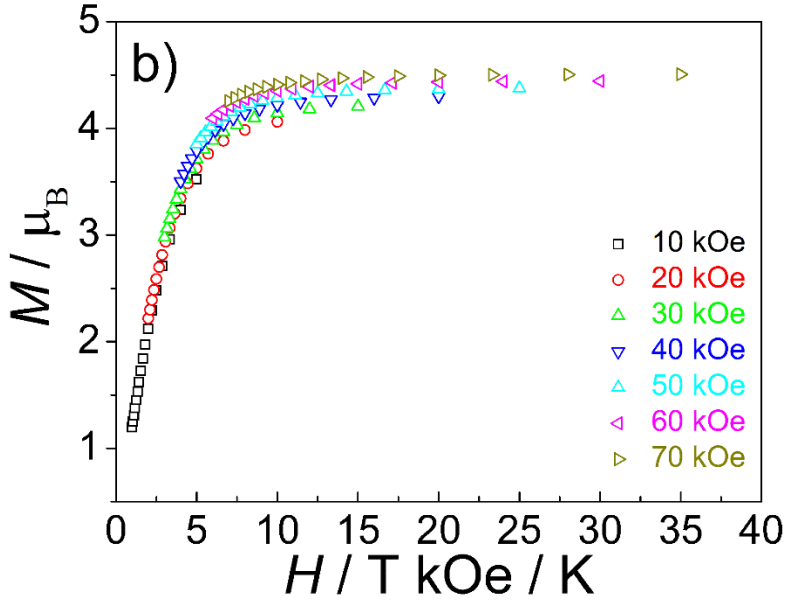

Fig. S13 The reduced magnetization data of **3** collected under various applied DC fields.

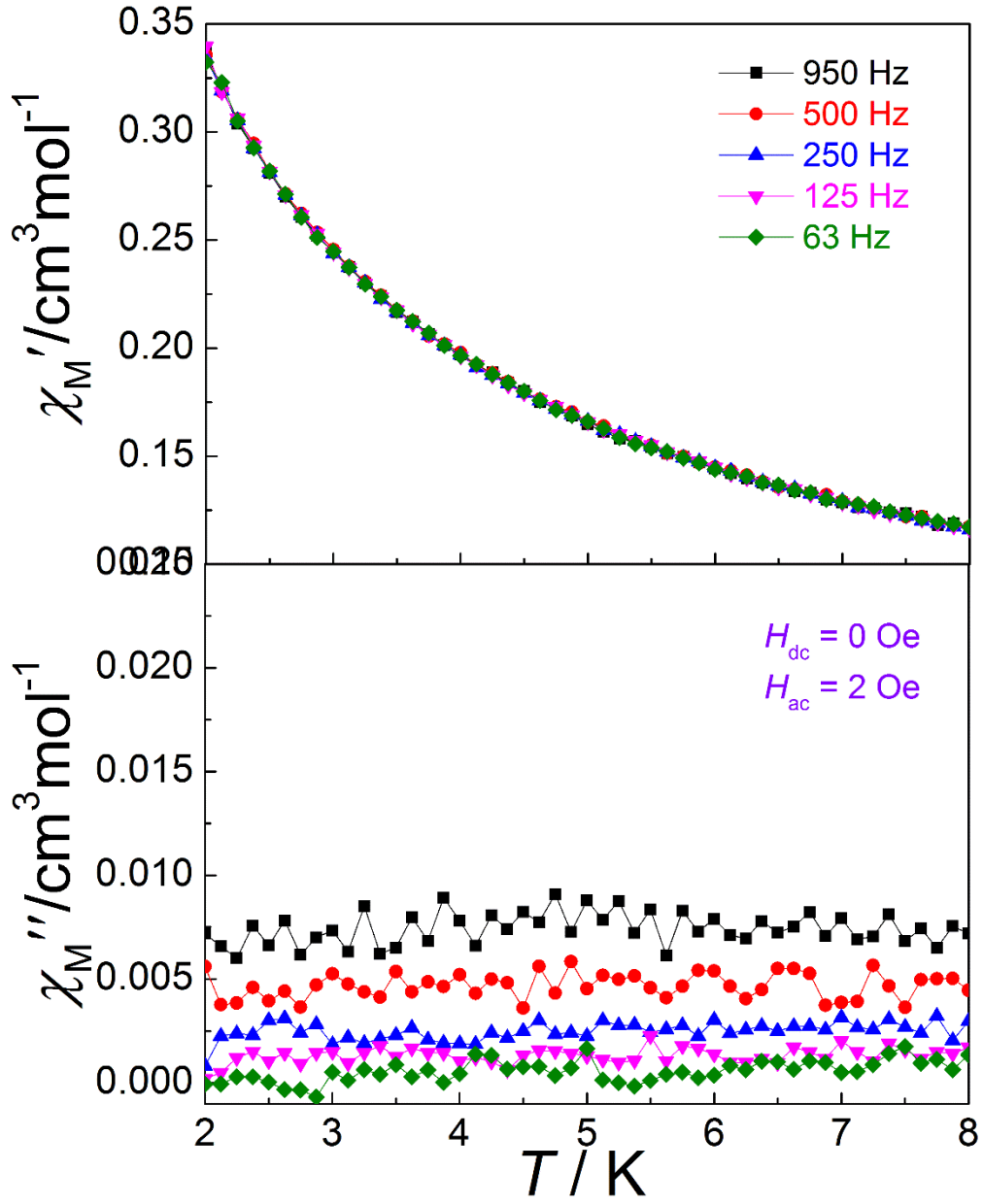

Fig. S14 Temperature dependent in-phase (top) and out-of-phase (bottom) a.c. susceptibility data of **2** measured under 0 Oe dc field (H_{ac} = 2 Oe). No out-of-phase signals were observed.

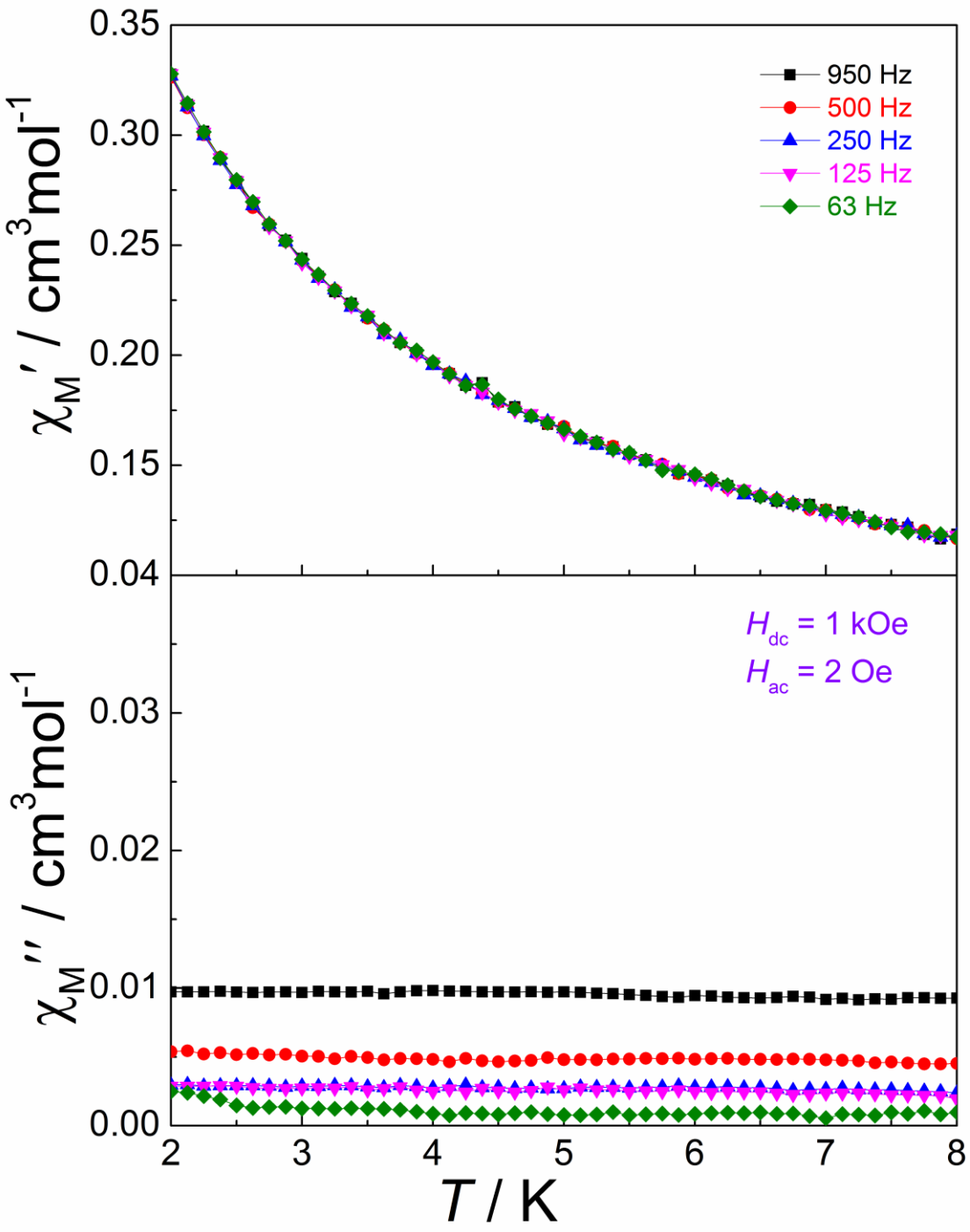

Fig. S15 Temperature dependent in-phase (top) and out-of-phase (bottom) a.c. susceptibility data of **2** measured under 1 kOe dc field (H_{ac} = 2 Oe). No out-of-phase signals were observed.

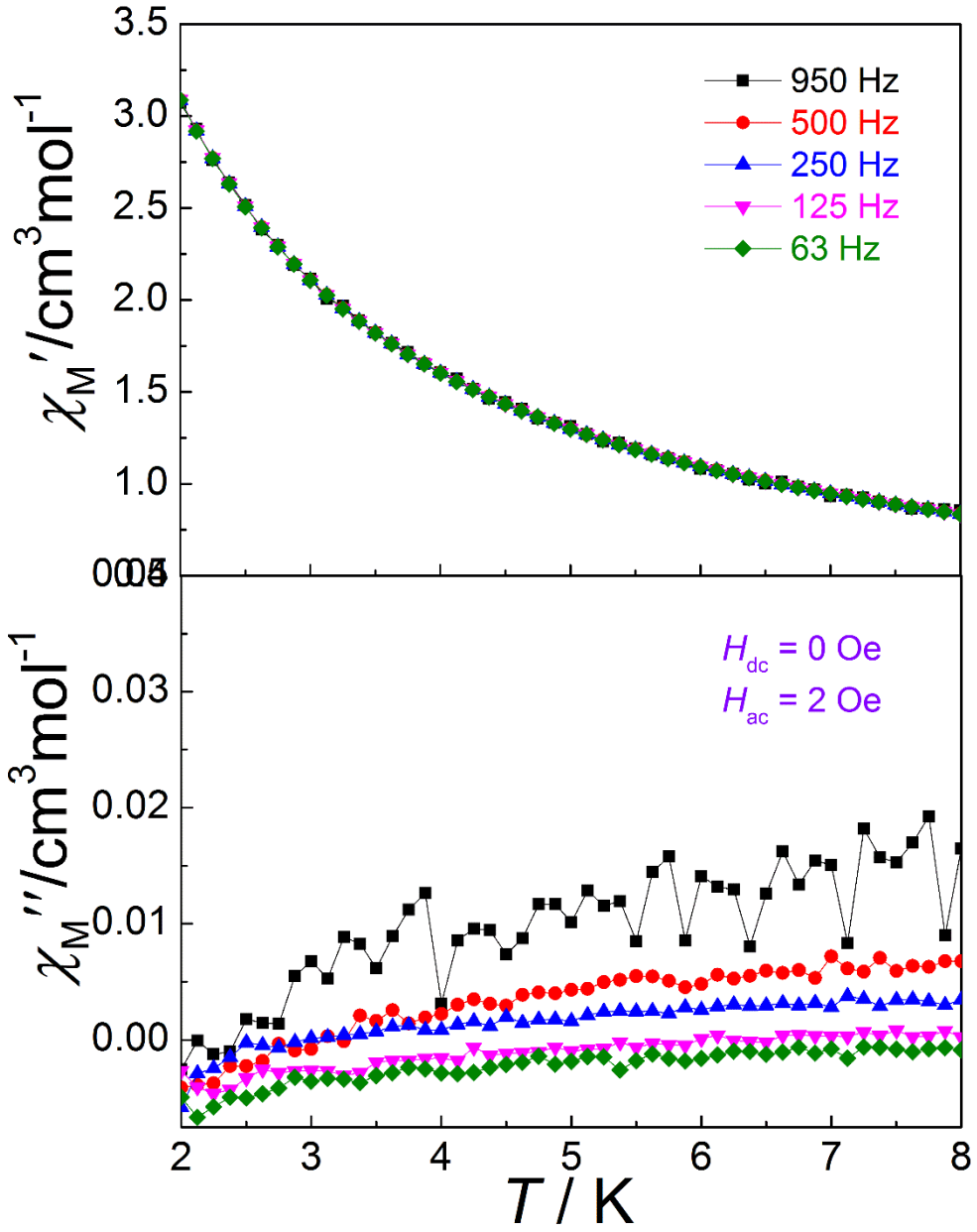

Fig. S16 Temperature dependent in-phase (top) and out-of-phase (bottom) a.c. susceptibility data of **3** measured under 0 Oe dc field (H_{ac} = 2 Oe). No out-of-phase signals were observed.

Table S5 Relaxation fitting parameters from the least-square fitting of the Cole-Cole plots of **3** according to the generalized Debye model.

Temperature / K	χS / cm^{3}mol−1K	χT / cm^{3}mol−1K	τ / s	α
1.8	0.14676	3.06860	0.00063	0.10517
2.0	0.12290	2.83739	0.00051	0.10835
2.2	0.12345	2.69056	0.00043	0.12150
2.4	0.13810	2.44926	0.00032	0.08777
2.6	0.17507	2.28701	0.00025	0.06897

2.8	0.10657	2.15376	0.00018	0.07319
3.0	0.12491	2.01730	0.00014	0.04976
3.2	0.12390	1.90413	0.00010	0.04022
3.4	0.16281	1.80818	0.00008	0.02634
3.6	0.21249	1.72229	0.00006	0.02662
3.8	0.15275	1.64185	0.00005	0.02547

5 References

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