

Electronic Supplementary Information

Carborane-incorporated mononuclear Co(II) complex showing zero-field slow magnetic relaxation

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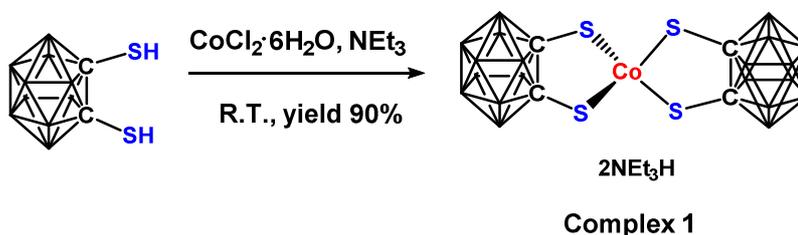
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I. General method

All reactions were carried out under an argon atmosphere. 1,2-dithiol-*o*-carborane ^{s1} and compound **2** were synthesized according to literature process. The starting material $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were purchased from Aldrich. IR spectra were measured with KBr pellets using a Bruker Vector 22 FT-IR spectrometer in $4000\text{--}400\text{ cm}^{-1}$ range. Elemental analyses for C, H, and N were performed on a Vario MICRO elemental analyzer. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu-K α) over the 2θ range of 5° to 40° at room temperature. Magnetic susceptibility measurements were performed in temperature range 1.8–300 K using a vibrating sample magnetometer (VSM) of Quantum Design MPMS SQUID-VSM system. The diamagnetic contribution of the sample itself was estimated from Pascal's constant.

II. Synthesis



Scheme S1 Preparation of target Co(II) complex **1**.

Synthesis of complex 1: 1,2- dithiol-*o*-carborane (124.8 mg, 0.6 mmol) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (68.3 mg, 0.25 mmol) were dissolved in 20 mL mixed solvents (CH_2Cl_2 10 mL, CH_3OH 10 mL). Then, 1 mL NEt_3 was added to the above solution at room temperature. The color of the reaction mixture was changed immediately. Then diethyl ether (40 mL) was added and the resulting green precipitate was filtered and washed. Yield: 151.6 mg (90%). Recrystallization in CH_2Cl_2 and CH_3CN under N_2 atmosphere gave green crystals of complex **1** (suitable for X-ray diffraction). Yield: 101.1 mg (60%). Anal. Calcd (%) for $\text{C}_{22}\text{H}_{52}\text{B}_{20}\text{CoN}_2\text{S}_4$: C, 28.43; H, 7.75; N, 4.14. Found: C, 28.36; H, 7.71; N, 4.05. IR (KBr pellet, cm^{-1}): 2517 (B–H).

III. X-ray structure determination

Single crystal X-ray crystallographic data were collected on a Bruker APEX II or APEX Duo diffractometer with a CCD area detector (Mo-K α radiation, $\lambda = 0.71073\text{ \AA}$). APEXII 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. Absorption corrections were applied with SADABS. The structures were solved by direct method and refined by full-matrix least-squares method on F^2 using the SHELXTL crystallographic software package. 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 data collections and structural refinement parameters are provided in Table S1. CCDC-1495750 (**1**) and CCDC-196006 (**2**) 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**

Empirical formula	C16 H52 B20 Co N2 S4	
Formula weight	675.96	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pna2 ₁	
Unit cell dimensions	a = 36.4636(15) Å	α = 90°.
	b = 9.9056(4) Å	β = 90°.
	c = 9.9210(4) Å	γ = 90°.
Volume	3583.4(3) Å ³	
Z	4	
Density (calculated)	1.253 Mg/m ³	
Absorption coefficient	0.728 mm ⁻¹	
F(000)	1412	
Crystal size	0.280 x 0.260 x 0.240 mm ³	
Theta range for data collection	2.056 to 27.609°.	
Index ranges	-45 ≤ h ≤ 47, -12 ≤ k ≤ 12, -12 ≤ l ≤ 12	
Reflections collected	32643	
Independent reflections	8168 [R(int) = 0.0578]	
Completeness to theta = 25.008°	99.9 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8168 / 14 / 397	
Goodness-of-fit on F ²	1.019	
Final R indices [I > 2σ(I)]	R1 = 0.0458, wR2 = 0.1076	
R indices (all data)	R1 = 0.0549, wR2 = 0.1123	
Largest diff. peak and hole	0.905 and -0.484 e.Å ⁻³	

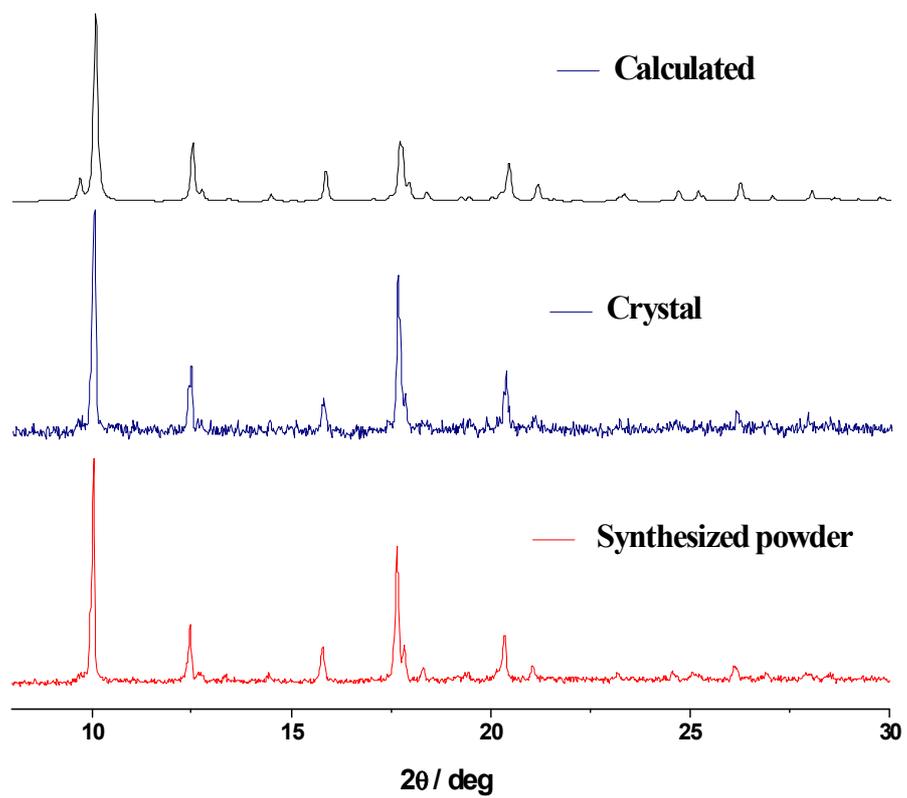


Fig. S1 Powder X-ray diffraction pattern of complex 1 at room temperature with the calculated pattern.

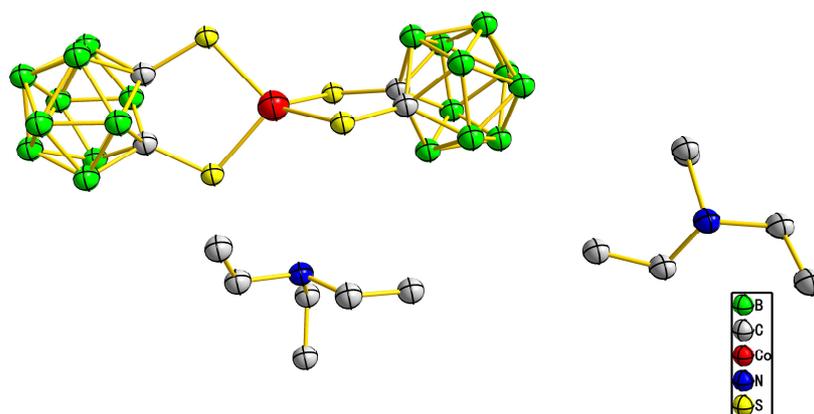


Fig. S2 The asymmetric unit of complex 1. All hydrogen atoms are omitted for clarity.

IV. Magnetic property measurements

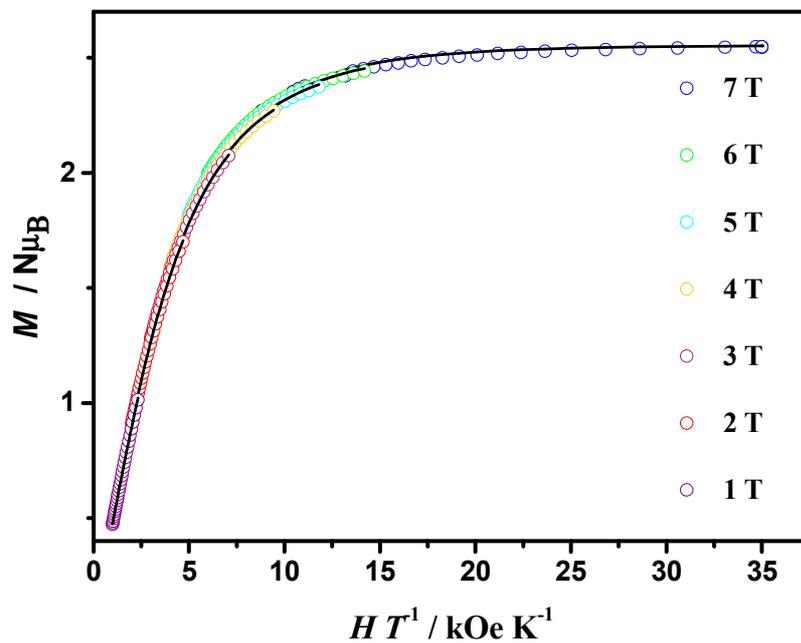


Fig. S3 Reduced magnetization data for **1** collected in the temperature range of 2–10 K under various applied dc fields of 1–7 T.

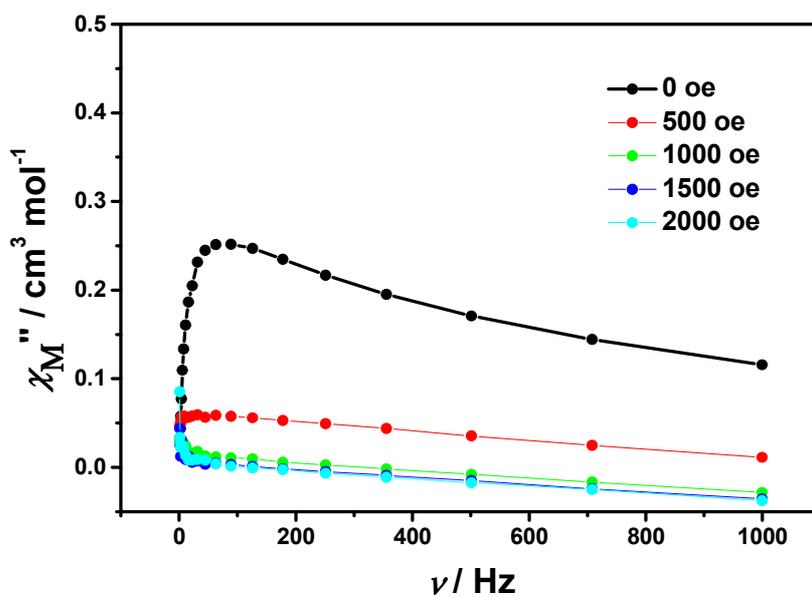


Fig. S4 Variable-frequency out-of phase (χ_M'') ac magnetic susceptibility data for **1** in different dc field ($H_{ac} = 2$ Oe).

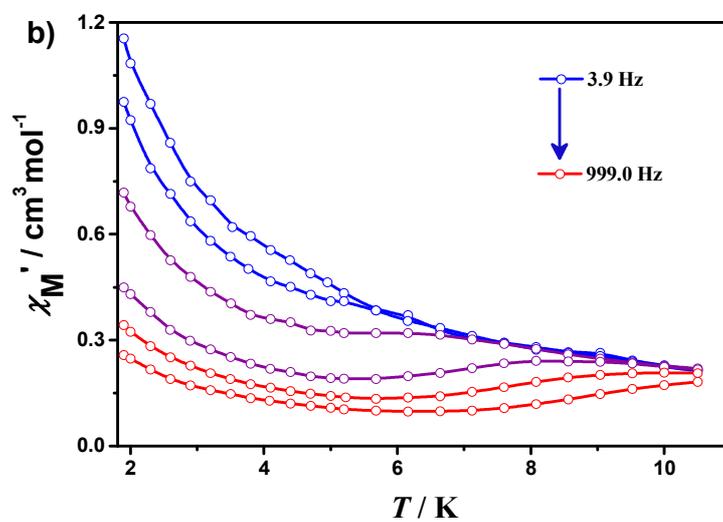
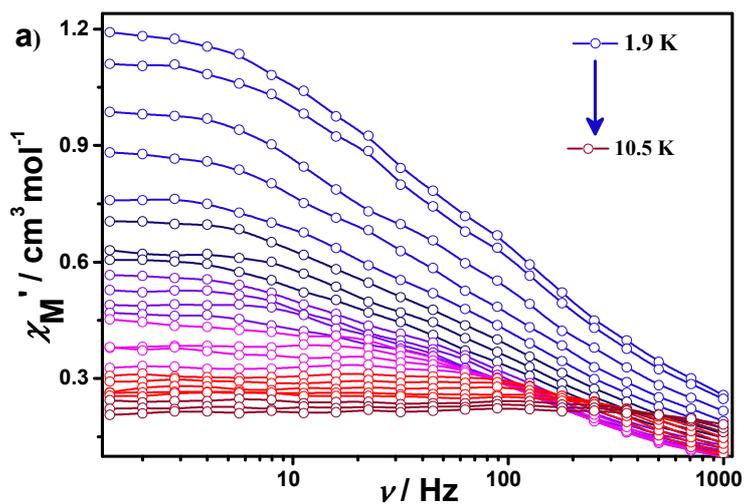
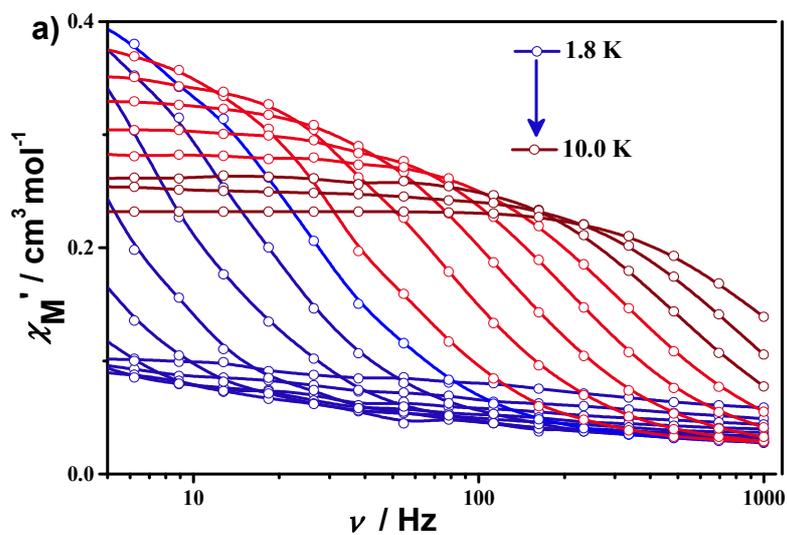


Fig. S5 Variable-temperature (a) and variable-frequency (b) out-of phase (χ_M'') ac magnetic susceptibility data for **1** at zero dc field ($H_{ac} = 2$ Oe).



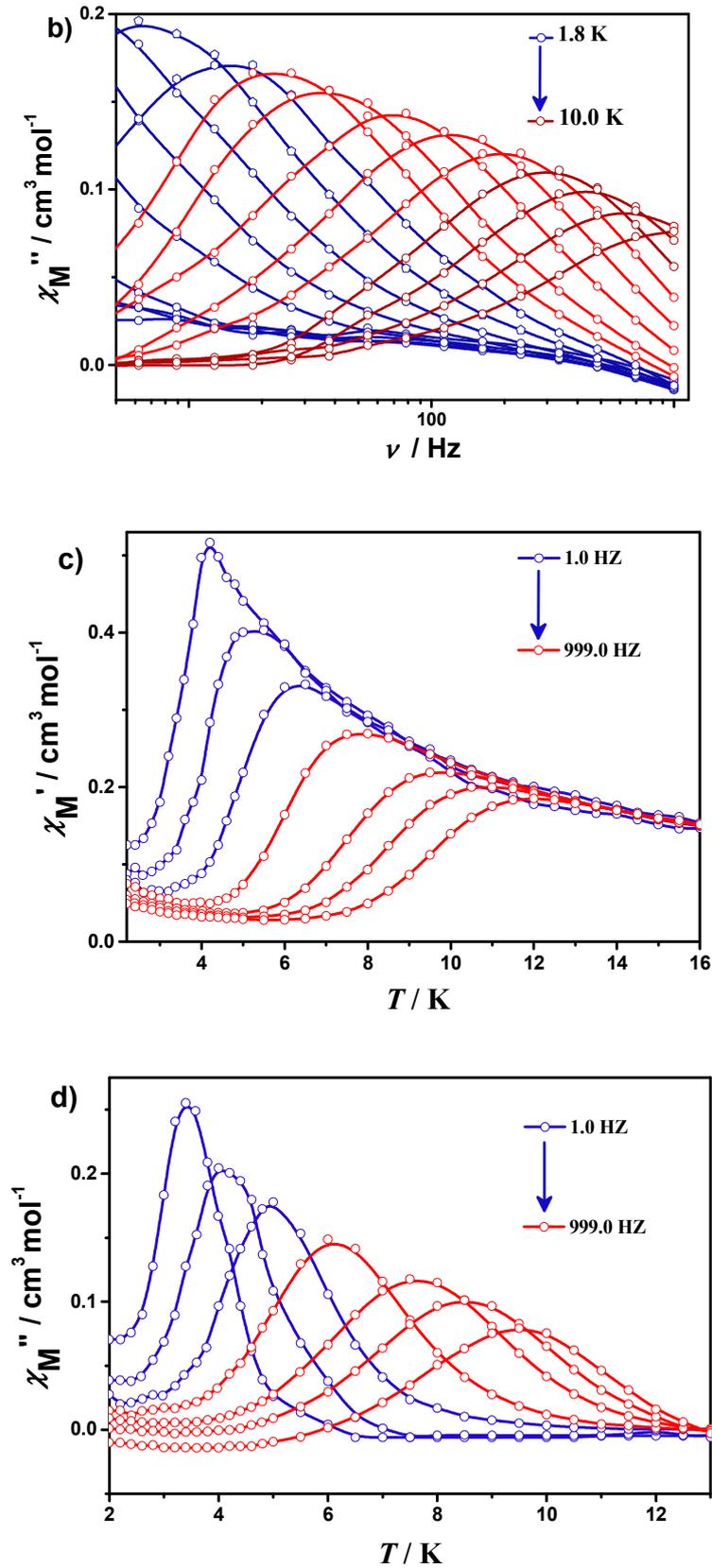


Fig. S6. Variable-temperature ((a), (b)) and variable-frequency ((c), (d)) ac magnetic susceptibility data for **1** under a 1000 Oe dc field ($H_{ac} = 2$ Oe).

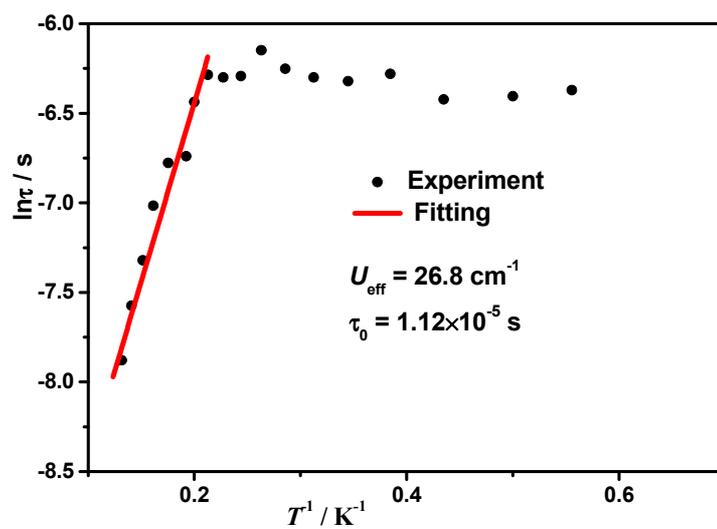


Fig. S7 Arrhenius plot of $\ln(\tau)$ vs T^{-1} for **1**. Solid line represents a fit to the high temperature region.

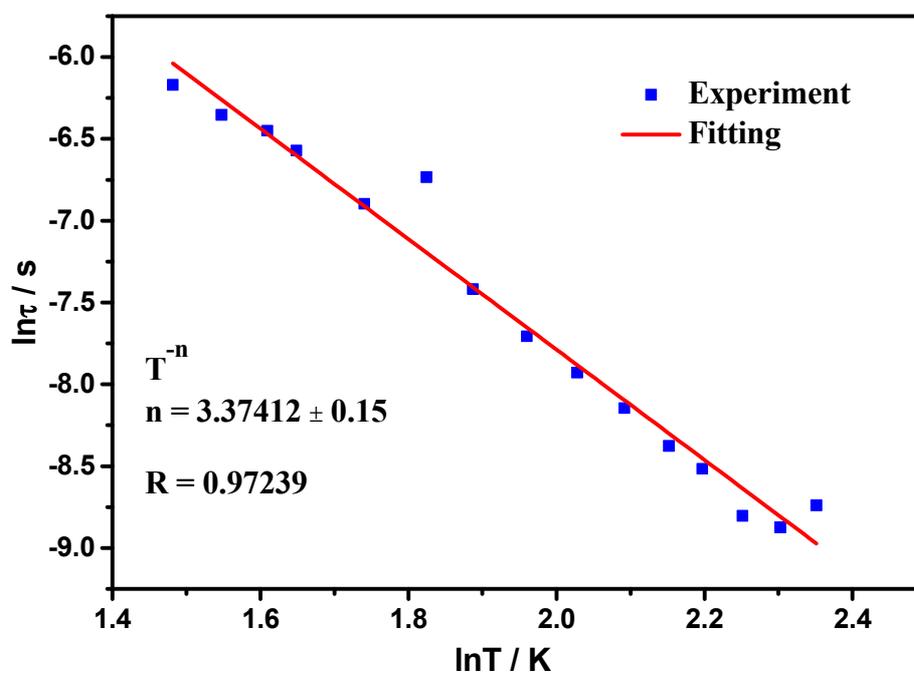


Fig. S8. Power law analysis in the form $\ln(\tau)$ vs $\ln(T)$.

Table S2. Relaxation fitting parameters from the least-square fitting of the Cole-Cole plots of **1** according to the generalized Debye model.

T/K	χ_s	χ_t	τ	α
1.9	0.19634	1.20747	0.00255	0.29995
2	0.18852	1.15079	0.00267	0.29988
2.3	0.15681	0.97222	0.00237	0.29922
2.6	0.13937	0.87832	0.00249	0.29616
2.9	0.12207	0.75725	0.00224	0.2921
3.2	0.10622	0.70399	0.00228	0.29736
3.5	0.1025	0.62709	0.00205	0.28896
3.8	0.09327	0.59976	0.00219	0.29646
4.1	0.07969	0.56118	0.00203	0.29688
4.4	0.08495	0.52878	0.00209	0.27672
4.7	0.06577	0.49831	0.00174	0.28461
5	0.05573	0.46688	0.00158	0.28715
5.2	0.07147	0.44292	0.0014	0.23332
5.7	0.07616	0.39089	0.00101	0.14161
6.2	0.10047	0.38677	0.00119	0.29936
6.6	0.06312	0.33913	6.00E-04	0.1976
7.1	0.0658	0.31167	4.50E-04	0.06936
7.6	0.06165	0.29481	3.60E-04	0.09839
8.1	0.07687	0.27646	2.90E-04	0.00372
8.6	0.06065	0.26251	2.30E-04	0.06564
9	0.07855	0.2591	2.00E-04	0.01349
9.5	0.06511	0.24507	1.50E-04	0.18801
10	0.10168	0.22802	1.40E-04	0.06662

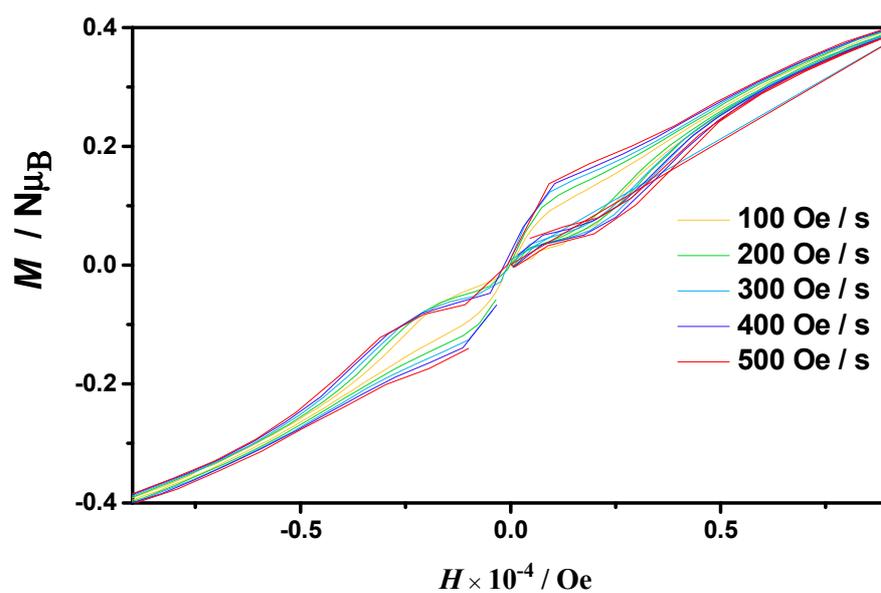


Fig. S9 Magnetic hysteresis loops of **1** under various field sweep rates at 1.8 K.

V. Reference

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