Slow magnetic relaxation in a cobalt magnetic chain

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Synthesis:

A solution of 2,3-dihydroxyquinoxaline (164.3 mg, 1.0 mmol) and $Co(OAc)_2 \cdot 4H_2O$ (251.8 mg, 0.99 mmol) in 10 mL of THF and 0.25 mL of NEt_3 was sealed in a Teflon-lined stainless steel vessel (23 mL). The mixture was heated according to the following temperature program: increasing the temperature to 140 °C at 18.3 °C/h, holding at 140 °C for 72 h, and then cooling to 30 °C at a rate of 2.3 °C/h. The deep purple block crystals suitable for single-crystal X-ray diffraction analysis were obtained. The crystals were rinsed a few times with DMF and ether, and dried in air. Yield: 67.8%. Anal.calcd for $C_{10}H_8CoN_2O_4$: C, 43.03; H, 2.89; N, 10.04. Found: C, 42.63; H, 2.62; N, 9.73.

X-ray Crystallography. Diffraction measurements for complex **1** were carried out using a Brucker APEXII CCD diffractometer with graphite-monochromated Mo K_α radiation ($\lambda = 0.7107$ Å). Data collation parameters of **1** are listed in Table S1. Structure was solved by direct methods and refined using the SHELXL-97[1] program by full-matrix least-squares on F^2 values. All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were placed in ideal, calculated positions, with isotropic thermal parameters riding on their respective carbon atoms.

Magnetic measurement. Variable temperature dc magnetic susceptibility measurements were collected on microcrystalline samples, restrained in eicosane to prevent torquing, on a Quantum Design MPMS SQUID-VSM magnetometer equipped with a 7.0 Tesla magnet and operating in the range of 1.8–300.0 K. AC magnetic susceptibility were performed on algid on a Quantum Design MMPS magnetometer. Diamagnetic corrections were estimated from

Pascal's constants[2] and subtracted from the experimental susceptibility data to obtain the molar paramagnetic susceptibility of the compounds. Measurements of the heat capacity for a polycrystalline sample (pellet piece) of complex **1** between T = 1.8 K and T = 20 K were made by a Quantum Design PPMS instrument using a hybrid adiabatic relaxation method. The two-tau relaxation method was used to determine the heat capacity with the PPMS software.

Other Studies. Infrared spectra were recorded in the solid state (KBr pellets) on a Perkin-Elmer PARAGON 1000 FT-IR spectrometer in the 400–4000 cm^{-1} range. Elemental analyses have been carried out by using a Perkin-Elmer TGA-7 TG analyzer.

1. Sheldrick, G. M. *SHELXL-97*; University of Gottingen: Gottingen, Germany, 1997.
2. Boudreaux, E. A.; Mulay, L. N. *Theory and Application of Molecular Paramagnetism*, Wiley J. & Sons, New York, 1976; p. 491.

Table 1S. Crystallographic data for complex **1**

	1	
Empirical formula	$C_{10}H_8CoN_2O_4$	
Formula weight	279.11	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.840(3) Å	
	b = 4.8670(14) Å	β = 94.139(4)°
	c = 19.354(6) Å	
Volume	1018.4(5) Å^3	
Z	4	
Density (calculated)	1.365 Mg/m^3	
Absorption coefficient	1.266 mm^{-1}	
F(000)	423	
Crystal size	0.4 x 0.1 x 0.3 mm^3	
Theta range for data collection	1.88 to 28.58°	
Index ranges	-14<=h<=14, -5<=k<=6, -17<=l<=26	
Reflections collected	7171	
Independent reflections	2579 [R(int) = 0.0343]	
Completeness to theta =25.00°	99.0%	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2579 / 0 / 156	
Goodness-of-fit on F^2	1.045	
Final R indices [$I > 2\sigma(I)$]	$R1$[a] = 0.0354, $wR2$[b] = 0.0911	
R indices (all data)	$R1$ = 0.0444, $wR2$ = 0.0962	
Largest diff. peak and hole	0.743 and –0.711 e.Å^{-3}	

[a] $R1 = (\Sigma||F_O|-|F_C||)/\Sigma|F_O|$ [b] $wR2 = [\Sigma[w(F_O^2-F_C^2)^2]/\Sigma[w(F_O^2)^2]]^{1/2}$

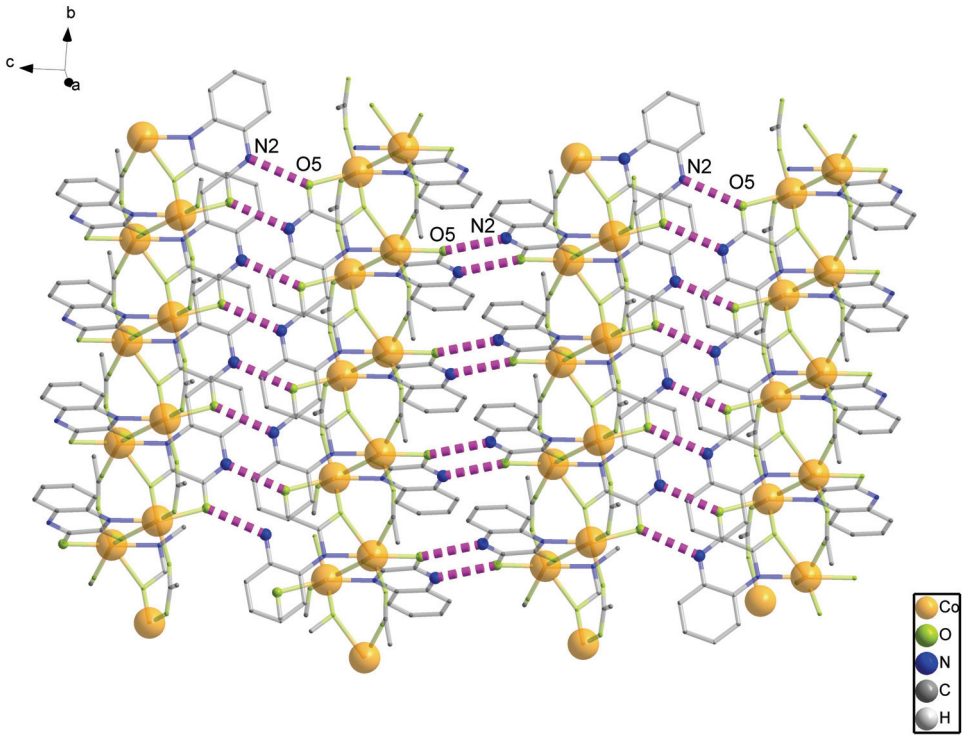

Figure 1S. 2D layer structure of **1** connected by H bonding.

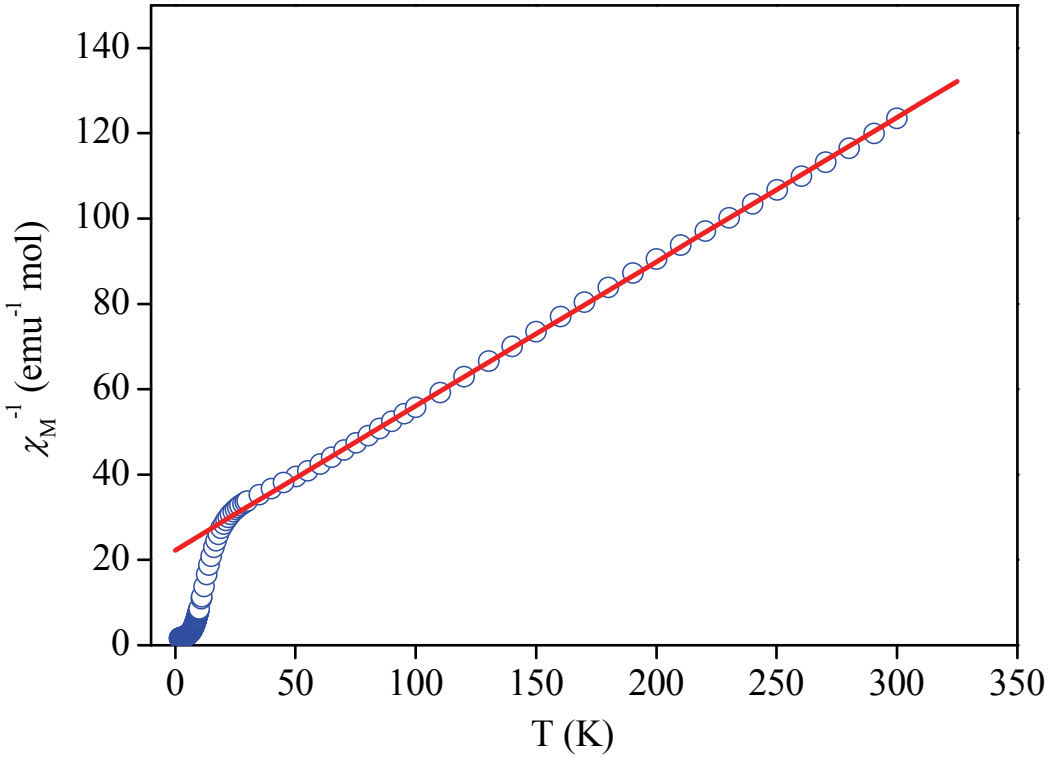

Figure 2S. Plot of χ_M^{-1} (○) vs. temperature for a microcrystalline sample of complex **1**. The solid line represents the best fit χ_M^{-1} above 50 K with a Curie–Weiss law.

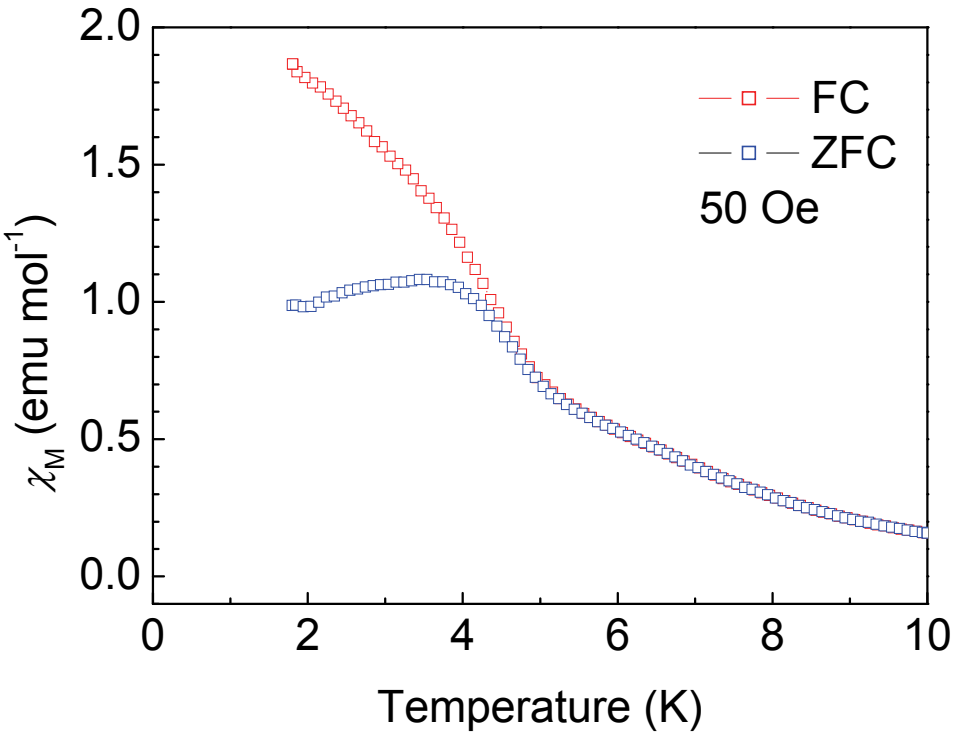

Figure 3S. ZFC/FC magnetization for **1** at an applied field of 50 G.

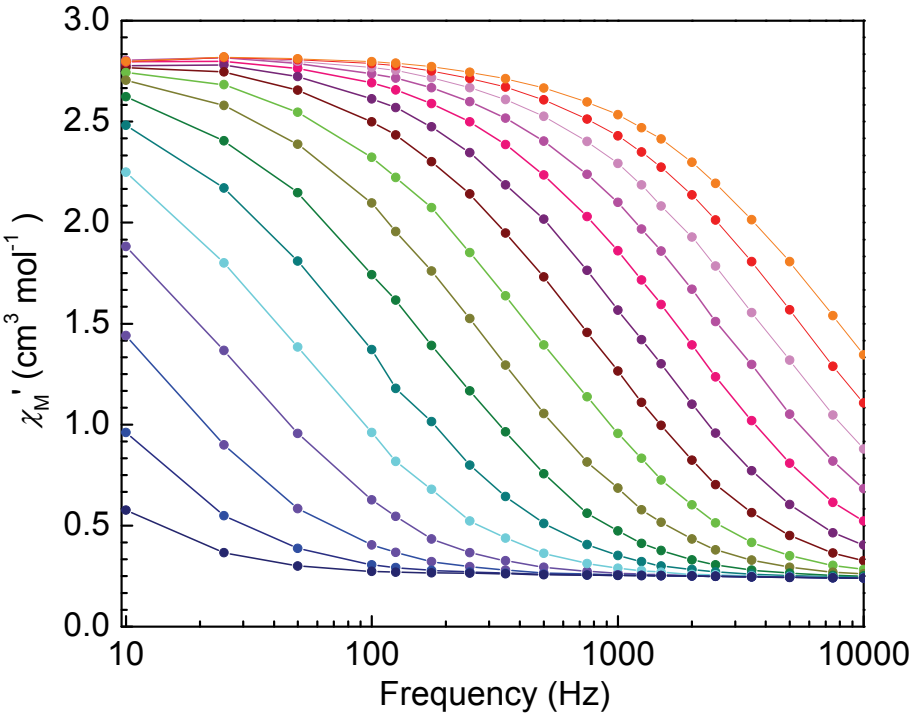

Figure 4S. Plots of in-phase (χ_M') of ac susceptibility vs. frequency in a 3.5 G ac field oscillating at the indicate temperatures for complex **1**.

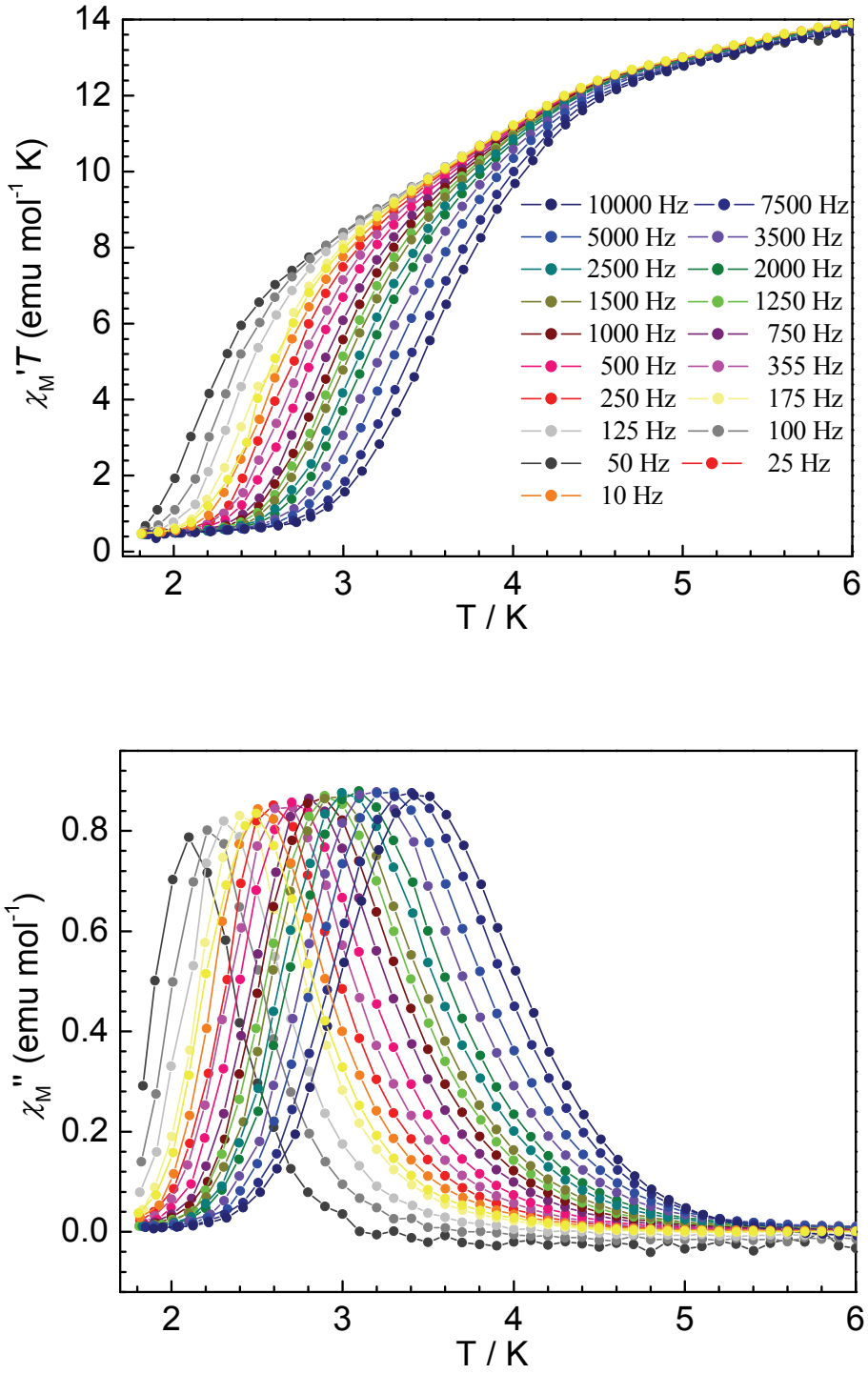

Figure 5S. Plots of in-phase ($\chi_M'T$) (Top) and out-off-phase (χ_M'') (Bottom) of ac susceptibility vs. T in a 3.5 G ac field oscillating at the indicate frequencies for complex **1**.

A scaling procedure of the $\chi_M T$ data for **1** (Figure 6S) clearly indicates a linear regime characteristic of Ising 1D systems. The ln($\chi_M'T$) versus 1/T plot increases linearly between 8 and 14 K, with an energy gap, Δ_ξ, of 16 K. It should be noted that the ΔE barrier extracted from the ac data is significantly larger than Δ_ξ, suggesting that the relaxation mechanism in this SCM cannot be described by a simple Glauber model.[3]

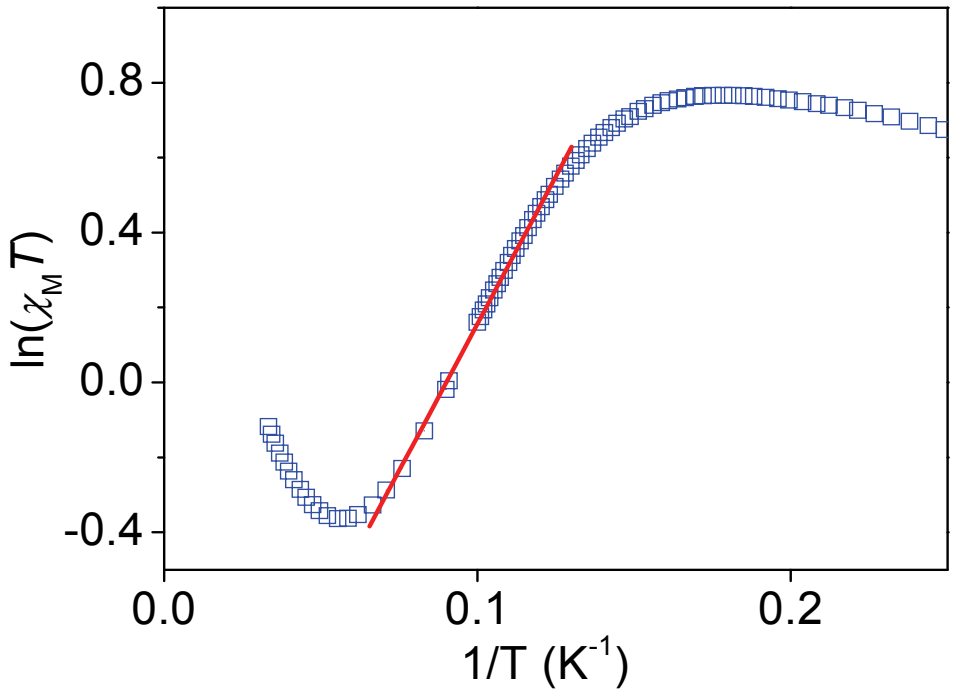

Figure 6S. Plot of ln ($\chi_M'T$) vs. T^{-1} for **1**. Solid line represents the fit of $\chi T = C_{eff}\exp(\Delta_\xi/k_B T)$ between 8 and 14 K.

3. C. Coulon, R. Clérac, L. Lecren, W. Wernsdorfer, H. Miyasaka, *Phys. Rev. B* 2004, **69**, 132408.

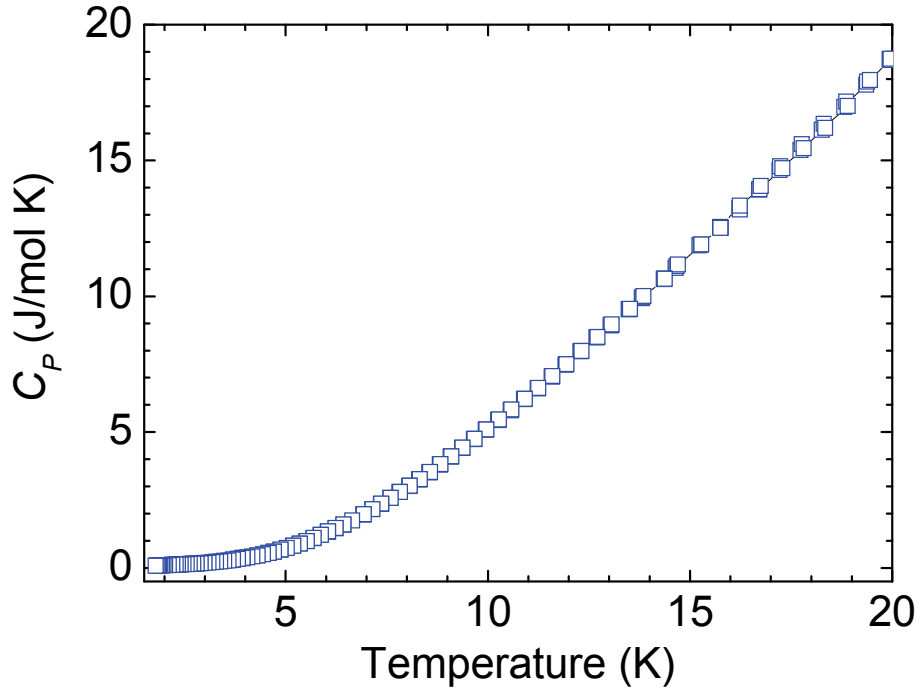

Figure 7S. Plot of C_p vs. *T* for a pellet piece polycrystalline of **1** measured on grounded crystals under zero applied field.