Electronic supplementary information (ESI)

Field-modified multiple slow relaxation in a metamagnet composed of cobalt(II) chains with mixed azide and tetrazolate bridges

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Synthesis of [Co(tzpo)(N$_3$)(H$_2$O)$_2$]$_n$·nH$_2$O (1). A mixture of CoCl$_2$·4H$_2$O (0.30 mmol, 72 mg), 4-cyanopyridine N-oxide (0.20 mmol, 24 mg), NaN$_3$ (1.0 mmol, 65 mg) and H$_2$O (6 mL) was sealed in a Teflon-lined autoclave, heated at 100°C for 24 h, and then cooled to room temperature in 12 h. Dark red crystals of **1** were collected in 52% yield. Anal. Calcd for C$_6$H$_{10}$CoN$_8$O$_4$: C, 22.72; H, 3.18; N, 35.33%. Found: C, 22.51; H, 3.49; N, 35.68%. IR (KBr pellets, cm-1): 3137(br,s), 2078(s), 1654(m), 1628(m), 1529(w), 1437(m), 1301(w), 1212(m), 1188(m), 863(m), 838(m), 655(m).

The synthesis reaction involves the [3+2] cycloaddition of azide and cyano groups to generate in situ the tetrazolate ligand:
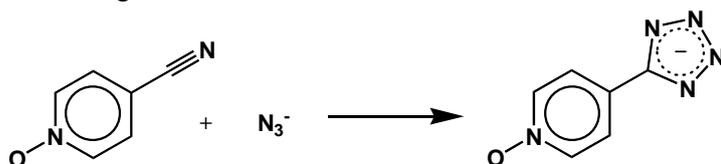
Physical Measurements. Elemental analyses were performed on an Elementar Vario ELIII analyzer. The FT-IR spectra were recorded in the range 500–4000 cm^{-1} using KBr pellets on a Nicolet NEXUS 670 spectrophotometer. Magnetic measurements were carried out with crushed crystals of **1** on a Quantum Design SQUID MPMS-5 magnetometer with an applied field of 1 kOe, and diamagnetic corrections were made with Pascal's constants. Thermogravimetric analyses were carried out on a Mettler Toledo TGA/SDTA851 instrument under flowing air at a heating rate of 1°C/min. The powder X-ray diffraction was recorded on a Rigaku D/Max-2500 diffractometer at 35 kV, 25mA for a Cu-target tube.

Crystal Data Collection and Refinement. Diffraction intensity data were collected at 293 K on a Bruker APEX II diffractometer equipped with graphite-monochromated Mo-Kα radiation (0.71073 Å) and a CCD area detector. Empirical absorption corrections were applied using the SADABS program.[1] The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXL program,[1] with anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms attached to carbon atoms were placed in calculated positions and refined using the riding model. The water hydrogen atoms were located from the difference Fourier map.

Crystal data: C$_6$H$_{10}$CoN$_8$O$_4$, M = 317.15, monoclinic $P2_1/c$, a = 7.2716(13), b = 21.676(4), c = 7.3030(13) Å, α = 90, β = 93.965(2), γ = 90°, V = 1148.3(4) Å^3, Z = 4, D_c = 1.834 g cm^{-3}. μ(Mo-Kα) = 1.713 mm^{-1}, T = 296(2) K, 2204 unique reflections with R_{int} = 0.0603, GOF on F^2 = 1.049, final R_1 = 0.0713 for $I \geq 2\sigma(I)$, wR_2 = 0.2220 for all data. CCDC 906889

References

1 G. M. Sheldrick, *SHELXTL* Version 5.1. Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1998.
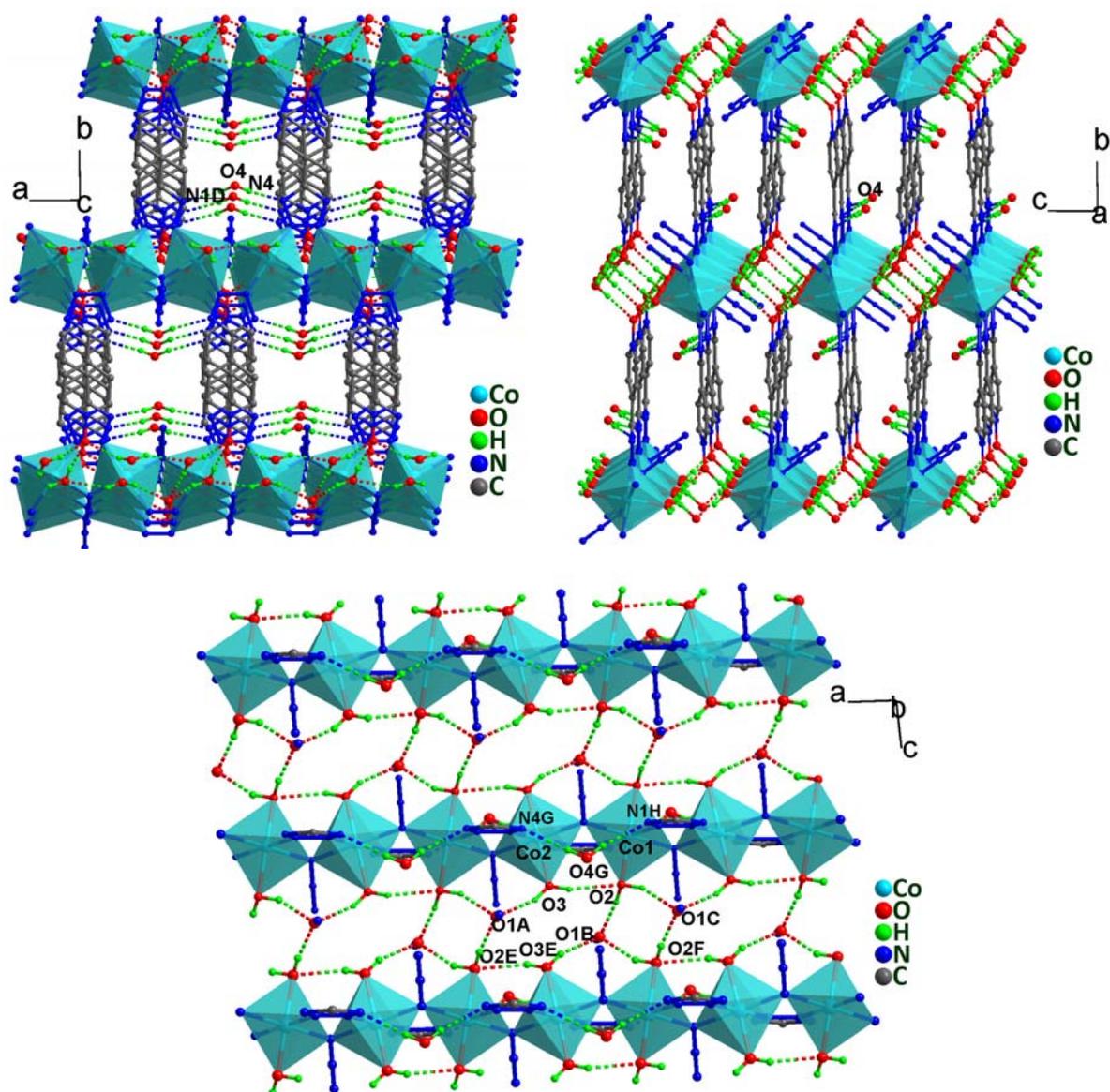
Fig. S1. The packing of the chains through hydrogen bonds in **1**. Top: the 3D structure viewed from different directions; bottom: the 2D hydrogen-bonded layer along the ac plane. Symmetry codes: A, -x+1, y-1/2, -z+5/2; B, x, -y+3/2, z+1/2; C, -x, y-1/2, -z+5/2;D, x+1, y, z; E, 1-x, 1-y, 3-z; F, -x, 1-y, 3-z; G, 1-x, 1-y, 2-z; H, -x, 1-y, 2-z. For parameters, see Table S1.

Table S1 Parameters for hydrogen bonds

	D-H	H...A	D...A	<(DHA)	note
O3-H3B...O2	0.81(8)	2.12(8)	2.880(7)	157(8)	Intrachain, between coordinated waters
O3-H3A...O1A	0.74(8)	2.14(8)	2.767(6)	143(9)	Between the N-oxide O atom and
O2-H2B...O1B	0.89(7)	1.94(7)	2.816(6)	170(8)	coordinated waters
O2-H2C...O1C	0.88(8)	1.94(8)	2.749(6)	153(7)	
O4-H4C...N4	0.82(11)	2.15(11)	2.965(8)	172(10)	Between uncoordinated water and tetrazole
O4-H4B...N1D	0.75(10)	2.26(10)	3.008(7)	176(12)	N atoms

A, -x+1, y-1/2, -z+5/2; B, x, -y+3/2, z+1/2; C, -x, y-1/2, -z+5/2;D, x+1, y, z
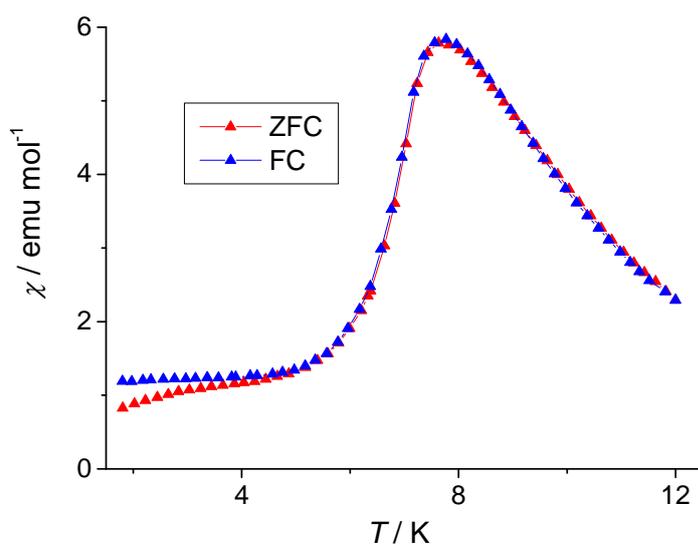
Fig. S2. FC and ZFC χ-T plots for **1** at 50 Oe.
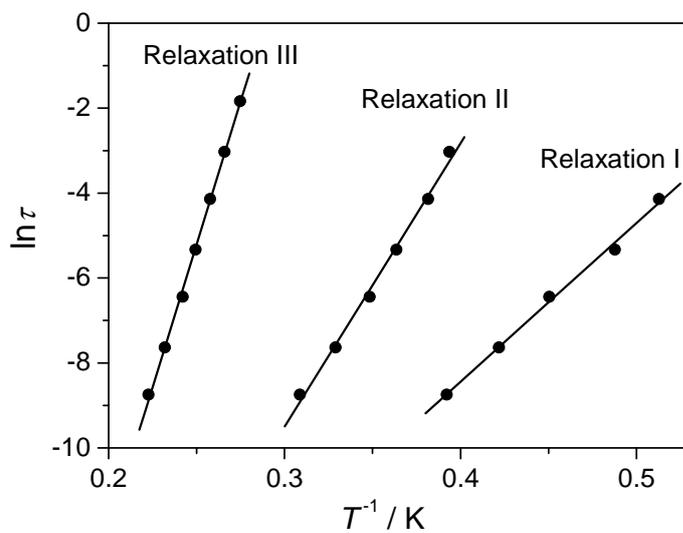
Fig. S3. Lnτ-1/T plots and the fits to the Arrhenius equation.
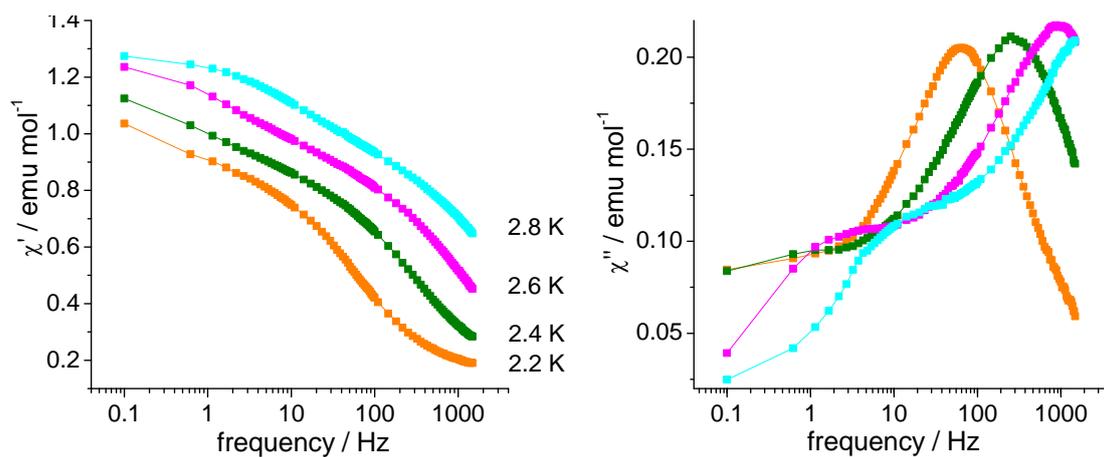
Fig. S4. Frequency-scan ac susceptibilities at different temperatures for **1** at zero dc field.
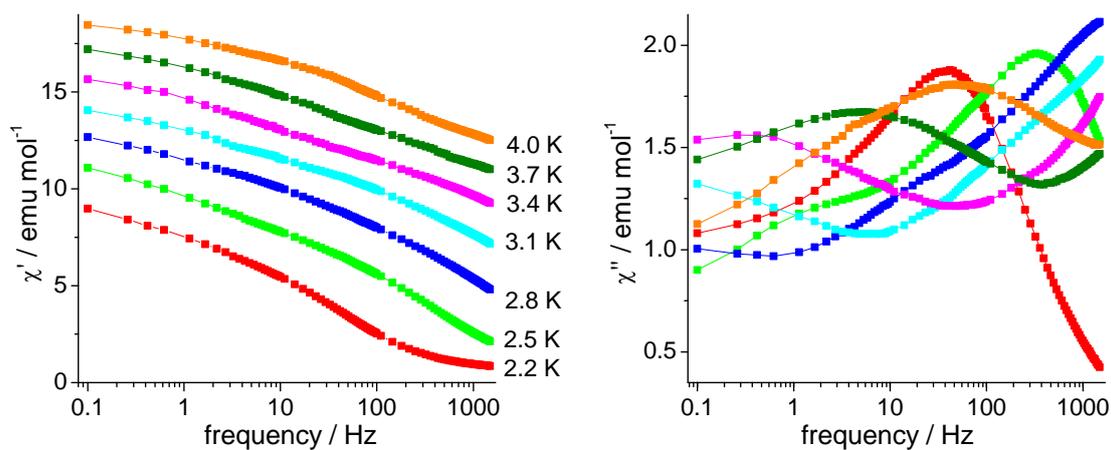
Fig. S5. Frequency-scan ac susceptibilities at different temperatures for **1** at 500 Oe.
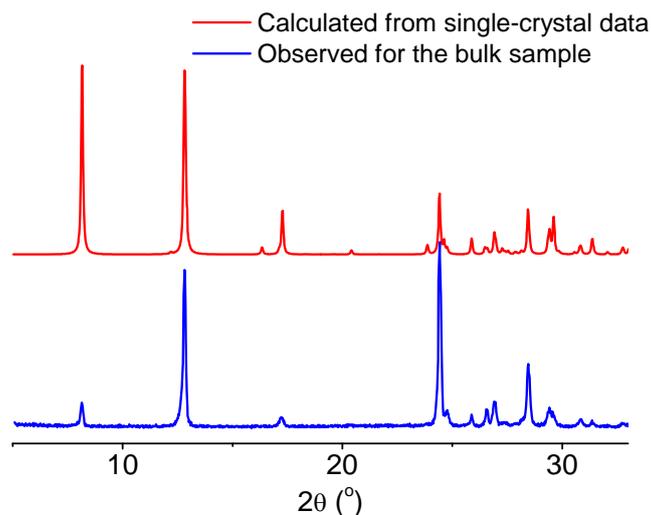
Fig. S6 Powder X-ray diffraction patterns for **1**, suggesting the phase purity of the bulk crystalline sample for magnetic and other physical measurements. The differences in intensity are attributable to preferred orientations in the sample.
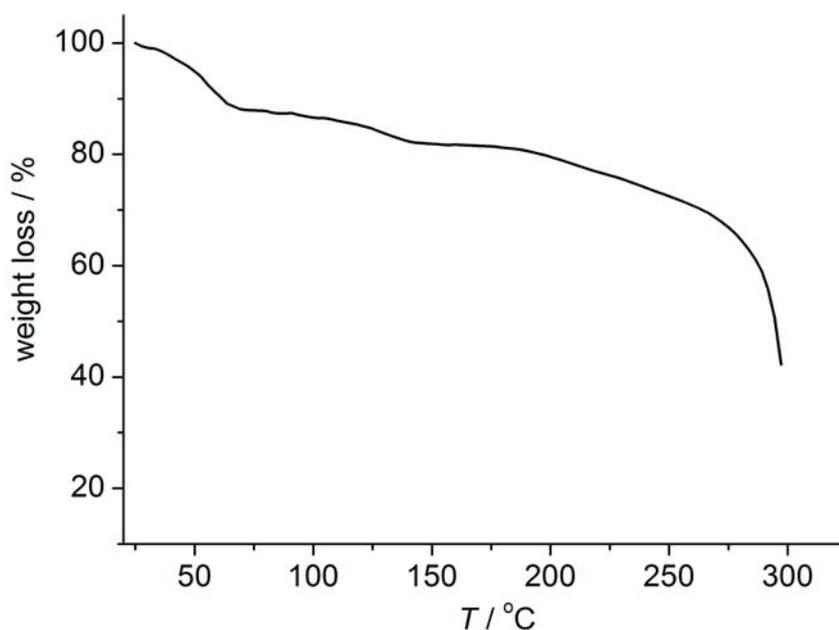
Fig. S7 Thermogravimetric plot for **1**. The weight loss from room temperature to 150°C is attributable to the release of all water molecules (coordinated and uncoordinated) in the compound (observed 18.1 %, calculated 17.0%). ***CAUTION***: The compound, containing both azide and tetrazole components, is potentially explosive. A small amount of the sample (< 2 mg) was used for thermogravimetric measurements. The sample was heated slowly at a rate (1°C/min), and the temperature was controlled below 300 °C.