A cyano-bridged coordination nanotube showing field-induced slow magnetic relaxation

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EXPERIMENTAL SECTION

Materials and Synthesis. All reagents were obtained from commercially available sources and used as received unless otherwise noted. The staring material, $[Co(L_{N3O2})(H_2O)_2](ClO_4)_2$, was prepared according the literature methods.[1]

Caution! Cyanides are highly toxic and dangerous. They should be handled in small quantities with great care.

$[Co(L_{N3O2})][Co(CN)_6]\cdot 26H_2O$. $K_3(Co(CN)_6)$ (0.1 mmol) dissolved in water-acetonitrile (1: 3) was added to one arm of an H-shaped tube, and a solution of water-acetonitrile (1: 3) containing $[Co(L_{N3O2})(H_2O)_2](ClO_4)_2$ (0.05 mmol) was put in the other arm. The orange crystals generated suitable for X-ray diffraction were grown out in the middle of the H-shaped tube after one week. Yield: ~62%. Elemental analysis (%) calculated for $C_{114}H_{173}Co_{10}N_{42}O_{38}$: C, 41.12; H, 5.23; N, 17.67. Found: C, 41.24; H, 5.01; N, 17.51. IR (KBr, cm^{-1}): 3418(vs), 2928(s), 2881(s), 2136(vs), 1649(s), 1591(s), 1422(w), 1355(w), 1271(s), 1204(w), 1097(vs), 1081(vs), 1046(w), 1020(w), 957(w), 819(s), 746(w), 560(w), 412(w).

Physical measurements.

Infrared spectra (IR) data were measured on KBr pellets using a Nexus 870 FT-IR spectrometer in the range of 4000-400 cm^{-1}. Elemental analyses of C, H, and N were performed at an Elementar Vario MICRO analyzer. Powder X-ray diffraction data (PXRD) were recorded at 298 K on a Bruker D8 Advance diffractometer with Cu Kα X-ray source (λ = 1.54056 Å) operated at 40 kV and 40 mA. Thermal gravimetric analysis (TGA) was measured in Al_2O_3 crucibles using a PerkinElmer Thermal Analysis in the temperature range of 20-700 °C under a nitrogen atmosphere. Magnetic measurements from 2 to 300 K with applied direct current (dc) field up to 7 T were performed using a Quantum Design SQUID VSM magnetometer on the ground samples from the single crystals of the compounds. Alternative current (ac) magnetic susceptibility data were collected in a zero dc field or different applied dc fields in the temperature range of 2-10 K, under an ac field of 2 Oe, oscillating at frequencies in the range of 1-1000 Hz. All magnetic data were corrected for the diamagnetic contributions of the sample holder and of core diamagnetism of the sample using Pascal's constants.

X-ray Crystallography.

Single crystal X-ray diffraction data were collected on a Bruker APEX Duo diffractometer with a CCD area detector (Mo-Kα radiation, λ = 0.71073 Å) at 123 K. 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.[2] Absorption corrections were applied with SADABS.[3] The structure was solved by direct methods and refined by full-matrix least-squares method on F2 using the SHELXTL crystallographic software package.[4] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the organic ligands were refined as riding on the corresponding non-hydrogen atoms. We used the methods of DIF-Fourier maps and HADD instructions to add the hydrogen atoms of the water molecules. Additional details of the data collections and structural refinement parameters are provided in Table 1. Selected bond lengths and angles of **1** are listed in Table S2. CCDC 1567196 is the supplementary crystallographic data for this paper. They can be obtained freely 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**

complex	**1**
Formula	$C_{114}H_{173}Co_{10}N_{42}O_{38}$
Mr /gmol^{-1}	3351.3603
Crystal system	Monoclinic
Space group	P2(1)/c
a /Å	17.249(3)
b /Å	28.481(5) A
c /Å	31.388(6) A
α /deg	90
β /deg	97.584(3)
γ /deg	90
V /Å^3	15285(5)
Z	4
T (K)	123
d_{calc}/g cm^{-1}	1.446
μ(Mo–*K*α) (mm^{-1})	1.140
F (000)	6892
Refl.collected/unique	100663 / 33718
data/restraints/parameters	33718 / 73 / 1718
R_1[a]/wR_2[b] ($I > 2\sigma(I)$)	0.0792/ 0.2324
R_1/ wR_2 (all data)	0.1351/ 0.2770
GOF[c] on F^2	1.025
Max/min /e [Å^{-3}]	1.255/ -0.761

[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) and bond angles (°) for **1**.

	1		
Co(2)-N(6)	2.115(4)	Co(4)-N(2)#1	2.058(5)
Co(2)-N(41)	2.128(4)	Co(4)-N(11)	2.073(5)
Co(2)-N(7)	2.137(4)	Co(4)-N(37)	2.104(7)
Co(2)-N(40)	2.181(4)	Co(4)-N(39)	2.153(7)
Co(2)-N(42)	2.181(5)	Co(4)-N(38)	2.216(9)
Co(2)-O(1)	2.267(4)	Co(4)-O(4)	2.290(6)
Co(2)-O(2)	2.279(4)	Co(4)-O(3)	2.309(8)
Averrage Co(2)-X	2.184(4)	Averrage Co(4)-X	2.172(5)
Co(5)-N(12)	2.074(5)	Co(7)-N(18)	2.083(5)
Co(5)-N(10)	2.096(5)	Co(7)-N(31)	2.110(6)
Co(5)-N(35)	2.119(5)	Co(7)-N(17)	2.112(4)
Co(5)-N(36)	2.180(6)	Co(7)-N(32)	2.156(6)
Co(5)-N(34)	2.181(6)	Co(7)-N(33)	2.179(6)
Co(5)-O(5)	2.277(5)	Co(7)-O(8)	2.295(5)
Co(5)-O(6)	2.297(5)	Co(7)-O(7)	2.302(5)
Averrage Co(5)-X	2.175(3)	Averrage Co(7)-X	2.177(2)
Co(8)-N(23)	2.073(5)	Co(10)-N(22)	2.078(4)
Co(8)-N(24)	2.101(5)	Co(10)-N(22)	2.079(5)
Co(8)-N(27)	2.142(8)	Co(10)-N(13)#1	2.089(5)
Co(8)-N(26)	2.165(7)	Co(10)-N(30)	2.115(7)
Co(8)-O(9)	2.204(6)	Co(10)-N(29)	2.212(7)
Co(8)-N(25)	2.231(8)	Co(10)-O(12)	2.235(7)
Co(8)-O(10)	2.264(6)	Co(10)-O(11)	2.299(6)
Averrage Co(8)-X	2.169(2)	Averrage Co(10)-X	2.158(7)
C(21)-Co(9)-C(20)	176.8(2)	C(19)-Co(9)-C(23)	179.1(3)
C(22)-Co(9)-C(24)	177.2(2)	C(12)-Co(3)-C(8)	176.6(3)
C(10)-Co(3)-C(7)	178.6(3)	C(11)-Co(3)-C(9)	177.7(2)
N(6)-Co(2)-N(7)	164.72(18)	N(7)-Co(2)-N(40)	100.46(16)

N(40)-Co(2)-N(42)	144.58(18)	N(41)-Co(2)-O(1)	144.92(17)
N(40)-Co(2)-O(1)	142.59(18)	N(41)-Co(2)-O(2)	143.88(16)
N(42)-Co(2)-O(2)	143.19(17)	N(30)-Co(10)-N(29)	147.6(4)
N(28)-Co(10)-O(12)	142.8(3)	N(30)-Co(10)-O(12)	141.0(4)
N(28)-Co(10)-O(11)	147.0(3)	N(29)-Co(10)-O(11)	141.2(4)
C(13)-Co(6)-C(16)	177.8(3)	C(15)-Co(6)-C(18)	178.2(3)
C(14)-Co(6)-C(17)	178.0(3)	C(5)-Co(1)-C(2)	175.6(3)
C(1)-Co(1)-C(6)	176.4(3)	C(3)-Co(1)-C(4)	179.0(3)
N(12)-Co(5)-N(10)	170.8(2)	N(36)-Co(5)-N(34)	144.8(2)
N(35)-Co(5)-O(5)	144.6(2)	N(34)-Co(5)-O(5)	142.3(2)
N(35)-Co(5)-O(6)	143.1(2)	N(36)-Co(5)-O(6)	144.1(2)
N(18)-Co(7)-N(17)	170.3(2)	N(32)-Co(7)-N(33)	146.3(3)
N(31)-Co(7)-O(8)	145.0(3)	N(33)-Co(7)-O(8)	141.0(3)
N(31)-Co(7)-O(7)	144.2(3)	N(32)-Co(7)-O(7)	143.2(3)
N(23)-Co(8)-N(24)	167.0(2)	N(26)-Co(8)-O(9)	149.2(3)
N(27)-Co(8)-N(25)	142.4(3	O(9)-Co(8)-N(25)	140.7(3)
N(27)-Co(8)-O(10)	148.3(3)	N(26)-Co(8)-O(10)	138.6(3)
N(39)-Co(4)-N(38)	146.4(3)	N(37)-Co(4)-O(4)	144.5(3)
N(39)-Co(4)-O(4)	143.1(3)	N(37)-Co(4)-O(3)	144.8(3)
N(38)-Co(4)-O(3)	141.1(3)	N(12)-C(13)-Co(6)	175.2(6)
C(6)-N(6)-Co(2)	147.9(4)	C(18)-N(17)-Co(7)	160.6(5)
C(20)-N(22)-Co(10)	146.8(5)	C(7)-N(7)-Co(2)	149.8(4)
C(19)-N(18)-Co(7)	156.7(5)	C(13)-N(12)-Co(5)	169.5(5)
C(12)-N(11)-Co(4)	154.6(5)	C(21)-N(23)-Co(8)	151.9(5)

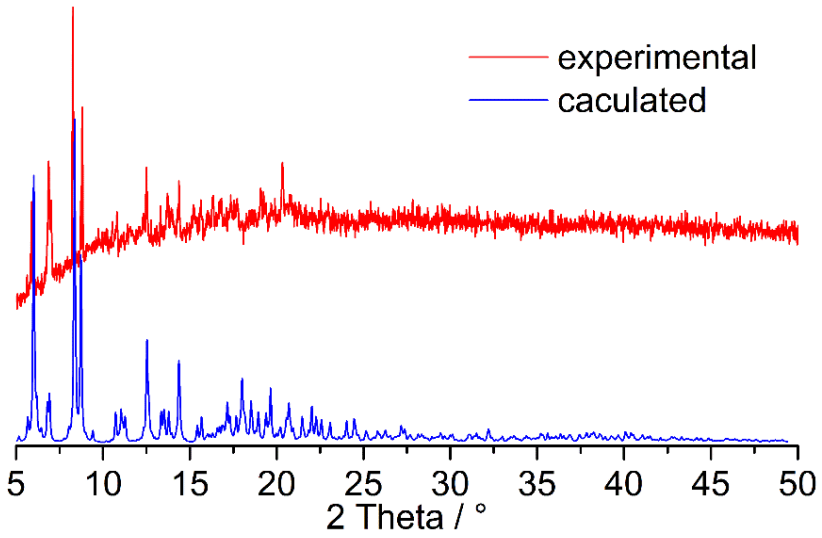

Figure S1. The Powder X-ray Diffraction (PXRD) of **1**

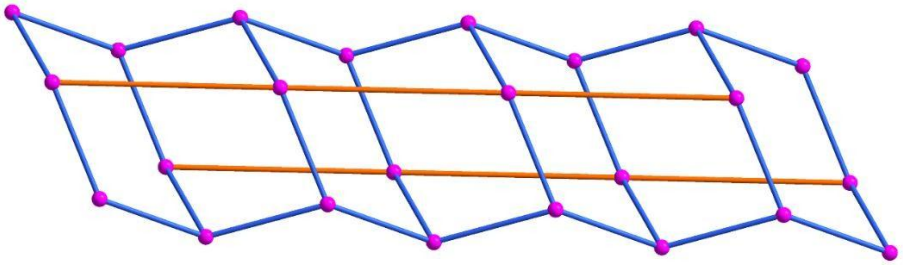

Figure S2. The topology of the 1D nanotubular of **1**

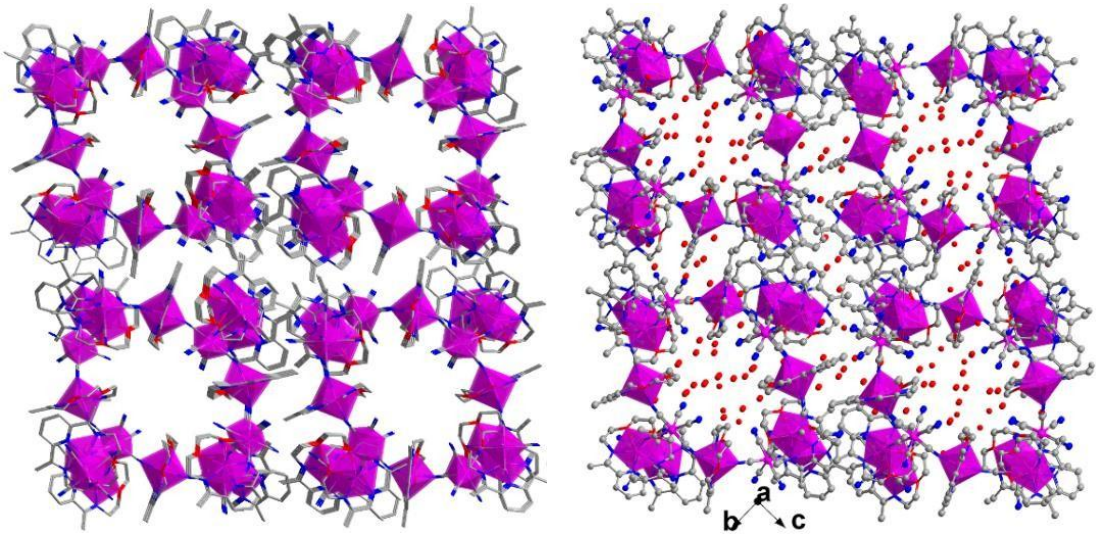

Figure S3. The packing of the tubes of **1** without or with water molecules.

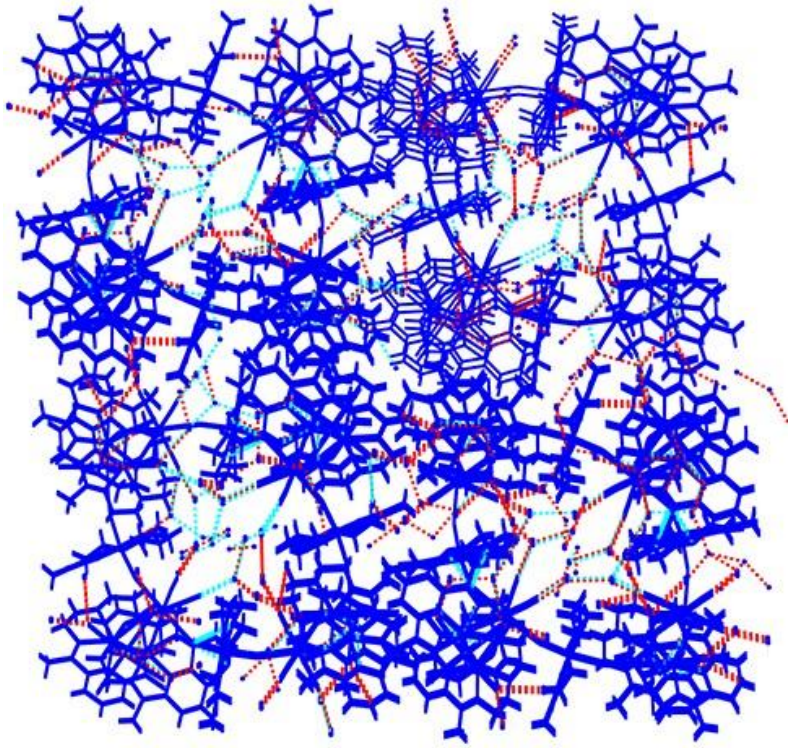

Figure S4. Rich hydrogen bonds in **1**.

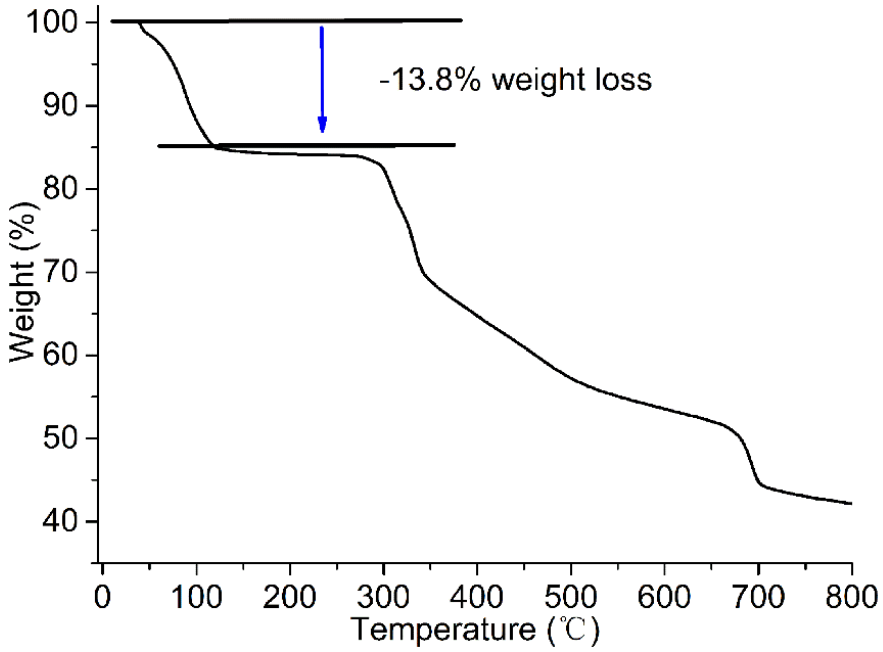

Figure S5. Thermal gravimetric analysis **1** under a N_2 atmosphere.

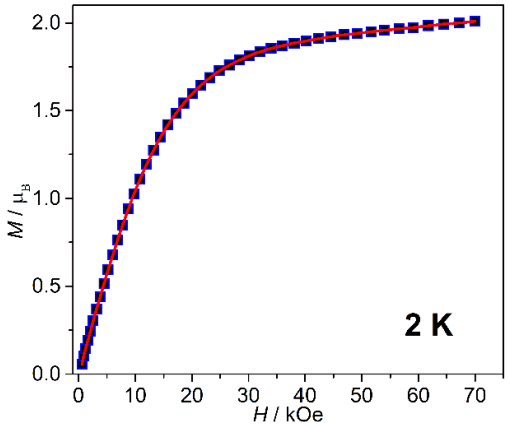

Figure S6. The magnetization curve for **1** measured at 2 K. The red solid lines represent the best fits by PHI program.

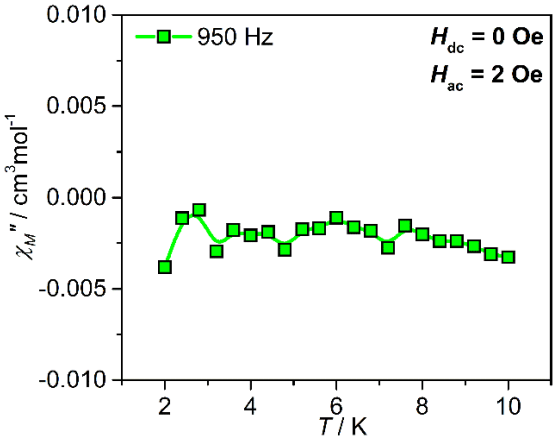

Figure S7. Temperature dependence of out-of-phase (χ″) ac susceptibility data for **1** measured under zero dc field

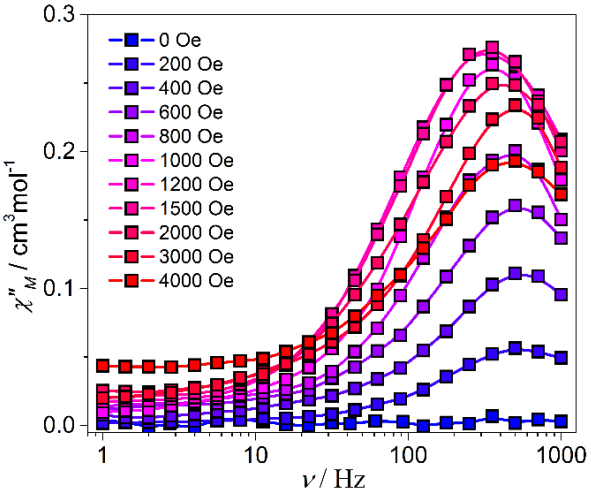

Figure S8. Frequency dependence of out-of-phase (χ″) ac magnetic susceptibility of **1** measured at 2 K in various applied fields from 0 to 4000 Oe.

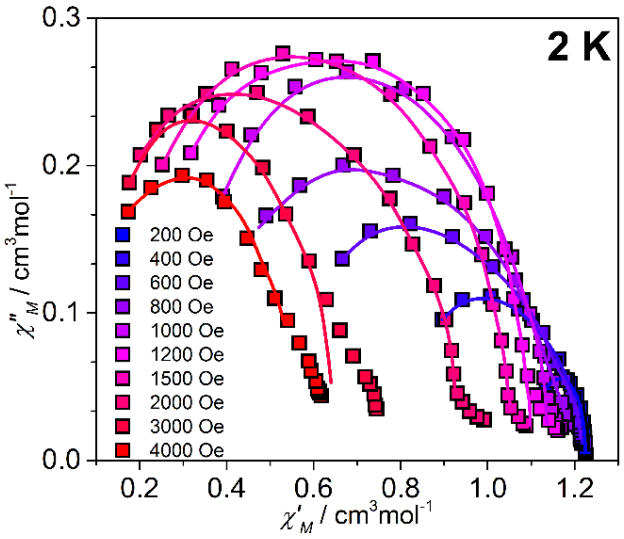

Figure S9. Cole–Cole plots of **1** at 2 K under various applied dc fields. The solid lines represent the best fit of the experimental results with the generalized Debye model.

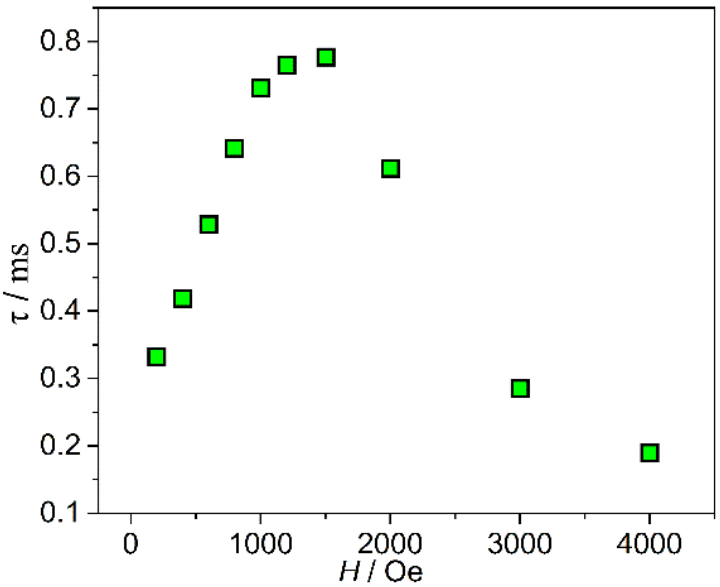

Figure S10. Field dependence of the magnetic relaxation time under various applied dc fields at 2 K for **1**.

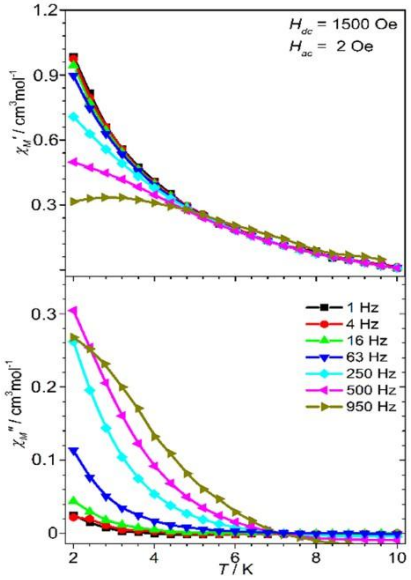

Figure S11. Temperature dependence of ac susceptibility data for **1** measured under a 1.5 kOe dc field.

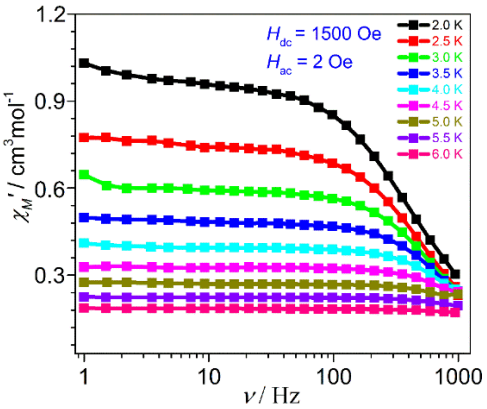

Figure S12. Frequency dependence of the in phase ac magnetic susceptibilities for **1** collected under a 1.5 kOe dc field in the temperature range 2 to 6 K.

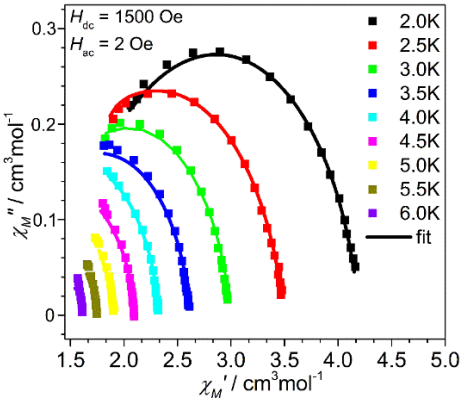

Figure S13. Cole-Cole plots of **1** at 2-6 K at 1500 Oe dc field. The solid lines represent the best fits according to the generalized Debye model.

Table S3. Relaxation fitting parameters from the least-square fitting of the Cole-Cole plots of compound **1** according to the generalized Debye model.

T / K	χ_S / $cm^3mol^{-1}K$	χ_T / $cm^3mol^{-1}K$	τ / s	α
2.0	1.40076	4.19550	0.00043	0.15172
2.5	0.97528	3.49134	0.00028	0.17984
3.0	0.96664	2.98698	0.00021	0.15163
3.5	0.81417	2.61925	0.00014	0.15072
4.0	0.70168	2.33024	0.00009	0.15059
4.5	0.79042	2.10330	0.00008	0.15853
5.0	1.02785	1.92061	0.00007	0.15109
5.5	1.23579	1.75906	0.00006	0.15686
6.0	1.20117	1.62401	0.00005	0.15093

Table S4. Compilation of pentagonal bipyramidal Co^{II} single-ion magnets.

Compound	Cshm's	D/cm^{-1}	E/cm^{-1}	U_{eff}/K (H/Oe)	Ref.
$[Co^{II}(H_2dapb)(H_2O)\ (NO_3)](NO_3)$	0.417	32.4	0	81.2(1000)	1a
$[Co^{II}L_{N5}(H_2O)_2]Cl_2{\cdot}4H_2O$	0.289	24.6	-1.4×10^{-2}	29.8(1000)	1a
$[Co^{II}(dapb)(im)_2]{\cdot}H_2O$	0.364	24.8	1.6×10^{-3}	89.6(1000)	1a
$[Co^{II}(tdmmb)(H_2O)_2][BF_4]_2$	0.101	25.6	-1.0	42.2(1500)	5
$[Co^{II}(tdmmb)(CN)_2]{\cdot}2H_2O$	0.109	17.4	-0.6	48.9(1500)	5
$[Co^{II}(tdmmb)(NCS)_2]$	0.195	26.3	-0.1	49.2(1500)	5
$[Co^{II}(tdmmb)(SPh)_2]$	0.667	34.5	-1.8	54.7(1500)	5
$[Co^{II}(tdmmb)(bpe)][BF_4]_2{\cdot}3CH_3CN$	0.167	21.7	-0.43	19.0(1000)	6
$[Co^{III}(CN)_6]_2[Co^{II}(TODA)]_3{\cdot}9H_2O$	0.499	29.9	0.8×10^{-3}	18.1(1500)	7
$[Co^{II}(tbp)_3(NO_3)_2]$	1.410	35.8	0.21	25.4(1000)	8
$[Co^{II}(isq)_3(NO_3)_2]$	1.542	35.7	0.02	15.8(1200)	8
$[Co^{II}(L)](ClO4)2$	0.0941	34	0.046	24.3(1000)	9
$[Co^{II}(H_2dapb)(SCN)_2]{\cdot}3H_2O$	-	15.9	0	-	10
$[Co^{II}(H_2dapb)(H_2O)_2]$	-	13.1	0	-	10
$[Co^{II}(L_{N3O2})Cl_2]{\cdot}2CH_3OH$	-	38	0		11
$[Co^{II}(L_{N3O2})Br_2]$	-	41	0	4.2(1000)	11
$[Co^{II}(L_{N3O2})I_2]$	-	35	0	4.5(1000)	11
$[Co^{II}(L_{N3O2})]_6[Co^{III}(CN)_6]_4{\cdot}26H_2O$	0.497, 0.257, 0.348, 0.262, 0.362, 0.234	21.4	-0.08	9.1(1000)	this work

H_2dapb = 2,6-diacetylpyridine bis(benzoylhydrazine); **L_{N5}** = 2,13-dimethyl-3,6,9,12-tetraaza-1(2,6)-pyridina-cyclotridecaphane-2,12-diene ; **L_{N3O2}** = 3,12,18-triaza-6,9-dioxabicyclo[12.3.1]octadeca-1(18),14,16-triene; **tdmmb** = 1,3,10,12-tetramethyl-1,2,11,12-tetra-aza[3](2,6)pyridino[3](2,9)-1,10-phenanthrolinophan-2,10-diene; **isq** = isoquinoline; **tbp** = 4-tert-butylpyridine; **TODA** = 1, 4, 10-trioxa-7, 13-diazacyclopentadecane; **bpe** = 1,2-di(4-pyridyl)ethane; **L** = 3,12-bis(2-methylpyridine)- 3,12,18-triaza-6,9 dioxabicyclo[12.3.1]octadeca-1,14,16-triene.

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