Hexacoordinated Co(II) complex exhibiting strong magnetic anisotropy and field-induced slow magnetization relaxation: synthesis, magnetic characterization, and quantum-chemical modelling

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Table S1. *Crystallographic data and details of the crystallographic experiment and refinement procedure for* ***1***

Parameters	Values
Empirical formula, moieties	$C_{24}H_{20}CoN_8S_2$, $2(C_2H_6OS)$
Formula weight	699.79
Temperature (K)	100.01(10)
λ, Å	MoK_α (0.71073)
Crystal system	Monoclinic
Space group	C 2/c
a, Å	14.6399(8)
b, Å	13.9674(5)
c, Å	17.1940(16)
β °	114.285(5)
V, Å^3	3204.7(4)
Z	4
d_{calc} (Mg/m^3)	1.450
μ, mm^{-1}	0.836
F(000)	1452
Crystal shape, size	Prism, 0.34 x 0.32 x 0.27 mm.
θ range, °	3.05-32.07
Index ranges	-21<=*h*<=19, -20<=*k*<=20, -25<=*l*<=24
Reflections collected/unique	23560/5529
Reflections $I > 2\sigma(I)$	4802

Refinement procedure	Full-matrix least squares on F^2.
Number of refined parameters	233
GooF	1.148
R indices $F^2 > 2\sigma(F^2)$	$R_1 = 0.0468$, w$R_2 = 0.0947$
R indices (all data)	$R_1 = 0.0564$, w$R_2 = 0.0984$
Min. and Max. Resd. Dens. [e/Ang^3]	-0.58, 0.54

Table S2. Selected bond lengths (Å), bond and torsion angles (degrees) of **1** (symmetry code a: 1-x, y, 1/2-z)

Bond lengths, Å					
Co-N1	2.1172(14)	N2-C3	1.373(2)	C9-C10	1.377(2)
Co-N3	2.2209(14)	N3-C3	1.324(2)	C10-C11	1.409(2)
Co-N4	2.0706(15)	C3-C4	1.420(2)	N3-C11	1.380(2)
N4-C12	1.153(2)	C4-C5	1.355(2)	C6-C11	1.414(2)
S1-C12	1.6315(19)	C5-C6	1.420(2)	C1-C2	1.489(2)
C1-C1_a	1.478(3)	C6-C7	1.412(2)	S2-O1	1.380(5)
N1-C1	1.292(2)	C7-C8	1.373(3)	S2-C13	1.776(3)
N1-N2	1.3530(19)	C8-C9	1.405(3)	S2-C14	1.764(4)
Bond angles, deg					
N1-Co-N3	73.87(5)	Co-N4-C12	169.79(14)	N1-Co-N4	98.30(6)
N1-C1-C1_a	113.22(15)	N1-Co-N1_a	72.30(5)	N1-C1-C2	125.56(15)
N1-Co-N3_a	145.53(5)	C1_a-C1-C2	121.20(15)	N1-Co-N4_a	91.08(6)
N3-Co-N4	87.39(6)	N3-C3-C4	124.29(16)	N3-Co-N3_a	140.44(5)
N2-C3-C4	117.46(15)	N3-Co-N4_a	88.69(6)	N2-C3-N3	118.24(14)
C3-C4-C5	118.08(16)	C4-C5-C6	120.45(16)	N4-Co-N4_a	168.39(6)
C7-C6-C11	119.34(16)	C5-C6-C11	117.37(15)	C5-C6-C7	123.25(16)
C6-C7-C8	120.38(17)	C7-C8-C9	120.32(18)	C8-C9-C10	120.21(18)
Co-N1-N2	116.77(10)	Co-N3-C3	113.24(11)	Co-N3-C11	128.52(11)
Co-N1-C1	120.59(11)	S1-C12-N4	179.62(16)		
Torsion angles, deg					
N3-Co-N1-N2	-8.27(14)	C2-C1-C1a-C2_a	7.0(3)	N3_a-Co-N3-C11	2.5(2)
N3-Co-N1-C1	174.35(18)	N2-C3-C4-C5	176.2(2)	N4_a-Co-N3-C3	-81.73(14)
N4-Co-N1-N2	-93.09(14)	N3-C3-C4-C5	-2.7(3)	N4_a-Co-N3-C11	86.85(17)
N4-Co-N1-C1	89.52(17)	C3-C4-C5-C6	2.9(3)	Co-N1-N2-C3	5.9(2)
N1_a-Co-N1-N2	178.43(16)	C4-C5-C6-C7	178.6(2)	C1-N1-N2-C3	-176.8(2)
N1_a-Co-N1-C1	1.05(16)	C4-C5-C6-C11	0.7(3)	Co-N1-C1-C2	175.44(18)
N3_a-Co-N1-N2	167.02(13)	C5-C6-C7-C8	-176.5(2)	Co-N1-C1-C1_a	-2.6(2)
N3_a-Co-N1-C1	-10.4(2)	C11-C6-C7-C8	1.3(3)	N2-N1-C1-C2	-1.8(3)
N4_a-Co-N1-N2	80.06(14)	C5-C6-C11-N3	-5.1(3)	N2-N1-C1-C1_a	-179.86(18)
N4_a-Co-N1-C1	-97.33(17)	C5-C6-C11-C10	173.79(19)	N1-N2-C3-N3	3.4(3)
N1-Co-N3-C3	9.78(14)	C7-C6-C11-N3	176.97(19)	N1-N2-C3-C4	-175.52(18)

N1-Co-N3-C11	178.35(18)	C7-C6-C11-C10	-4.1(3)	Co-N3-C3-N2	-10.4(2)
N4-Co-N3-C3	109.20(14)	C6-C7-C8-C9	2.0(3)	Co-N3-C3-C4	168.49(16)
N4-Co-N3-C11	-82.23(17)	C7-C8-C9-C10	-2.4(4)	C11-N3-C3-N2	179.70(18)
N1_a-Co-N3-C3	21.1(2)	C8-C9-C10-C11	-0.5(3)	C11-N3-C3-C4	-1.5(3)
N1_a-Co-N3-C11	-170.33(15)	C9-C10-C11-N3	-177.29(19)	Co-N3-C11-C6	-162.77(15)
N3_a-Co-N3-C3	-166.03(13)	C9-C10-C11-C6	3.8(3)	Co-N3-C11-C10	18.4(3)
C3-N3-C11-C10	-173.48(18)	N1-C1-C1_a-N1_a	3.3(3)	C3-N3-C11-C6	5.4(3)
N1-C1-C1_a-C2_a	-174.9(2)	C2-C1-C1_a-N1_a	-174.9(2)		

Table S3. Nuclei coordinates of **1** used for CASSCF/NEVPT2 calculations. Non-hydrogen atoms coordinates are taken from single crystal diffraction experiment, hydrogen atoms position are optimized at BP86/ def2-TZVP level of theory.

27	0.000000000	0.000000000	0.598280000
16	1.341144000	4.628719000	0.190851000
7	1.197206000	-0.357581000	2.307750000
7	2.466267000	-0.770990000	2.088461000
1	3.006701000	-1.242448000	2.810990000
7	2.060646000	-0.355510000	-0.153585000
7	0.375816000	2.030852000	0.387931000
6	0.702355000	-0.230230000	3.494560000
6	1.412666000	-0.544531000	4.766571000
1	1.027619000	0.043951000	5.605838000
1	2.488089000	-0.315391000	4.694094000
1	1.320700000	-1.611017000	5.037867000
6	2.886688000	-0.795925000	0.780135000
6	4.182427000	-1.318888000	0.521459000
1	4.814403000	-1.645489000	1.348472000
6	4.579716000	-1.423350000	-0.771643000
1	5.554284000	-1.849180000	-1.019359000
6	3.743980000	-0.962478000	-1.821852000
6	4.109300000	-1.014956000	-3.184092000
1	5.060655000	-1.477207000	-3.455627000
6	3.287699000	-0.487897000	-4.146167000
1	3.577651000	-0.534876000	-5.197209000
6	2.087504000	0.148442000	-3.782455000
1	1.462646000	0.610622000	-4.547601000
6	1.705439000	0.205048000	-2.460301000
1	0.801937000	0.730177000	-2.155675000
6	2.505699000	-0.383640000	-1.460236000
6	0.779330000	3.102195000	0.305523000
7	-1.197206000	0.357581000	2.307750000
7	-2.466267000	0.770990000	2.088461000
1	-3.006701000	1.242447000	2.810990000
7	-2.060646000	0.355510000	-0.153585000
6	-0.702355000	0.230230000	3.494560000
6	-1.412666000	0.544531000	4.766571000
1	-1.027617000	-0.043948000	5.605838000
1	-2.488089000	0.315388000	4.694095000
1	-1.320703000	1.611018000	5.037865000

6	-2.886688000	0.795925000	0.780135000
6	-4.182427000	1.318888000	0.521459000
1	-4.814403000	1.645489000	1.348472000
6	-4.579716000	1.423350000	-0.771644000
1	-5.554284000	1.849180000	-1.019359000
6	-3.743980000	0.962478000	-1.821852000
6	-4.109300000	1.014957000	-3.184093000
1	-5.060655000	1.477207000	-3.455627000
6	-3.287699000	0.487897000	-4.146168000
1	-3.577651000	0.534877000	-5.197209000
6	-2.087504000	-0.148442000	-3.782455000
1	-1.462647000	-0.610622000	-4.547601000
6	-1.705439000	-0.205048000	-2.460301000
1	-0.801937000	-0.730177000	-2.155675000
6	-2.505699000	0.383641000	-1.460236000
16	-1.341144000	-4.628719000	0.190850000
7	-0.375816000	-2.030852000	0.387930000
6	-0.779330000	-3.102195000	0.305522000

Table S4. Best fit parameters of the generated Debye model for the Cole-Cole plot of complex **1** at H_{DC} =1000 Oe

T, K	χ_S, cm^3 mol^{-1}	χ_T, cm^3 mol^{-1}	τ, s	α	R_1 [a]
1.8	0.152	1.285	4.14E-03	0.130	3.2E-03
2.0	0.138	1.179	2.85E-03	0.128	2.0E-03
2.2	0.124	1.084	1.93E-03	0.129	1.6E-03
2.4	0.113	1.020	1.25E-03	0.124	1.6E-03
2.5	0.105	0.949	1.07E-03	0.125	8.8E-04
2.7	0.093	0.880	7.81E-04	0.125	6.6E-04
2.8	0.091	0.844	6.66E-04	0.118	7.2E-04
3.0	0.083	0.794	5.25E-04	0.123	4.7E-04
3.5	0.069	0.682	3.12E-04	0.112	3.1E-04
4.0	0.060	0.611	2.05E-04	0.105	1.5E-04
5.0	0.032	0.484	1.00E-04	0.105	6.5E-04

[a] The mean residual sum of squares

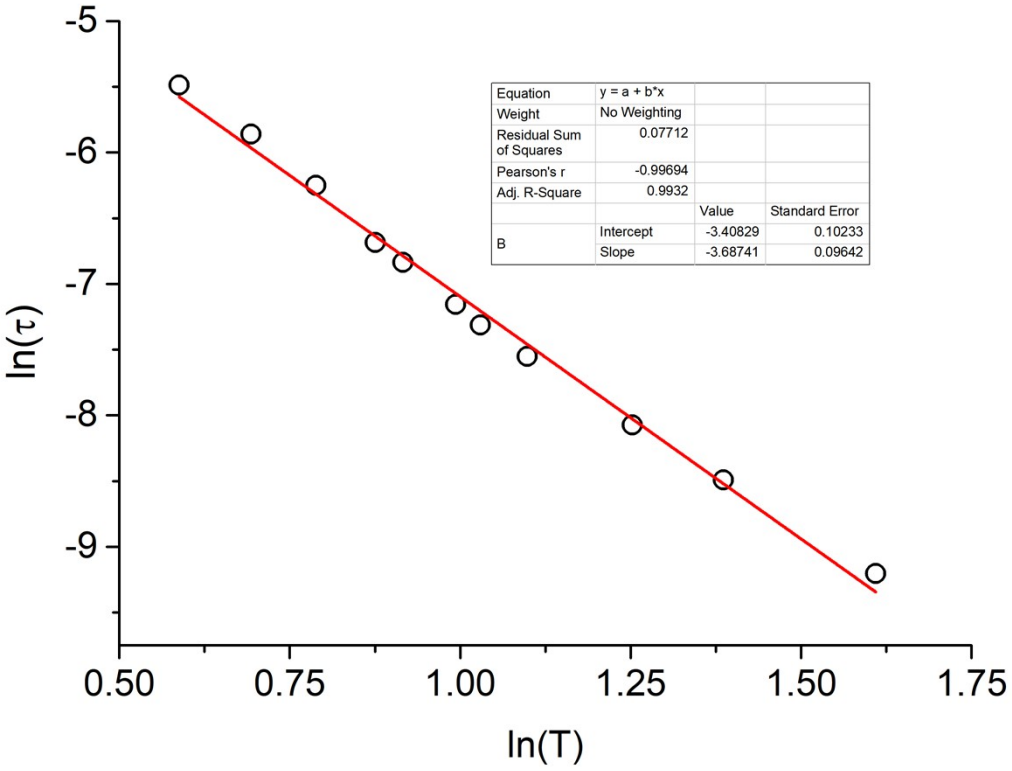

Fig.S1. ln(τ) versus ln(T) dependence: open circles – experiment, red solid line – linear fit.