

Supporting Information

Syntheses, structures, and magnetic properties of three two-dimensional cobalt(II) single-ion magnets with a $\text{Co}^{\text{II}}\text{N}_4\text{X}_2$ octahedral geometry

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Details of the physical measurements.

Infrared spectra (IR) data were measured on KBr pellets using a Nexus 870 FT-IR spectrometer in the 4000-400 cm⁻¹ range. 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 K α X-ray source ($\lambda = 1.5405 \text{ \AA}$) operated at 40 kV and 40 mA. Thermal gravimetric analysers (TGA) were measured in Al₂O₃ crucibles using a PerkinElmer Thermal analysis in the temperature range of 20-700 °C under a nitrogen atmosphere. Magnetic susceptibility data were collected using Quantum Design SQUID VSM magnetometer on samples of crushed crystals. Direct current (dc) magnetic susceptibility measurements were performed in the temperature range of 2-300 K under an applied field of 1000 Oe. Alternative current (ac) susceptibility measurements were performed with a 2 Oe ac oscillating field in an operating frequency range of 1-1000 Hz under a dc field of 0 or 1000 Oe. Magnetization data were collected in the 0 to 70 kOe field range at 2.0 K. Experimental susceptibilities were corrected for diamagnetism of the sample holders and that of the compounds according to Pascal's constants.

Details of the X-ray Crystallography.

Single crystal X-ray crystallographic data were collected on a Bruker APEX DUO diffractometer with a CCD area detector (Mo-K α radiation, $\lambda = 0.71073 \text{ \AA}$) at room temperature. 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.¹ Absorption corrections were applied with SADABS.² The structures were solved by direct methods and refined by full-matrix least-squares method on F^2 using the SHELXTL crystallographic software package.³ All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the organic ligands were refined as riding on the corresponding non-hydrogen atoms.

Computational details

Complete-active-space self-consistent field (CASSCF) calculations with MOLCAS 8.2 program package⁴ was performed on individual Co^{II} fragment on the basis of X-ray determined geometry of **1–3**. During the calculations, the basis sets for all atoms are atomic natural orbitals from the MOLCAS ANO-RCC library: ANO-RCC-VTZP for CoII ion; VTZ for close N and A; VDZ for distant atoms. The calculations employed the second order Douglas-Kroll-Hess Hamiltonian, where scalar relativistic contractions were taken into account in the basis set and the spin-orbit couplings were handled separately in the restricted active space state interaction (RASSI-SO) procedure. For **1–3**, the active electrons in 10 active spaces considering the 3d-double shell effect (5+5') include all seven 3d electrons (CAS(7 in 5+5')). The mixed spin-free states are 50 (all from 10 quadruplets and all from 40 doublets). And then, SINGLE_ANISO⁵ program was used to obtain the **g** tensors, energy levels, magnetic axes, *et al.*, based on the above CASSCF/RASSI-SO calculations.

References

- 1 SAINT Software Users Guide, Version 7.0; Bruker Analytical X-Ray Systems: Madison, WI, **1999**.
- 2 Sheldrick, G. M. SADABS, Version 2.03; Bruker Analytical X-Ray Systems, Madison, WI, **2000**.
- 3 Sheldrick, G. M. SHELXTL, Version 6.14, Bruker AXS, Inc.; Madison, WI 2000-2003.
- 4 F. Aquilante, J. Autschbach, R. K. Carlson, L. F. Chibotaru, M. G. Delcey, L. De Vico, I. Fdez. Galván, N. Ferré L. M. Frutos, L. Gagliardi, M. Garavelli, A. Giussani, C. E. Hoyer, G. Li Manni, H. Lischka, D. Ma, P. Å. Malmqvist, T. Müller, A. Nenov, M. Olivucci, T. B. Pedersen, D. Peng, F. Plasser, B. Pritchard, M. Reiher, I. Rivalta, I. Schapiro, J. Segarra - Martí M. Stenrup, D. G. Truhlar, L. Ungur, A. Valentini, S. Vancoillie, V. Veryazov, V. P. Vysotskiy, O. Weingart, F. Zapata, R. Lindh, MOLCAS 8: New Capabilities for Multiconfigurational Quantum Chemical Calculations across the Periodic Table, *J. Comput. Chem.*, **2016**, *37*, 506.
- 5 (a) Chibotaru, L. F.; Ungur, L.; Soncini, A. *Angew. Chem. Int. Ed.*, **2008**, *47*, 4126. (b) Ungur, L.; Van den Heuvel, W.; Chibotaru, L. F. *New J. Chem.*, **2009**, *33*, 1224. (c) Chibotaru, L. F.; Ungur, L.; Aronica, C.; Elmoll, H.; Pilet, G.; Luneau, D. *J. Am. Chem. Soc.*, **2008**, *130*, 12445.

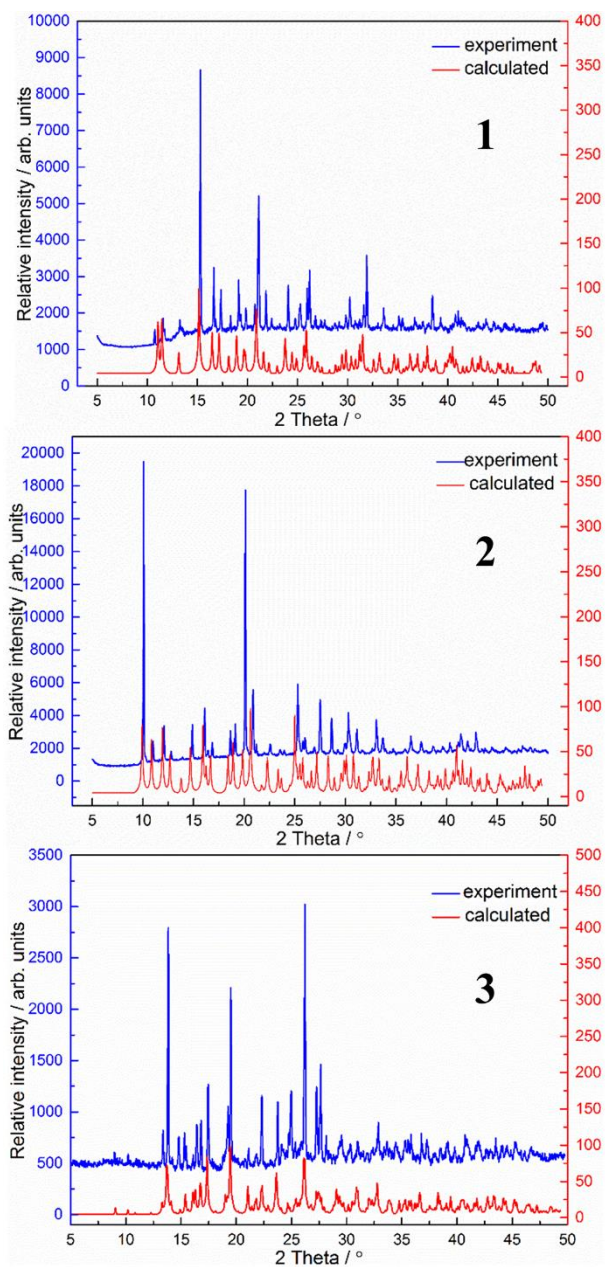


Figure S1 | Experimental and calculated PXRD patterns for **1-3**

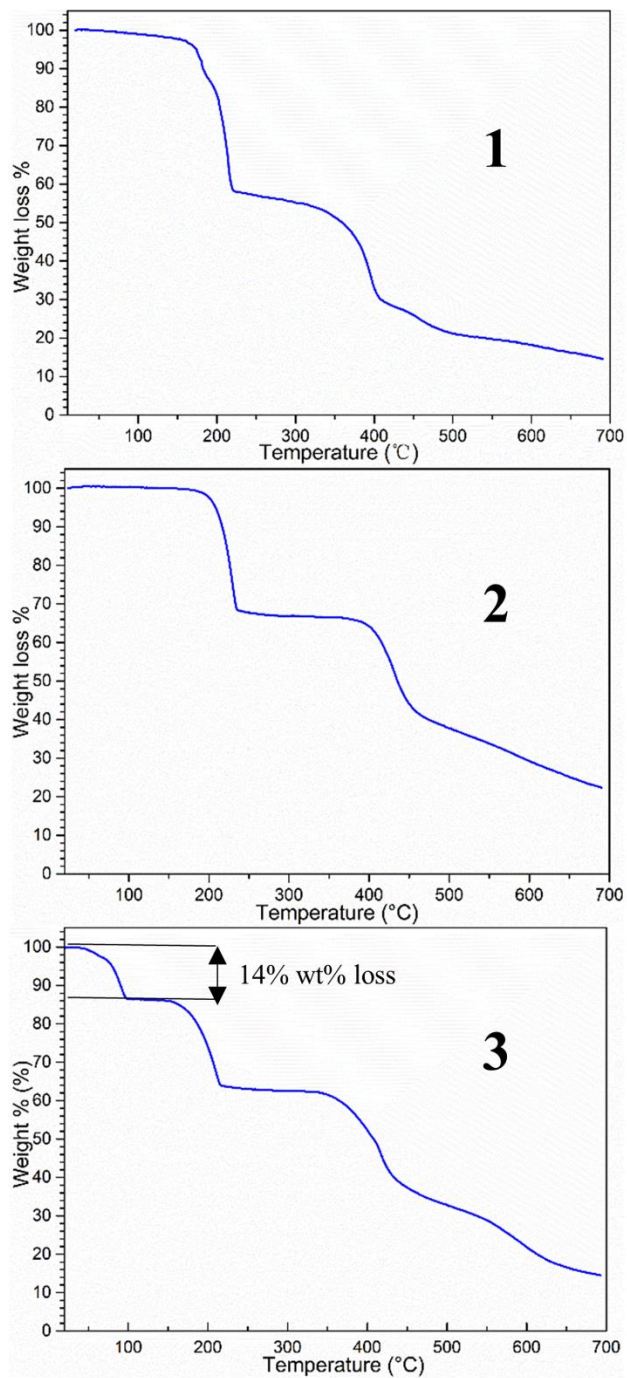


Figure S2 | TGA curves for 1-3

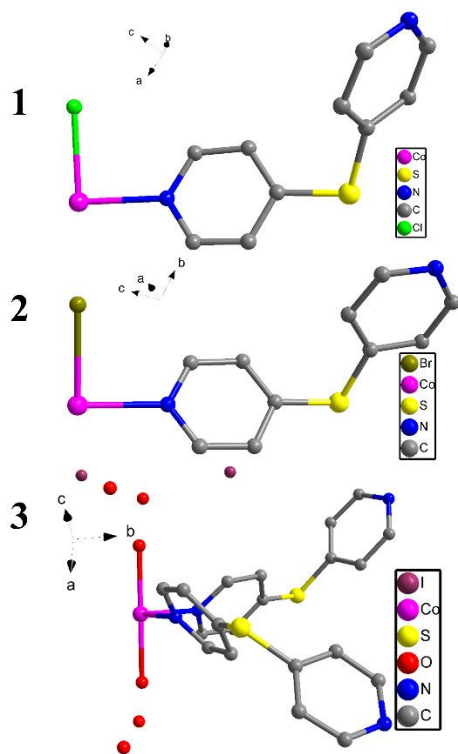


Figure S3 | The asymmetric units of **1-3**

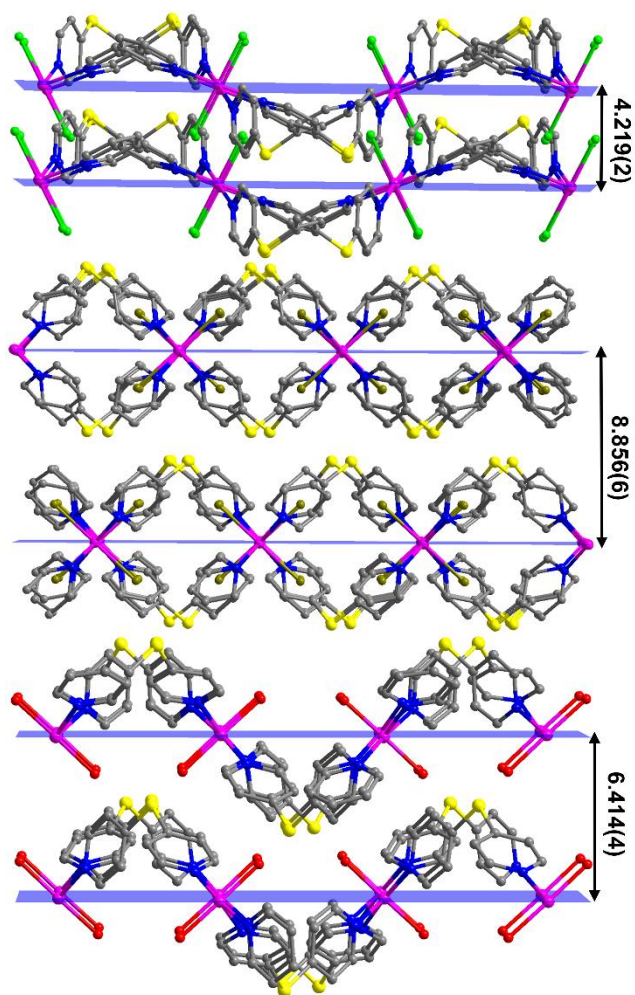


Figure S4 | The shortest distance of the neighboring 2D sheets for **1-3**.

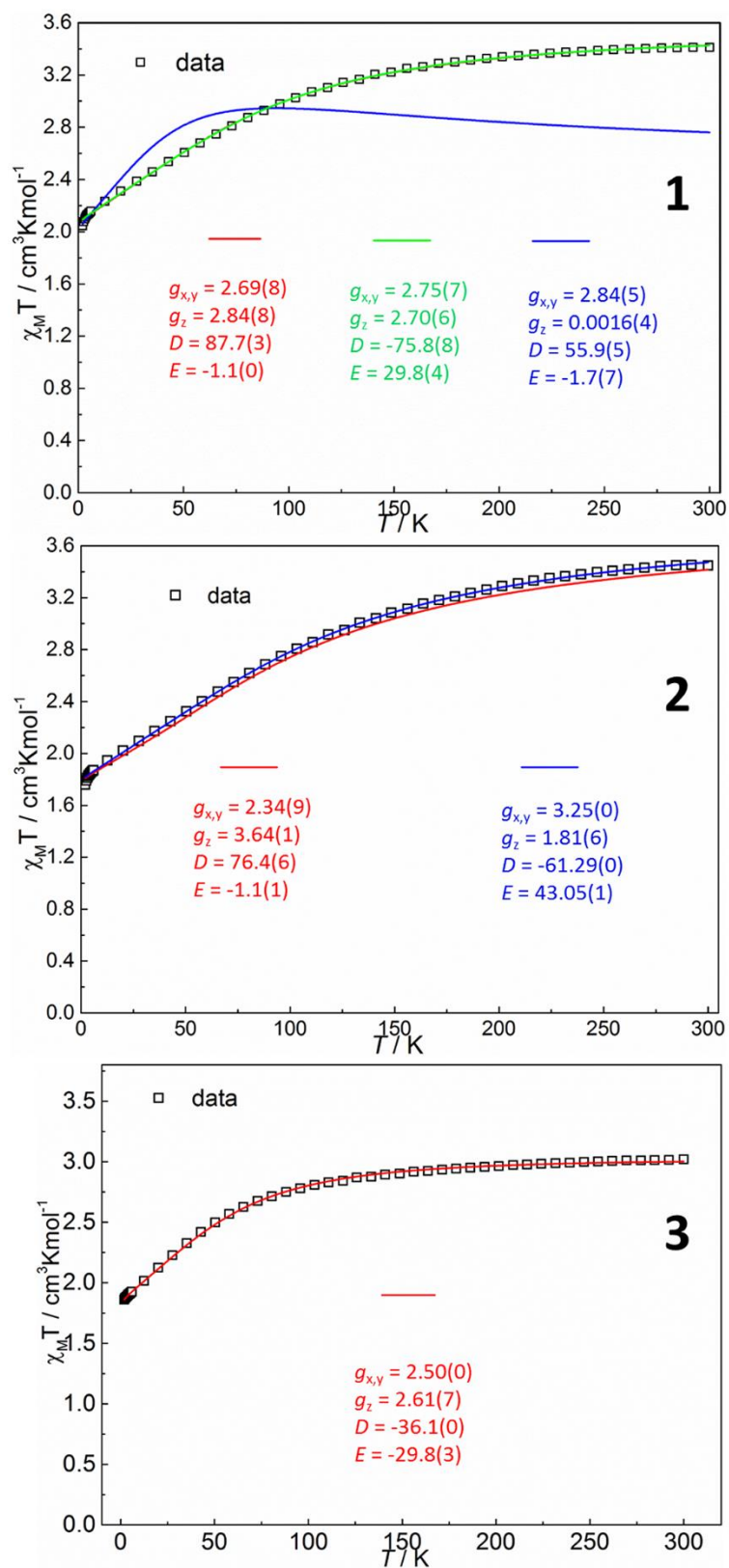


Figure S5 | Fitting results of the experimental magnetic data using PHI software with free g_z values.

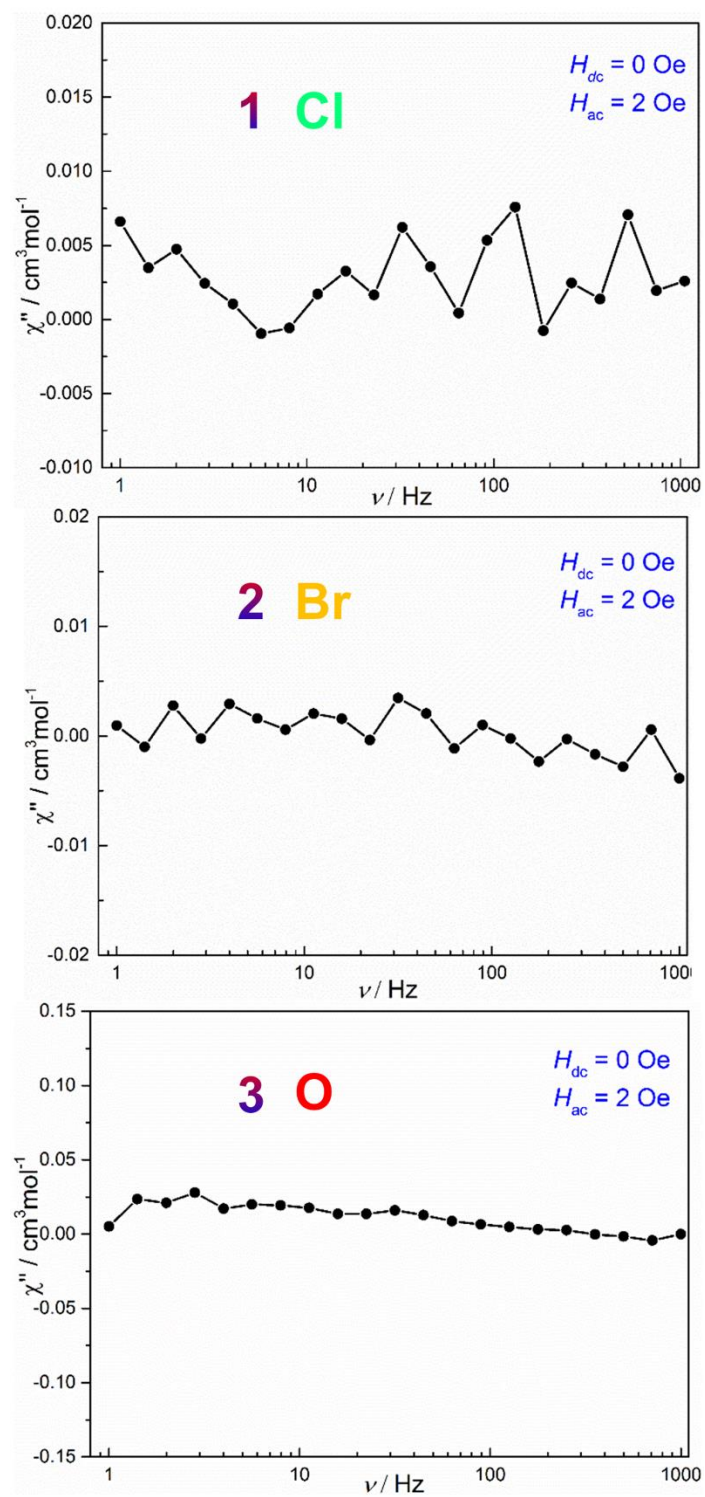


Figure S6 | Frequency dependence of out-of-phase signals (χ'') of the ac magnetic susceptibilities for **1-3** in 0 kOe dc field at 2 K.

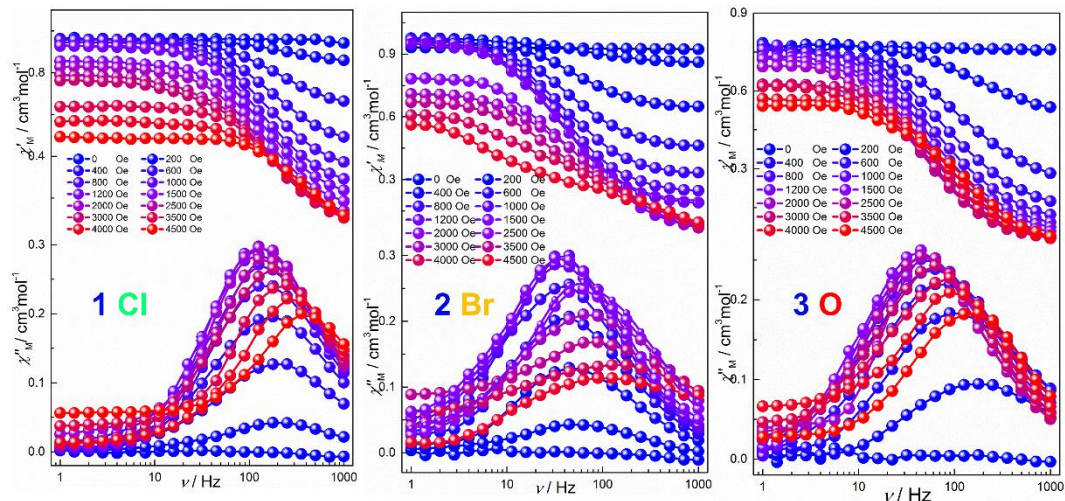


Figure S7 | Frequency dependence of the ac magnetic susceptibilities of **1-3** (1-1000Hz) measured at 2.0K in various applied dc fields from 0 to 4500 Oe.

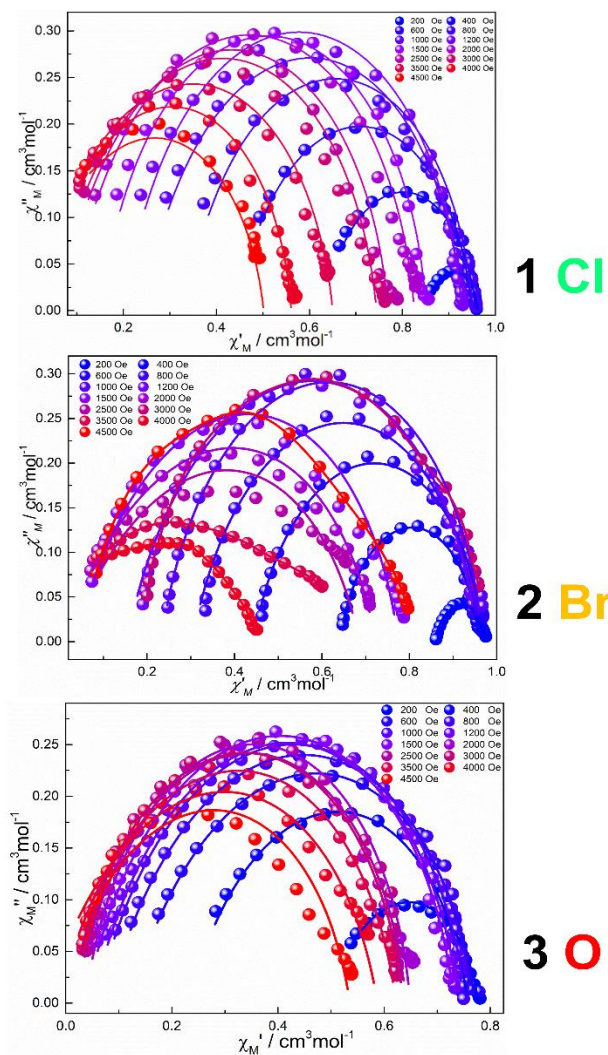


Figure S8 | Cole–Cole plots of **1-3** at 2.0 K under various applied dc fields. The solid lines represent the best fits of the experimental results with the generalized Debye model.

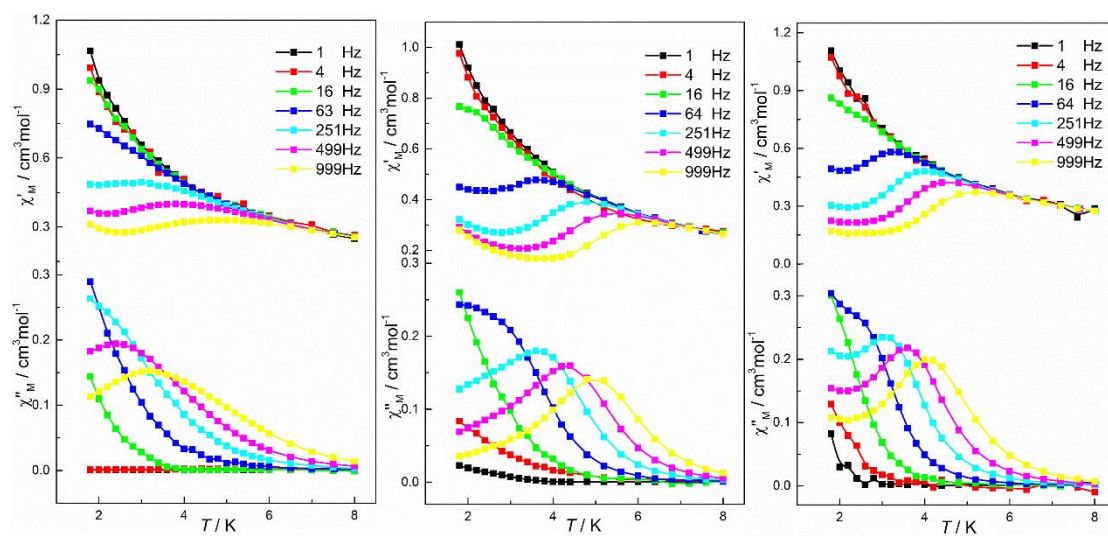


Figure S9 | Variable-temperature ac susceptibility data for **1-3** collected under a 1500 Oe dc field over the frequency range of 1 to 1000 Hz. The solid lines are simply guides for the eye.

Table S1. Crystallographic data and structure refinement parameters for complexes **1-3**.

	1	2	3
Formula	C ₂₀ H ₁₆ N ₄ Cl ₂ S ₂ Co ₁	C ₂₀ H ₁₆ N ₄ Br ₂ S ₂ Co ₁	C ₂₀ H ₁₆ N ₄ O ₆ S ₂ Co ₁ I ₂
Mr /gmol ⁻¹	506.34	595.24	797.31
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	<i>P2₁/c</i>	<i>Pccn</i>	<i>Pbca</i>
<i>a</i> [Å]	7.5000(17)	17.7131(9)	12.8028(5)
<i>b</i> [Å]	15.318(3)	7.5346(4)	18.2985(7)
<i>c</i> [Å]	9.384(2)	16.1950(8)	25.4610(10)
α [°]	90	90.00	90
β [°]	98.293(4)	90.00	90
γ [°]	90	90.00	90
<i>V</i> [Å ³]	1066.8(4)	2161.40(19)	5964.8(4)
<i>Z</i>	2	4	8
<i>T</i> [K]	296(2)	296(2)	296(2)
ρ_{calcd} [g cm ⁻³]	1.576	1.829	1.776
<i>F</i> (000)	514	1172	3112
Refl. collected / unique	7148 / 2462	17113 / 2458	48624 / 6849
<i>R</i> _{int}	0.0326	0.0513	0.0350
<i>T</i> _{max} / <i>T</i> _{min}	0.7682 / 0.7183	0.6024 / 0.4851	0.5755 / 0.5052
data/restraints/parameters	2462 / 0 / 133	2458 / 0 / 132	17735 / 6 / 1168
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b (<i>I</i> > 2 σ (<i>I</i>))	0.0321 / 0.0820	0.0257 / 0.0643	0.0295 / 0.0580
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0372 / 0.0853	0.0301 / 0.0669	0.0457 / 0.0636
GOF on <i>F</i> ²	1.0080	1.071	1.042

^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 angles (°) for **1-3**

1					
Co(1)-N(1)#1	2.2155(15)	N(1)#1-Co(1)-N(1)	180.0	N(1)#1-Co(1)-Cl(1)	90.52(5)
Co(1)-N(1)	2.2155(16)	N(1)#1-Co(1)-N(2)#2	93.97(6)	N(1)-Co(1)-Cl(1)	89.48(5)
Co(1)-N(2)#2	2.2780(15)	N(1)-Co(1)-N(2)#2	86.03(6)	N(2)#2-Co(1)-Cl(1)	89.97(4)
Co(1)-N(2)#3	2.2780(15)	N(1)#1-Co(1)-N(2)#3	86.03(6)	N(2)#3-Co(1)-Cl(1)	90.03(4)
Co(1)-Cl(1)	2.4169(6)	N(1)-Co(1)-N(2)#3	93.97(6)	N(1)#1-Co(1)-Cl(1)#1	89.48(5)
Co(1)-Cl(1)#1	2.4169(6)	N(2)#2-Co(1)-N(2)#3	180.0	N(1)-Co(1)-Cl(1)#1	90.52(5)
N(2)#2-Co(1)-Cl(1)#1	90.03(4)	N(2)#3-Co(1)-Cl(1)#1	89.97(4)	Cl(1)-Co(1)-Cl(1)#1	180.00(3)
Symmetry transformations used to generate equivalent atoms: #1 -x+2, -y+1,-z+1 #2 x+1,-y+1/2,z+1/2 #3 -x+1,y+1/2,-z+1/2					
2					
Br(1)-Co(1)	2.5696(2)	N(2)#1-Co(1)-N(2)#2	95.51(9)	N(2)#1-Co(1)-Br(1)	90.58(5)
Co(1)-N(2)#1	2.1826(18)	N(2)#1-Co(1)-N(1)#3	176.67(7)	N(2)#2-Co(1)-Br(1)	90.58(5)
Co(1)-N(2)#2	2.1826(18)	N(2)#2-Co(1)-N(1)#3	87.51(7)	N(1)#3-Co(1)-Br(1)	90.94(5)
Co(1)-N(1)#3	2.2066(18)	N(2)#1-Co(1)-N(1)	87.51(7)	N(1)-Co(1)-Br(1)	90.58(5)
Co(1)-N(1)	2.2066(18)	N(2)#2-Co(1)-N(1)	176.67(7)	N(2)#1-Co(1)-Br(1)#3	87.99(5)
Co(1)-Br(1)#3	2.5696(2)	N(1)#3-Co(1)-N(1)	89.50(9)	N(2)#2-Co(1)-Br(1)#3	90.58(5)
N(1)#3-Co(1)-Br(1)#3	90.94(5)	N(1)-Co(1)-Br(1)#3	90.58(5)	Br(1)-Co(1)-Br(1)#3	177.870(19)
Symmetry transformations used to generate equivalent atoms: #1 x, -y+1/2,z+1/2 #2 -x+1/2,y+1,z+1/2 #3 -x+1/2,-y+3/2,z					
3					
Co(1)-O(2)	2.092(2)	O(2)-Co(1)-O(1)	178.63(9)	O(2)-Co(1)-N(2)#1	87.42(8)
Co(1)-O(1)	2.099(2)	O(2)-Co(1)-N(3)	88.57(8)	O(1)-Co(1)-N(2)#1	93.18(8)
Co(1)-N(3)	2.133(2)	O(1)-Co(1)-N(3)	90.76(9)	N(3)-Co(1)-N(2)#1	174.53(8)
Co(1)-N(1)	2.153(2)	O(2)-Co(1)-N(1)	92.13(8)	N(1)-Co(1)-N(2)#1	89.62(8)
Co(1)-N(2)#1	2.176(2)	O(1)-Co(1)-N(1)	89.11(8)	O(2)-Co(1)-N(4)#2	93.12(8)
Co(1)-N(4)#2	2.193(2)	N(3)-Co(1)-N(1)	94.24(8)	O(1)-Co(1)-N(4)#2	85.68(8)
N(3)-Co(1)-N(4)#2	90.00(8)	N(1)-Co(1)-N(4)#2	173.33(8)	N(2)#1-Co(1)-N(4)#2	86.52(8)
Symmetry transformations used to generate equivalent atoms: #1 -x+3/2,y-1/2,z #2 -x+1/2,y-1/2,z					

Table S3 Continuous Shape Measure values calculated for **1-3**

Structure [ML6]	HP-6	PPY-6	OC-6	TPR-6	JPPY-5
1	23.153	25.224	7.146	17.282	25.075
2	25.918	30.927	16.838	20.121	31.582
3	18.203	24.200	6.841	16.063	25.705

HP-6 1 D_{6h} Hexagon;
 PPY-6 2 C_{5v} Pentagonal pyramid;
 OC-6 3 O_h Octahedron;
 TPR-6 4 D_{3h} Trigonal prism;
 JPPY-5 5 C_{5v} Johnson pentagonal pyramid(J2).

Table S4. Relaxation fitting parameters from the Cole-Cole plots at various applied dc fields at 2 K of **1-3** according to the generalized Debye model.

1				
H / Oe	$\chi_S / \text{cm}^3\text{mol}^{-1}\text{K}$	$\chi_T / \text{cm}^3\text{mol}^{-1}\text{K}$	τ / s	α
200	0.83936	0.96256	0.00081	0.33441
400	0.60257	0.96938	0.00088	0.27167
600	0.42088	0.95229	0.00096	0.20035
800	0.29627	0.96153	0.00105	0.20000
1000	0.20749	0.93468	0.00115	0.20038
1200	0.15203	0.93815	0.00120	0.20022
1500	0.14226	0.85381	0.00121	0.10063
2000	0.08651	0.82287	0.00117	0.12210
2500	0.05898	0.77421	0.00105	0.14508
3000	0.03134	0.74558	0.00091	0.17619
3500	0.07031	0.64674	0.00071	0.13449
4000	0.06897	0.64660	0.00051	0.12784
4500	0.06340	0.64797	0.00034	0.13223
2				
H / Oe	$\chi_S / \text{cm}^3\text{mol}^{-1}\text{K}$	$\chi_T / \text{cm}^3\text{mol}^{-1}\text{K}$	τ / s	α
200	0.86199	0.97417	0.00295	0.16083
400	0.63310	0.96773	0.00319	0.16772
600	0.44422	0.96865	0.00375	0.15109
800	0.44422	0.96865	0.00412	0.15109
1000	0.23062	0.96855	0.00437	0.14424
1200	0.16578	0.95727	0.0045	0.18112
1500	0.16315	0.97804	0.0046	0.20208
2000	0.03994	0.77613	0.00389	0.21981
2500	0.02745	0.78028	0.00289	0.24534
3000	0.01768	0.72152	0.00253	0.28619
3500	0.11270	2.52627	0.00186	0.09058
4000	0.10897	0.93645	0.00152	0.16970
4500	0.35015	8.12720	0.00123	0.60349
3				
H / Oe	$\chi_S / \text{cm}^3\text{mol}^{-1}\text{K}$	$\chi_T / \text{cm}^3\text{mol}^{-1}\text{K}$	τ / s	α
200	0.48239	0.78552	0.00126	0.28587

400	0.24358	0.75037	0.00144	0.17417
600	0.11653	0.77316	0.00200	0.24742
800	0.07738	0.76370	0.00242	0.21879
1000	0.04931	0.76599	0.00279	0.22460
1200	0.04361	0.74733	0.00308	0.19817
1500	0.03756	0.73629	0.00349	0.19047
2000	0.02171	0.65617	0.00365	0.15938
2500	0.04901	0.63976	0.00314	0.17121
3000	0.03816	0.63746	0.00273	0.18267
3500	0.01574	0.61656	0.00222	0.16148
4000	0.02986	0.58137	0.00177	0.24966
4500	0.01217	0.52954	0.00135	0.16123

Table S5. Relaxation fitting parameters from the least-square fitting of the Cole-Cole plots of **1-3** according to the generalized Debye model.

1				
T / K	$\chi_S / \text{cm}^3\text{mol}^{-1}\text{K}$	$\chi_T / \text{cm}^3\text{mol}^{-1}\text{K}$	τ / s	α
2.0	0.24264	0.94364	0.00117	0.14404
2.2	0.22630	0.84669	0.00090	0.13825
2.4	0.20334	0.78608	0.00073	0.13398
2.6	0.20514	0.73948	0.00062	0.12757
2.8	0.18236	0.70423	0.00053	0.16406
3.0	0.20319	0.64938	0.00045	0.10744
3.2	0.16191	0.62022	0.00035	0.18717
3.4	0.17867	0.57400	0.00032	0.13443
3.6	0.17406	0.54746	0.00026	0.13530
3.8	0.20000	0.53099	0.00024	0.09433
4.0	0.21140	0.49849	0.00021	0.06654
2				
T / K	$\chi_S / \text{cm}^3\text{mol}^{-1}\text{K}$	$\chi_T / \text{cm}^3\text{mol}^{-1}\text{K}$	τ / s	α
2.0	0.24786	0.92658	0.00395	0.09562
2.2	0.21564	0.84154	0.00308	0.11901
2.4	0.20498	0.77330	0.00254	0.08259
2.6	0.19602	0.74809	0.00230	0.09212
2.8	0.16789	0.70205	0.00199	0.11464
3.0	0.15247	0.67950	0.00174	0.15685

3.2	0.15129	0.63019	0.00147	0.12895
3.4	0.14344	0.60054	0.00116	0.10160
3.6	0.15244	0.56356	0.00094	0.05906
3.8	0.14136	0.53670	0.00073	0.05280
4.0	0.11685	0.50855	0.00057	0.08462
4.2	0.11288	0.48642	0.00045	0.07561
4.4	0.11064	0.46917	0.00036	0.07303
4.8	0.10938	0.43012	0.00024	0.05786
5.2	0.08616	0.40021	0.00014	0.05101

3				
T / K	$\chi_S / \text{cm}^3\text{mol}^{-1}\text{K}$	$\chi_T / \text{cm}^3\text{mol}^{-1}\text{K}$	τ / s	α
2.0	0.11783	1.03407	0.00317	0.24274
2.2	0.10787	0.96408	0.00268	0.23424
2.4	0.11506	0.86676	0.00206	0.19603
2.6	0.10826	0.80336	0.00159	0.18488
2.8	0.10488	0.75188	0.00120	0.15942
3.0	0.11314	0.70467	0.00089	0.11390
3.2	0.11173	0.66632	0.00068	0.09901
3.4	0.12132	0.61896	0.00051	0.04620
3.6	0.08088	0.59393	0.00036	0.08824
3.8	0.10587	0.55787	0.00029	0.02877
4.0	0.09142	0.53749	0.00022	0.06149
4.2	0.11555	0.50835	0.00018	0.00054
4.4	0.12276	0.48715	0.00014	0.01864
4.8	0.04144	0.44813	0.00007	0.06566
5.2	0.08668	0.41252	0.00006	0.05322

Table S6. Summary of the obtained parameters of the magnetic relaxation for complexes **1-3**.

compound	$A(\text{s}^{-1}\text{K}^{-1}\text{kOe}^{-4})$	$B_1(\text{s}^{-1})$	$B_2(\text{kOe}^{-2})$	$C(\text{s}^{-1}\text{K}^{-n})$	n	$\tau_0(\text{s})$	$U_{\text{eff}}/\text{cm}^{-1}$
1	3.56	1068	0.127	244.65	2.5	2.38×10^{-5}	11.0cm^{-1}
2	1.665	282	0.131	90.44	1.5	7.40×10^{-7}	28.9cm^{-1}
3	1.285	562	0.369	69.55	2.1	5.54×10^{-7}	25.3cm^{-1}

Table S7. Calculated spin-free energies (cm^{-1}) of the lowest ten terms ($S = 3/2$) of the Co^{II} ion of complexes **1-3**.

spin-free states	1	2	3
	E/cm^{-1}	E/cm^{-1}	E/cm^{-1}
1	0.0	0.0	0.0
2	372.4	175.8	143.4
3	983.6	410.1	650.3
4	5948.1	5528.8	7098.7
5	6419.3	7159.6	7567.0
6	6958.9	7239.3	8261.1
7	13436.4	14218.3	16297.2
8	21299.8	21635.4	23860.2
9	21771.5	21743.0	24157.2
10	22989.9	22985.5	25503.3

Table S8. Calculated weights of the five most important spin-orbit-free states for the lowest two spin-orbit states of the Co^{II} ion of complexes **1-3**.

	Spin-orbit states	Energy (cm^{-1})	Spin-free states, Spin, Weights				
1	1	0.0	1,1.5,0.6705	2,1.5,0.2545	3,1.5,0.0707	6,1.5,0.0015	5,1.5,0.0009
	2	199.3	1,1.5,0.8640	2,1.5,0.0823	3,1.5,0.0466	4,1.5,0.0041	6,1.5,0.0012
2	1	0.0	1,1.5,0.4926	2,1.5,0.3089	3,1.5,0.1954	4,1.5,0.0007	5,1.5,0.0007
	2	259.3	1,1.5,0.7740	2,1.5,0.1375	3,1.5,0.0809	4,1.5,0.0037	5,1.5,0.0017
3	1	0.0	1,1.5,0.5228	2,1.5,0.3620	3,1.5,0.1123	4,1.5,0.0008	6,1.5,0.0007
	2	243.6	1,1.5,0.6984	2,1.5,0.2349	3,1.5,0.0610	5,1.5,0.0024	4,1.5,0.0014

Table S9. Calculated energy levels (cm^{-1}), \mathbf{g} (g_x, g_y, g_z) tensors of the ground and first excited doublets of the Co^{II} of complexes **1–3** using CASSCF/RASSI-SO with MOLCAS 8.2.

	1		2		3	
	E/cm^{-1}	\mathbf{g}	E/cm^{-1}	\mathbf{g}	E/cm^{-1}	\mathbf{g}
1	0.0	2.575	0.0	3.442	0.0	2.480
		3.217		4.342		2.977
		6.985		5.359		7.128
2	199.3	3.718	259.3	0.025	243.6	3.742
		2.132		0.432		2.332
		0.356		4.840		0.527