Supporting Information

Switching of easy-axis to easy-plane anisotropy in cobalt(II) complexes

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Table S1 Crystal Data and Structure Refinement Details for **1-5**

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{64}H_{60}Co_4F_{12}O_{16}$	$C_{30}H_{24}CoF_6O_6$	$C_{38}H_{24}CoF_6N_2O_4$	$C_{40}H_{28}CoF_6N_2O_4$	$C_{40}H_{28}CoF_6N_2O_4$
Formula weight	1548.84	653.42	745.52	773.57	773.57
Crystal system	monoclinic	triclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/c$	P-1	P-1	P-1	$P2_1/c$
a (Å)	18.650(3)	5.2383(6)	11.2640(7)	9.8446(17)	17.8736(6)
b (Å)	19.130(3)	10.7061(13)	11.3866(8)	10.4886(18)	12.7580(4)
c (Å)	18.079(3)	12.8155(17)	13.4453(10)	17.502(2)	17.6747(7)
α (°)	90	109.816(12)	70.958(7)	81.985(12)	90
β (°)	93.562(15)	91.495(10)	89.366(6)	79.972(13)	116.774(5)
γ (°)	90	92.628(9)	88.289(5)	70.659(16)	90
V (Å^3)	6437.7(18)	674.79(15)	1629.4(2)	1672.6(5)	3598.3(3)
Z	4	1	2	2	4
μ (mm^{-1})	1.115	5.768	0.606	0.594	4.398
Unique reflections	11342	2340	7569	7849	6294
Observed reflections	44581	3631	14020	13236	12011
R_{int}	0.0957	0.0920	0.063	0.0594	0.0449
Final R indices	R_1 = 0.0821	R_1 = 0.0728	R_1 = 0.0757	R_1 = 0.0787	R_1 = 0.0735
[$I > 2\sigma(I)$]	wR_2 = 0.2895	wR_2 = 0.1739	wR_2 = 0.1137	wR_2 = 0.1582	wR_2 = 0.1935
Goodness-of-fit on F^2	1.046	1.024	1.031	1.048	1.033

Table S2 Selected Bond Lengths (Å) and Bond Angles (°) for **1**.

1			
Co(1)-O(6)	2.055(6)	O(6)-Co(1)-O(8)	85.1(2)
Co(1)-O(8)	2.062(6)	O(6)-Co(1)-O(B)	89.7(2)
Co(1)-O(B)	2.186(6)	O(6)-Co(1)-O(15)	81.6(2)
Co(1)-O(13)	2.045(6)	O(8)-Co(1)-O(B)	90.8(2)
Co(1)-O(14)	2.018(6)	O(8)-Co(1)-O(15)	82.3(2)
Co(1)-O(15)	2.135(6)	O(13)-Co(1)-O(15)	93.5(2)
Co(2)-O(1)	2.025(6)	O(2)-Co(2)-O(6)	92.0(3)
Co(2)-O(2)	2.036(6)	O(2)-Co(2)-O(3)	95.9(3)
Co(2)-O(3)	2.196(6)	O(1)-Co(2)-O(3)	91.3(2)
Co(2)-O(6)	2.078(6)	O(1)-Co(2)-O(7)	95.1(3)
Co(2)-O(7)	2.049(6)	O(3)-Co(2)-O(7)	89.0(2)
Co(2)-O(8)	2.131(6)	O(7)-Co(2)-O(8)	81.7(2)
Co(3)-O(4)	2.039(7)	O(4)-Co(3)-O(7)	93.2(3)
Co(3)-O(5)	2.022(6)	O(4)-Co(3)-O(9)	95.1(3)
Co(3)-O(6)	2.158(7)	O(5)-Co(3)-O(9)	88.5(3)
Co(3)-O(7)	2.054(6)	O(5)-Co(3)-O(6)	98.6(3)
Co(3)-O(9)	2.209(6)	O(7)-Co(3)-O(15)	84.3(2)
Co(3)-O(15)	2.043(6)	O(9)-Co(3)-O(15)	90.3(2)
Co(4)-O(7)	2.129(6)	O(7)-Co(4)-O(8)	81.8(2)
Co(4)-O(8)	2.046(6)	O(7)-Co(4)-O(15)	82.2(2)
Co(4)-O(10)	2.050(6)	O(10)-Co(4)-O(12)	94.2(2)
Co(4)-O(11)	2.024(6)	O(10)-Co(4)-O(15)	92.0(2)
Co(4)-O(12)	2.173(6)	O(11)-Co(4)-O(12)	89.7(3)
Co(4)-O(15)	2.056(6)	O(12)-Co(4)-O(15)	92.2(2)

Table S3 Selected Bond Lengths (Å) and Bond Angles (°) for **2**

2			
Co(1)-O(1)	2.036(4)	O(1)-Co(1)-O(3)#1	88.39(16)
Co(1)-O(1)#1	2.036(4)	O(1)#1-Co(1)-O(3)#1	91.61(16)
Co(1)-O(2)	2.048(4)	O(1)#1-Co(1)-O(3)	88.39(16)
Co(1)-O(2)#1	2.261(4)	O(2)-Co(1)-O(3)#1	90.10(15)
Co(1)-O(3)	2.129(4)	O(2)#1-Co(1)-O(3)	90.10(15)
Co(1)-O(3)#1	2.129(4)	O(2)-Co(1)-O(2)#1	180
O(1)-Co(1)-O(1)#1	180	O(2)-Co(1)-O(3)	89.90(15)
O(1)-Co(1)-O(2)	90.65(15)	O(2)#1-Co(1)-O(1)#1	90.65(15)
O(1)-Co(1)-O(2)#1	89.35(15)	O(2)#1-Co(1)-O(2)	89.35(15)
O(1)-Co(1)-O(3)	91.61(16)	O(3)-Co(1)-O(3)#1	180
#1 1-x, -y, -z			

Table S4 Selected Bond Lengths (Å) and Bond Angles (°) for **3**

3			
Co(1)-O(1)	2.055(2)	O(1)-Co(1)-O(5)	90.58(11)
Co(1)-O(2)	2.063(3)	O(5)-Co(1)-O(6)	86.83(12)
Co(1)-O(5)	2.051(3)	O(5)-Co(1)-N(1)	97.94(11)
Co(1)-O(6)	2.059(3)	O(5)-Co(1)-N(2)	82.70(13)
Co(1)-N(1)	2.118(3)	N(1)-Co(1)-N(2)	76.89(13)
Co(1)-N(2)	2.117(4)	N(2)-Co(1)-O(1)	94.32(12)
O(1)-Co(1)-O(2)	87.92(10)	O(2)-Co(1)-O(6)	93.18(11)
N(1)-Co(1)-O(2)	83.57(11)	N(1)-Co(1)-O(6)	93.97(12)
N(2)-Co(1)-O(2)	97.58(12)	O(2)-Co(1)-O(5)	178.49(10)
O(1)-Co(1)-O(6)	96.58(11)	N(2)-Co(1)-O(6)	164.94(12)

Table S5 Selected Bond Lengths (Å) and Bond Angles (°) for **4**

4			
Co(1)-O(1)	2.033(3)	O(1)-Co(1)-N(2)	94.19(13)
Co(1)-O(2)	2.115(3)	O(2)-Co(1)-N(1)	175.36(13)
Co(1)-O(3)	2.059(3)	O(2)-Co(1)-N(2)	100.40(12)
Co(1)-O(4)	2.085(3)	O(3)-Co(1)-O(2)	88.38(12)
Co(1)-N(1)	2.143(3)	O(3)-Co(1)-O(4)	86.71(12)
Co(1)-N(2)	2.150(3)	O(3)-Co(1)-N(1)	87.63(13)
O(1)-Co(1)-O(2)	88.34(12)	O(3)-Co(1)-N(2)	92.66(13)
O(1)-Co(1)-O(3)	172.84(11)	O(4)-Co(1)-O(2)	80.24(11)
O(1)-Co(1)-O(4)	86.46(12)	O(4)-Co(1)-N(1)	101.88(12)
O(1)-Co(1)-N(1)	95.89(13)	N(1)-Co(1)-N(2)	77.44(12)

Table S6 Selected Bond Lengths (Å) and Bond Angles (°) for **5**

5			
Co(1)-O(1)	2.055(4)	O(1)-Co(1)-N(2)	174.02(14)
Co(1)-O(2)	2.069(4)	O(2)-Co(1)-O(4)	170.46(14)
Co(1)-O(3)	2.060(3)	O(2)-Co(1)-N(1)	96.12(16)
Co(1)-O(4)	2.071(3)	O(2)-Co(1)-N(2)	92.98(15)
Co(1)-N(1)	2.097(4)	O(3)-Co(1)-O(2)	88.46(14)
Co(1)-N(2)	2.106(4)	O(3)-Co(1)-O(4)	87.62(13)
O(1)-Co(1)-O(2)	85.87(14)	O(3)-Co(1)-N(1)	172.22(17)
O(1)-Co(1)-O(3)	89.84(14)	O(3)-Co(1)-N(2)	96.00(15)
O(1)-Co(1)-O(4)	85.43(14)	O(4)-Co(1)-N(1)	88.78(15)
O(1)-Co(1)-N(1)	96.74(16)	N(1)-Co(1)-N(2)	77.53(17)

Table S7 Co^{II} ion geometry analysis of **1** by SHAPE 2.1 software

Configuration	ABOXIY, **1**(Co1)	ABOXIY, **1**(Co2)	ABOXIY, **1**(Co3)	ABOXIY, **1**(Co4)
OC-6	0.445	0.448	0.533	0.417
TPR-6	14.975	14.850	14.654	15.418
JPPY-6	30.580	30.551	30.069	30.805

Table S8 Co^{II} ion geometry analysis of **2-5** by SHAPE 2.1 software

Configuration	ABOXIY, **2**	ABOXIY, **3**	ABOXIY, **4**	ABOXIY, **5**
OC-6	0.057	1.030	0.857	0.698
TPR-6	16.501	11.429	15.141	13.371
JPPY-6	33.140	26.937	29.656	28.689

Table S9 Fitted *D*, *E*, and g value for complexes **2-5**

Complex	D (cm^{-1})	E (cm^{-1})	$g_{x,y}$	g_z	R
2	-60.48	-9.559	3.56	2.20	5.35×10^{-4}
3	70.77	9.898	2.21	2.16	8.96×10^{-4}
4	35.71	13.470	2.14	2.12	3.64×10^{-4}
5	51.28	6.386	2.57	2.56	6.28×10^{-4}

Table S10 Relaxation fitting parameters from least-squares fitting of $\chi(f)$ data under 2000 Oe dc field of **1**

T(K)	χ_T	χ_S	α
2	0.849	0.024	0.180
2.25	0.807	0.026	0.177
2.5	0.769	0.027	0.173
2.75	0.734	0.027	0.170
3	0.692	0.027	0.164
3.25	0.641	0.031	0.156
3.5	0.602	0.028	0.150
3.75	0.564	0.023	0.145
4	0.532	0.024	0.138
4.25	0.501	0.025	0.131
4.5	0.473	0.026	0.125
4.75	0.436	0.024	0.118
5	0.397	0.026	0.111
5.25	0.349	0.027	0.102
5.5	0.306	0.027	0.101
5.75	0.264	0.029	0.101
6	0.232	0.030	0.101

Table S11 Relaxation fitting parameters from least-squares fitting of $\chi(f)$ data under 2000 Oe dc field of **2**

T(K)	χ_T	χ_S	α
2	0.444	0.072	0.344
2.1	0.436	0.067	0.349
2.2	0.422	0.066	0.337
2.3	0.422	0.071	0.338
2.4	0.394	0.071	0.289
2.5	0.383	0.066	0.290
2.6	0.370	0.070	0.257
2.7	0.359	0.71	0.236
2.8	0.345	0.075	0.197
2.9	0.335	0.071	0.194
3	0.336	0.064	0.215
3.1	0.327	0.062	0.202
3.2	0.316	0.060	0.187
3.3	0.304	0.064	0.147
3.4	0.294	0.065	0.115
3.5	0.289	0.060	0.117
3.6	0.285	0.052	0.130
3.7	0.276	0.053	0.099
3.8	0.269	0.049	0.090
3.9	0.264	0.049	0.073
4	0.259	0.040	0.080
4.2	0.248	0.031	0.064
4.4	0.238	0.015	0.060
4.6	0.229	0.004	0.047
4.8	0.220	0.002	0.032
5	0.212	0.001	0.012

Table S12 Relaxation fitting parameters from least-squares fitting of $\chi(f)$ data under 2000 Oe dc field of **3**

T(K)	χ_T	χ_S	α
2	0.032	0.532	0.006
2.25	0.031	0.528	0.006
2.5	0.030	0.523	0.007
2.75	0.030	0.509	0.010
3	0.031	0.495	0.008
3.25	0.029	0.469	0.009
3.5	0.028	0.445	0.009
3.75	0.028	0.419	0.014
4	0.029	0.400	0.012
4.25	0.023	0.384	0.013
4.5	0.024	0.364	0.011
4.75	0.023	0.328	0.008
5	0.027	0.305	0.008
5.25	0.026	0.269	0.007
5.5	0.024	0.231	0.006

Table S13 Relaxation fitting parameters from least-squares fitting of $\chi(f)$ data under 2000 Oe dc field of **4**

T(K)	χ_T	χ_S	α
2	0.364	0.002	0.123
2.1	0.353	0.003	0.115
2.2	0.344	0.004	0.114
2.3	0.336	0.006	0.112
2.4	0.323	0.001	0.093
2.5	0.316	0.002	0.093
2.6	0.307	0.003	0.084
2.7	0.299	0.003	0.081
2.8	0.292	0.004	0.080
2.9	0.286	0.006	0.081
3	0.277	0.008	0.068
3.1	0.269	0.002	0.061
3.2	0.263	0.002	0.058
3.3	0.254	0.003	0.053
3.4	0.249	0.007	0.050
3.5	0.244	0.008	0.047
3.6	0.238	0.001	0.044
3.7	0.232	0.001	0.039
3.8	0.228	0.002	0.033
3.9	0.222	0.003	0.019
4	0.217	0.002	0.016

Table S14 Relaxation fitting parameters from least-squares fitting of $\chi(f)$ data under 2000 Oe dc field of **5**

T(K)	χ_T	χ_S	α
2	0.397	0.006	0.265
2.5	0.327	0.002	0.202
3	0.282	0.002	0.161
3.3	0.259	0.004	0.134
3.6	0.239	0.007	0.108
4	0.218	0.001	0.077
4.3	0.204	0.002	0.068
4.6	0.192	0.003	0.059
5	0.177	0.006	0.052
5.3	0.168	0.002	0.045
5.6	0.160	0.003	0.039
6	0.150	0.002	0.033
6.5	0.139	0.002	0.027
7	0.129	0.003	0.015
7.5	0.121	0.004	0.013

Table S15 The B3LYP/def2-TZVP calculated net Mulliken spin densities, the $<S^2>$ values and relative energies of the high-spin (HS) and the broken-symmetry spin (BS) states for a molecular fragment [Co_4] of **1**

Spin states	$\Delta^a_{i/cm^{-1}}$	$<S^2>$	ρ(Co1)	ρ(Co2)	ρ(Co3)	ρ(Co4)
HS, |αααα>	0	42.0395	2.751	2.753	2.747	2.752
BS1, |βααα>	96.510	15.0273	-2.749	2.747	2.747	2.755
BS2, |ββαβ>	101.934	6.0238	-2.755	2.747	2.750	-2.745

Table S16 The CASSCF/NEVPT2/def2-TZVP(-f) (Co and O atoms, def2-QZVP) computed Individual contributions to *D*-tensor for in complex **2**

2*S*+1	Root	*D*	*E*	2*S*+1	Root	*D*	*E*
4	0	0.000	0.000	2	15	1.168	-0.011
4	1	-13.045	-4.620	2	16	-0.646	-0.453
4	2	-29.746	0.094	2	17	-0.220	0.332
4	3	-8.838	-0.004	2	18	-0.386	-0.063
4	4	0.047	-0.026	2	19	-0.576	-0.441
4	5	3.238	-1.314	2	20	-0.218	0.207
4	6	0.016	0.002	2	21	-0.613	0.157
4	7	0.086	-0.027	2	22	0.319	-0.009
4	8	-0.005	0.001	2	23	-0.038	0.041
4	9	-0.024	-0.001	2	24	-0.253	0.155
2	0	-11.425	-4.708	2	25	0.011	0.002
2	1	-1.315	-0.410	2	26	-0.025	0.024
2	2	-0.025	0.008	2	27	-0.076	-0.044
2	3	0.009	0.002	2	28	0.000	0.000
2	4	1.796	-0.002	2	29	0.005	-0.001
2	5	-1.060	0.356	2	30	0.220	0.002
2	6	-0.017	0.013	2	31	-0.030	-0.019
2	7	0.005	-0.003	2	32	-0.040	0.037
2	8	0.884	-0.000	2	33	0.080	-0.000
2	9	0.186	-0.000	2	34	-0.003	-0.003
2	10	-0.067	0.026	2	35	0.000	0.000
2	11	-1.018	-0.495	2	36	-0.011	-0.002
2	12	0.070	-0.009	2	37	0.000	0.000
2	13	0.168	-0.001	2	38	-0.004	-0.002
2	14	0.000	0.000	2	39	-0.071	-0.024

Table S17 The CASSCF/NEVPT2/def2-TZVP(-f) (Co, N and O atoms, def2-QZVP) computed Individual contributions to *D*-tensor for in complex **3**

2*S*+1	Root	*D*	*E*	2*S*+1	Root	*D*	*E*
4	0	-0.000	0.000	2	15	-0.454	0.434
4	1	41.699	41.650	2	16	-0.581	-0.601
4	2	30.099	-29.974	2	17	-0.001	-0.000
4	3	-18.858	0.048	2	18	-0.639	0.618
4	4	2.079	-2.056	2	19	-0.420	-0.419
4	5	1.309	2.501	2	20	-0.324	0.060
4	6	0.000	0.000	2	21	-0.212	0.013
4	7	0.028	-0.023	2	22	0.992	-0.046
4	8	0.070	0.069	2	23	-0.002	-0.005
4	9	0.049	-0.039	2	24	0.077	-0.041
2	0	-2.404	2.357	2	25	-0.007	-0.009
2	1	-2.149	-2.086	2	26	-0.034	-0.059
2	2	-0.006	0.006	2	27	-0.067	0.060
2	3	-1.033	-1.025	2	28	0.214	-0.018
2	4	-0.523	0.523	2	29	-0.026	0.039
2	5	-0.248	-0.080	2	30	0.038	-0.013
2	6	-0.644	0.629	2	31	-0.010	0.009
2	7	-0.027	0.003	2	32	-0.041	0.034
2	8	3.117	-0.000	2	33	-0.055	-0.049
2	9	-0.045	-0.025	2	34	-0.001	0.001
2	10	-0.049	-0.010	2	35	-0.034	-0.035
2	11	-0.036	0.035	2	36	-0.019	0.012
2	12	0.822	-0.000	2	37	-0.012	0.007
2	13	-0.020	0.016	2	38	-0.000	0.000
2	14	0.012	-0.013	2	39	-0.027	0.022

Table S18 The CASSCF/NEVPT2/def2-TZVP(-f) (Co, N and O atoms, def2-QZVP) computed Individual contributions to *D*-tensor for in complex **4**

2*S*+1	Root	*D*	*E*	2*S*+1	Root	*D*	*E*
4	0	0.000	0.000	2	15	-0.392	0.330
4	1	21.500	20.283	2	16	-0.237	-0.372
4	2	15.673	-15.177	2	17	-0.010	0.010
4	3	-7.536	0.307	2	18	-0.868	0.902
4	4	0.340	1.035	2	19	0.395	-0.002
4	5	2.241	1.973	2	20	1.015	-0.004
4	6	0.010	-0.010	2	21	-0.189	-0.267
4	7	0.079	-0.074	2	22	-0.014	0.010
4	8	0.107	0.102	2	23	-0.035	0.035
4	9	0.012	-0.010	2	24	-0.225	-0.217
2	0	-4.750	5.964	2	25	0.004	-0.005
2	1	2.984	0.633	2	26	-0.113	0.114
2	2	-0.014	-0.012	2	27	0.006	-0.001
2	3	-1.073	-1.075	2	28	-0.090	-0.091
2	4	-0.089	0.034	2	29	-0.006	0.005
2	5	-0.839	0.868	2	30	0.157	-0.013
2	6	-0.085	0.089	2	31	-0.042	0.038
2	7	-0.344	0.292	2	32	-0.023	0.023
2	8	-0.234	-0.206	2	33	-0.005	0.005
2	9	-0.007	-0.001	2	34	-0.036	-0.036
2	10	-0.087	0.083	2	35	0.031	0.005
2	11	3.115	0.008	2	36	-0.012	0.019
2	12	0.093	-0.049	2	37	0.002	0.012
2	13	-0.221	-0.284	2	38	-0.025	0.024
2	14	-0.022	-0.004	2	39	-0.005	0.005

Table S19 The CASSCF/NEVPT2/def2-TZVP(-f) (Co, N and O atoms, def2-QZVP) computed Individual contributions to *D*-tensor for in complex **5**

2*S*+1	Root	*D*	*E*	2*S*+1	Root	*D*	*E*
4	0	0.000	0.000	2	15	-0.195	0.204
4	1	24.480	24.566	2	16	-0.220	0.220
4	2	22.301	-22.254	2	17	-0.262	-0.329
4	3	-13.121	-0.023	2	18	-0.061	0.029
4	4	3.413	3.484	2	19	-0.900	0.907
4	5	0.897	0.802	2	20	0.175	-0.064
4	6	0.004	-0.004	2	21	0.767	-0.166
4	7	0.050	-0.047	2	22	-0.094	0.071
4	8	0.084	0.058	2	23	0.025	-0.250
4	9	0.037	0.001	2	24	-0.007	0.006
2	0	1.566	-0.024	2	25	-0.152	-0.221
2	1	-4.006	3.832	2	26	-0.133	0.133
2	2	-0.019	-0.016	2	27	0.009	-0.001
2	3	-0.470	-0.462	2	28	-0.048	0.045
2	4	-0.487	-0.388	2	29	-0.038	-0.078
2	5	-0.611	-0.141	2	30	0.219	-0.032
2	6	-1.153	1.102	2	31	-0.019	0.002
2	7	0.016	-0.010	2	32	-0.005	0.002
2	8	3.430	0.003	2	33	-0.069	0.066
2	9	-0.012	0.012	2	34	-0.054	-0.053
2	10	-0.084	-0.085	2	35	0.000	-0.000
2	11	-0.071	0.070	2	36	0.003	0.011
2	12	0.484	-0.094	2	37	0.003	0.011
2	13	-0.287	-0.286	2	38	-0.001	0.000
2	14	24.480	24.566	2	39	-0.039	0.042

Table S20 Energy levels (cm^{-1}) of ligand field multiplets in zero field derived from CASSCF/def2-TZVP(-f) (Co and O atoms, def2-QZVP) computed for complex **2**

KDs	E/cm^{-1}	KDs	E/cm^{-1}	KDs	E/cm^{-1}	KDs	E/cm^{-1}
1	0.0	31	17259.9	61	29290.1	91	43415.0
2	70.6	32	19120.4	62	30113.2	92	43844.4
3	70.6	33	19120.4	63	30113.2	93	43844.4
4	2020.9	34	19713.8	64	30187.5	94	44370.4
5	2020.9	35	19713.8	65	30187.5	95	44370.4
6	2141.7	36	20339.0	66	32262.4	96	44679.4
7	2141.7	37	20339.0	67	32262.4	97	44679.4
8	3080.1	38	21860.3	68	32524.6	98	45153.8
9	3080.1	39	21860.3	69	32524.6	99	45153.8
10	3245.3	40	22190.3	70	33026.0	100	42918.3
11	3245.3	41	22190.3	71	33026.0	101	42918.3
12	5293.1	42	23069.4	72	33334.5	102	45974.4
13	5293.1	43	23069.4	73	33334.5	103	45974.4
14	10752.3	44	23517.7	74	33541.8	104	46620.5
15	10752.3	45	23517.7	75	33541.8	105	46620.5
16	10800.0	46	23777.2	76	35702.8	106	46782.9
17	10800.0	47	23777.2	77	35702.8	107	46782.9
18	10876.2	48	24104.5	78	36394.2	108	47348.7
19	10876.2	49	24104.5	79	36394.2	109	47348.7
20	13365.8	50	26742.2	80	37862.4	110	65209.8
21	13365.8	51	26742.2	81	37862.4	111	65209.8
22	13464.3	52	26807.6	82	38478.8	112	65974.8
23	13464.3	53	26807.6	83	38478.8	113	65974.8
24	15517.3	54	26903.1	84	38958.3	114	67244.8
25	15517.3	55	26903.1	85	38958.3	115	67244.8
26	16191.0	56	26919.4	86	40011.2	116	67638.8
27	16191.0	57	26919.4	87	40011.2	117	67638.8
28	16368.5	58	28766.8	88	41644.3	118	68459.7
29	16368.5	59	28766.8	89	41644.3	119	68459.7
30	17259.9	60	29290.1	90	43415.0		

Table S21 Energy levels (cm^{-1}) of ligand field multiplets in zero field derived from CASSCF/def2-TZVP(-f) (Co, N and O atoms, def2-QZVP) computed for complex **3**

KDs	*E*/cm^{-1}	KDs	*E*/cm^{-1}	KDs	*E*/cm^{-1}	KDs	*E*/cm^{-1}
1	0.0	31	16327.9	61	26981.2	91	37380.5
2	161.0	32	20255.6	62	27405.7	92	37621.0
3	161.0	33	20255.6	63	27405.7	93	37621.0
4	709.3	34	20533.5	64	29700.1	94	38054.6
5	709.3	35	20533.5	65	29700.1	95	38054.6
6	1013.9	36	20931.0	66	30127.0	96	47841.1
7	1013.9	37	20931.0	67	30127.0	97	47841.1
8	1324.3	38	21154.1	68	30329.9	98	48290.5
9	1324.3	39	21154.1	69	30329.9	99	48290.5
10	1450.7	40	21328.8	70	30656.8	100	48397.2
11	1450.7	41	21328.8	71	30656.8	101	48397.2
12	7650.5	42	21474.9	72	30747.5	102	49366.9
13	7650.5	43	21474.9	73	30747.5	103	49366.9
14	7680.1	44	24284.0	74	30974.3	104	49523.4
15	7680.1	45	24284.0	75	30974.3	105	49523.4
16	7981.6	46	24349.7	76	32910.4	106	49850.1
17	7981.6	47	24349.7	77	32910.4	107	49850.1
18	8015.9	48	24765.0	78	33200.1	108	50342.6
19	8015.9	49	24765.0	79	33200.1	109	50342.6
20	8152.5	50	24838.1	80	35834.6	110	73665.7
21	8152.5	51	24838.1	81	35834.6	111	73665.7
22	8254.2	52	24968.3	82	36028.2	112	73939.9
23	8254.2	53	24968.3	83	36028.2	113	73939.9
24	14712.8	54	25306.0	84	36286.6	114	74279.6
25	14712.8	55	25306.0	85	36286.6	115	74279.6
26	14857.9	56	25917.1	86	37005.1	116	74506.4
27	14857.9	57	25917.1	87	37005.1	117	74506.4
28	16326.4	58	26871.4	88	37257.8	118	74843.2
29	16326.4	59	26871.4	89	37257.8	119	74843.2
30	16327.9	60	26981.2	90	37380.5		

Table S22 Energy levels (cm^{-1}) of ligand field multiplets in zero field derived from CASSCF/def2-TZVP(-f) (Co, N and O atoms, def2-QZVP) computed for complex **4**

KDs	*E*/cm^{-1}	KDs	*E*/cm^{-1}	KDs	*E*/cm^{-1}	KDs	*E*/cm^{-1}
1	0.0	31	18202.0	61	27348.5	91	42366.4
2	83.4	32	18715.5	62	29098.1	92	42756.6
3	83.4	33	18715.5	63	29098.1	93	42756.6
4	1400.6	34	19266.2	64	30327.0	94	43164.5
5	1400.6	35	19266.2	65	30327.0	95	43164.5
6	1540.0	36	19520.2	66	30574.5	96	43345.9
7	1540.0	37	19520.2	67	30574.5	97	43345.9
8	2239.4	38	19698.6	68	31503.7	98	43544.1
9	2239.4	39	19698.6	69	31503.7	99	43544.1
10	2325.3	40	22369.2	70	32243.3	100	43746.5
11	2325.3	41	22369.2	71	32243.3	101	43746.5
12	6903.8	42	22699.1	72	32760.2	102	47579.9
13	6903.8	43	22699.1	73	32760.2	103	47579.9
14	7565.8	44	23679.0	74	33123.3	104	48383.3
15	7565.8	45	23679.0	75	33123.3	105	48383.3
16	12585.2	46	24506.7	76	34312.3	106	48469.0
17	12585.2	47	24506.7	77	34312.3	107	48469.0
18	12637.6	48	24631.8	78	35545.9	108	49422.9
19	12637.6	49	24631.8	79	35545.9	109	49422.9
20	13633.6	50	25933.7	80	37890.4	110	66063.8
21	13633.6	51	25933.7	81	37890.4	111	66063.8
22	13681.7	52	26069.1	82	38629.0	112	67115.5
23	13681.7	53	26069.1	83	38629.0	113	67115.5
24	13778.1	54	26210.7	84	38897.8	114	68806.4
25	13778.1	55	26210.7	85	38897.8	115	68806.4
26	13914.9	56	26255.5	86	39930.0	116	69253.4
27	13914.9	57	26255.5	87	39930.0	117	69253.4
28	17545.1	58	27287.3	88	40696.7	118	70176.5
29	17545.1	59	27287.3	89	40696.7	119	70176.5
30	18202.0	60	27348.5	90	42366.4		

Table S23 Energy levels (cm^{-1}) of ligand field multiplets in zero field derived from CASSCF/def2-TZVP(-f) (Co, N and O atoms, def2-QZVP) computed for complex **5**

KDs	*E*/cm^{-1}	KDs	*E*/cm^{-1}	KDs	*E*/cm^{-1}	KDs	*E*/cm^{-1}
1	0.0	31	18316.7	61	24124.2	91	37779.0
2	98.3	32	18555.8	62	26151.6	92	37834.5
3	98.3	33	18555.8	63	26151.6	93	37834.5
4	1134.4	34	19103.7	64	28073.8	94	38442.8
5	1134.4	35	19103.7	65	28073.8	95	38442.8
6	1355.5	36	19377.4	66	28601.0	96	41491.0
7	1355.5	37	19377.4	67	28601.0	97	41491.0
8	1742.7	38	20067.3	68	28970.8	98	41920.2
9	1742.7	39	20067.3	69	28970.8	99	41920.2
10	1861.9	40	20528.8	70	29485.9	100	42214.9
11	1861.9	41	20528.8	71	29485.9	101	42214.9
12	9169.9	42	20597.9	72	30091.9	102	44521.9
13	9169.9	43	20597.9	73	30091.9	103	44521.9
14	9221.3	44	21883.4	74	30419.6	104	44676.2
15	9221.3	45	21883.4	75	30419.6	105	44676.2
16	9957.3	46	22165.3	76	31702.5	106	45029.7
17	9957.3	47	22165.3	77	31702.5	107	45029.7
18	10384.4	48	22461.3	78	32591.6	108	45132.8
19	10384.4	49	22461.3	79	32591.6	109	45132.8
20	10436.5	50	22682.8	80	34809.7	110	64697.3
21	10436.5	51	22682.8	81	34809.7	111	64697.3
22	10740.4	52	22828.2	82	35202.6	112	65053.2
23	10740.4	53	22828.2	83	35202.6	113	65053.2
24	10829.6	54	23050.8	84	35516.3	114	65442.0
25	10829.6	55	23050.8	85	35516.3	115	65442.0
26	10917.4	56	23654.3	86	36742.7	116	65811.7
27	10917.4	57	23654.3	87	36742.7	117	65811.7
28	17901.0	58	23852.9	88	37110.5	118	66216.7
29	17901.0	59	23852.9	89	37110.5	119	66216.7
30	18316.7	60	24124.2	90	37779.0		

Table S24 Calculated energy levels (cm^{-1}) and g (g_x, g_y, g_z) tensors of the lowest Kramers doublets (KDs) for complexes 2-5 within ORCA/CASSCF+NEVPT2+SINGLE_ANISO.

KDs	**2**				**3**			
	energy levels /cm^{-1}	g_x	g_y	$\mathbf{g_z}$	energy levels /cm^{-1}	g_x	g_y	$\mathbf{g_z}$
1	0.000	1.482	2.207	6.494	0.000	2.360	3.860	6.336
2	70.628	1.746	2.280	5.651	160.989	1.065	1.111	5.826
3	2020.890	0.604	0.681	7.288	709.261	4.475	3.715	1.676
4	2141.744	4.152	3.304	2.438	1013.906	0.094	0.176	3.750
KDs	**4**				**5**			
	energy levels /cm^{-1}	g_x	g_y	$\mathbf{g_z}$	energy levels /cm^{-1}	g_x	g_y	$\mathbf{g_z}$
1	0.000	1.632	2.496	6.672	0.000	2.077	3.770	6.039
2	83.363	1.718	2.159	5.647	98.256	0.956	1.097	6.047
3	1400.614	5.156	3.807	1.614	1134.435	1.780	3.263	5.972
4	1539.982	0.465	0.615	4.692	1355.506	0.775	0.926	4.323

Table S25 Mulliken atomic charges on the metal atoms and donor atoms in the ground state of complexes **2-5** calculated within CASSCF.

atoms	**2**	atoms	**3**	**4**	**5**
Co	1.7908	Co	1.2551	1.4821	1.2576
O1	-0.9990	O1	-0.9181	-0.9744	-0.9501
O2	-0.9643	O2	-0.9761	-1.0212	-0.9618
O3	-0.9643	O3	-0.9428	-0.9975	-0.9988
O4	-0.9989	O4	-0.9854	-0.9571	-0.9767
O5	-0.8271	N1	-0.7493	-0.8074	-0.6873
O6	-0.8271	N2	-0.7200	-0.1388	-0.6650

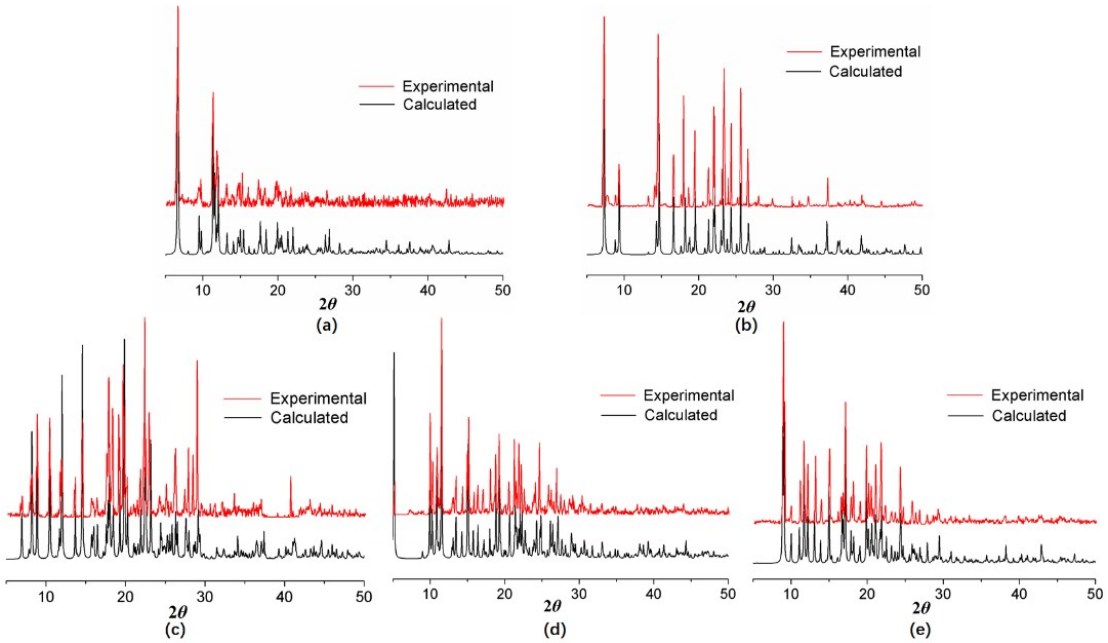

Fig. S1 PXRD patterns for complexes **1**(a), **2**(b), **3**(c), **4**(d) and **5**(e).

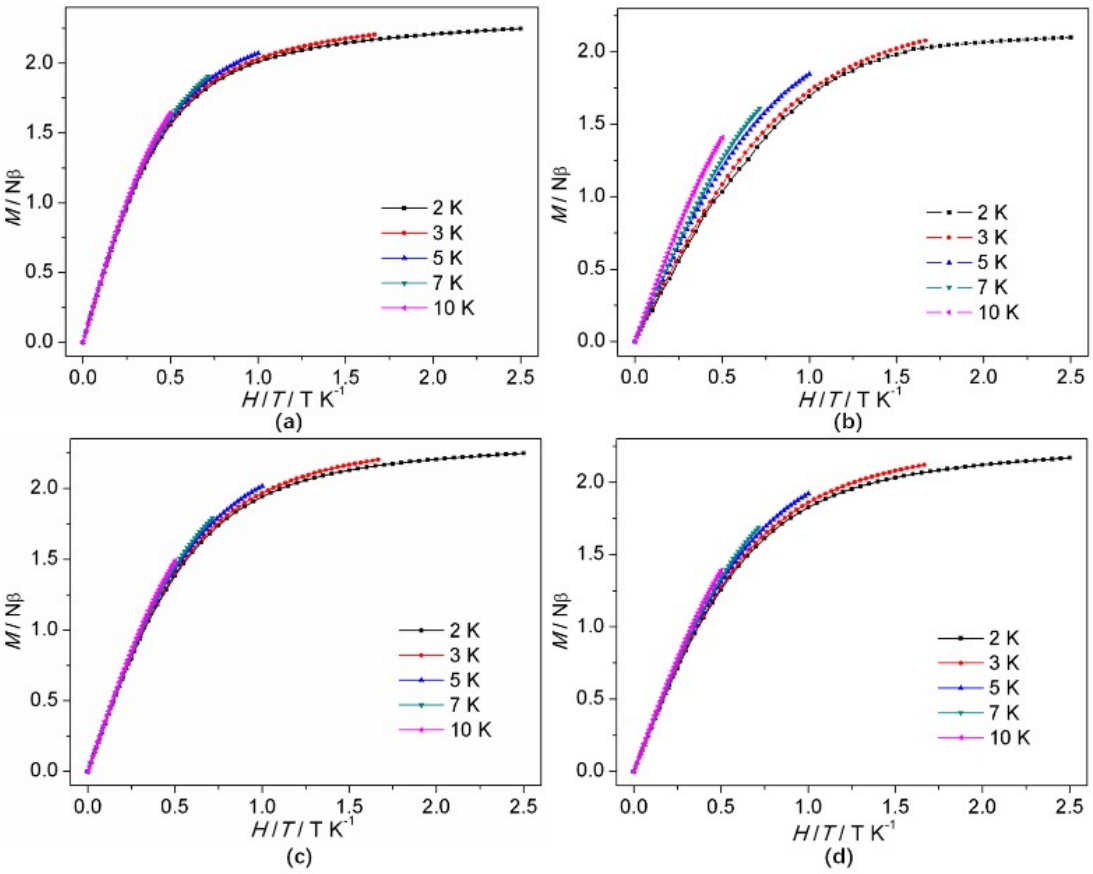

Fig. S2 Plots of *M* vs *H*/*T* for **2-5** at different temperatures.

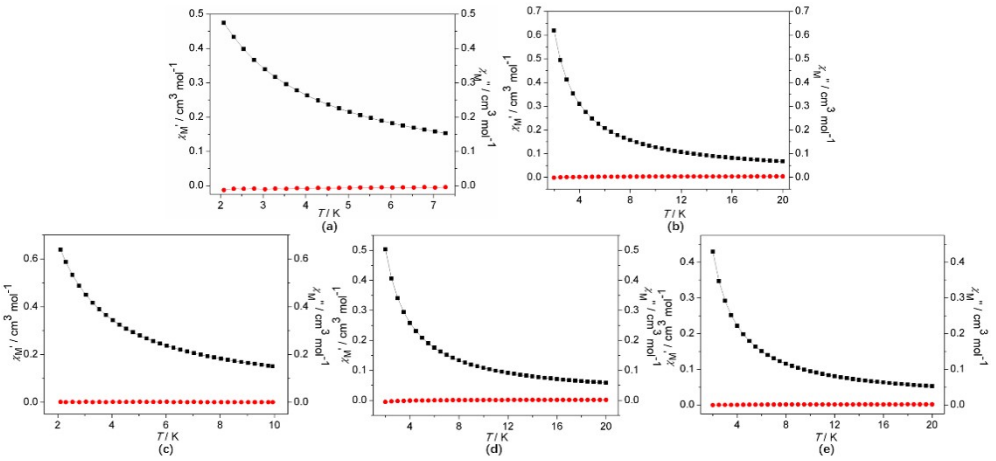

Fig. S3 Ac magnetic susceptibility measurements for **1-5** in 0 Oe static field.

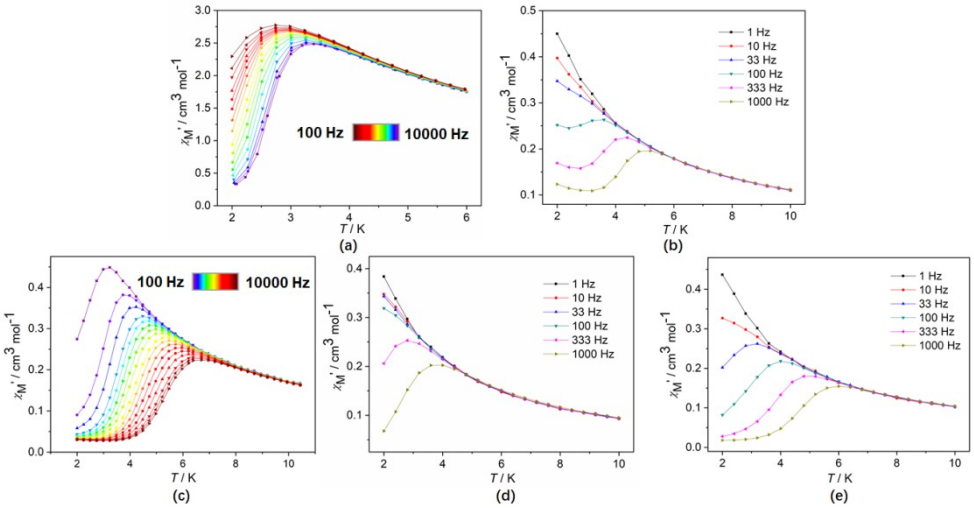

Fig. S4 Temperature dependence of the in-phase ac susceptibilities at different frequencies with a dc field of 2000 Oe for complexes **1-5**.

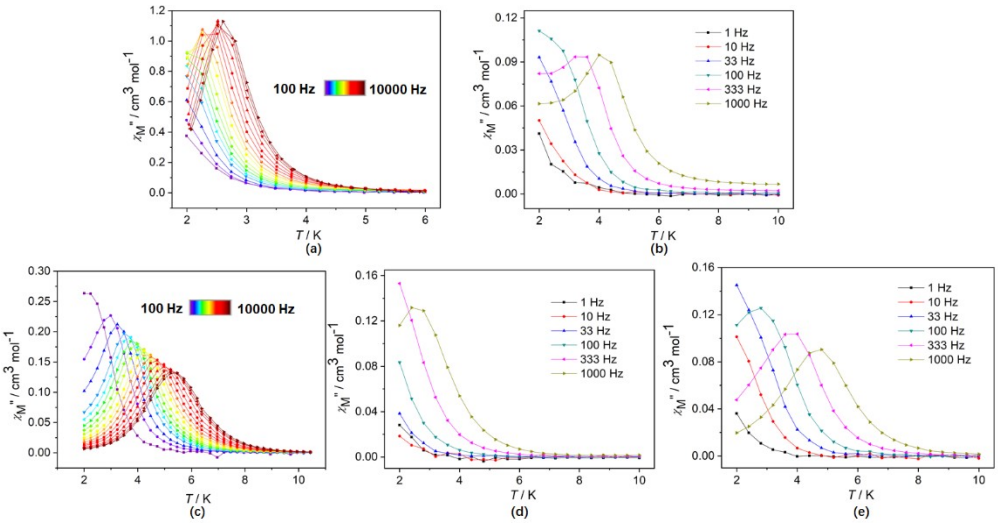

Fig. S5 Temperature dependence of the out-of-phase ac susceptibilities at different frequencies with a dc field of 2000 Oe for complexes **1-5**.

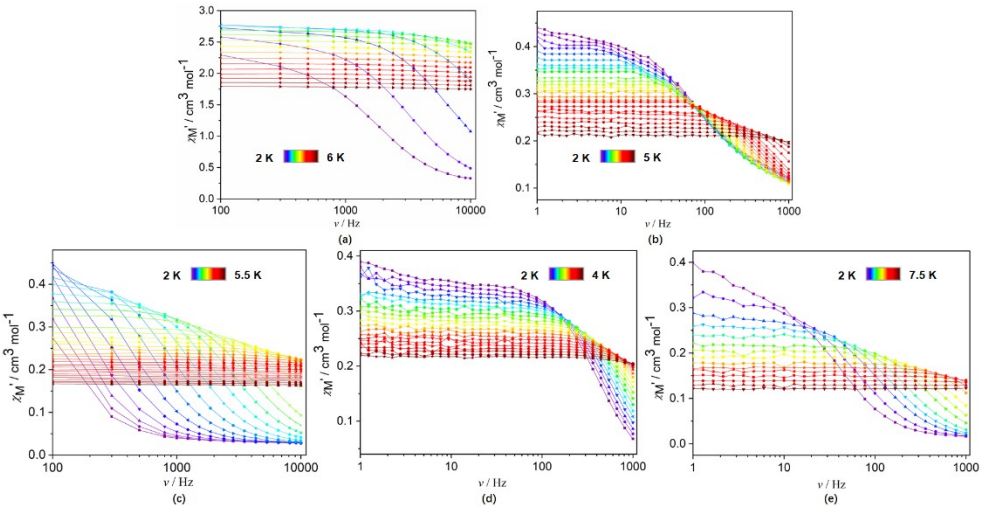

Fig. S6 Frequency dependence of the in-phase ac susceptibility signals for complexes **1**-**5** under a 2000 Oe dc field.

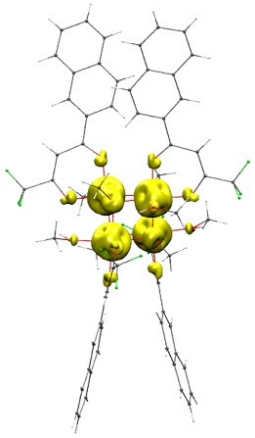

Fig. S7 B3LYP calculated spin density for the high spin state with the cutoff values of 0.008 $e \cdot a_0^{-3}$ of complex **1**.

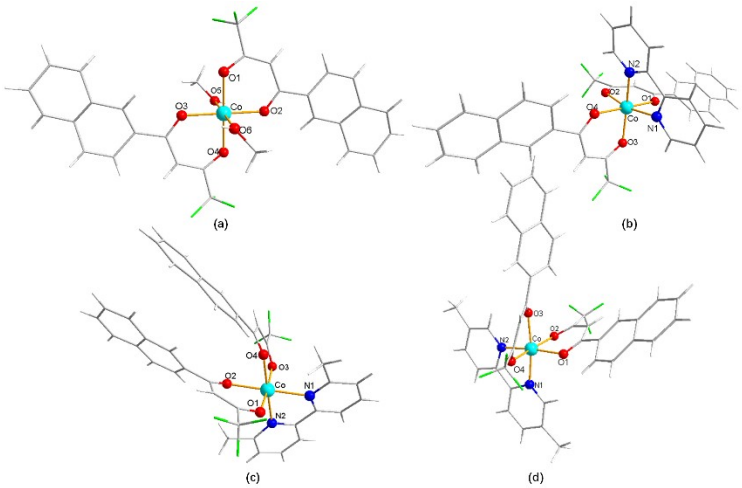

Fig. S8 Calculated complete structure of complexes **2**-**5**.