Supporting Information

Coligand effects on the architectures and magnetic properties of octahedral cobalt(II) complexes with easy-axis magnetic anisotropy

Yuewei Wu,[a#] Jing Xi,[a#] Jinhui Yang,[a] Weiming Song,[a] Shuchang Luo,*[b] Zheng Wang [a] and Xiangyu Liu*[a c]

[a] State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering, National Demonstration Center for Experimental Chemistry Education, College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, China

[b] School of Chemical Engineering, Guizhou University of Engineering Science, Bijie, 551700, China

[c] State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210023, China.

# These authors contributed equally to this work.

***Corresponding author**

Dr. Xiangyu Liu

E-mail: xiangyuliu432@126.com

***Corresponding author**

Dr. Shuchang Luo

E-mail: luosc@gues.edu.cn

Table of contents

Table S1 Selected crystallographic data for complexes **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{24}H_{22}CoN_{16}O_2$	$C_{24}H_{22}CoN_{18}O$
Formula weight	625.50	637.52
Temperature	100 K	100 K
Crystal system	monoclinic	monoclinic
Space group	*P*21/*n*	*P*21/*n*
a (Å)	7.7569(6)	13.1218(7)
b (Å)	15.7881(12)	14.2515(7)
c (Å)	10.9425(11)	14.6292(8)
α (°)	90	90
β (°)	91.562(8)	102.327(5)
γ (°)	90	90
V (Å^3)	1339.59(19)	2672.7(2)
Z	2	4
D (g/cm^3)	1.551	1.584
Mu (mm^{-1})	0.698	0.701
F(0 0 0)	642	1308
Unique reflections	3171	4557
Observed reflections	6107	6389
R_{int}	0.0536	0.0433
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0687$ $wR_2 = 0.1284$	$R_1 = 0.0595$ $wR_2 = 0.1223$
R indices (all data)	$R_1 = 0.1142$ $wR_2 = 0.1558$	$R_1 = 0.0927$ $wR_2 = 0.1386$
Goodness-of-fit on F^2	1.060	1.060

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

		1	
Co(1)-O(1)	2.043(2)	O(1)-Co(1)-O(1)#1	180
Co(1)-O(1)#1	2.043(2)	O(1)-Co(1)-N(1)	91.75(12)
Co(1)-N(1)	2.175(3)	O(1)-Co(1)-N(6)	94.71(12)
Co(1)-N(1)#1	2.175(3)	O(1)-Co(1)-N(1)#1	88.25(12)
Co(1)-N(6)	2.131(3)	O(1)-Co(1)-N(6)	85.29(12)
Co(1)-N(6)#1	2.131(3)	N(1)-Co(1)-N(6)	92.28(13)
#1 1-x,1-y,-z;			

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

		2	
Co(1)-N(5)	2.096(3)	N(5)-Co(1)-N(6)	77.29(10)
Co(1)-N(6)	2.136(3)	N(5)-Co(1)-N(7)	103.01(10)
Co(1)-N(7)	2.143(3)	N(5)-Co(1)-N(8)	176.49(10)
Co(1)-N(8)	2.092(3)	N(6)-Co(1)-N(7)	178.95(10)
Co(1)-N(13)	2.144(3)	N(6)-Co(1)-N(8)	102.61(10)
Co(1)-N(16)	2.120(3)	N(6)-Co(1)-N(16)	93.34(10)

Table S4 Co(II) ion geometry analysis of **1** and **2** by SHAPE 2.1 software

Configuration	ABOXIY, **1**	ABOXIY, **2**
OC-6	0.219	0.886
TPR-6	15.903	15.162
JPPY-6	32.199	30.312

Table S5 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	0.359	0.001	0.334
2.5	0.316	0.002	0.333
3	0.280	0.004	0.330
4	0.227	0.0004	0.306

Table S6 ORCA/CASSCF computed Individual contributions to *D*-tensor for complex **1**

2*S*+1	Root	*D*	*E*	2*S*+1	Root	*D*	*E*
4	0	0.000	-0.000	2	15	-0.207	0.299
4	1	-83.460	0.028	2	16	0.833	0.017
4	2	19.085	-19.221	2	17	0.013	0.008
4	3	6.156	6.175	2	18	-0.948	0.959
4	4	-9.218	0.455	2	19	0.011	-0.120
4	5	0.081	-0.204	2	20	-0.529	-0.560
4	6	-0.002	0.000	2	21	-0.132	0.044
4	7	0.066	-0.069	2	22	0.512	-0.019
4	8	-0.011	-0.002	2	23	-0.054	0.070
4	9	-0.132	-0.002	2	24	-0.121	0.137
2	0	-4.522	4.579	2	25	0.001	-0.018
2	1	-0.306	-1.141	2	26	0.470	-0.016

2	2	-0.018	0.018	2	27	-0.013	0.014
2	3	2.448	0.006	2	28	0.051	-0.019
2	4	-0.006	0.012	2	29	0.084	-0.006
2	5	0.001	0.004	2	30	-0.069	-0.090
2	6	-0.004	0.001	2	31	-0.043	0.051
2	7	-1.247	1.282	2	32	0.009	0.003
2	8	-1.653	-1.654	2	33	0.130	0.003
2	9	0.190	-0.001	2	34	-0.001	0.002
2	10	0.032	0.001	2	35	-0.005	-0.018
2	11	-0.063	0.061	2	36	-0.009	0.010
2	12	-0.335	-0.355	2	37	-0.002	-0.004
2	13	0.158	0.098	2	38	-0.003	0.000
2	14	0.013	0.000	2	39	-0.064	0.063

Table S7 Energy levels (cm^{-1}) of ligand field multiplets in zero field derived from ORCA/CASSCF computed for complex **1**

0	0.0	30	18780.6	60	24790.2	90	37725.9
1	0.0	31	18780.6	61	24790.2	91	37725.9
2	164.8	32	19285.7	62	26368.9	92	37939.5
3	164.8	33	19285.7	63	26368.9	93	37939.5
4	769.1	34	19427.8	64	28666.3	94	38368.5
5	769.1	35	19427.8	65	28666.3	95	38368.5
6	992.2	36	19841.6	66	29153.5	96	43017.1
7	992.2	37	19841.6	67	29153.5	97	43017.1
8	1843.4	38	19940.4	68	29433.0	98	43419.9
9	1843.4	39	19940.4	69	29433.0	99	43419.9
10	1894.1	40	20121.9	70	29796.0	100	43846.6
11	1894.1	41	20121.9	71	29796.0	101	43846.6
12	9032.3	42	20216.3	72	30744.6	102	45607.9
13	9032.3	43	20216.3	73	30744.6	103	45607.9
14	9079.8	44	21988.7	74	30961.0	104	46089.6
15	9079.8	45	21988.7	75	30961.0	105	46089.6
16	9972.6	46	22274.2	76	31947.6	106	46417.3
17	9972.6	47	22274.2	77	31947.6	107	46417.3
18	9992.9	48	22847.9	78	33246.4	108	46475.3
19	9992.9	49	22847.9	79	33246.4	109	46475.3
20	10294.6	50	23111.3	80	35028.5	110	65756.9

21	10294.6	51	23111.3	81	35028.5	111	65756.9
22	10367.8	52	23464.8	82	35484.2	112	66580.2
23	10367.8	53	23464.8	83	35484.2	113	66580.2
24	10686.8	54	23767.7	84	36019.8	114	66827.8
25	10686.8	55	23767.7	85	36019.8	115	66827.8
26	11342.9	56	24145.9	86	36901.4	116	67270.9
27	11342.9	57	24145.9	87	36901.4	117	67270.9
28	18413.4	58	24473.5	88	37644.3	118	67642.5
29	18413.4	59	24473.5	89	37644.3	119	67642.5

Table S8 ORCA/CASSCF computed Individual contributions to D-tensor for complex **2**

2*S*+1	Root	*D*	*E*	2*S*+1	Root	*D*	*E*
4	0	0.000	-0.000	2	15	0.005	0.004
4	1	-42.394	-0.018	2	16	0.480	-0.001
4	2	12.210	-12.109	2	17	0.108	-0.000
4	3	5.828	5.678	2	18	-1.068	1.068
4	4	-4.965	-0.010	2	19	-0.033	-0.035
4	5	-3.339	-0.013	2	20	-0.707	-0.689
4	6	0.006	-0.006	2	21	0.284	-0.007
4	7	0.063	-0.063	2	22	0.058	0.001
4	8	-0.168	-0.001	2	23	-0.020	-0.004
4	9	-0.020	0.000	2	24	0.560	0.051
2	0	-4.187	4.188	2	25	0.044	0.118
2	1	-1.906	-1.094	2	26	-0.007	-0.010
2	2	0.000	0.000	2	27	0.016	0.000
2	3	2.072	0.001	2	28	0.211	-0.001
2	4	0.243	0.000	2	29	0.007	-0.000
2	5	0.030	0.003	2	30	-0.090	-0.084
2	6	-0.076	0.057	2	31	-0.077	0.075
2	7	-1.338	1.348	2	32	-0.001	0.002
2	8	0.450	-0.025	2	33	0.086	0.003
2	9	-1.836	-1.836	2	34	0.023	0.002
2	10	0.036	-0.002	2	35	-0.031	-0.031
2	11	-0.073	0.071	2	36	-0.001	0.001
2	12	-0.200	-0.130	2	37	0.001	-0.000
2	13	0.717	0.013	2	38	-0.010	0.009
2	14	-0.165	0.192	2	39	-0.054	0.055

Table S9 Energy levels (cm^{-1}) of ligand field multiplets in zero field derived from ORCA/CASSCF computed for complex **2**

0	0.0	30	18896.0	60	26060.5	90	39947.7
1	0.0	31	18896.0	61	26060.5	91	39947.7
2	80.0	32	19295.9	62	27258.1	92	40088.2
3	80.0	33	19295.9	63	27258.1	93	40088.2
4	1511.1	34	19959.0	64	29244.3	94	40617.1
5	1511.1	35	19959.0	65	29244.3	95	40617.1
6	1615.4	36	20771.0	66	29806.2	96	43334.7
7	1615.4	37	20771.0	67	29806.2	97	43334.7
8	2967.5	38	21157.1	68	30362.5	98	44029.6
9	2967.5	39	21157.1	69	30362.5	99	44029.6
10	3008.2	40	21820.0	70	31060.0	100	44602.3
11	3008.2	41	21820.0	71	31060.0	101	44602.3
12	9818.1	42	21866.7	72	31929.3	102	46512
13	9818.1	43	21866.7	73	31929.3	103	46512
14	9831.5	44	22513.2	74	32473.0	104	47158.6
15	9831.5	45	22513.2	75	32473.0	105	47158.6
16	10047.5	46	22877.3	76	32698.8	106	47648.5
17	10047.5	47	22877.3	77	32698.8	107	47648.5
18	10944.3	48	23450.9	78	34974.5	108	47830.2
19	10944.3	49	23450.9	79	34974.5	109	47830.2
20	11481.4	50	23680.2	80	35806.5	110	65973.3
21	11481.4	51	23680.2	81	35806.5	111	65973.3
22	11562.1	52	24399.6	82	36769.2	112	66901.7
23	11562.1	53	24399.6	83	36769.2	113	66901.7
24	12206.4	54	25068.2	84	37225.0	114	68145.6
25	12206.4	55	25068.2	85	37225.0	115	68145.6
26	12294.4	56	25289.4	86	38076.5	116	68496.4
27	12294.4	57	25289.4	87	38076.5	117	68496.4
28	18213.1	58	25833.5	88	39002.3	118	68722.5
29	18213.1	59	25833.5	89	39002.3	119	68722.5

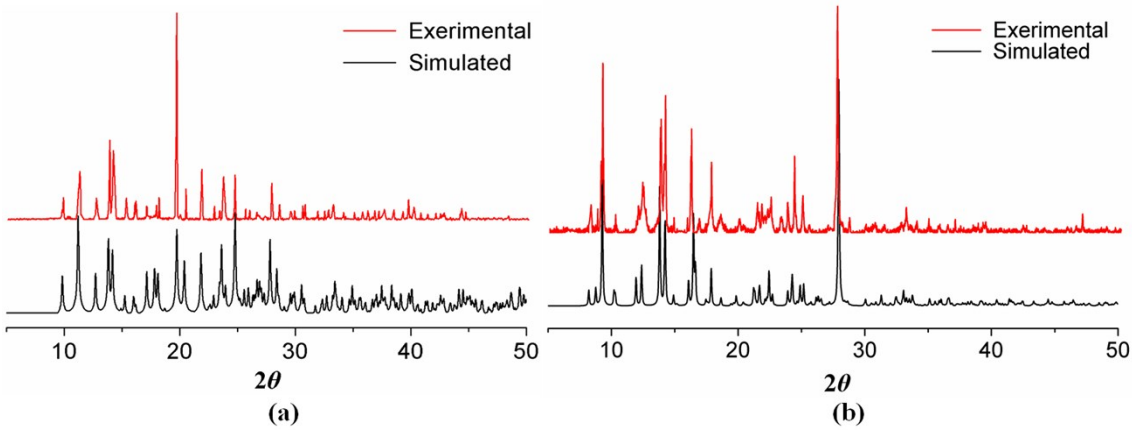

Fig. S1 PXRD patterns for complexes **1** (a) and **2** (b).

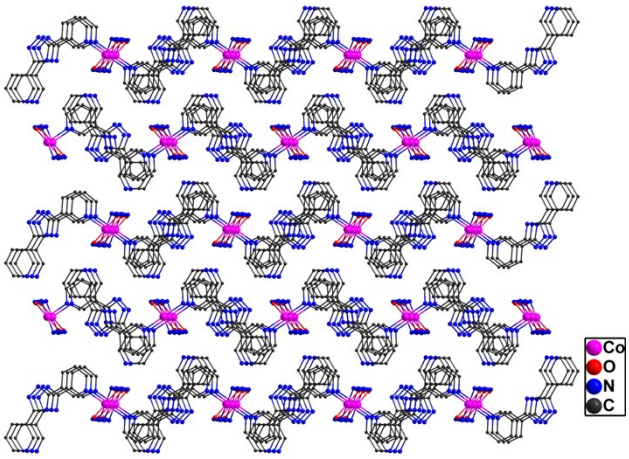

Fig. S2 3D supramolecular networks of complex **1** (H atoms have been deleted for clarity).

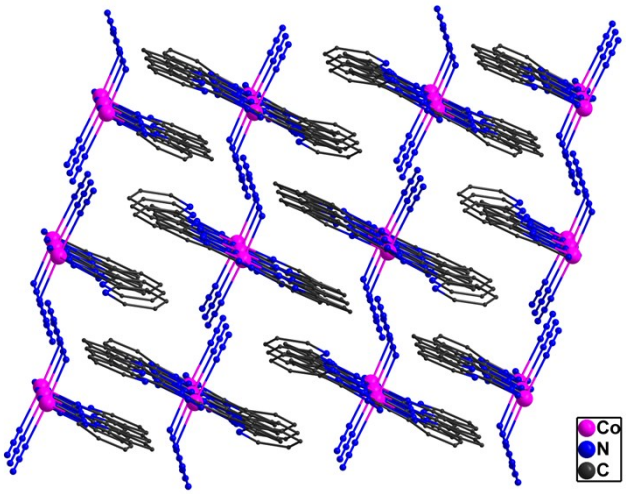

Fig. S3 3D supramolecular networks of complex **2** (H atoms have been deleted for clarity).

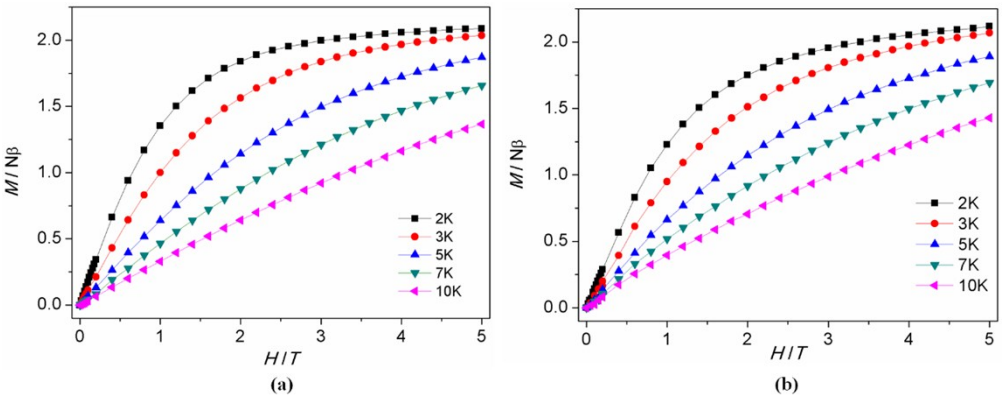

Fig. S4 *M* versus *H* at different temperatures.

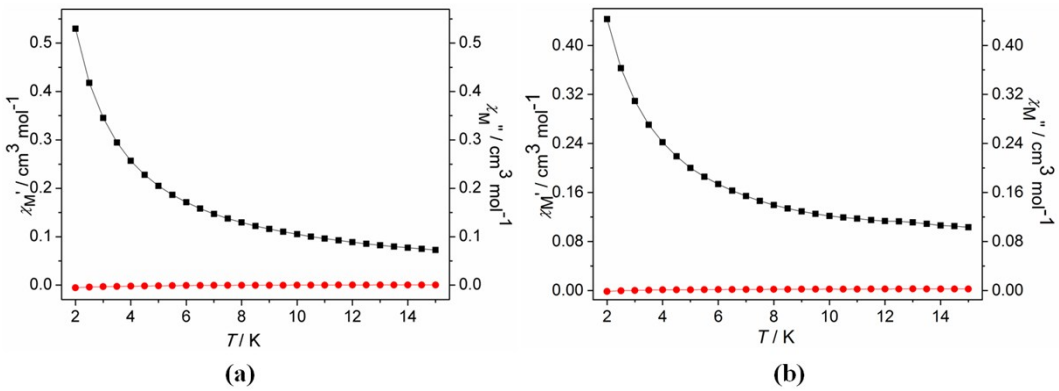

Fig. S5 Ac magnetic susceptibility measurements for **1** (a) and **2** (b) in 0 Oe static field.

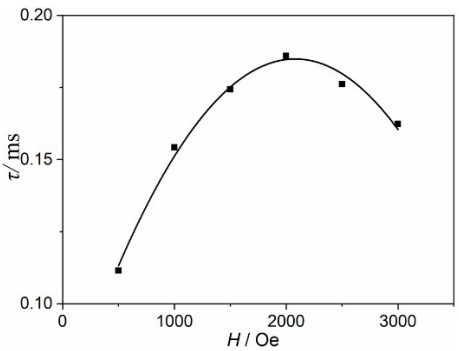

Fig. S6 Field dependence of the magnetic relaxation time at 2 K for **2**.

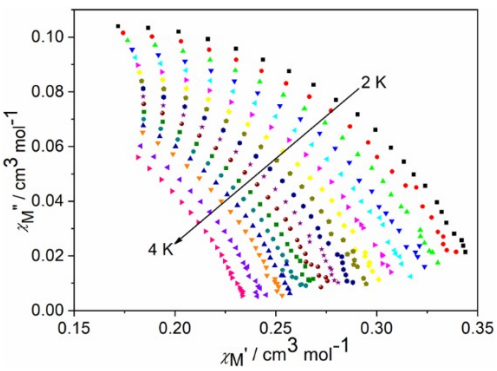

Fig. S7 Cole–Cole plots under 2000 Oe for **2**.