Supporting Information

Modulation of the magnetic dynamics of pentagonal-bipyramidal Co(II) complexes by fine-tuning of the coordination microenvironment

Yuanyuan Qin,[a‡] Yuewei Wu,[a‡] Shuchang Luo,*[b] Jing Xi,[a] Yan Guo,[a] Yi Ding,[a] Jun Zhang[a] and Xiangyu Liu*[a]

[a] State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering, College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, China. E-mail: xiangyuliu432@126.com

[b] College of Chemical Engineering, Guizhou University of Engineering Science, Bijie 551700, China. E-mail: luosc@gues.edu.cn

‡ These authors contributed equally to this work.

***Corresponding author**

Dr. Xiangyu Liu

E-mail: xiangyuliu432@126.com

***Corresponding author**

Prof. Shuchang Luo

E-mail: luosc@gues.edu.cn

Contents:

Fig. S6 Plots of *M* vs *H*/*T* for **1-4** at different temperatures.

Fig. S7 Temperature dependence of the in-phase (χ') and out-phase (χ'') ac magnetic susceptibility at 1000 Hz without static field for **1**-**4**.

Fig. S8 Temperature dependence of the in-phase (top) and out-phase (bottom) ac susceptibilities at different frequencies with a dc field of 2000 Oe for complexes **1**(a), **2**(b) and **4**(c).

Fig. S9 Frequency dependence of the in-phase ac susceptibility signals for complexes **1**(a), **2**(b) and **4**(c) under a 2000 Oe dc field.

Fig. S10 Cole-Cole plots under 2000 Oe for **1**. The solid lines show the best fitting according to the generalized Debye model.

Fig. S11 Cole-Cole plots under 2000 Oe for **2**(a) and **4**(b). The solid lines show the best fitting according to the generalized Debye model.

Fig. S12 Calculated complete structure of complexes **1**-**4**.

Fig. S13 The molecular structure for **1** (a) and **2** (b).

Table S1 Selected crystallographic data and structure refinement for complexes **1**-**4**.

complex	**1**	**2**	**3**	**4**
Empirical formula	$C_{24}H_{25}CoN_5O_4$	$C_{25}H_{28}CoN_8O_4$	$C_{13}H_{21}CoN_7O_{10}$	$C_{17}H_{19}N_6O_6Co$
Formula weight	506.42	563.48	494.30	462.31
Temperature	100.00(10) K	150.0 K	296.0 K	296.0 K
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$	$P2_1/c$	$P2_1/c$
a (Å)	9.9206(8)	25.621(3)	7.6670(19)	16.0546(12)
b (Å)	24.0797(17)	8.0234(12)	15.405(3)	8.0594(5)
c (Å)	10.0515(8)	24.820(3)	18.209(5)	15.2612(10)
α (°)	90	90	90	90
β (°)	109.445(9)	90.826(5)	96.489(9)	95.807(2)
γ (°)	90	90	90	90
V (Å^3)	2264.2(3)	5101.7(12)	2136.9(9)	1964.5(2)
Z	4	8	4	4
D (g/cm^3)	1.486	1.467	1.536	1.610
Mu (mm^{-1})	0.800	0.722	0.868	0.922
F(0 0 0)	1052.0	2344.0	1020.0	952.0
Completeness	86.3	99.7	97.5	99.8
Unique reflections lections	5438	5878	4738	4502
Observed reflections	14627	66456	10263	30050
R_{int}	0.0536	0.0986	0.0603	0.0490
Final R indices [$I>2\sigma(I)$]	R_1 =0.0532 wR_2 =0.0919	R_1 =0.0503 wR_2 =0.1398	R_1 =0.0900 wR_2 =0.2580	R_1 =0.0417 wR_2 =0.1051
R indices (all data)	R_1 =0.0850 wR_2 =0.1035	R_1 =0.0754 wR_2 =0.1596	R_1 =0.1113 wR_2 =0.2766	R_1 =0.0553 wR_2 =0.1145
Goodness-of-fit on F^2	1.039	1.049	1.057	1.042

Table S2 Selected Bond Lengths (Å) and Bond Angles (°) for **1-4**.

Complex 1			
Co(1)-O(1)	2.183(17)	O(3)-Co(1)-O(2)	91.32(8)
Co(1)-O(2)	2.148(18)	O(3)-Co(1)-O(4)	178.44(7)
Co(1)-O(3)	2.133(18)	O(3)-Co(1)-N(2)	92.66(8)
Co(1)-O(4)	2.146(17)	O(3)-Co(1)-N(3)	91.69(8)
Co(1)-N(2)	2.200(2)	O(3)-Co(1)-N(4)	86.50(7)
Co(1)-N(3)	2.175(2)	O(4)-Co(1)-O(1)	88.73(7)
Co(1)-N(4)	2.218(2)	O(4)-Co(1)-O(2)	88.99(7)
O(1)-Co(1)-N(2)	69.77(7)	O(4)-Co(1)-N(2)	86.28(7)
O(1)-Co(1)-N(4)	148.06(7)	O(4)-Co(1)-N(3)	89.05(7)
O(2)-Co(1)-O(1)	78.56(7)	O(4)-Co(1)-N(4)	95.04(7)
O(2)-Co(1)-N(2)	148.05(7)	N(2)-Co(1)-N(4)	142.06(8)
O(2)-Co(1)-N(3)	140.50(7)	N(3)-Co(1)-O(1)	140.81(8)
O(2)-Co(1)-N(4)	69.83(7)	N(3)-Co(1)-N(2)	71.04(8)
O(3)-Co(1)-O(1)	89.83(7)	N(3)-Co(1)-N(4)	71.07(8)

Complex 2			
Co(1)-O(1)	2.113(2)	O(2)-Co(1)-N(4)	69.73(8)
Co(1)-O(2)	2.168(2)	O(2)-Co(1)-N(6)	92.56(9)
Co(1)-O(3)	2.179(2)	O(3)-Co(1)-N(4)	91.39(8)
Co(1)-N(1)	2.161(2)	N(1)-Co(1)-O(2)	138.65(9)
Co(1)-N(2)	2.146(2)	N(1)-Co(1)-O(3)	85.93(9)
Co(1)-N(4)	2.233(2)	N(1)-Co(1)-N(4)	70.10(9)
Co(1)-N(6)	2.172(3)	N(1)-Co(1)-N(6)	94.11(9)
O(1)-Co(1)-O(2)	76.31(8)	N(2)-Co(1)-O(2)	147.11(9)
O(1)-Co(1)-O(3)	93.50(8)	N(2)-Co(1)-O(3)	86.11(9)
O(1)-Co(1)-N(1)	144.63(9)	N(2)-Co(1)-N(1)	72.17(9)
O(1)-Co(1)-N(2)	72.50(9)	N(2)-Co(1)-N(4)	142.28(9)
O(1)-Co(1)-N(4)	145.18(9)	N(2)-Co(1)-N(6)	96.43(9)
O(1)-Co(1)-N(6)	87.99(9)	N(6)-Co(1)-O(3)	177.36(9)
O(2)-Co(1)-O(3)	85.60(9)	N(6)-Co(1)-N(4)	86.14(9)

Complex 3			
Co(1)-O(1)	2.218(4)	O(9)-Co(1)-N(2)	89.95(18)
Co(1)-O(2)	2.147(4)	O(9)-Co(1)-N(4)	91.66(18)
Co(1)-O(9)	2.140(4)	O(10)-Co(1)-O(1)	89.9(2)
Co(1)-O(10)	2.129(5)	O(10)-Co(1)-O(2)	88.8(2)
Co(1)-N(1)	2.176(4)	O(10)-Co(1)-O(9)	177.3(2)
Co(1)-N(2)	2.202(5)	O(10)-Co(1)-N(1)	91.36(19)
Co(1)-N(4)	2.206(5)	O(10)-Co(1)-N(2)	88.7(2)
O(2)-Co(1)-O(1)	76.00(18)	O(10)-Co(1)-N(4)	90.8(2)
O(2)-Co(1)-N(1)	142.04(17)	N(1)-Co(1)-O(1)	141.95(16)
O(2)-Co(1)-N(2)	147.67(17)	N(1)-Co(1)-N(2)	70.25(16)
O(2)-Co(1)-N(4)	72.14(17)	N(1)-Co(1)-N(4)	69.91(16)
O(9)-Co(1)-O(1)	87.50(18)	N(2)-Co(1)-O(1)	71.76(16)
O(9)-Co(1)-O(2)	91.11(19)	N(2)-Co(1)-N(4)	140.13(17)
O(9)-Co(1)-N(1)	90.40(16)	N(4)-Co(1)-O(1)	148.11(16)

Complex 4			
Co(1)-N(2)	2.172(2)	O(1)-Co(1)-N(4)	70.41(7)
Co(1)-N(3)	2.175(2)	O(2)-Co(1)-N(4)	147.59(8)
Co(1)-N(4)	2.207(2)	O(2)-Co(1)-O(1)	77.2(7)
Co(1)-O(1)	2.2033(18)	O(3)-Co(1)-N(2)	100.25(8)
Co(1)-O(2)	2.1817(19)	O(3)-Co(1)-N(3)	89.55(8)
Co(1)-O(3)	2.1612(18)	O(3)-Co(1)-N(4)	83.00(8)
Co(1)-O(9)	2.101(2)	O(3)-Co(1)-O(1)	84.85(7)
N(2)-Co(1)-N(3)	70.61(8)	O(3)-Co(1)-O(2)	92.79(8)
N(2)-Co(1)-N(4)	140.66(8)	O(9)-Co(1)-N(2)	88.97(9)
N(2)-Co(1)-O(1)	148.72(8)	O(9)-Co(1)-N(3)	93.03(10)
N(2)-Co(1)-O(2)	71.74(8)	O(9)-Co(1)-N(4)	89.51(10)
N(3)-Co(1)-N(4)	70.23(8)	O(9)-Co(1)-O(1)	87.53(9)
N(3)-Co(1)-O(1)	140.62(8)	O(9)-Co(1)-O(2)	90.62(10)
N(3)-Co(1)-O(2)	142.08(8)	O(9)-Co(1)-O(3)	170.76(8)

Table S3 Hydrogen-bonded parameters /Å, ° for complexes **1-3**.

Complex	D-H A	D-H	H A	D-A	DHA
1	O3-H3 N5[1]	0.846	1.941	2.784	173.6
	O4-H4A O2[2]	0.860	2.020	2.747	142.4
	O4-H4B O1[2]	0.860	1.890	2.694	154.6
2	O3-H3 N8[1]	0.881	1.928	2.785	164.0
	N5-H5 N6[2]	0.880	2.110	2.928	154.7
	O4-H4A O1	0.840	2.150	2.965	164.5
3	O9-H9 O4	0.856	1.918	2.759	167.0
	O10-H10 O6	0.820	1.940	2.754	175.7
	N3-H3 O3[1]	0.860	1.960	2.817	170.7
	N5-H5 O7[2]	0.860	1.980	2.829	168.2

Table S4 Co(II) ions geometry analysis of **1-4** by SHAPE 2.1 software.

Configuration	ABOXIY, **1**	ABOXIY, **2**	ABOXIY, **3**	ABOXIY, **4**
PBPY-7	**0.197**	**0.285**	**0.104**	**0.335**
COC-7	7.246	7.028	7.782	6.727
CTPR-7	5.510	5.505	6.097	4.913
JPBPY-7	3.465	4.008	3.287	3.447
JETPY-7	22.459	22.424	23.901	22.644

Table S5 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
2.4	0.204	0.191	0.168
2.8	0.184	0.168	0.208
3.2	0.167	0.151	0.100
3.4	0.161	0.141	0.200
3.8	0.148	0.131	0.095

4.2	0.138	0.117	0.147
4.4	0.114	0.133	1.889
5	0.120	0.081	0.235

Table S6 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	0.312	0.192	0.111
2.5	0.272	0.155	0.115
3	0.239	0.131	0.096
3.5	0.213	0.110	0.109
4	0.191	0.097	0.091
4.5	0.172	0.087	0.071
5	0.157	0.073	0.082
5.5	0.144	0.062	0.067
6	0.133	0.037	0.088
6.5	0.123	0.012	0.046

Table S7 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
2.5	0.246	6.84E-18	0.422
3	0.218	1.06E-17	0.420
3.5	0.197	1.42E-17	0.416
4	0.178	1.95E-17	0.406
4.5	0.160	2.84E-17	0.370
5	0.146	4.44E-17	0.325
5.5	0.132	4.68E-17	0.254
6	0.121	8.36E-17	0.184
6.5	0.111	6.79E-16	0.095

Table S8 The CASSCF/NEVPT2/def2-TZVP(-f) computed Individual contributions to D-tensor for complexes.

		1				**2**				**3**				**4**	
2S+1	**Root**	***D***	***E***	**2S+1**	**Root**	***D***	***E***	**2S+1**	**Root**	***D***	***E***	**2S+1**	**Root**	***D***	***E***
4	0	0.000	0.000	4	0	0.000	0.000	4	0	0.000	0.000	4	0	0.000	0.000
4	1	9.283	8.961	4	1	8.704	9.008	4	1	10.434	10.001	4	1	9.051	7.914
4	2	3.250	-2.630	4	2	2.798	-3.244	4	2	2.513	-1.887	4	2	1.808	-1.740
4	3	7.312	5.772	4	3	10.809	-3.275	4	3	10.363	2.871	4	3	16.008	-13.810
4	4	10.896	-10.257	4	4	9.202	0.582	4	4	12.198	-8.491	4	4	9.031	7.798
4	5	0.005	-0.002	4	5	0.030	-0.012	4	5	0.001	-0.001	4	5	0.008	-0.000

4	6	0.003	-0.000	4	6	0.013	0.002	4	6	0.000	0.001	4	6	0.003	0.001
4	7	0.028	0.008	4	7	0.054	-0.013	4	7	0.036	-0.033	4	7	0.032	-0.026
4	8	0.040	-0.020	4	8	0.053	-0.002	4	8	0.041	0.034	4	8	0.050	0.041
4	9	0.000	-0.000	4	9	0.000	-0.000	4	9	0.000	0.000	4	9	0.000	-0.000
2	0	0.088	-0.001	2	0	0.106	-0.000	2	0	1.082	0.001	2	0	0.856	0.004
2	1	-0.000	0.007	2	1	3.431	-0.019	2	1	0.175	0.000	2	1	1.769	-0.007
2	2	-0.002	-0.005	2	2	0.021	0.006	2	2	0.048	-0.002	2	2	-0.003	-0.001
2	3	0.010	-0.000	2	3	-0.008	0.003	2	3	0.123	0.001	2	3	-0.006	0.000
2	4	14.001	-0.003	2	4	-0.035	-0.062	2	4	12.374	0.000	2	4	0.015	-0.006
2	5	-0.017	-0.011	2	5	-0.038	0.019	2	5	-0.005	-0.001	2	5	0.241	0.074
2	6	0.006	0.013	2	6	1.229	-1.120	2	6	0.073	0.016	2	6	9.925	-0.091
2	7	-1.536	-0.214	2	7	5.903	-0.287	2	7	-1.637	-1.541	2	7	-0.798	-1.212
2	8	-1.525	0.106	2	8	-0.455	1.366	2	8	-1.540	1.435	2	8	-1.589	1.343
2	9	-0.000	0.000	2	9	-0.003	0.002	2	9	-0.000	-0.000	2	9	-0.001	-0.001
2	10	-0.043	0.021	2	10	-0.028	0.026	2	10	-0.045	0.038	2	10	-0.118	-0.092
2	11	-0.005	-0.002	2	11	-0.019	-0.007	2	11	-0.066	-0.037	2	11	-0.008	0.001
2	12	-0.040	0.041	2	12	-0.059	0.053	2	12	-0.046	-0.043	2	12	-0.042	0.040
2	13	-0.069	-0.069	2	13	-0.118	-0.083	2	13	-0.047	-0.013	2	13	-0.069	-0.060
2	14	-0.005	0.004	2	14	-0.146	0.111	2	14	-0.032	0.032	2	14	-0.083	0.069
2	15	-0.003	-0.003	2	15	-0.112	-0.082	2	15	0.000	-0.000	2	15	-0.024	-0.021
2	16	-0.499	0.498	2	16	0.009	-0.000	2	16	-0.466	0.463	2	16	-0.010	-0.006
2	17	-0.445	-0.439	2	17	-0.210	0.112	2	17	-0.164	-0.141	2	17	-0.275	-0.300
2	18	0.015	-0.002	2	18	-0.148	-0.078	2	18	-0.210	-0.212	2	18	-0.182	0.256
2	19	-0.007	-0.005	2	19	-0.012	-0.015	2	19	-0.006	-0.006	2	19	0.061	0.045
2	20	0.005	0.000	2	20	0.260	0.041	2	20	0.051	-0.000	2	20	-0.007	0.011
2	21	0.001	-0.000	2	21	-0.057	-0.047	2	21	0.040	-0.001	2	21	0.002	0.002
2	22	1.210	0.001	2	22	1.103	-0.005	2	22	1.459	-0.000	2	22	1.276	-0.000
2	23	-0.003	-0.002	2	23	-0.028	0.021	2	23	-0.002	0.003	2	23	-0.005	0.005
2	24	-0.130	-0.051	2	24	-0.153	-0.079	2	24	-0.015	-0.012	2	24	-0.257	0.186
2	25	-0.059	0.025	2	25	-0.125	0.054	2	25	-0.017	0.017	2	25	-0.249	0.261
2	26	-0.351	-0.252	2	26	-0.362	-0.264	2	26	-0.548	0.386	2	26	-0.040	-0.032
2	27	-0.462	0.331	2	27	-0.433	0.335	2	27	-0.504	-0.335	2	27	-0.510	-0.435
2	28	0.001	0.000	2	28	0.013	0.001	2	28	-0.000	-0.001	2	28	0.000	0.001
2	29	0.006	-0.000	2	29	0.003	-0.000	2	29	-0.001	0.001	2	29	0.003	-0.002
2	30	-0.004	0.004	2	30	-0.059	0.017	2	30	-0.001	0.002	2	30	-0.006	0.000
2	31	-0.009	-0.003	2	31	-0.150	-0.141	2	31	-0.002	-0.001	2	31	-0.132	0.088

2	32	-0.124	-0.110	2	32	-0.115	0.115	2	32	-0.146	-0.125	2	32	-0.031	0.024
2	33	-0.120	0.107	2	33	-0.001	0.001	2	33	-0.140	0.112	2	33	-0.139	-0.118
2	34	-0.000	0.000	2	34	-0.004	0.001	2	34	-0.000	0.000	2	34	-0.000	-0.000
2	35	0.000	-0.000	2	35	-0.000	-0.001	2	35	0.001	-0.000	2	35	0.007	0.000
2	36	0.001	0.000	2	36	-0.001	-0.001	2	36	0.001	-0.000	2	36	0.004	-0.000
2	37	-0.001	-0.000	2	37	0.003	-0.001	2	37	-0.002	-0.002	2	37	-0.002	-0.002
2	38	-0.001	0.000	2	38	0.006	0.002	2	38	-0.003	0.003	2	38	-0.002	0.003
2	39	0.211	0.000	2	39	0.199	0.000	2	39	0.221	0.000	2	39	0.209	0.000

Table S9 Energy levels (cm^{-1}) of ligand field multiplets in zero field derived from CASSCF/def2-TZVP(-f) computed for complexes.

1		**2**		**3**		**4**	
States	**Energy levels (cm^{-1})**	**States**	**Energy levels (cm^{-1})**	**States**	**Energy levels (cm^{-1})**	**States**	**Energy levels (cm^{-1})**
1	0.0	1	0.0	1	0.0	1	0.0
2	74.9	2	75.2	2	82.7	2	82.3
3	74.9	3	75.2	3	82.7	3	82.3
4	4510.3	4	3312.1	4	3825.2	4	3269.2
5	4510.3	5	3312.1	5	3825.2	5	3269.2
6	4921.5	6	3583.8	6	4205.9	6	3556.9
7	4921.5	7	3583.8	7	4205.9	7	3556.9
8	5378.7	8	4396.8	8	4576.3	8	4527.3
9	5378.7	9	4396.8	9	4576.3	9	4527.3
10	5481.7	10	4488.4	10	4654.1	10	4594.5
11	5481.7	11	4488.4	11	4654.1	11	4594.5
12	5889.2	12	6009.7	12	5440.4	12	4995.3
13	5889.2	13	6009.7	13	5440.4	13	4995.3
14	5965.9	14	6107.1	14	5539.2	14	5132.8
15	5965.9	15	6107.1	15	5539.2	15	5132.8
16	6298.9	16	6357.0	16	5616.9	16	6286.2
17	6298.9	17	6357.0	17	5616.9	17	6286.2
18	6624.4	18	6473.7	18	5801.3	18	6441.4
19	6624.4	19	6473.7	19	5801.3	19	6441.4
20	12649.9	20	11693.1	20	11080.4	20	10821.7
21	12649.9	21	11693.1	21	11080.4	21	10821.7

22	13023.2	22	11842.7	22	11315.7	22	11000.5
23	13023.2	23	11842.7	23	11315.7	23	11000.5
24	13471.1	24	14120.3	24	12479.4	24	12795.1
25	13471.1	25	14120.3	25	12479.4	25	12795.1
26	13764.5	26	14193.4	26	12630.1	26	12889.4
27	13764.5	27	14193.4	27	12630.1	27	12889.4
28	17937.7	28	15789.9	28	16684.5	28	17185.9
29	17937.7	29	15789.9	29	16684.5	29	17185.9
30	18271.6	30	17135.2	30	16719.5	30	17457.7
31	18271.6	31	17135.2	31	16719.5	31	17457.7
32	18346.1	32	17840.9	32	17706.5	32	18392.2
33	18346.1	33	17840.9	33	17706.5	33	18392.2
34	18745.1	34	18423.3	34	18002.5	34	18723.7
35	18745.1	35	18423.3	35	18002.5	35	18723.7
36	20668.1	36	20849.0	36	18155.0	36	19881.5
37	20668.1	37	20849.0	37	18155.0	37	19881.5
38	20790.3	38	20939.3	38	18827.4	38	19954.1
39	20790.3	39	20939.3	39	18827.4	39	19954.1
40	20885.9	40	21187.2	40	20056.0	40	20984.6
41	20885.9	41	21187.2	41	20056.0	41	20984.6
42	21272.5	42	21412.7	42	20161.3	42	21171.5
43	21272.5	43	21412.7	43	20161.3	43	21171.5
44	21438.5	44	21498.8	44	20949.8	44	21313.3
45	21438.5	45	21498.8	45	20949.8	45	21313.3
46	22482.8	46	21769.3	46	21814.0	46	21597.5
47	22482.8	47	21769.3	47	21814.0	47	21597.5
48	22905.8	48	21909.2	48	22129.5	48	21769.8
49	22905.8	49	21909.2	49	22129.5	49	21769.8
50	22967.9	50	22113.7	50	22262.3	50	22059.1
51	22967.9	51	22113.7	51	22262.3	51	22059.1
52	23362.1	52	22444.4	52	22717.0	52	22580.0
53	23362.1	53	22444.4	53	22717.0	53	22580.0
54	23464.0	54	23179.8	54	23000.6	54	23137.6
55	23464.0	55	23179.8	55	23000.6	55	23137.6
56	25562.1	56	23780.4	56	24316.7	56	23891.0
57	25562.1	57	23780.4	57	24316.7	57	23891.0

58	25814.8	58	24028.3	58	24496.3	58	24136.9
59	25814.8	59	24028.3	59	24496.3	59	24136.9
60	26987.5	60	25317.0	60	26111.2	60	25343.2
61	26987.5	61	25317.0	61	26111.2	61	25343.2
62	27099.1	62	25685.7	62	26433.4	62	26399.2
63	27099.1	63	25685.7	63	26433.4	63	26399.2
64	27336.6	64	27431.7	64	26778.3	64	26548.5
65	27336.6	65	27431.7	65	26778.3	65	26548.5
66	27738.2	66	27631.4	66	27140.4	66	27520.9
67	27738.2	67	27631.4	67	27140.4	67	27520.9
68	28592.2	68	28104.7	68	27672.8	68	27777.7
69	28592.2	69	28104.7	69	27672.8	69	27777.7
70	28652.8	70	28598.0	70	28050.7	70	28133.9
71	28652.8	71	28598.0	71	28050.7	71	28133.9
72	29107.9	72	29947.0	72	28379.3	72	28891.4
73	29107.9	73	29947.0	73	28379.3	73	28891.4
74	29465.6	74	30428.5	74	29336.8	74	29523.8
75	29465.6	75	30428.5	75	29336.8	75	29523.8
76	31243.0	76	30736.4	76	29573.4	76	29795.2
77	31243.0	77	30736.4	77	29573.4	77	29795.2
78	31578.9	78	31132.1	78	30671.4	78	30082.8
79	31578.9	79	31132.1	79	30671.4	79	30082.8
80	32177.3	80	31764.3	80	30926.6	80	30903.4
81	32177.3	81	31764.3	81	30926.6	81	30903.4
82	32335.8	82	31990.2	82	31276.1	82	31381.6
83	32335.8	83	31990.2	83	31276.1	83	31381.6
84	33040.8	84	32582.8	84	31679.7	84	31595.5
85	33040.8	85	32582.8	85	31679.7	85	31595.5
86	34103.7	86	33530.9	86	32702.2	86	32547.9
87	34103.7	87	33530.9	87	32702.2	87	32547.9
88	34334.3	88	33922.6	88	33080.8	88	32997.3
89	34334.3	89	33922.6	89	33080.8	89	32997.3
90	34633.9	90	34150.0	90	33177.9	90	33493.7
91	34633.9	91	34150.0	91	33177.9	91	33493.7
92	35137.1	92	34921.5	92	33865.4	92	33792.5
93	35137.1	93	34921.5	93	33865.4	93	33792.5

94	36019.7	94	35699.0	94	34578.0	94	34953.6
95	36019.7	95	35699.0	95	34578.0	95	34953.6
96	42854.2	96	42585.1	96	42136.0	96	42217.8
97	42854.2	97	42585.1	97	42136.0	97	42217.8
98	43153.8	98	42907.4	98	42434.8	98	42519.8
99	43153.8	99	42907.4	99	42434.8	99	42519.8
100	44407.6	100	43450.4	100	43377.7	100	43222.0
101	44407.6	101	43450.4	101	43377.7	101	43222.0
102	44785.0	102	43989.2	102	44011.4	102	43999.5
103	44785.0	103	43989.2	103	44011.4	103	43999.5
104	45511.5	104	44234.7	104	44379.2	104	44101.9
105	45511.5	105	44234.7	105	44379.2	105	44101.9
106	45658.2	106	44592.2	106	44486.2	106	44354.7
107	45658.2	107	44592.2	107	44486.2	107	44354.7
108	46189.2	108	44827.7	108	44968.8	108	44798.2
109	46189.2	109	44827.7	109	44968.8	109	44798.2
110	64302.9	110	63907.3	110	63115.4	110	63258.4
111	64302.9	111	63907.3	111	63115.4	111	63258.4
112	64432.0	112	64115.4	112	63396.8	112	63422.1
113	64432.0	113	64115.4	113	63396.8	113	63422.1
114	66176.0	114	64927.4	114	64922.3	114	64793.9
115	66176.0	115	64927.4	115	64922.3	115	64793.9
116	66524.9	116	65360.5	116	65291.3	116	65297.1
117	66524.9	117	65360.5	117	65291.3	117	65297.1
118	68286.7	118	66489.6	118	66776.0	118	66713.3
119	68286.7	119	66489.6	119	66776.0	119	66713.3

Table S10 Structural and magnetic parameters for the reported pentagonal-bipyramidal Co(II) complexes.

Molecular formula	Donors	Deviation[a]	Co-X_{axial} distance /Å	X_{axial}-Co-X_{axial} angle /°	Average Co-X_{eq} distance/ Å	Angular distortion [b]/°	The slow relaxation process		
							D exp. (cal.) /cm^{-1}	τ_0/s	U_{eff}/K
[Co(dapbh)(H_2O)(CH3OH)] (1)[this work]	N_3O_4	0.197	2.133	178.44	2.1848	12.85	27.6(37.338)	4.24×10^{-4}	22.16 (2000 Oe)

			2.146						
$[Co(dapbh)(N_3)(CH_3OH)]\cdot(CH_3OH)$ **(2)**[this work]	N_4O_3	0.285	2.179 2.172	177.36	2.1642	9.15	21.9(37.273)	2.15×10^{-8}	44.15 (2000 Oe)
$[Co(H_2aapbh)(CH_3OH)_2]\cdot(NO_3^-)_2$ **(3)**[this work]	N_3O_4	0.104	2.129 2.140	177.30	2.1898	9.22	31.9(41.138)	—	—
$[Co(H_2bapbh)(H_2O)(NO_3^-)]\cdot(NO_3^-)$ **(4)**[this work]	N_3O_4	0.335	2.101 2.161	170.76	2.1817	10.21	33.1(41.139)	1.03×10^{-8}	48.72 (2000 Oe)
$[Co(tdmmb)(H_2O)_2][BF_4]_2$ **(5)**[1]	N_5O_2	0.101	2.171 2.173	178.1	2.1624	9.878	25.6(34.5)	5.2×10^{-9}	85.2 (200 Oe)
$[Co(tdmmb)(CN)_2]2H_2O$ **(6)**[1]	N_5C_2	0.109	2.150 2.140	179.3	2.1744	7.458	17.4(35.1)	7.4×10^{-10}	76.4 (200 Oe)
$[Co(tdmmb)(NCS)_2]$ **(7)**[1]	N_7	0.195	2.123 2.123	175.5	2.1726	8.394	26.3(37.7)	8.2×10^{-8}	82.2 (200 Oe)
$[Co(tdmmb)(SPh)_2]$ **(8)**[1]	N_5S_2	0.667	2.5199 2.5456	176.5	2.17404	8.456	34.5(39.7)	6.5×10^{-8}	98.6 (200 Oe)
$[Co(H_4L)(DMF)(H_2O)](NO_3)_2\cdot(DMF)$ **(9)**[2]	N_3O_4	0.293	2.113 2.124	171.45	2.19656	11.69	35.92(36.29)	6.5×10^{-6}	25 (2000 Oe)
$[Co(H_4L)(MeOH)(H_2O)](NO_3)_2\cdot(MeOH)$ **(10)**[2]	N_3O_4	0.067	2.152 2.173	179.84	2.161	4.85	37.23(36.15)	3.5×10^{-6}	15 (2000 Oe)
$[Co(H_4L)(DEF)(H_2O)](NO_3)_2$ **(11)**[2]	N_3O_4	0.253	2.090 2.133	174.4	2.1886	9.9	43.76(37.43)	1.9×10^{-6}	4 (2000 Oe)
$[Co(H_2dapbh)(SCN)_2].3H_2O$ **(12)**[3]	N_5O_2	0.250	2.078 2.120	179.33	2.2214	10.68	15.9(14.6)	—	—
$[Co(dapbh)(H_2O)_2]$ **(13)**[3]	N_3O_4	0.342	2.096 2.119	175.18	2.213	14.81	13.1(12.4)	—	—
$[Co(H_2dapbh)(NO_3)(H_2O)](NO_3)$ **(14)**[4]	N_3O_4	0.417	2.129 2.140	173.44	2.1944	12.96	32.4	6×10^{-10}	81.2 (1000 Oe)
$[CoL_{N5}^1(H_2O)_2]Cl_2\cdot 4H_2O$ **(15)**[4]	N_5O_2	0.289	2.177	176.11	2.2373	7.24	24.6	1.2×10^{-6}	29.8 (1000 Oe)

			2.189						
[Co(dapbh)(im)$_2$]·H_2O (16) [4]	N_5O_2	0.364	2.131 2.131	174.97	2.23676	19.1	24.8	8.7×10^{-11}	89.6 (1000 Oe)
[Co(L5^H)Cl$_2$]·2CH_3OH(17) [5]	$N_3O_2Cl_2$	0.498	2.464 2.472	176.07	2.24542	7.46	38(44.8)	2.01×10^{-6}	7.9(3000 Oe)
[Co(L5^H)Br$_2$](18) [5]	$N_3O_2Br_2$	0.868	2.6441 2.6434	177.62	2.2354	8	41(44.0)	2.57×10^{-7}	17.6(1000 Oe)
[Co(L5^H)I$_2$](19) [5]	$N_3O_2I_2$	1.689	2.208 2.8155	176.74	2.2344	8.8	35(43.4)	1.06×10^{-7}	30.6(2000 Oe)
Co(L$^{2,2'\text{-bipy}}$)(NO_3)$_2$(CH_3CN)](20) [6]	N_3O_4	1.885	2.109 2.084	176.34	2.271	64.54	32.9(33.9)	7.73×10^{-9}	55.1(1000 Oe)
[Co(O_3N)(H_2O)$_3$](21) [7]	NO_6	0.490	2.0972 2.0898	174.447	2.2447	31.34	70.41()	1.35×10^{-5}	5.27(1500 Oe)

H_2dapbh = 2,6-diacetylpyridine bis(benzoyl hydrazine); tdmmb = 1,3,10,12-tetramethyl-1,2,11,12-tetraaza[[3](2,6)-pyridino[3](2,9)-1,10-phenanthrolinophane-2,10-diene; SPh$^-$ = thiophenol anion; H_4L = 2,2′-(pyridine-2,6-diylbis(ethan-1-yl-1-ylidene))bis(N-phenylhydrazinecarboxamide; $L_{N5}{}^1$ = 2,13-dimethyl-3,6,9,12-tetraaza-1(2,6)-pyridinacyclotridecaphane-2,12-diene; im = imidazole; L5^H = 15-membered pyridine-based macrocyclic ligand (3,12,18-triaza-6,9-dioxabicyclo[12.3.1]octadeca-1(18),14,16-triene); L^{CH2Py} = {3,12-bis(2-methylpyridine)-3,12,18-triaza-6,9-dioxabicyclo[12.3.1]octadeca-1,14,16-triene; L$^{2\text{-bzimi}}$ = 3,12-bis((1H-benzimidazol-2-yl)methyl)-6,9-dioxa3,12,18-triazabicyclo[12.3.1]octadeca-1(18),14,16-triene; L$^{2,2'\text{-bipy}}$ = 2,2′-bipyridine; O_3N = 8-carboxymethoxy-2-carboxylicquinoline.

[a] The extent of deviation is confirmed by the continuous shape measures (CShMs) calculated with SHAPE 2.1.

[b] Angular distortion parameter = average distortion of the equatorial donor-metal-donor angles from the ideal 72°.

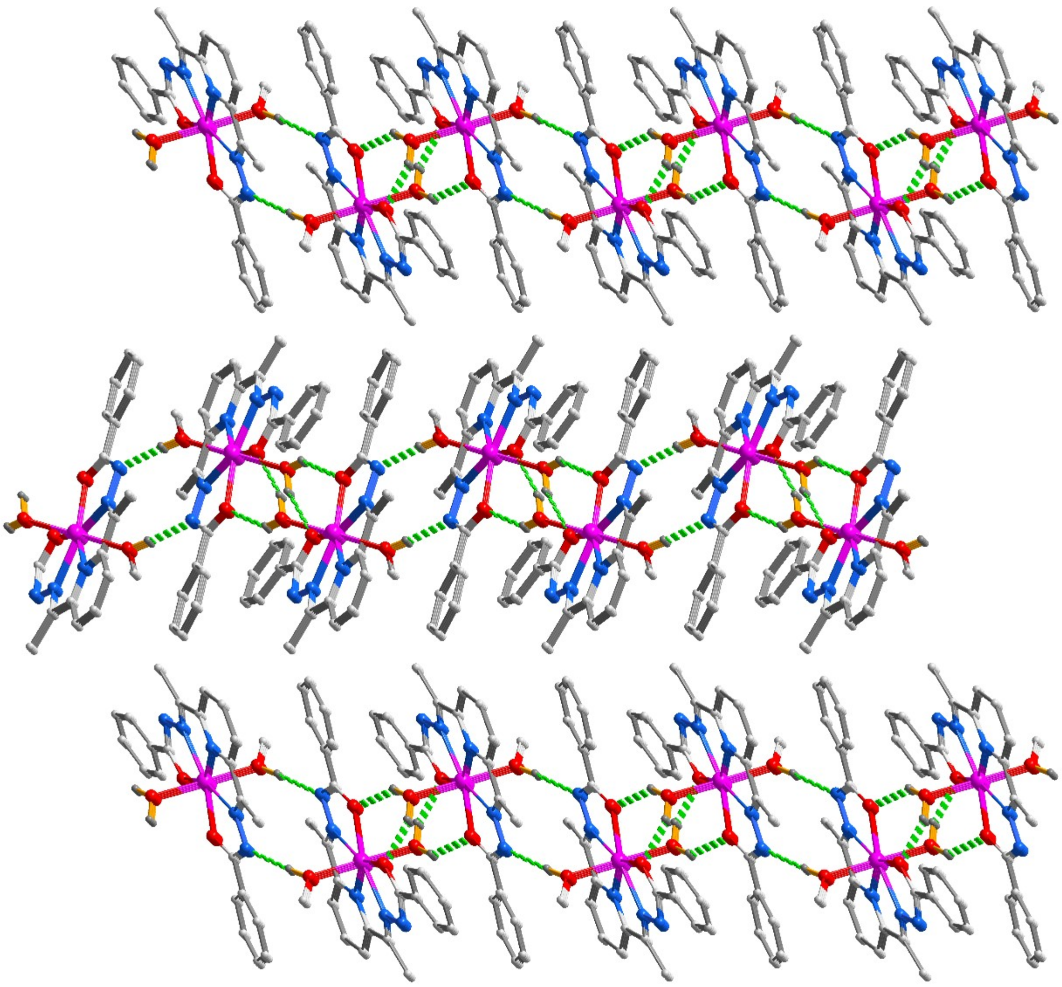
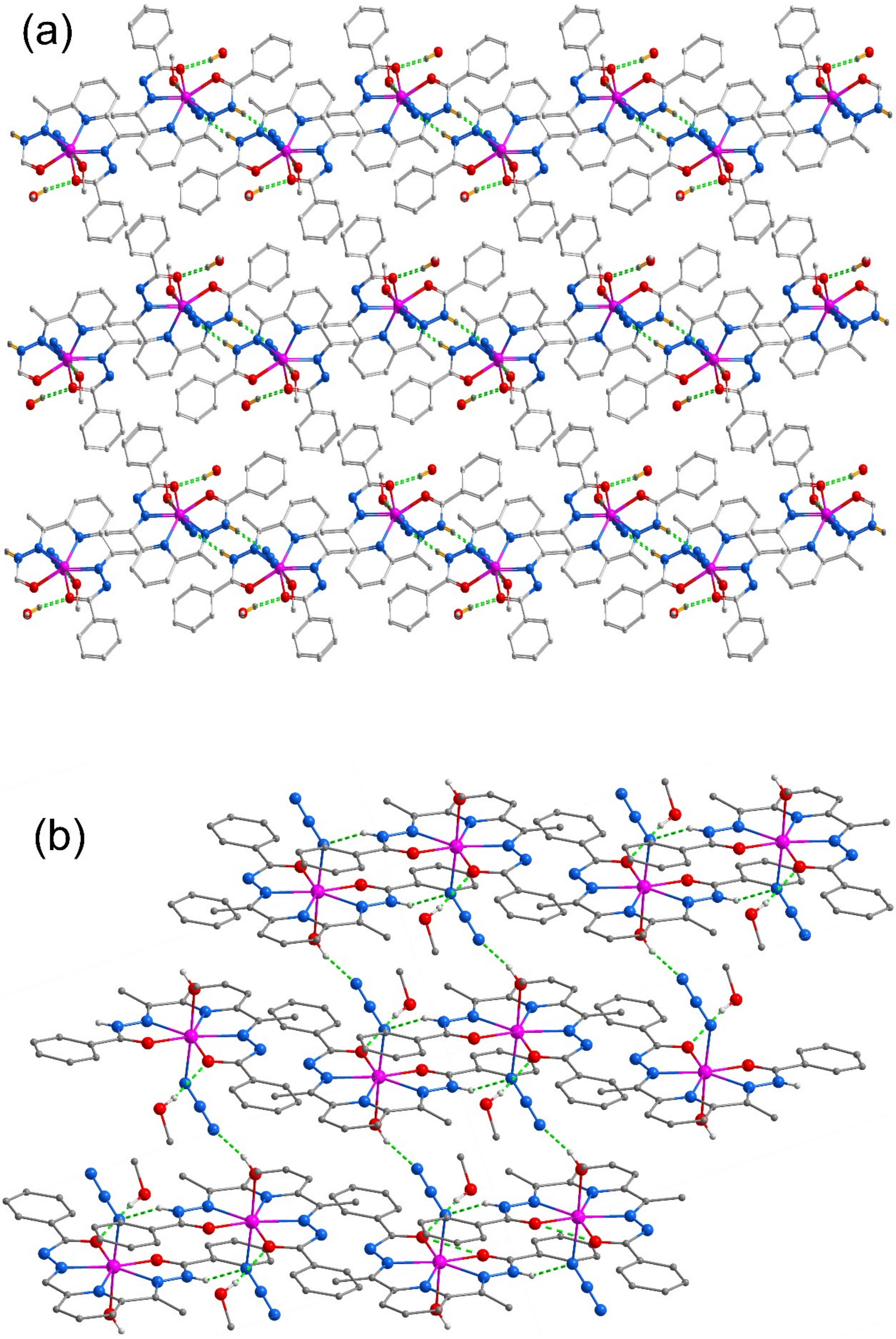


Fig. S1 1D chains formed via intermolecular hydrogen bonds and packing crystal structures of **1**.



(a)
(b)

Fig. S2 1D chains formed via intermolecular hydrogen bonds along the b-axis(a) and packing crystal structures, 1D chains formed via intermolecular hydrogen bonds along the c-axis (b) of **2**.

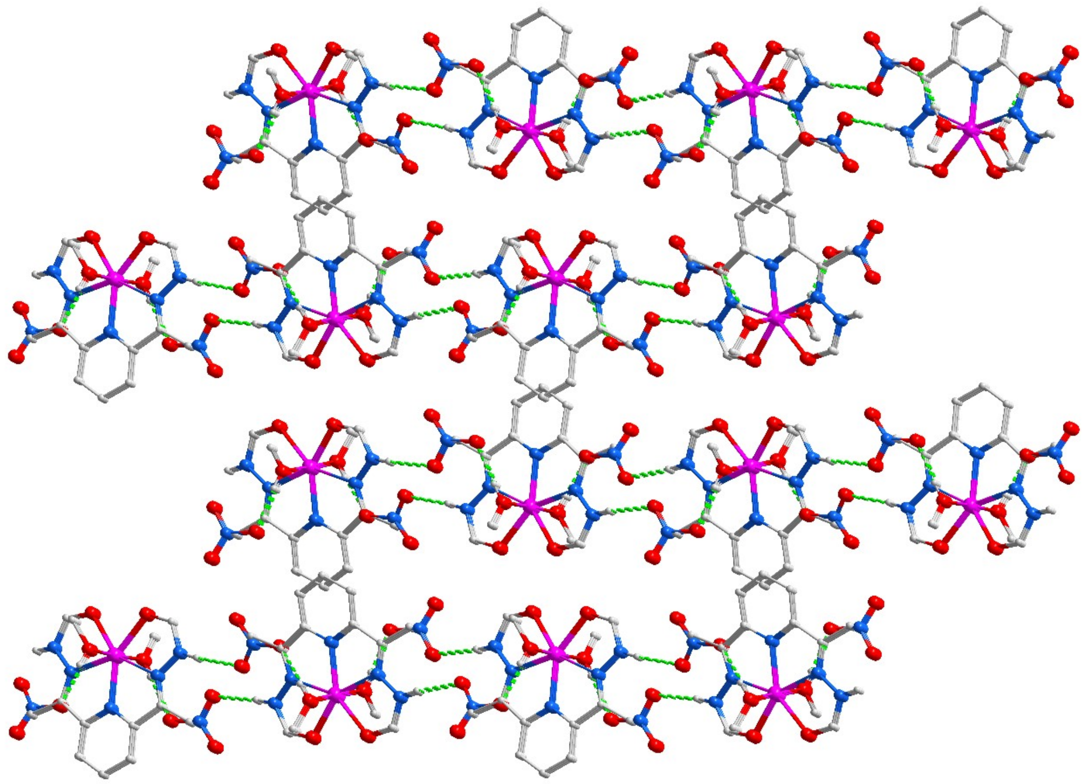


Fig. S3 1D chains formed via intermolecular hydrogen bonds and packing crystal structures of **3**.

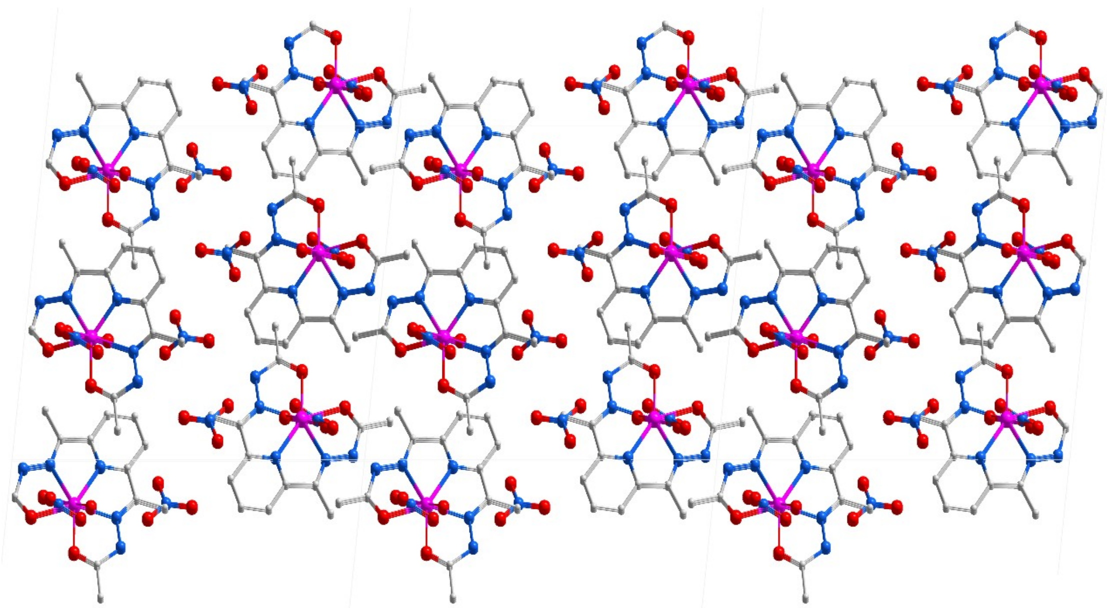


Fig. S4 The packing crystal structures of **4**.

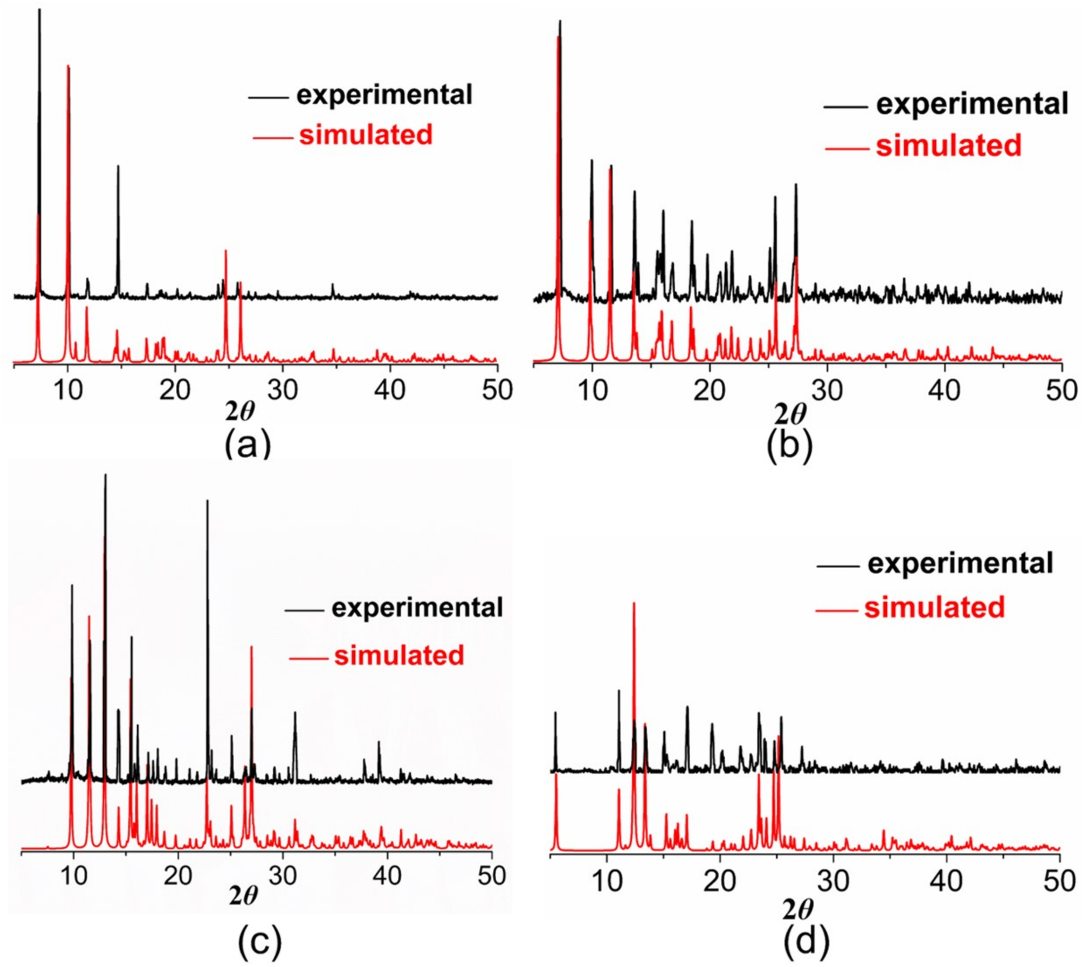


Fig. S5 PXRD patterns for complexes **1**(a), **2**(b), **3**(c), **4**(d).

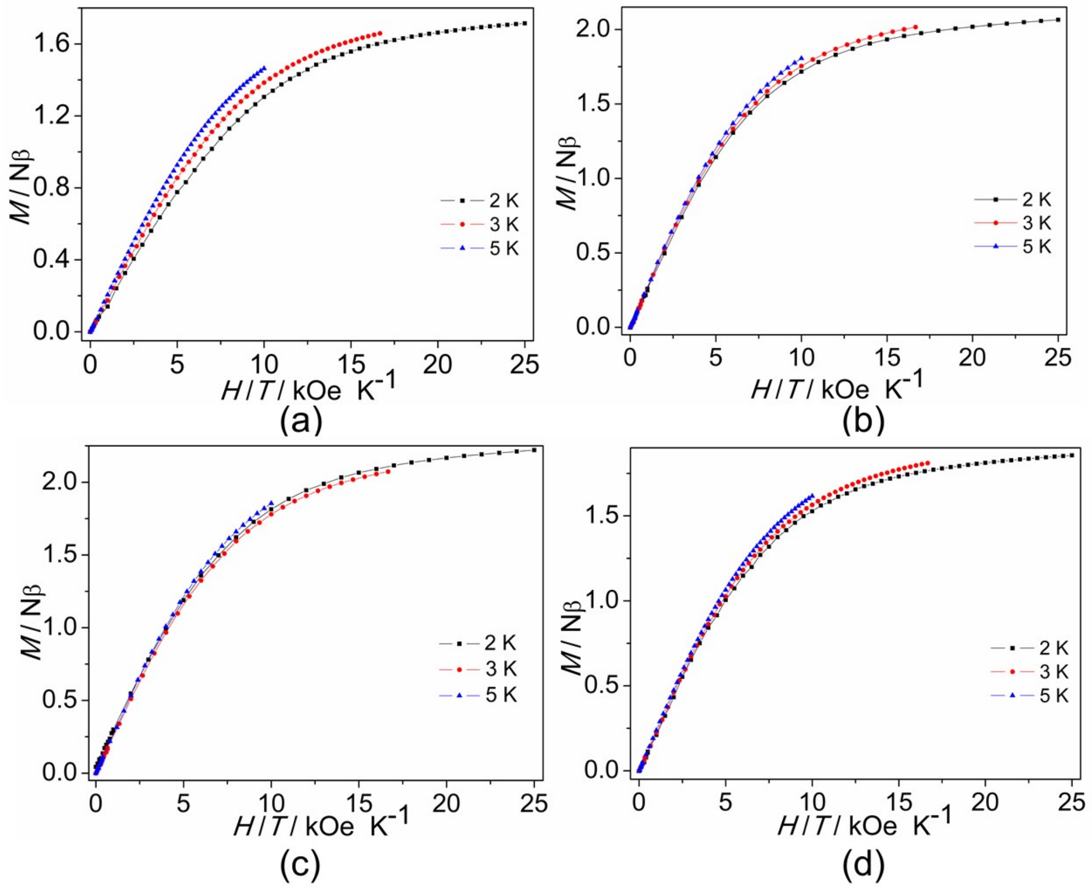


Fig. S6 Plots of M vs H/T for **1-4** at different temperatures.

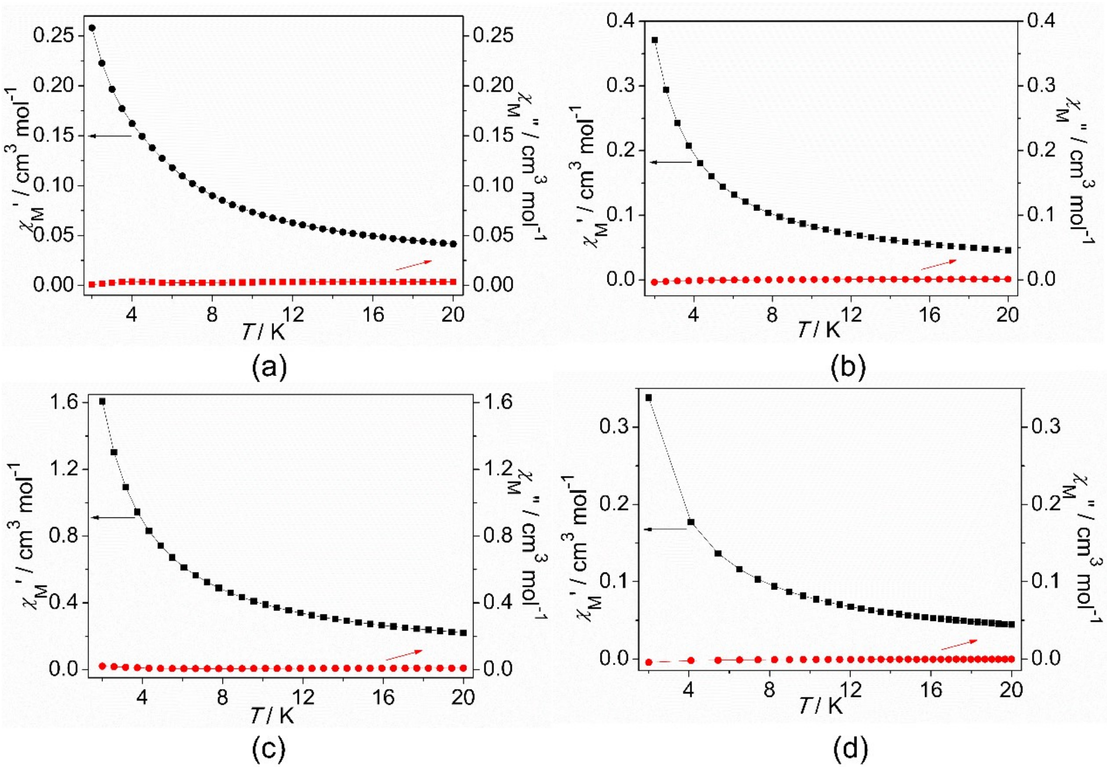


Fig. S7 Temperature dependence of the in-phase (χ') and out-phase (χ'') ac magnetic susceptibility at 1000 Hz without static field for **1**-**4**.

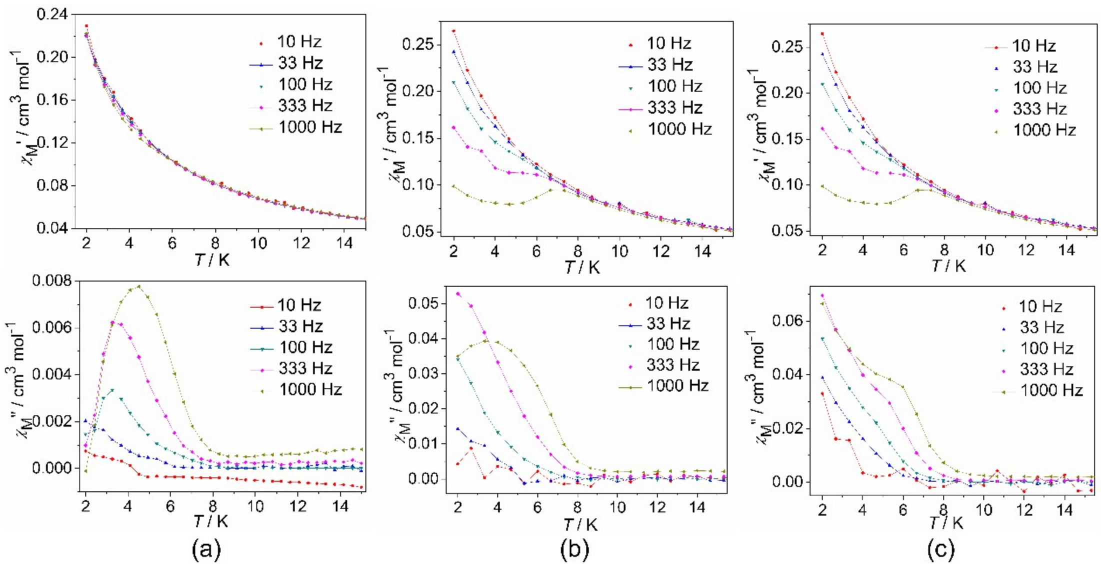


Fig. S8 Temperature dependence of the in-phase (top) and out-phase (bottom) ac susceptibilities at different frequencies with a dc field of 2000 Oe for complexes **1**(a), **2**(b) and **4**(c).

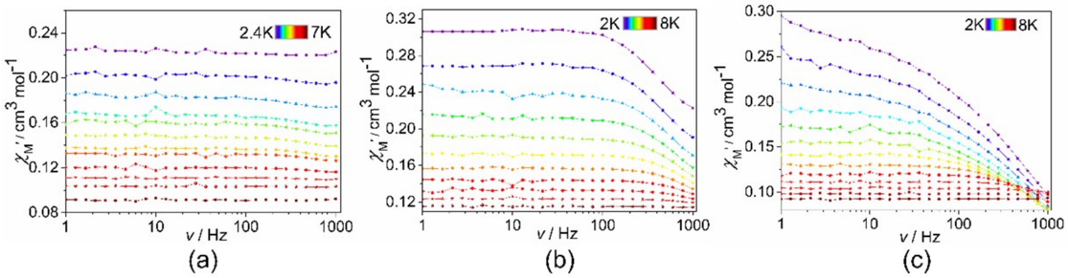


Fig. S9 Frequency dependence of the in-phase ac susceptibility signals for complexes **1**(a), **2**(b) and **4**(c) under a 2000 Oe dc field.

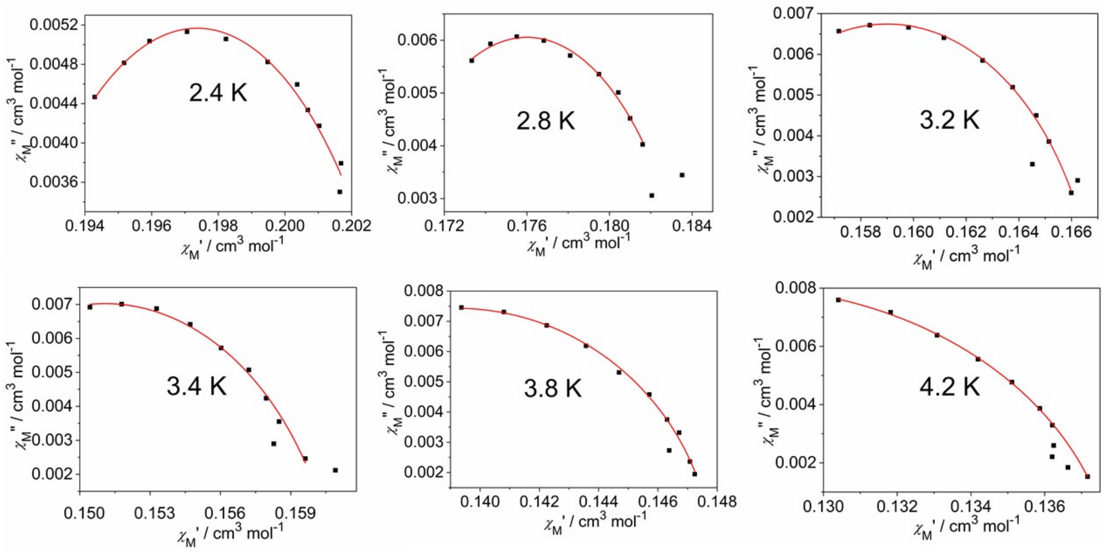


Fig. S10 Cole-Cole plots under 2000 Oe for **1**. The solid lines show the best fitting according to the generalized Debye model.

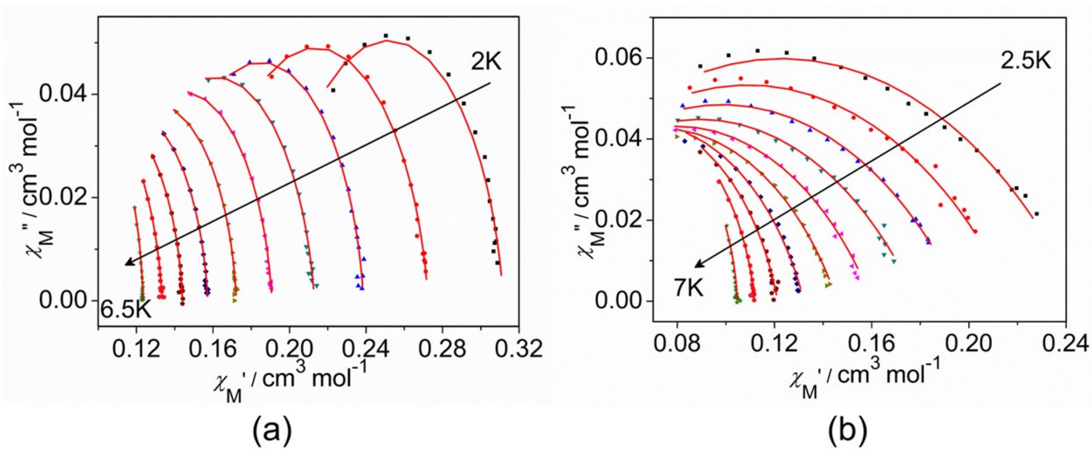


Fig. S11 Cole-Cole plots under 2000 Oe for **2**(a) and **4**(b). The solid lines show the best fitting according to the generalized Debye model.

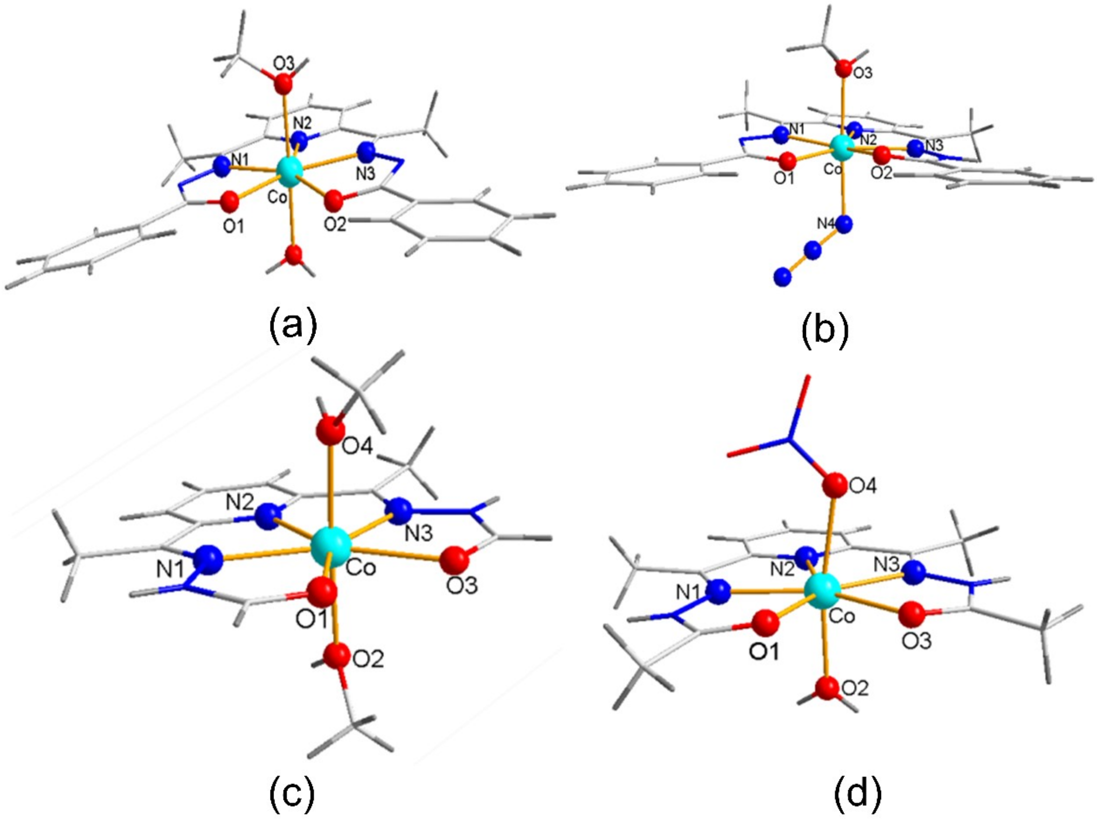


Fig. S12 Calculated complete structure of complexes **1**-**4**.

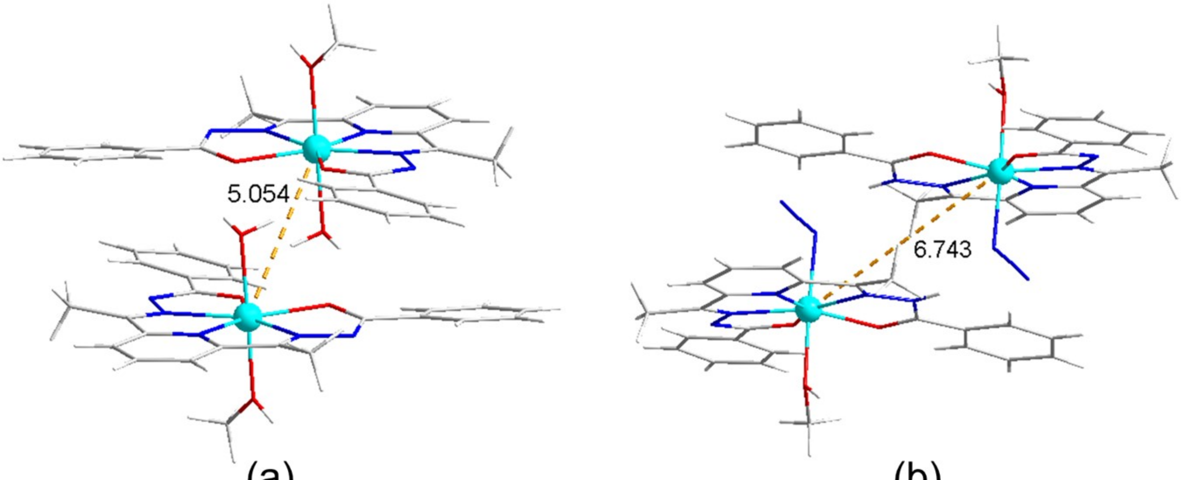


Fig. S13 The molecular structure for **1** (a) and **2** (b).

References

1. D. Shao, S.-L. Zhang, L. Shi, Y.-Q. Zhang, and X.-Y. Wang, *Inorg. Chem.,* 2016 **55**, 10859-10869.
2. A. Mondal, A. K. Kharwar, and S. Konar, *Inorg. Chem.* 2019 **58**, 10686-10693.
3. M. Dey, S. Dutta, B. Sarma, R. C. Deka and N. Gogoi, M. *Chem. Commun.*, 2016, **52**, 753-756.
4. X.-C. Huang, C. Zhou, D. Shao, and X.-Y. Wang, *Inorg. Chem*., 2014 **53**, 12671-12673.
5. B. Drahos ˇ, R. Herchel and Z, *Inorg. Chem.*, 2017, **56**, 5076–5088.
6. J. Wang, H.-H. Cui, Y.-Q. Zhang, L. Chen and X.-T. Chen, *Polyhedron*, 2018, **154**, 148–155
7. H. Lou, L. Yin, B. Zhang, Z.-W. Ouyang, B. Li and Z. Wang, *Inorg. Chem*., 2018, **57**, 7757–7762.