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Supporting information for article:

Crystal structure and spectroscopic characterization of a cobalt(II) tetraazamacrocycle

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Supporting information

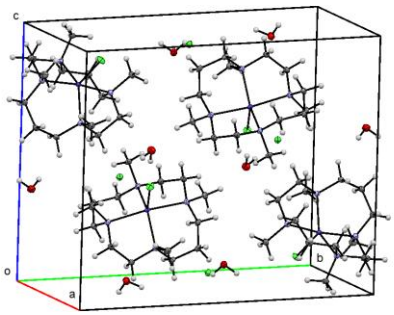

Figure S1 The crystal packing of complex **1**.

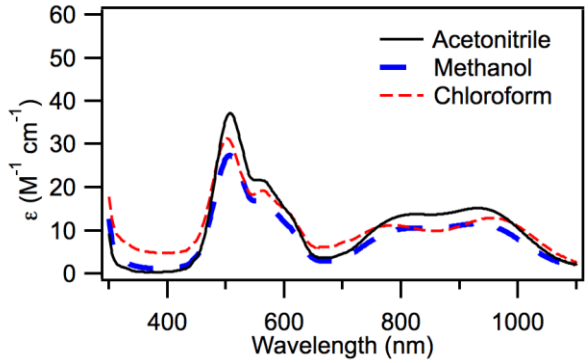

Figure S2 UV-visible spectra of complex **1** collected in acetonitrile (black solid line), methanol (thick blue dashed line), and chloroform (red dashed line).

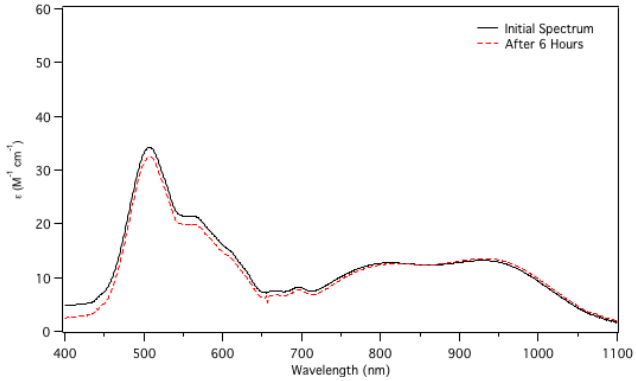

Figure S3 UV-visible spectra of complex **1** in acetonitrile at time point zero (black solid line) and after six hours at room temperature (red dashed line).

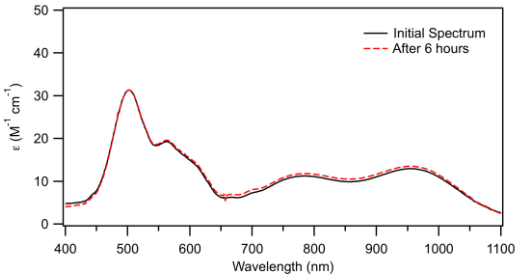

Figure S4 UV-visible spectrum of complex **1** in chloroform at time point zero (black solid line) and after six hours at room temperature (red dashed line).

Table S1 Complete geometric parameters of complex **1** (Å, º)

Cl1—Co1	2.3022 (3)	C12—H12C	0.9800
Co1—N3	2.1066 (8)	N3—C13	1.4877 (12)
Co1—N1	2.1158 (8)	N3—C6	1.4920 (12)
Co1—N2	2.2208 (9)	C6—C7	1.5218 (14)
Co1—N4	2.2427 (9)	C6—H6A	0.9900
N1—C10	1.4880 (13)	C6—H6B	0.9900
N1—C11	1.4883 (13)	C7—C8	1.5217 (14)
N1—C1	1.4953 (13)	C7—H7A	0.9900
C1—C2	1.5204 (14)	C7—H7B	0.9900
C1—H1A	0.9900	C8—N4	1.4937 (13)
C1—H1B	0.9900	C8—H8A	0.9900
C2—C3	1.5218 (14)	C8—H8B	0.9900
C2—H2A	0.9900	C13—H13A	0.9800
C2—H2B	0.9900	C13—H13B	0.9800
C3—N2	1.4934 (12)	C13—H13C	0.9800
C3—H3A	0.9900	N4—C14	1.4832 (13)
C3—H3B	0.9900	N4—C9	1.4880 (12)
C11—H11A	0.9800	C9—C10	1.5164 (14)
C11—H11B	0.9800	C9—H9A	0.9900
C11—H11C	0.9800	C9—H9B	0.9900
N2—C12	1.4828 (13)	C10—H10A	0.9900
N2—C4	1.4856 (12)	C10—H10B	0.9900
C4—C5	1.5152 (14)	C14—H14A	0.9800

C4—H4A	0.9900	C14—H14B	0.9800
C4—H4B	0.9900	C14—H14C	0.9800
C5—N3	1.4919 (12)	O2W—H2W2	0.820 (13)
C5—H5A	0.9900	O2W—H2W1	0.825 (13)
C5—H5B	0.9900	O1W—H1W1	0.869 (13)
C12—H12A	0.9800	O1W—H1W2	0.869 (12)
C12—H12B	0.9800		
N3—Co1—N1	137.57 (3)	H12A—C12—H12B	109.5
N3—Co1—N2	84.26 (3)	N2—C12—H12C	109.5
N1—Co1—N2	92.53 (3)	H12A—C12—H12C	109.5
N3—Co1—N4	91.52 (3)	H12B—C12—H12C	109.5
N1—Co1—N4	83.81 (3)	C13—N3—C5	108.51 (7)
N2—Co1—N4	169.13 (3)	C13—N3—C6	109.67 (7)
N3—Co1—Cl1	112.70 (2)	C5—N3—C6	107.56 (7)
N1—Co1—Cl1	109.71 (2)	C13—N3—Co1	108.07 (6)
N2—Co1—Cl1	96.12 (2)	C5—N3—Co1	107.42 (5)
N4—Co1—Cl1	94.75 (2)	C6—N3—Co1	115.42 (6)
C10—N1—C11	108.94 (8)	N3—C6—C7	115.18 (8)
C10—N1—C1	107.64 (7)	N3—C6—H6A	108.5
C11—N1—C1	109.33 (7)	C7—C6—H6A	108.5
C10—N1—Co1	107.28 (5)	N3—C6—H6B	108.5
C11—N1—Co1	108.64 (6)	C7—C6—H6B	108.5
C1—N1—Co1	114.86 (6)	H6A—C6—H6B	107.5
N1—C1—C2	115.32 (8)	C8—C7—C6	113.94 (8)
N1—C1—H1A	108.4	C8—C7—H7A	108.8
C2—C1—H1A	108.4	C6—C7—H7A	108.8
N1—C1—H1B	108.4	C8—C7—H7B	108.8
C2—C1—H1B	108.4	C6—C7—H7B	108.8
H1A—C1—H1B	107.5	H7A—C7—H7B	107.7
C1—C2—C3	114.11 (8)	N4—C8—C7	114.74 (8)
C1—C2—H2A	108.7	N4—C8—H8A	108.6

C3—C2—H2A	108.7	C7—C8—H8A	108.6
C1—C2—H2B	108.7	N4—C8—H8B	108.6
C3—C2—H2B	108.7	C7—C8—H8B	108.6
H2A—C2—H2B	107.6	H8A—C8—H8B	107.6
N2—C3—C2	114.95 (8)	N3—C13—H13A	109.5
N2—C3—H3A	108.5	N3—C13—H13B	109.5
C2—C3—H3A	108.5	H13A—C13—H13B	109.5
N2—C3—H3B	108.5	N3—C13—H13C	109.5
C2—C3—H3B	108.5	H13A—C13—H13C	109.5
H3A—C3—H3B	107.5	H13B—C13—H13C	109.5
N1—C11—H11A	109.5	C14—N4—C9	107.26 (8)
N1—C11—H11B	109.5	C14—N4—C8	108.50 (8)
H11A—C11—H11B	109.5	C9—N4—C8	108.42 (8)
N1—C11—H11C	109.5	C14—N4—Co1	116.11 (6)
H11A—C11—H11C	109.5	C9—N4—Co1	102.10 (6)
H11B—C11—H11C	109.5	C8—N4—Co1	113.85 (6)
C12—N2—C4	107.79 (8)	N4—C9—C10	110.88 (8)
C12—N2—C3	108.57 (8)	N4—C9—H9A	109.5
C4—N2—C3	108.68 (8)	C10—C9—H9A	109.5
C12—N2—Co1	116.32 (6)	N4—C9—H9B	109.5
C4—N2—Co1	102.02 (6)	C10—C9—H9B	109.5
C3—N2—Co1	112.94 (6)	H9A—C9—H9B	108.1
N2—C4—C5	111.35 (8)	N1—C10—C9	110.97 (8)
N2—C4—H4A	109.4	N1—C10—H10A	109.4
C5—C4—H4A	109.4	C9—C10—H10A	109.4
N2—C4—H4B	109.4	N1—C10—H10B	109.4
C5—C4—H4B	109.4	C9—C10—H10B	109.4
H4A—C4—H4B	108.0	H10A—C10—H10B	108.0
N3—C5—C4	110.45 (8)	N4—C14—H14A	109.5
N3—C5—H5A	109.6	N4—C14—H14B	109.5
C4—C5—H5A	109.6	H14A—C14—H14B	109.5

N3—C5—H5B	109.6	N4—C14—H14C	109.5
C4—C5—H5B	109.6	H14A—C14—H14C	109.5
H5A—C5—H5B	108.1	H14B—C14—H14C	109.5
N2—C12—H12A	109.5	H2W2—O2W—H2W1	103.8 (16)
N2—C12—H12B	109.5	H1W1—O1W—H1W2	101.5 (14)

Table S2 Selected hydrogen-bond parameters for complex **1**.

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
C2—H2A···Cl2^{i}	0.99	2.83	3.7784 (11)	160.3
C3—H3A···Cl2^{ii}	0.99	2.74	3.7054 (11)	166.4
C11—H11C···O1W^{i}	0.98	2.66	3.5203 (13)	147.0
C5—H5A···Cl2^{ii}	0.99	2.76	3.7452 (10)	171.1
C12—H12A···Cl1	0.98	2.77	3.3409 (11)	117.8
C7—H7A···Cl2^{iii}	0.99	2.94	3.6790 (10)	132.3
C8—H8A···O2W^{ii}	0.99	2.66	3.6324 (14)	168.4
C13—H13C···Cl2^{iv}	0.98	2.97	3.7640 (10)	138.4
C9—H9B···O1W^{v}	0.99	2.58	3.4736 (13)	150.1
C10—H10A···O2W^{ii}	0.99	2.54	3.5121 (14)	167.8
C14—H14A···Cl1	0.98	2.70	3.3189 (12)	121.7
O2W—H2W2···Cl2^{vi}	0.820 (13)	2.400 (13)	3.2158 (9)	173.0 (16)
O2W—H2W1···Cl2	0.825 (13)	2.388 (13)	3.2110 (9)	175.4 (15)
O1W—H1W1···Cl1	0.869 (13)	2.393 (13)	3.2568 (9)	173.0 (14)
O1W—H1W2···Cl2	0.869 (12)	2.334 (13)	3.2024 (9)	177.6 (14)

Symmetry code(s): (i) *x*+1, *y*, *z*; (ii) *x*+1, −*y*+3/2, *z*+1/2; (iii) −*x*+1, *y*−1/2, −*z*+3/2; (iv) *x*, −*y*+3/2, *z*+1/2; (v) −*x*+1, −*y*+1, −*z*+1; (vi) −*x*, −*y*+2, −*z*+1.

Table S3 Optimized coordinates for complex **1** (MO6, 6-31G on Co, 3-21G on all other atoms)

Cl	-0.00015800	-0.00045900	2.27102100
Co	0.00003900	0.00007500	0.00275300

N	-1.08108000	-1.81891200	-0.32410700
C	-2.05823700	-1.57029200	-1.44754900
H	-2.54569200	-2.53093200	-1.68638700
H	-1.44570100	-1.23870200	-2.30298300
C	-3.11170000	-0.49921900	-1.16952000
H	-3.70874900	-0.73224800	-0.27921300
H	-3.81368900	-0.53672400	-2.01660200
C	-2.56884200	0.93292300	-1.12940700
H	-1.89198200	1.07128300	-1.98583500
H	-3.40412200	1.65195100	-1.19406300
C	-1.77611800	-2.46427800	0.83761700
H	-2.48832500	-1.76244100	1.27697700
H	-1.04649300	-2.72419800	1.60892200
H	-2.30669100	-3.36953400	0.50481900
N	-1.78383500	1.26000200	0.11947100
C	-1.23500900	2.66243200	0.03289200
H	-0.99303100	2.97451400	1.05610000
H	-2.01511700	3.33832300	-0.35304000
C	-0.00155700	2.73035200	-0.84978500
H	-0.24009300	2.38769600	-1.86507200
H	0.38156400	3.76180800	-0.89806900
C	-2.71350700	1.21417400	1.30034700
H	-2.18002100	1.54713200	2.19320900
H	-3.05314700	0.19089000	1.46962100
H	-3.58144300	1.86572300	1.11428800
N	1.08092200	1.81889800	-0.32389300
C	2.05825300	1.57055800	-1.44724900
H	2.54570700	2.53128100	-1.68574500
H	1.44585200	1.23919500	-2.30288100

C	3.11178600	0.49948900	-1.16944200
H	3.81368500	0.53718600	-2.01658900
H	3.70892600	0.73242300	-0.27917400
C	2.56900700	-0.93267800	-1.12948100
H	1.89216800	-1.07094900	-1.98593300
H	3.40429700	-1.65168000	-1.19420500
C	1.77584800	2.46382300	0.83815000
H	2.48768600	1.76169700	1.27766500
H	1.04608400	2.72392400	1.60926400
H	2.30679700	3.36897400	0.50563900
N	1.78396800	-1.25982000	0.11935300
C	1.23499100	-2.66220700	0.03268400
H	0.99286300	-2.97421900	1.05586900
H	2.01510600	-3.33815400	-0.35314300
C	0.00163300	-2.73009600	-0.85009600
H	0.24019300	-2.38716900	-1.86527700
H	-0.38130600	-3.76162400	-0.89864700
C	2.71367300	-1.21436100	1.30023300
H	2.17991500	-1.54670900	2.19316200
H	3.05408500	-0.19127300	1.46919500

Table S4 Calculated energies used to determine the theoretical ground state configuration.

Functional	Basis Set (M, all other atoms)	Energy of S=3/2 State (kcal/mol)	Energy of S=1/2 State (kcal/mol)	Energy Difference (kcal/mol)
M06	6-31G, 3-21G	-1636363.3	-1636351.9	-11.4
M06	6-311G(d), 6-31G(d)	-1640238.6	-1640225.9	-12.7
M06	def2tzvpp, def2(svp)	-1639884.1	-1639870.0	-14.1

BP86	6-31G, 3-21G	-1636750.1	-1636747.6	-2.5
BP86	6-311G(d), 6-31G(d)	-1640785.1	-1640784.9	-0.2
BP86	def2tzvpp, def2(svp)	-1640430.1	-1640428.5	-1.6
PBEPBE	6-31G, 3-21G	-1635691.6	-1635687.7	-3.9
PBEPBE	6-311G(d), 6-31G(d)	-1639720.6	-1639719.5	-1.1
PBEPBE	def2tzvpp, def2(svp)	-1639369.0	-1639366.0	-3.0
B3LYP	6-31G, 3-21G	-1636638.0	-1636625.7	-12.4
B3LYP	6-311G(d), 6-31G(d)	-1640673.7	-1640663.9	-9.8
B3LYP	def2tzvpp, def2(svp)	-1640312.6	-1640300.9	-11.7
$[Co(13\text{-}TMC)(MeCN)]^{2+}$				
M06	6-31G, 3-21G	-1407059.7	-1407062.4	2.7