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Supporting Information

Synthesis, Characterization, and Reactivity of Cobalt(III)–Oxygen Complexes Bearing a Macrocyclic N-Tetramethylated Cyclam Ligand

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Table S1. Crystal data and structure refinements for $[Co(15\text{-}TMC)(CH_3CN)_2](ClO_4)_2$ and $[Co(15\text{-}TMC\text{-}CH_2\text{-}O)(OH)](ClO_4)\cdot CH_3CN$.

	$[Co(15\text{-}TMC)(CH_3CN)_2](ClO_4)_2$	$[Co(15\text{-}TMC\text{-}CH_2\text{-}O)(OH)](ClO_4)\cdot CH_3CN$
Empirical formula	$C_{19}H_0Cl_2CoN_6O_8$	$C_{17}H_{37}ClCoN_5O_6$
Formula weight	570.08	501.90
Temperature (K)	170(2)	170(2)
Wavelength (Å)	0.71073	0.71073
Crystal system/space group	Monoclinic, *P2(1)/n*	Monoclinic, *P2(1)/c*
Unit cell dimensions		
a (Å)	8.6493(8)	9.6291(3)
b (Å)	15.6174(13)	19.6761(6)
c (Å)	10.7612(9)	12.0095(4)
α (º)	90.00	90.00
β (º)	111.2190(10)	98.974(2)
γ (º)	90.00	90.00
Volume (Å^3)	1355.1(2)	2247.51(12)
Z	2	4
Calculated density (g/cm^{-3})	1.397	1.483
Absorption coefficient (mm^{-1})	0.880	0.925
Reflections collected	7479	29048
Independent reflections [*R*(int)]	2636 [0.1214]	4263 [0.0349]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2636/0/179	4263/0/276
Goodness-of-fit on F^2	1.080	1.104
Final *R* indices [$I > 2\text{sigma}(I)$]	$R_1 = 0.0865$, $wR_2 = 0.2603$	$R_1 = 0.0699$, $wR_2 = 0.2470$
R indices (all data)	$R_1 = 0.0941$, $wR_2 = 0.2671$	$R_1 = 0.0875$, $wR_2 = 0.2671$
Largest difference peak and hole (e/Å^3)	1.282 and –1.048	0.941 and –0.612

Table S2. Selected bond distances (Å) and angles (º) for $[Co(15\text{-}TMC)(CH_3CN)_2](ClO_4)_2$ and $[Co(15\text{-}TMC\text{-}CH_2\text{-}O)(OH)](ClO_4)\cdot CH_3CN$.

Bond Distances (Å)			
$[Co(15\text{-}TMC)(CH_3CN)_2](ClO_4)_2$		$[Co(15\text{-}TMC\text{-}O)(OH)](ClO_4)\cdot CH_3CN$	
Co1-N1	2.216(4)	Co1-N1	1.988(5)
Co1-N2	2.225(4)	Co1-N2	2.125(5)
Co1-N3	2.165(5)	Co1-N3	2.089(4)
		Co1-N4	2.082(5)
		Co1-O1	1.896(3)
		Co1-O2	1.878(4)
Bond Angles (°)			
$[Co(15\text{-}TMC)(CH_3CN)_2](ClO_4)_2$		$[Co(15\text{-}TMC\text{-}O)(OH)](ClO_4)\cdot CH_3CN$	
N1-Co1-N2	89.40(19)	N1-Co1-N2	91.1(2)
N1-Co1-N3	91.56(18)	N1-Co1-N3	171.10(18)
N2-Co1-N3	88.44(18)	N1-Co1-N4	85.0(2)
		N2-Co1-N3	92.0(2)
		N2-Co1-N4	175.5(2)
		N3-Co1-N4	92.2(2)
		N1-Co1-O1	74.04(18)
		N2-Co1-O1	91.24(16)
		N3-Co1-O1	97.56(16)
		N4-Co1-O1	89.87(15)
		N1-Co1-O2	100.09(19)
		N2-Co1-O2	85.73(18)
		N3-Co1-O2	88.46(17)
		N4-Co1-O2	92.71(17)
		Co1-O1-C1	92.7(3)
		O1-Co1-O2	173.36(17)

Table S3. Co-K Pre-edge analysis for **1**, **2**, and **3**.

	Pre-edge (1s→3d) (eV)[a]	Co K rising-edge (eV)[b]
1	7709.3(0.04)[c]	7720.4
2	7710.2(0.02)	7721.2
3	7710.2(0.02)	7721.0

[a]Intensity weighted average energy of pre-edge multiplet features. [b]Energy position of first inflection point. [c]Values in parentheses are the statistical standard deviations calculated from the individual acceptable fits used in the analysis. Fits performed using Edg-Fit (a peak fitting routine in EXAFSPAK, reference 6)

Table S4. EXAFS least squares fitting results for **2** and **3**.

Complex	Coordination/Path	R(Å)[a]	σ^2(Å^2)[b]	E_0 (eV)	F[c]
2	2 Co-O	1.89	154	-1.88	0.18
	4 Co-N	2.07	809		
	1 Co-N	2.40	784		
	8 Co-C[d]	2.94	1150		
	16 Co-C-N[d]	3.23	/1150		
	4 Co-C	3.49	340		
3	1 Co-O	1.86	176	-4.8	0.13
	4 Co-N	2.04	742		
	1 Co-N	2.19	164		
	8 Co-C	3.04	1851		
	16 Co-C-N	3.32	/1851		
	4 Co-C	3.47	644		
	2 Co-C-N	3.25	342		
	1 Co-C-N-C	/3.25	/342		

[a]The estimated standard deviations for the distances are in the order of ± 0.02 Å. [b]The σ^2 values are multiplied by 10^5. [c]Error is given by $\Sigma[(\chi_{obsd} - \chi_{calcd})^2 k^6]/\Sigma[(\chi_{obsd})^2 k^6]$. / indicates the σ^2 value for the path is linked to the preceding path. The S_0^2 factor was set at 1.

Table S5. Kinetic data obtained in the conversion of **3** (4.0 mM) to **4** performed with different amounts of $HClO_4$.

Amount of $HClO_4$	k_{obs}, s^{-1}
40 mM	$3.9(4) \times 10^{-3}$
120 mM	$3.9(3) \times 10^{-3}$
240 mM	$4.0(3) \times 10^{-3}$

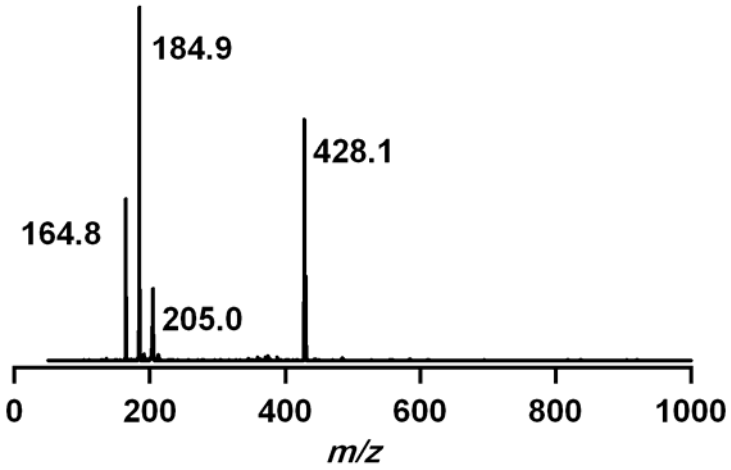

Figure S1. ESI MS of **1** in CH_3CN: Mass peaks at *m/z* of 164.8, 184.9, 205.0, and 428.1 are assigned to $[Co(15\text{-}TMC)]^{2+}$, $[Co(15\text{-}TMC)(CH_3CN)]^{2+}$, $[Co(15\text{-}TMC)(CH_3CN)_2]^{2+}$, and $[Co(15\text{-}TMC)(ClO_4)]^{+}$, respectively.

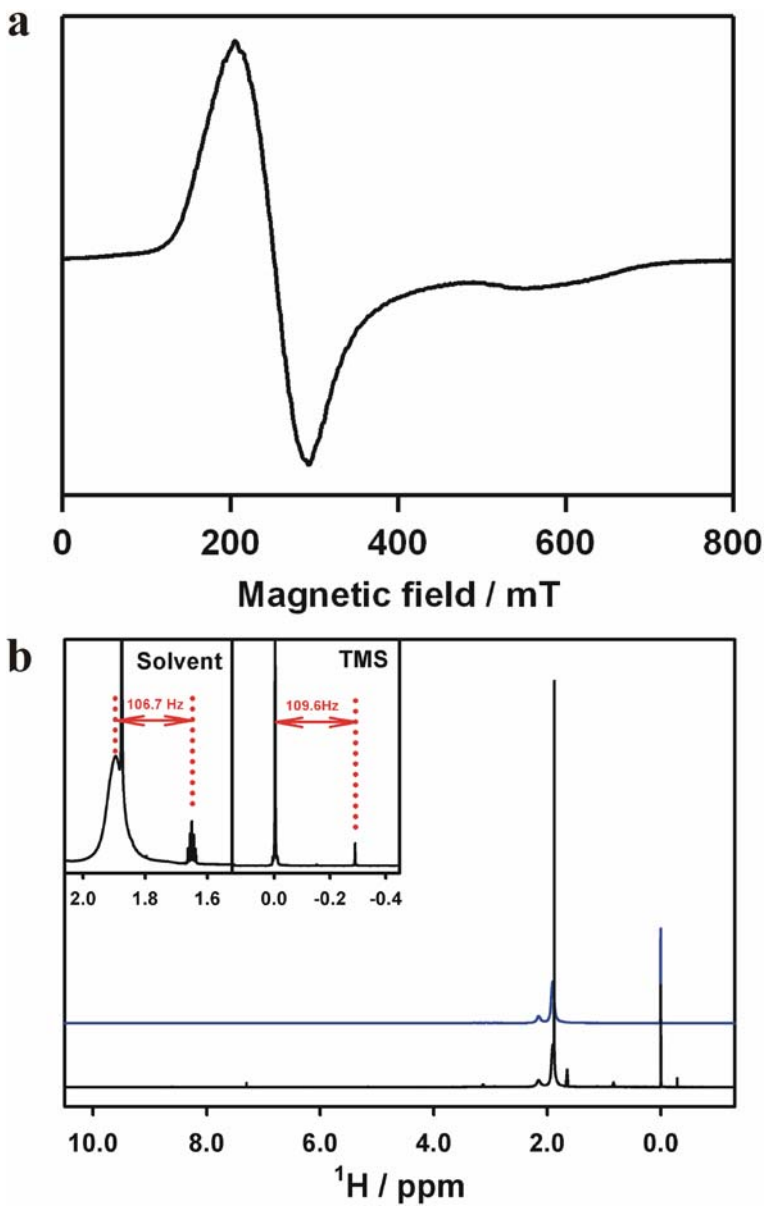

Figure S2. (a) X-band EPR spectrum of **1** (*g* values of 4.6 and 2.3) in frozen CH_3CN at 4.3 K. Instrumental parameters: microwave power = 1.0 mW, frequency = 9.101 GHz, sweep width = 0.5 T, modulation amplitude = 0.2 mT. (b) ^{1}H NMR spectra of **1** (8.0 mM) with common (blue) and Evans (black) techniques at 298 K. Insets show that the $\Delta\nu$ values of solvent and TMS peaks were 106.7 and 109.6 Hz, respectively. The magnetic moment of **1** determined to be 4.4(2) B.M. from both $\Delta\nu$ values indicates spin state of $S = 3/2$ for **1**.

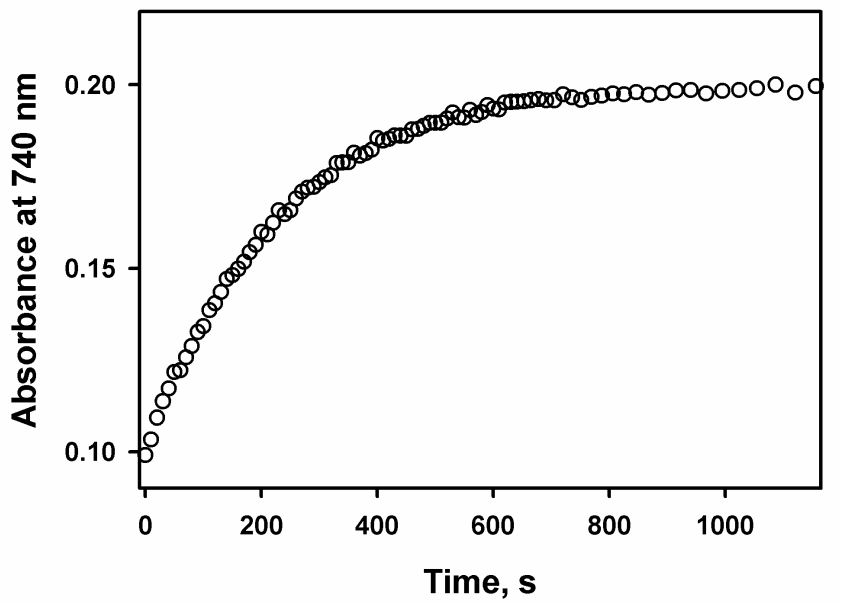

Figure S3. Time trace monitored at 740 nm in the conversion of **3** to **4** in CH_3CN at 0 ^oC.

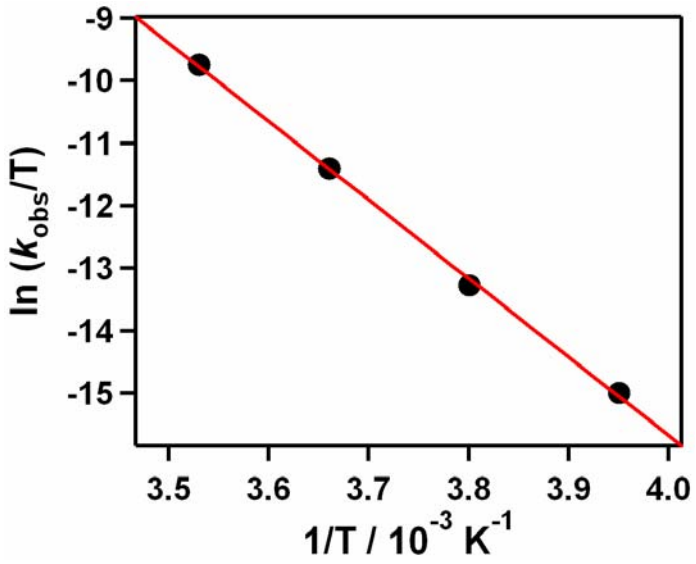

Figure S4. Plot of first-order rate constants against 1/*T* to determine activation parameters for the conversion of **3** to **4**.