Electronic Supplementary Material (ESI) for Chemical Science

– Supporting Information –

Proton-Coupled Electron Transfer at a $[Co\text{-}OH_x]^z$ Unit in Aqueous Media: Evidence for a Concerted Mechanism

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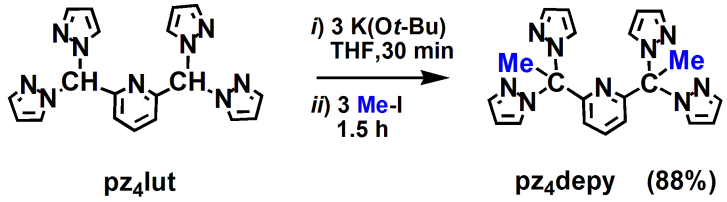
Experimental Section

Materials. Reagents (including those used in the preparation of buffer solutions) were purchased from Sigma Aldrich or Alfa Aesar and used as received unless otherwise noted. All solutions for electrochemical studies were prepared from Milli-Q water with a solution resistance of 18.2 MΩ. D_2O was obtained from Cambridge Isotope Laboratories.

Synthesis. The ligand pz_4lut was prepared as previously described,[1] but purification by column chromatography on neutral Al_2O_3 required ethyl acetate as the eluent (R_f = 0.7) rather than Et_2O (R_f = 0.15).[2,3] The complexes $[Co(H_2O)_6](OTs = p\text{-}O_3SC_6H_4CH_3)_2$ and $[Co(H_2O)(\mathbf{PY5})](ClO_4)_2$, $[\mathbf{1}](ClO_4)_2$, were prepared by literature procedures.[4-6]

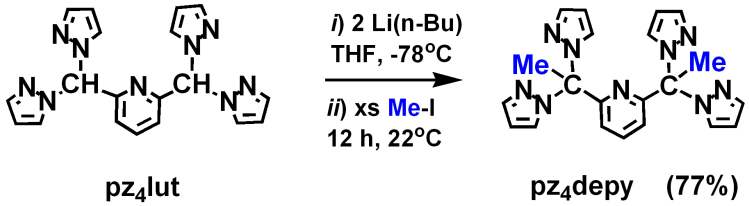
Ligand:

Method A.



pz_4lut pz_4depy (88%)

Method B.

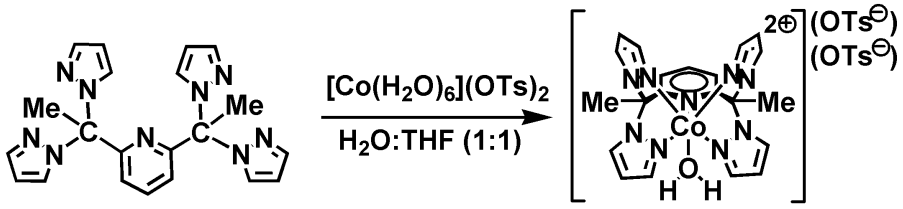


pz_4lut pz_4depy (77%)

Method A. Under a nitrogen blanket, a solid portion of 0.682 g (6.08 mmol) K(Ot-Bu) was added to a solution of 0.752 g (2.02 mmol) pz_4lut in 25 mL THF. The reaction mixture became orange immediately upon mixing and was allowed to stir at room temperature for 30 min. Then, 0.38 mL (0.86 g, 6.1 mmol) CH_3I was added by syringe whereupon a colorless precipitate formed. After the reaction mixture had been stirred for an additional 90 min, 25 mL each of water and Et_2O were added sequentially. The organic and aqueous layers were separated. The aqueous layer was extracted with two 25 mL portions Et_2O. The combined organic fractions were dried over $MgSO_4$, filtered, and solvent

was removed to leave a colorless solid with a trace of yellow oil. The yellow oil was by removed trituration with 5 mL Et_2O, decanting the yellow solution, and drying the colorless solid at room temperature under vacuum for 30 min. Yield: 0.710 g (88 % based on pz_4lut).

Method B. A 5.05 mL aliquot of Li^{n}Bu (1.6 M in hexane, 8.08 mmol) was added to a cold (-78^{o}C) solution of 1.50 g (4.04 mmol) of pz_4lut in 40 mL THF affording a red brown solution. After the solution had been stirred for 30 min, 1 mL (2.28 g, 16.1 mmol) iodomethane was added, the external cold bath was removed, and the reaction mixture was stirred at room temperature for 12 h. Next, 50 mL each of water and CH_2Cl_2 were carefully added and the organic fraction was separated. The aqueous fraction was extracted twice more with 50 mL aliquots of CH_2Cl_2. The combined organic fractions were dried over $MgSO_4$, filtered and solvent was removed by vacuum distillation. The resulting oily residue was purified by column chromatography on silica using Et_2O as an eluent. The desired product elutes in the first major band after the solvent front (R_f 0.55 on a silica plate). Evaporation of solvent, trituration of the waxy solid with minimal Et_2O, and drying under vacuum for 30 min afforded 1.242 g (77%) of the desired product as a fluffy, colorless powder. Mp, 157-159°C. Anal. Calcd. (obsd.) for $C_{21}H_{21}N_9$: C, 63.14 (63.17); H, 5.30 (5.10); N, 31.56 (31.50). ^{1}H NMR ($CDCl_3$): δ 7.65 (t, J = 7.8 Hz, 1H, H_4-py), 7.61 (d, J = 2Hz, 4H, H_3-pz), 7.13 (d, J = 1 Hz, 4H, H_5-pz), 6.45 (d, J = 7.8 Hz, 2H, $H_{3,5}$-py), 6.27 (dd, J = 1; 2Hz, 4H, H_4-pz), 2.65 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 159.1, 140.3, 138.5, 129.6, 121.1, 106.1, 82.5, 26.4. UV-Vis (CH_3CN) λ_{max}, nm (ε, $M^{-1}cm^{-1}$): 212 (35,000), 263 (6,500).



[**2**](OTs)$_2$·2H$_2$O

[Co(H$_2$O)(pz$_4$depy)](OTs)$_2$·xH$_2$O, [**2**](OTs)$_2$·**2H$_2$O.** A colorless solution of 0.252g (0.631 mmol) pz_4depy in 5 mL THF was added via cannula transfer to a pink solution of 0.291 g (0.630 mmol) $[Co(H_2O)_6](OTs)_2$ in 5 mL de-ionized H_2O, which gave a yellow solution upon complete mixing. After stirring 5 min, solvents were removed under vacuum via rotary evaporation. The resulting orange solid was triturated with hot acetone to give a pale yellow powder of the desired product that was isolated after decanting the acetone solution and drying the remaining solid under vacuum. The pale yellow

solid was recrystallized by dissolution in minimal (ca. 2 mL) H_2O and allowing the solution to cool to room temperature over the course of several hours. In this way, large yellow crystals of **2**·3H_2O suitable for X-ray diffraction are obtained. Drying the crystals under vacuum causes the crystals to desolvate and shatter into 0.372g (69% based on cobalt) of [**2**](OTs)$_2$·2H_2O as a pale orange powder.

Mp, 135 – 137 ºC (decomp. to orange residue with apparent gas evolution). Anal. Calcd. (obsd.) for [**2**](OTs)$_2$·2H_2O, $C_{35}H_{41}CoN_9O_9S_2$: C, 49.17 (49.27); H, 4.83 (4.45); N, 14.75(14.72). μ_{eff} (solid, 297 K): 4.4 ± 0.1 μ_B. UV-Vis (H_2O) λ_{max}, nm (ε, $M^{-1}cm^{-1}$): 221 (51,200), 262 (5,600), 458 (28), 508 sh (11), 862 (6), 935 (6).

Crystallographic Structure Determinations

X-ray intensity data from a yellow plate of **2**·2H_2O were collected at 101.1 K with an Oxford Diffraction Ltd. Supernova diffractometer equipped with a 135 mm Atlas CCD detector using Cu(Ka) radiation. Raw data frame integration and Lp corrections were performed with CrysAlis Pro (Oxford Diffraction, Ltd.).[7] Final unit cell parameters were determined by least-squares refinement of 10696 reflections from the data set of **2**·3H_2O with I > 2σ(I). Analysis of the data showed negligible crystal decay during collection in each case. Direct methods structure solutions, difference Fourier calculations and full-matrix least-squares refinements against F^2 were performed with SHELXL-97.[8] .A numerical absorption correction based on gaussian integration over a multifaceted crystal model was applied to the data. The structure contains several symmetry-inequivalent moieties in the asymmetric unit, including: two dications, four anions, and six solvated water molecules. There is extensive disorder of the anions and three of the solvate water molecules partially populated among at least two positions each. The carbon atoms of disordered *p*-toluenesulfonate ions were refined isotropically. All other non-hydrogen atoms were refined with anisotropic displacement parameters. Since the positions of hydrogen atoms on the partially occupied disordered water molecules could not be satisfactorily modeled, they were omitted from the refinement. All other hydrogen atoms were placed in geometrically idealized positions and were included as riding atoms.

Electrochemical Methods. Electrochemical measurements were recorded using Milli-Q H_2O (R = 18.2 MΩ) with a CH Instruments 660D potentiostat; a CH Instruments glassy carbon working electrode (area = 0.071 cm2) or a ALS glassy carbon ultramicorelectrode (area = 8.6 × 10^{-6} cm^2), a Pt wire counter electrode; and a CH Instruments Ag/AgCl reference electrode, calibrated against both a commercial (PAR K0077) saturated calomel electrode (SCE) and against the $[Fe^{III}(CN)_6]^{3-}/[Fe^{II}(CN)_6]^{2-}$ redox

couple in 1 M $HClO_4$ (0.72 V vs NHE).[4] Potentials reported herein are referenced to a normal hydrogen electrode (NHE) according to the calibration. The glassy carbon working electrode was polished between each pH measurement with an alumina slurry (0.05 micron particle size) on a felt mesh to achieve a mirror finish and thoroughly rinsed with water and left to air dry. Several polishing trials were repeated at each pH to ensure reasonably reproducible voltammograms were being recorded. Pourbaix diagrams for **1** – **3** were recorded in 0.1 M Britton-Robinson buffer due to the near linear response of pH to titration volume for this buffer system. Values for the formal potentials ($E°'$) for **1** – **3** were recorded at a scan rate of 0.05 V s^{-1}.

Scan rate dependent studies were conducted at scan rates ranging from 0.02 – 1 Vs^{-1} for complexes **1** and **2** using the CH Instruments glassy carbon electrode (area = 0.071 cm^2). Typically, 5 – 10 scan rates were averaged at a single pH value to obtain the reported value of k_S. The electron transfer was sufficiently sluggish such that relatively slow scan rates could be used and complications in measured potentials arising from solution resistance are negligible (< 3 mV). However, complex **3** displayed much faster kinetics, and therefore the use of an ultramicroelectrode was necessary because higher scan rates (1 – 500 Vs^{-1}) were needed in order to observe appreciable ΔE_p values. Solution resistance was determined to be negligible under our conditions and *iR* compensation had no observable effect on the voltammograms. Buffer solutions were used to achieve the various pH ranges; *i.e.*, an acetate buffer (0.1 M) solution at pH < 6, a phosphate buffer at pH 6-10, and borate buffer at pH 10-12. The pH was adjusted by adding aliquots of 5 M KOH or 5 M HNO_3 prepared from Milli-Q H_2O. Satisfactory reproducibility was not observed in the kinetic experiments using the Britton-Robinson buffer. An example of scan-rate dependent data for **1** is shown below (Table S2) at pH 7.03 in phosphate buffer. Values of k_S were approximated based on Equation 4 in the text of the manuscript.

Table S1. Crystallographic data collection and structure refinement for **2**·3H_2O.

Compound	**2**·3H_2O
Formula	$C_{35}H_{40}CoN_9O_{10.02}S_2$
Formula weight	870.21
Crystal system	monoclinic
Space group	P 2/c
Temp. [K]	101.1
a [Å]	30.9019(10)
b [Å]	12.4380(3)
c [Å]	21.0739(6)
α[°]	90.00
β[°]	108.631(4)
γ [°]	90.00
V [Å^3]	7675.4(4)
Z	8
$D_{calcd.}$ [gcm^{-3}]	1.506
λ [Å] (Cu Kα)	1.5418
μ.[mm^{-1}]	5.119
Abs. Correction	numerical
F(000)	3618
2θ range [°]	7.10 to 148.00
Reflections collected	42973
Independent reflections	15195[R(int) = 0.0322]
T_min/max	0.556/0.787
Data/restraints/ parameters	15195/94/1214
Goodness-of-fit on F^2	1.017
$R1/wR2[I>2\sigma(I)]$[a]	0.0536/0.1322
$R1/wR2$ (all data)[a]	0.0688/0.1428
Largest diff. peak/hole / e Å^{-3}	0.877/-0.656

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$ $wR2 = [\Sigma w(|Fo| - |Fc|)2/\Sigma w|Fo|2]^{1/2}$.

Table S2. Example of determined values of k_S for **1** at pH 7.03 in phosphate buffer.

v (mV s^{-1})	E_{pa} (V vs Ag/AgCl)	E_{pc} (V vs Ag/AgCl)	$v^{1/2}$ (x 10^3 $V^{1/2}$ $s^{-1/2}$)	ΔE_p (V)	k_S (× 10^{-3} cm s^{-1})
20	0.120	0.002	0.141	0.118	0.853
30	0.120	0.005	0.173	0.115	1.14
40	0.121	0.001	0.200	0.120	1.09
50	0.128	-0.008	0.224	0.136	1.17
60	0.130	-0.008	0.245	0.138	1.06
70	0.133	-0.016	0.265	0.149	1.14
80	0.133	-0.021	0.283	0.154	1.07
90	0.139	-0.027	0.300	0.166	1.08
100	0.140	-0.032	0.316	0.172	1.00
150	0.147	-0.046	0.387	0.193	0.99
200	0.152	-0.061	0.447	0.213	0.97
				average k_S (one std dev)	1.04(1)

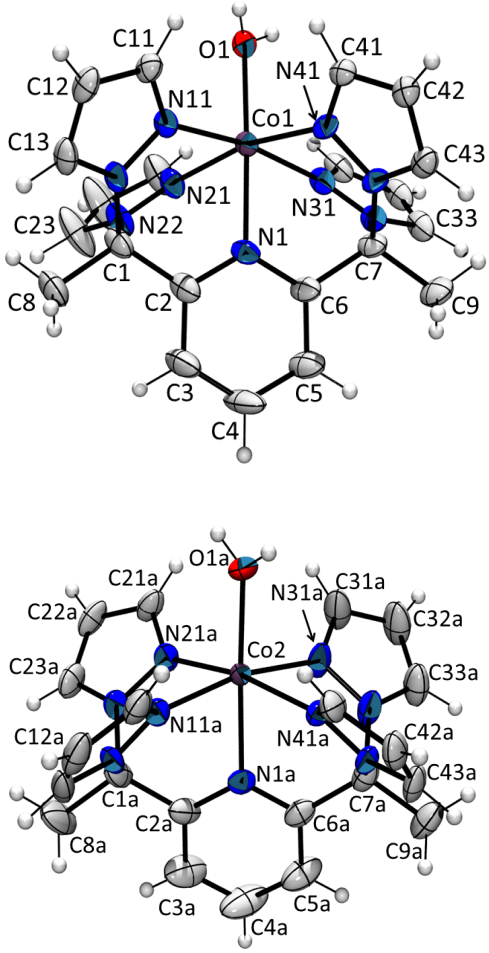


Figure S1. View the two dications in $[Co(H_2O)(pz_4depy)](OTs)_2 \cdot 3H_2O$, **2**$\cdot 3H_2O$. Selected bond distances (Å): Co1-O1, 2.044(2); Co1-N1, 2.132(2); Co1-N11, 2.091(2); Co1-N21, 2.102(2); Co1-N31, 2.101(2); Co1-N41, 2.101(2). Co2-O1a, 2.032(3); Co2-N1a, 2.135(2); Co2-N11a, 2.094(2); Co2-N21a, 2.098(2); Co2-N31a, 2.100(3); Co2-N41a, 2.096(2). Selected interatomic angles (°): O1-Co1-N1, 178.18(9); N11-Co1-N31, 170.05(10); N21-Co1-N41, 166.83(10); N11-Co1-N21, 85.08(9); N21-Co1-N31, 93.75(9); N31-Co1-N41, 84.82(9); N41-Co1-N11, 93.41(9); N1-Co1-N11, 85.23(9); N11-Co1-O1, 93.35(9); O1a-Co2-N1a, 177.60(10); N11a-Co2-N31a, 168.46(12); N21a-Co2-N41a, 169.65(10); N11a-Co2-N21a, 84.39(10); N21a-Co2-N31a, 95.67(11); N31a-Co2-N41a, 84.61(11); N41a-Co2-N11a, 93.27(10); N1a-Co2-N11a, 84.78(10); N11a-Co2-O1a, 96.27(12).

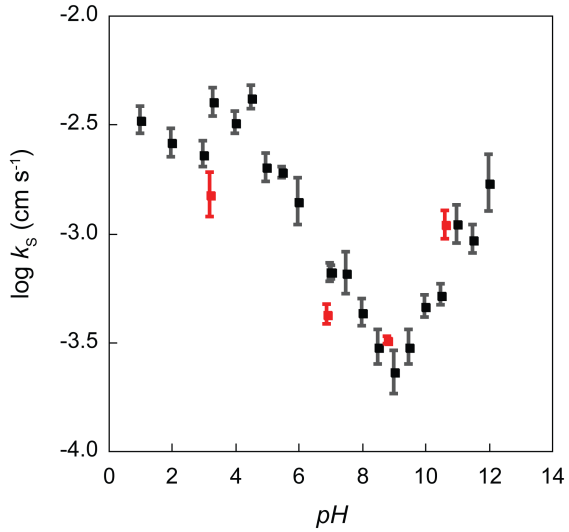


Figure S2. Data from Figure 5 showing values of log(k_S) as a function of pH for $[Co^{II}(\mathbf{PY5})(OH_2)]^{2+}$ (**1**) as a function of solution pH in buffered H_2O (black) and D_2O (red) with error bars representing one standard deviation.

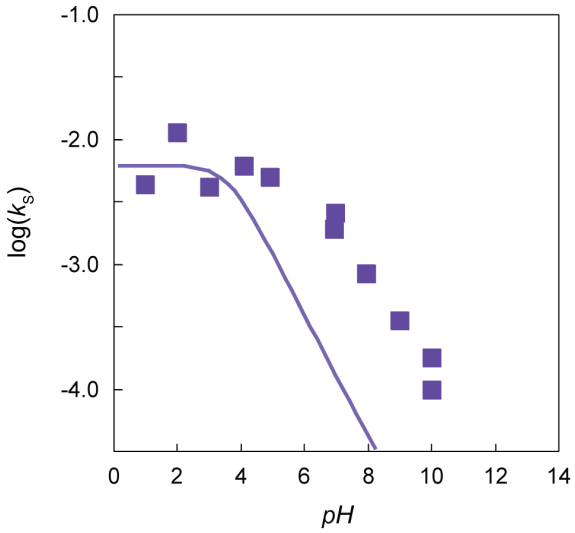


Figure S3. Variation of k_S for the Co(III)/Co(II) redox couple of $[Co^{II}(\mathbf{pz_4depy})(OH_2)]^{2+}$ (**2**) as a function of solution pH. Experimental data (purple squares) and predicted values of log(k_S) based on the step-wise mechanism corresponding to Eqs 1-3 from the manuscript (purple line) are shown.

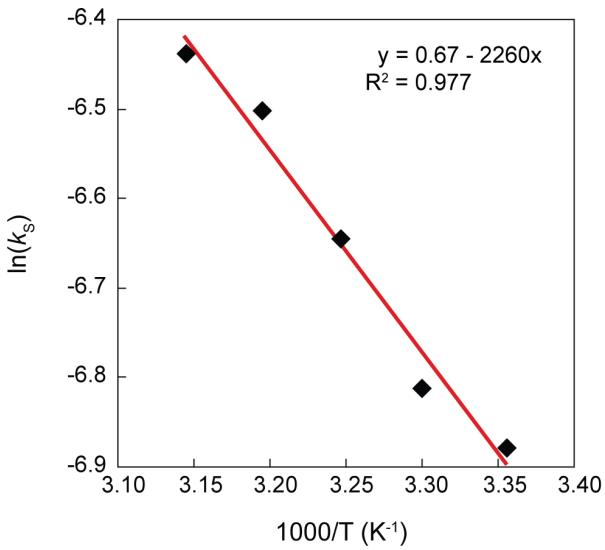


Figure S4. Arrhenius plot ($\ln(k_S)$ *vs* 1000/T) taken between 25 and 60 C° of **1** at pH 7, yielding a value for ΔG^* of 19 kJ mol^{-1} or $\lambda = 0.25$ eV from the equation $\ln(k_S) = \ln(Z^{het}) - (\lambda/4RT)$ where λ is the apparent reorganization energy; Z^{het} is the heterogeneous pre-exponential factor; R is the gas constant; and T is the absolute temperature.[9]

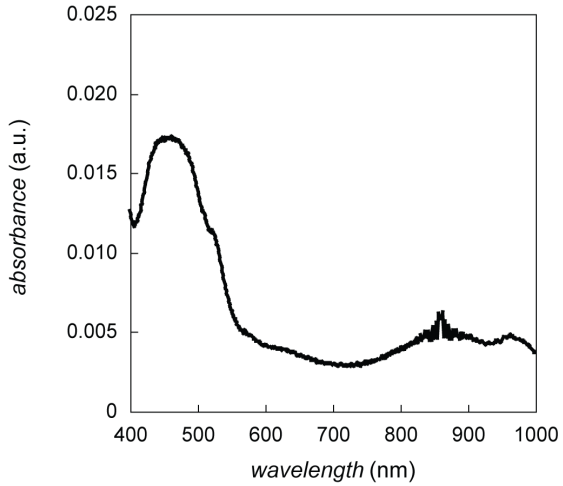


Figure S5. UV-vis spectrum of **1** (2.0 mM) in MeOH. Note solubility of **1** in neat water is limited to ~0.5 mM prompting us to record the data in MeOH.

References

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– SECTION 2; Computational Details –

Calculations.

DFT calculations were performed with the M06 meta-hybrid GGA functional[40] using the Def2-SV(P) double-zeta basis set.[41] Solvent (H_2O) effects were accounted for by using the polarizable continuum model IEFPCM,[42] as implemented in Gaussian 09.[43] The chosen model proved superior over other combinations of functionals (M06 or B3LYP[44]) and basis sets (Def2-SV(P) or 6311-G*/LANL2DZ[45]) for reproducing bond distances and spectroscopic data. Analytical vibrational frequency calculations were also carried out to verify that the optimized geometries were stationary points.

Table S3. Summary of SCF energies and thermochemical data from theoretical calculations (M06/Def2-SV(P)).

		L1 = PY5				L2 = pz_4depy			
	H^+	$L1Co^{II}(H_2O)$	$L1Co^{III}(H_2O)$	$L1Co^{II}(OH)$	$L1Co^{III}(OH)$	$(L2)Co^{II}(H_2O)$	$(L2)Co^{III}(H_2O)$	$(L2)Co^{II}(OH)$	$(L2)Co^{III}(OH)$
E_{SCF}(hartree)	-0.164564	-3000.75073	-3000.538644	-3000.29184	-3000.123156	-2762.349408	-2762.147122	-2761.884089	-2761.723628
E_{SCF}(kcal/mol)	-103.2653911	-1882998.09	-1882865.004	-1882710.132	-1882604.281	-1733399.115	-1733272.178	-1733107.123	-1733006.432
E_{SCF}(eV)	-4.477901635	-81652.52789	-81646.75688	-81640.04117	-81635.45116	-75165.46104	-75159.95669	-75152.79938	-75148.43312
E+ZPE	-0.163147	-3000.234691	-3000.018283	-2999.788765	-2999.615537	-2761.911796	-2761.70565	-2761.45842	-2761.294565
H (hartree)	-0.162203	-3000.201493	-2999.986654	-2999.756903	-2999.584502	-2761.884024	-2761.679828	-2761.43142	-2761.269169
G (hartree)	-0.174563	-3000.296442	-3000.075269	-2999.848302	-2999.672126	-2761.967829	-2761.756168	-2761.514698	-2761.345457
G (kcal/mol)	-109.5398536	-1882713.02	-1882574.232	-1882431.808	-1882321.256	-1733159.67	-1733026.851	-1732875.327	-1732769.126
G (eV)	-4.749981424	-81640.16639	-81634.14812	-81627.97219	-81623.17832	-75155.078	-75149.31856	-75142.74799	-75138.14283

Figure S6. Free energy diagram for various species associated with PCET events associated with $[(PY5)Co(OH_x)]^{n+}$ (green) and $[(pz_4depy)Co(OH_x)]^{n+}$ (red) from theoretical calculations (M06/Def2-S

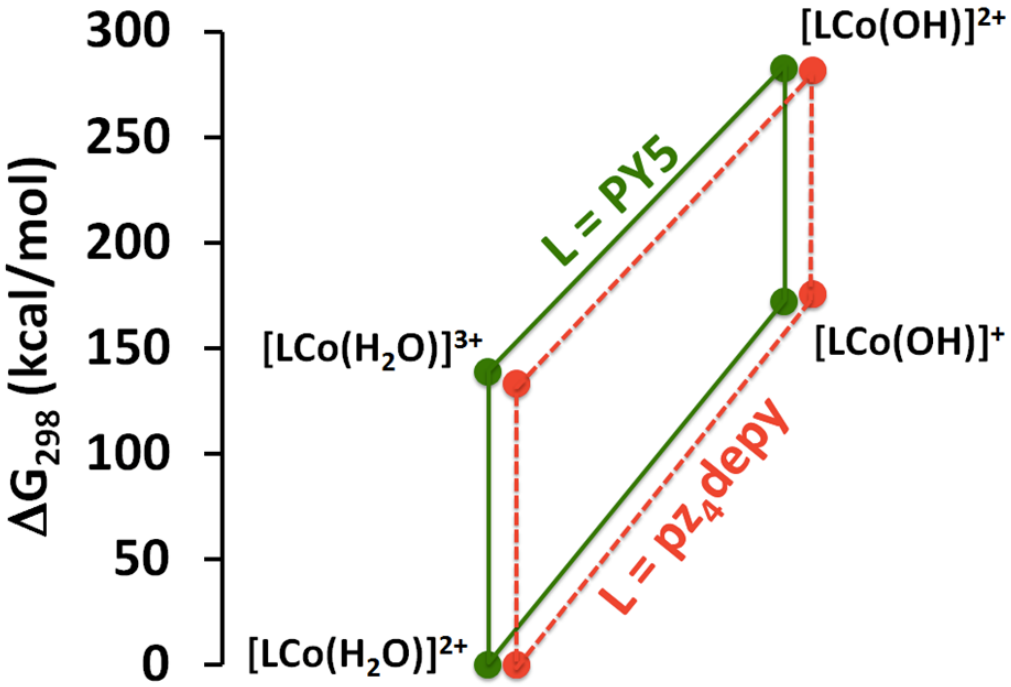

Table S4. Cartesian Coordinates for $[(PY5)Co^{II}(H_2O)]^{2+}$

Label	x	y	z
N	0.066	0.036	1.379
C	-1.249	0.006	3.795
C	-0.203	-1.133	1.969
C	-0.251	1.192	1.972
C	-0.930	1.214	3.189
C	-0.880	-1.187	3.186
C	0.059	-2.441	1.212
C	-0.034	2.512	1.222
C	1.302	-2.525	0.307
C	3.355	-2.800	-1.507
C	2.066	-3.693	0.305
N	1.531	-1.548	-0.583
C	2.525	-1.689	-1.467
C	3.113	-3.824	-0.601
C	-1.136	-2.611	0.264
C	-3.182	-2.851	-1.531
N	-1.297	-1.653	-0.662
C	-1.980	-3.712	0.359
C	-3.025	-3.828	-0.555
C	-2.292	-1.784	-1.545
C	1.214	2.640	0.328
C	3.292	2.973	-1.445
N	1.486	1.670	-0.558
C	1.940	3.831	0.337
C	2.999	3.993	-0.549
C	2.495	1.838	-1.420
C	-1.227	2.649	0.268
C	-3.262	2.834	-1.547
C	-2.104	3.723	0.357
N	-1.350	1.690	-0.664
C	-2.340	1.794	-1.556
C	-3.144	3.811	-0.565
O	-0.086	3.579	2.118
O	0.048	-3.513	2.102
C	0.878	3.636	3.155
C	1.018	-3.539	3.135
Co	0.119	0.042	-0.707
H	2.659	1.038	-2.149
H	-2.396	1.020	-2.329
H	-4.054	2.870	-2.300
H	-3.851	4.646	-0.519
H	-1.961	4.475	1.136
H	4.106	3.057	-2.171
H	3.581	4.921	-0.546
H	1.667	4.641	1.014
H	2.648	-0.888	-2.204
H	-2.379	-1.007	-2.313
H	-3.980	-2.907	-2.277
H	-3.707	-4.683	-0.506
H	-1.808	-4.461	1.134
H	4.155	-2.862	-2.250
H	3.723	-4.734	-0.606
H	1.831	-4.510	0.988
H	1.733	2.958	2.970
H	1.255	4.671	3.221
H	0.425	3.371	4.128
H	-1.250	2.161	3.628
H	-1.810	-0.007	4.734
H	-1.161	-2.147	3.623
H	1.851	-2.837	2.945
H	0.562	-3.287	4.109
H	1.426	-4.563	3.200
O	0.119	0.048	-2.779
H	0.134	-0.738	-3.356
H	0.130	0.840	-3.348

Table S5. Cartesian Coordinates for $[(PY5)Co^{II}(OH)]^{+}$.

Label	x	y	z
N	0.078	0.040	1.363
C	-1.388	-0.003	3.704
C	-0.224	-1.126	1.939
C	-0.282	1.187	1.946
C	-1.036	1.207	3.119
C	-0.972	-1.190	3.115
C	0.081	-2.441	1.213
C	-0.025	2.517	1.230
C	1.317	-2.511	0.298
C	3.319	-2.782	-1.571
C	2.117	-3.656	0.311
N	1.498	-1.553	-0.619
C	2.458	-1.693	-1.536
C	3.141	-3.782	-0.622
C	-1.118	-2.668	0.284
C	-3.171	-2.972	-1.491
N	-1.334	-1.709	-0.625
C	-1.908	-3.810	0.373
C	-2.959	-3.955	-0.530
C	-2.325	-1.867	-1.503
C	1.228	2.632	0.344
C	3.285	2.959	-1.454
N	1.460	1.684	-0.572
C	1.997	3.798	0.387
C	3.049	3.952	-0.511
C	2.449	1.850	-1.453
C	-1.211	2.704	0.276
C	-3.210	2.947	-1.570
C	-2.038	3.821	0.338
N	-1.369	1.740	-0.639
C	-2.332	1.868	-1.553
C	-3.062	3.934	-0.600
O	-0.053	3.567	2.153
O	0.113	-3.495	2.129
C	0.890	3.547	3.207
C	1.072	-3.438	3.168
Co	0.071	0.051	-0.820
H	2.553	1.070	-2.215
H	-2.367	1.082	-2.317
H	-3.989	3.012	-2.335
H	-3.733	4.799	-0.579
H	-1.872	4.583	1.103
H	4.085	3.047	-2.194
H	3.665	4.857	-0.483
H	1.766	4.591	1.100
H	2.517	-0.910	-2.300
H	-2.434	-1.077	-2.256
H	-3.975	-3.056	-2.228
H	-3.604	-4.840	-0.488
H	-1.695	-4.563	1.135
H	4.094	-2.850	-2.340
H	3.779	-4.672	-0.618
H	1.929	-4.457	1.028
H	1.744	2.876	2.993
H	1.274	4.572	3.345
H	0.422	3.222	4.155
H	-1.381	2.155	3.537
H	-2.005	-0.020	4.608
H	-1.268	-2.156	3.531
H	1.911	-2.759	2.927
H	0.614	-3.101	4.117
H	1.473	-4.455	3.319
O	-0.031	0.079	-2.705
H	-0.031	-0.827	-3.050

Table S6. Cartesian Coordinates for $[(PY5)Co^{III}(H_2O)]^{3+}$.

Label	x	y	z
N	-0.037	0.041	1.356
C	-0.972	0.018	3.959
C	-0.182	-1.122	2.010
C	-0.254	1.197	2.004
C	-0.746	1.218	3.302
C	-0.668	-1.168	3.309
C	0.037	-2.409	1.239
C	-0.096	2.496	1.237
C	1.269	-2.421	0.334
C	3.211	-2.627	-1.599
C	2.100	-3.535	0.308
N	1.400	-1.433	-0.571
C	2.325	-1.565	-1.536
C	3.106	-3.629	-0.646
C	-1.142	-2.490	0.272
C	-3.115	-2.640	-1.606
N	-1.252	-1.491	-0.628
C	-2.016	-3.564	0.305
C	-3.032	-3.636	-0.643
C	-2.205	-1.594	-1.565
C	1.150	2.552	0.353
C	3.272	2.722	-1.377
N	1.396	1.523	-0.479
C	1.912	3.713	0.314
C	2.997	3.800	-0.550
C	2.435	1.619	-1.322
C	-1.263	2.532	0.262
C	-3.186	2.628	-1.666
C	-2.187	3.564	0.294
N	-1.300	1.545	-0.655
C	-2.226	1.628	-1.622
C	-3.183	3.603	-0.677
O	-0.190	3.597	2.065
O	-0.007	-3.515	2.063
C	0.768	3.804	3.098
C	0.954	-3.681	3.101
Co	0.074	0.043	-0.572
H	2.618	0.799	-2.011
H	-2.187	0.893	-2.425
H	-3.915	2.631	-2.480
H	-3.930	4.403	-0.673
H	-2.098	4.325	1.071
H	4.104	2.726	-2.085
H	3.607	4.708	-0.582
H	1.640	4.561	0.942
H	2.344	-0.825	-2.335
H	-2.245	-0.827	-2.336
H	-3.870	-2.659	-2.396
H	-3.735	-4.474	-0.637
H	-1.875	-4.334	1.066
H	3.943	-2.665	-2.409
H	3.769	-4.499	-0.663
H	1.943	-4.351	1.012
H	1.555	3.029	3.104
H	1.237	4.793	2.962
H	0.257	3.804	4.076
H	-0.992	2.168	3.776
H	-1.391	0.007	4.969
H	-0.849	-2.130	3.789
H	1.712	-2.877	3.105
H	0.442	-3.698	4.078
H	1.458	-4.653	2.970
O	0.085	0.078	-2.527
H	0.115	-0.714	-3.100
H	0.298	0.871	-3.060

Table S7. Cartesian Coordinates for $[(PY5)Co^{III}(OH)]^{2+}$.

Label	x	y	z
N	-0.024	0.052	1.405
C	-1.019	0.045	3.984
C	-0.199	-1.104	2.055
C	-0.249	1.209	2.042
C	-0.770	1.243	3.330
C	-0.718	-1.149	3.344
C	0.032	-2.380	1.269
C	-0.074	2.496	1.250
C	1.274	-2.384	0.363
C	3.149	-2.617	-1.639
C	2.136	-3.475	0.352
N	1.368	-1.427	-0.578
C	2.234	-1.576	-1.588
C	3.113	-3.572	-0.634
C	-1.138	-2.471	0.286
C	-2.998	-2.694	-1.701
N	-1.214	-1.503	-0.647
C	-2.016	-3.544	0.312
C	-2.984	-3.641	-0.686
C	-2.083	-1.649	-1.652
C	1.171	2.539	0.360
C	3.266	2.693	-1.409
N	1.386	1.522	-0.494
C	1.963	3.682	0.332
C	3.035	3.757	-0.550
C	2.402	1.610	-1.364
C	-1.252	2.530	0.283
C	-3.225	2.582	-1.599
C	-2.183	3.558	0.321
N	-1.303	1.536	-0.624
C	-2.254	1.591	-1.566
C	-3.201	3.575	-0.628
O	-0.157	3.613	2.065
O	-0.009	-3.500	2.083
C	0.789	3.804	3.109
C	0.932	-3.653	3.135
Co	0.069	0.053	-0.587
O	0.109	0.047	-2.427
H	0.134	0.966	-2.741
H	2.523	0.798	-2.077
H	-2.217	0.830	-2.345
H	-3.981	2.566	-2.389
H	-3.952	4.371	-0.618
H	-2.086	4.330	1.086
H	4.083	2.699	-2.135
H	3.668	4.650	-0.573
H	1.726	4.527	0.977
H	2.110	-0.873	-2.414
H	-1.990	-0.933	-2.470
H	-3.696	-2.759	-2.540
H	-3.694	-4.474	-0.685
H	-1.914	-4.295	1.097
H	3.846	-2.684	-2.479
H	3.803	-4.422	-0.638
H	2.029	-4.273	1.086
H	1.567	3.019	3.122
H	1.274	4.787	2.981
H	0.271	3.808	4.083
H	-1.019	2.195	3.800
H	-1.458	0.041	4.986
H	-0.924	-2.105	3.824
H	1.687	-2.845	3.148
H	0.408	-3.667	4.107
H	1.446	-4.623	3.018

Table S8. Cartesian Coordinates for $[(pz_4depy)Co^{II}(H_2O)]^{2+}$

Label	x	y	z
N	0.010	-0.084	0.936
C	-0.132	-0.314	3.667
C	-0.120	-1.298	1.486
C	0.080	1.019	1.692
C	0.009	0.937	3.081
C	-0.194	-1.448	2.869
C	-0.197	-2.521	0.543
C	0.230	2.383	0.979
N	0.992	-2.568	-0.327
N	-1.394	-2.413	-0.310
N	1.425	2.375	0.116
N	-0.952	2.635	0.136
N	1.231	-1.576	-1.206
N	-1.567	-1.343	-1.109
N	1.511	1.518	-0.920
N	-1.287	1.773	-0.844
C	-2.362	2.275	-1.435
C	-2.745	3.484	-0.831
C	-1.819	3.683	0.169
C	2.659	1.779	-1.529
C	3.345	2.819	-0.880
C	2.524	3.176	0.168
C	2.323	-1.918	-1.874
C	2.818	-3.153	-1.423
C	1.940	-3.539	-0.434
C	-2.703	-1.540	-1.762
C	-3.292	-2.758	-1.383
C	-2.425	-3.290	-0.454
C	-0.275	-3.821	1.322
C	0.363	3.519	1.974
Co	-0.037	0.110	-1.190
O	-0.127	0.296	-3.233
H	-0.121	-0.449	-3.860
H	0.043	1.117	-3.729
H	-2.816	1.750	-2.280
H	2.948	1.217	-2.421
H	4.310	3.254	-1.138
H	2.659	3.936	0.935
H	-3.586	4.128	-1.088
H	-1.728	4.491	0.894
H	0.490	4.482	1.455
H	-0.535	3.584	2.607
H	1.232	3.359	2.630
H	0.058	1.822	3.717
H	-0.191	-0.405	4.756
H	-0.303	-2.425	3.341
H	-1.181	-3.844	1.946
H	0.599	-3.926	1.984
H	-0.302	-4.685	0.639
H	-2.482	-4.220	0.110
H	1.940	-4.430	0.191
H	3.698	-3.693	-1.769
H	-4.225	-3.194	-1.739
H	-3.052	-0.800	-2.487
H	2.710	-1.268	-2.663

Table S9. Cartesian Coordinates for $[(pz_4depy)Co^{II}(OH)]^+$.

Label	x	y	z
N	0.019	-0.066	0.927
C	-0.186	-0.286	3.663
C	-0.128	-1.274	1.481
C	0.073	1.035	1.684
C	-0.028	0.961	3.074
C	-0.235	-1.421	2.865
C	-0.191	-2.507	0.551
C	0.238	2.400	0.978
N	0.997	-2.552	-0.324
N	-1.392	-2.424	-0.301
N	1.434	2.384	0.115
N	-0.947	2.669	0.145
N	1.203	-1.579	-1.227
N	-1.590	-1.349	-1.084
N	1.507	1.538	-0.928
N	-1.315	1.799	-0.813
C	-2.388	2.312	-1.393
C	-2.740	3.540	-0.802
C	-1.792	3.737	0.179
C	2.667	1.774	-1.520
C	3.378	2.787	-0.850
C	2.556	3.154	0.193
C	2.268	-1.932	-1.927
C	2.785	-3.158	-1.468
C	1.942	-3.528	-0.443
C	-2.680	-1.595	-1.792
C	-3.220	-2.852	-1.461
C	-2.364	-3.357	-0.506
C	-0.252	-3.801	1.341
C	0.387	3.532	1.976
Co	-0.070	0.139	-1.316
O	-0.146	0.285	-3.190
H	-0.243	-0.609	-3.553
H	-2.861	1.778	-2.221
H	2.943	1.210	-2.414
H	4.357	3.198	-1.090
H	2.701	3.902	0.970
H	-3.573	4.196	-1.053
H	-1.674	4.554	0.889
H	0.534	4.494	1.460
H	-0.514	3.613	2.605
H	1.249	3.355	2.637
H	0.011	1.847	3.708
H	-0.269	-0.375	4.750
H	-0.357	-2.396	3.338
H	-1.163	-3.835	1.959
H	0.620	-3.887	2.009
H	-0.261	-4.672	0.668
H	-2.393	-4.301	0.036
H	1.964	-4.407	0.198
H	3.654	-3.704	-1.833
H	-4.114	-3.329	-1.861
H	-3.023	-0.855	-2.519
H	2.610	-1.292	-2.744

Table S10. Cartesian Coordinates for $[(pz_4depy)Co^{III}(H_2O)]^{3+}$.

Label	x	y	z
N	0.005	-0.085	0.989
C	0.011	-0.326	3.731
C	-0.106	-1.304	1.549
C	0.114	1.018	1.753
C	0.122	0.925	3.137
C	-0.105	-1.453	2.929
C	-0.233	-2.500	0.606
C	0.219	2.362	1.033
N	0.941	-2.514	-0.274
N	-1.406	-2.290	-0.248
N	1.384	2.317	0.144
N	-0.966	2.516	0.182
N	1.198	-1.435	-1.044
N	-1.434	-1.199	-1.038
N	1.442	1.369	-0.813
N	-1.200	1.589	-0.770
C	-2.255	2.005	-1.467
C	-2.723	3.217	-0.949
C	-1.875	3.516	0.097
C	2.523	1.626	-1.547
C	3.185	2.753	-1.049
C	2.428	3.171	0.025
C	2.249	-1.743	-1.801
C	2.688	-3.039	-1.511
C	1.828	-3.502	-0.538
C	-2.489	-1.321	-1.839
C	-3.174	-2.507	-1.549
C	-2.451	-3.104	-0.538
C	-0.349	-3.821	1.330
C	0.334	3.538	1.974
Co	0.002	0.084	-0.927
O	-0.098	0.268	-2.857
H	0.080	-0.489	-3.451
H	0.175	1.099	-3.297
H	-2.635	1.440	-2.317
H	2.788	1.012	-2.408
H	4.101	3.203	-1.428
H	2.565	4.009	0.707
H	-3.574	3.801	-1.295
H	-1.866	4.368	0.776
H	0.403	4.482	1.410
H	-0.546	3.588	2.635
H	1.233	3.443	2.602
H	0.210	1.817	3.759
H	0.015	-0.421	4.820
H	-0.197	-2.439	3.387
H	-1.242	-3.827	1.975
H	0.536	-3.993	1.962
H	-0.429	-4.652	0.611
H	-2.616	-4.044	-0.012
H	1.795	-4.460	-0.020
H	3.527	-3.569	-1.960
H	-4.080	-2.881	-2.022
H	-2.704	-0.576	-2.603
H	2.654	-1.043	-2.532

Table S11. Cartesian Coordinates for $[(pz_4depy)Co^{III}(OH)]^{2+}$.

Label	x	y	z
N	0.003	-0.100	1.029
C	0.011	-0.356	3.768
C	-0.105	-1.317	1.581
C	0.110	0.993	1.797
C	0.119	0.899	3.183
C	-0.104	-1.481	2.961
C	-0.226	-2.501	0.617
C	0.216	2.335	1.067
N	0.954	-2.513	-0.259
N	-1.397	-2.290	-0.246
N	1.389	2.297	0.182
N	-0.965	2.493	0.205
N	1.198	-1.445	-1.046
N	-1.417	-1.209	-1.052
N	1.434	1.377	-0.804
N	-1.166	1.600	-0.785
C	-2.158	2.059	-1.533
C	-2.636	3.269	-1.008
C	-1.843	3.523	0.091
C	2.463	1.685	-1.580
C	3.123	2.817	-1.077
C	2.402	3.188	0.038
C	2.227	-1.759	-1.822
C	2.678	-3.053	-1.524
C	1.837	-3.507	-0.530
C	-2.470	-1.333	-1.848
C	-3.168	-2.509	-1.542
C	-2.450	-3.100	-0.524
C	-0.345	-3.830	1.327
C	0.325	3.511	2.009
Co	0.014	0.078	-0.950
O	0.019	0.285	-2.773
H	-0.047	-0.605	-3.159
H	-2.471	1.516	-2.425
H	2.671	1.097	-2.474
H	4.010	3.304	-1.481
H	2.546	4.014	0.734
H	-3.452	3.884	-1.386
H	-1.853	4.357	0.791
H	0.395	4.457	1.448
H	-0.557	3.558	2.667
H	1.223	3.417	2.640
H	0.206	1.787	3.812
H	0.016	-0.458	4.857
H	-0.192	-2.469	3.416
H	-1.237	-3.840	1.974
H	0.539	-4.009	1.959
H	-0.426	-4.655	0.601
H	-2.623	-4.031	0.014
H	1.814	-4.459	-0.001
H	3.508	-3.589	-1.981
H	-4.079	-2.884	-2.007
H	-2.669	-0.587	-2.617
H	2.596	-1.056	-2.570

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