Supporting Information

Bidirectional and Unidirectional PCET in a Molecular Model of a Cobalt-Based Oxygen Evolving Catalyst

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Experimental Section

Materials. KOH 98.5% (Mallinckrodt), K₂SO₄ and KNO₃ (Fluka) were reagent grade and used as received. All electrolyte solutions were prepared with reagent grade water (Ricca Chemical, 18 MΩ-cm resistivity). H₂SO₄ (99.999%), D₂SO₄ (96-98% in D₂O), [Ru(bpy)₃]Cl₂ (99.9%), and ammonium cerium nitrate (99.99%) were obtained from Aldrich. D₂O (99.9%) was supplied by Cambridge Isotope Laboratories. 2,2-dimethyl-2-silapentane-5-sulfonate (sodium salt) was purchased from Santa Cruz Biotechnology. $[Co_4O_4(CO_2Me)_2(bpy)_4][Ce(NO_3)_6]$ (2)² were synthesized as reported.

Electrochemical Studies. Electrochemical measurements were performed on a CH Instruments (Austin, Texas) 760C Electrochemical Workstation using CHI Version 10.03 software. pH values were determined using a VWR symphony SP70P meter with a temperature-correcting probe (14002-860). Electrochemical experiments for constructing the Pourbaix diagram were conducted at 295 K using a CH Instruments glassy carbon button working electrode (area = 0.071 cm^2), BASi Ag/AgCl reference electrode, and Pt mesh counter electrode. For scan rate dependency studies, a Princeton Applied Research glassy carbon microelectrode (area = $8 \times 10^{-6} \text{ cm}^2$) was substituted as the working electrode. All electrode potentials were converted to the NHE scale using E(NHE) = E(Ag/AgCl) + 0.197 V. All electrochemical experiments were conducted in electrolyte solutions prepared using reagent grade water.

Data collection for the Pourbaix plot (at pH = 0) began with a measurement of a 1 mM solution of **1** in 1 M H₂SO₄, The pH was incremented between CV scans by titration with 1 M KOH and all peak potential values were compensated for solution resistance. Values for $E_{1/2}$ were obtained from the average of anodic and cathodic peak potentials, $E_{p,a}$ and $E_{p,c}$ measured by cyclic voltammetry (CV) performed on quiescent solutions in a single compartment cell at a scan rate of 100 mV sec⁻¹. CV scans were performed over a range of pH values from 0 to 7 to produce the Pourbaix diagram (Figure 2).

Scan rate dependency studies were performed on 0.5 mM solutions of cubane **1** in a single compartment cell in various buffers, namely; i) 0.1 M H₂SO₄ with 0.2 M KNO₃, ii) 0.1 mM H₂SO₄ with 0.2 M KNO₃ and 0.05 M K₂SO₄, and iii) 0.1 M D₂SO₄ with 0.2 M KNO₃. pH (pD) measurements were taken before and after each set of experiments and were not found to vary over the course of the experiment. The pH-dependent rate constant for cubane oxidation was determined by measuring the scan rate dependence of the CV taken at pH = 1. The pH-independent rate constant for cubane oxidation was determined by measuring the scan rate measurement. However, limited solubility of the cubane at higher pHs made such measurements more problematic. All experiments were repeated at least four times using freshly prepared

^{1.} Dimitrou, K.; Folting, K.; Streib, W. E.; Christou, G. J. Am. Chem. Soc. 1993, 115, 6432.

^{2.} Dimitrou, K.; Brown, A. D.; Concolino, T. E.; Rheingold, A. L.; Christou, G. Chem. Commun. 2001, 1284.

samples of **1** and the results reported are averages. Appropriate background scans were subtracted from all CVs. Solutions were stirred between acquisition of individual CVs. AC impedance measurements were used to gauge uncompensated resistance, which was determined to have a negligible effect on the reported values of $E_{1/2}$ due to the low currents (nA) obtained on the microelectrode.

The diffusion coefficient, D_o , of species $1-H^+$ was calculated using the equation:³

$$i_{p,a}(\text{rev}) = [(2.72 \times 10^5) \text{n}^{3/2} \text{D}_0^{1/2} \text{C}^0] v^{1/2}$$

where $i_{p,a}(\text{rev})$ is the magnitude the anodic peak current density (A cm⁻²) at a scan rate, v (V s⁻¹), in the electrochemically reversible limit (linear region of the plot of $E_{p,a} - E_{1/2} vs. v$), n is the number of electrons involved in the redox process, C^o is the bulk concentration of the reactant (mol cm⁻³), and D_o is the diffusion coefficient (cm² s⁻¹). Values of v chosen for this determination were 0.1 V s⁻¹, 1 V s⁻¹ and 10 V s⁻¹, giving an averaged value of D_o = 3.6 × 10⁻⁶ cm² s⁻¹. The diffusion coefficients of **1** and **2** were assumed to have the same value, as has been assumed previously for protonated and oxidized forms of the same molecule.⁴ Using this value of D and assuming a transfer coefficient of $\alpha = 0.5$,³ the electrochemical rate constant for the forward process (herein referred to as simply "k") was obtained by simulating CVs using the CH v. 10.03 computer software package using these parameters and varying values of k, with the resulting fits being the product of numerous rounds of trial and error.

¹**H NMR studies.** ¹H NMR data were obtained on a Bruker Avance-600 NMR spectrometer fitted with a 5 mm ¹H{¹³C, ¹⁵N} TXI cryo-probe at 295 K (RT measurements only) and a Varian Inova-500 NMR spectrometer fitted with a gHX inverse broadband probe (for 295 K and elevated temperature measurements). All ¹H NMR data sets were collected at least in triplicate, at 295 K (unless stated otherwise). Typical pH-dependence titrations were performed as follows. To 0.5 mL of a 0.5 mM solution of **1** in 0.1 M D₂SO₄ in D₂O (pD = 1) or 0.1 mM D₂SO₄ in D₂O (pD = 4) containing 1% 2,2-dimethyl-2-silapentane-5-sulfonate (sodium salt) (DSS), was added aliquots of a 1 mM solution of **2** in either 0.1 M D₂SO₄ in D₂O (pD = 1) or 0.1 mM D₂SO₄ in D₂O (pD = 4) also containing 1% DSS. After thorough mixing, ¹H NMR spectra were recorded after each aliquot was added.

Typical kinetic isotope assays were performed in equimolar (0.5 mM / 0.5 mM) solutions of **1** and **2** in either 0.1 M D₂SO₄ in D₂O (pD = 1) or 0.1 mM D₂SO₄ in D₂O (pD = 4) containing 1% DSS (total volume = 1 mL). Aliquots of 0.1 M H₂SO₄ in H₂O (pH = 1) or 0.1 mM H₂SO₄ in H₂O (pH = 4) containing 1% DSS were then added and the solutions thoroughly mixed before acquisition of ¹H NMR spectra.

^{3.} Gileadi, E. *Electrode Kinetics for Chemists, Chemical Engineers and Materials Scientists;* Wiley-VCH: New York, 1993.

^{4.} Costentin, C.; Robert, M.; Savéant, J.-M.; Teillout, A.-L. Proc. Nat. Acad. Sci. USA 2009, 106, 18129.

Variable temperature (VT-¹H NMR) experiments were performed in equimolar (0.5 mM / 0.5 mM) solutions of **1** and **2** in 0.1 M D₂SO₄ in D₂O (pD = 1) containing 1% DSS (total volume = 1 mL). The temperature was controlled to ± 0.2 °C over the time course of each acquisition.

In all cases, the apparent rate constant for self-exchange, k_{obs} , was obtained by fitting parts of the acquired spectra to simulations generated using WINDNMR-Pro NMR Spectrum Calculations Version 7.1.13 (2008);⁵ the value for k_{obs} was iteratively varied with comparison of both the overlaid spectra and residuals until the best fit was obtained by eye. Figures S1, S2, and S3 show representative fits. The peaks fitted were one bipyridine–based triplet in $1/1-H^+$ and its magnetization self-exchange partner in cubane 2, as determined by a 1D EXSY magnetization transfer experiment. The relevant self-exchange rate constant, k_{SE} , was then calculated for the oxidized cubane 2 and all such values reported are normalized for the population of 2 vs. 1 (or 1- H^+) in solution.⁶

Figure S4 shows an overlay of plots of $\ln(k_{obs}/T)$ vs. 1/T for the values of k_{SE} found from computational fitting of the VT-¹H NMR spectra acquired in 0.1 M D₂SO₄/D₂O. Values for the enthalpy and entropy of activation were obtained by fitting the gradients and *y*-intercepts of these lines respectively to the Eyring equation.

Figure S5 shows an overlay of plots of k_{SE} vs. [2] for the values of k_{SE} found from computational fitting of the ¹H NMR spectra acquired in 0.1 M D₂SO₄/D₂O and pD 4 for titrations of 2 into 1-H⁺ and 1 respectively. The rate of self-exchange was obtained by analysis of the gradients of these curves.

Figure S6 shows an overlay of $k_{SE}/k_D vs.$ fractional content of H₂O (χ H₂O) for the values of k_{SE} found from computational fitting of the ¹H NMR spectra acquired at (a) pH/D 1 for titrations of 0.1 M H₂SO₄/H₂O into equimolar solutions of **2** and **1**-H⁺ in 0.1 M D₂SO₄/D₂O and (b) pH/D 4 for titrations of 0.1 mM H₂SO₄/H₂O into equimolar solutions of **2** and **1** in 0.1 mM D₂SO₄/D₂O. k_{SE} is the observed value of the rate constant for self-exchange. KIEs were obtained by analysis of the gradients of these curves.

Stopped-Flow and Absorbance Studies. Electronic absorbance spectra were recorded at room temperature in quartz cuvettes on a Varian Cary 5000 UV-vis-NIR spectrophotometer, and are reproduced in Figure S7. These show that a 10:1 solution of cubane **2** and $[Ru(bpy)_3]Cl_2$ in 0.1 M H₂SO₄/H₂O does not have the absorbance peak at ~450 nm that would be expected by simple summation of the individual spectra for **2** and $[Ru(bpy)_3]Cl_2$. Instead, the spectrum obtained on mixing **2** and $[Ru(bpy)_3]Cl_2$ in a 10:1 ratio closely resembles that of **2** (and/or reduced, protonated cubane **1-H**⁺ (10%) with **2** (90%), which would be the expected cubane products of a redox reaction at this stoichiometry). This demonstrates that oxidation of $[Ru(bpy)_3]Cl_2$ (which

^{5.} Reich, H. J. J. Chem. Educ. Software **1996**, 3D, 2. This program is available for free download on the internet at http://www.chem.wisc.edu/areas/reich/plt/windnmr.htm

^{6.} Sandström, J. Dynamic NMR Spectroscopy; Academic Press: London, 1982.

absorbs at 450 nm) to $[Ru(bpy)_3]^{3+}$ (which does not absorb strongly at 450 nm)⁷ occurs rapidly upon mixing **2** and $[Ru(bpy)_3]Cl_2$ in 0.1 M H₂SO₄/H₂O, such that no absorption from $[Ru(bpy)_3]Cl_2$ can be detected.

Kinetic absorbance assays were performed on a Hi-Tech Scientific (Salisbury, U.K.) SF-61 DX2 stopped-flow spectrophotometer at a constant temperature of 295 K. In mixing experiments, a 5.0 μ M solution of [Ru(bpy)₃]Cl₂ in 0.1 M H₂SO₄/H₂O was mixed rapidly on the stopped-flow apparatus with an equal volume of a solution of cubane **2**, also in 0.1 M H₂SO₄/H₂O. Concentrations of **2** used were 50, 75, 100 and 150 μ M. As equal volumes of each solution were mixed in every run, the final concentrations of all species at the detector were half of that of the as-prepared solutions (hereafter all concentrations are given as concentrations at the detector; "final concentrations using 0.1 M D₂SO₄/D₂O as solvent. Data were collected using a photomultiplier under monochromatic halogen lamp illumination ($\lambda = 450$ nm), and time-dependent absorbance data (at 450 nm) were analyzed by the software package Kinetic Studio (TgK Scientific). Representative averaged traces (of at least 30 runs per set of conditions) and fits to these traces are shown in Figure S8. Rates constants, *k*_{obs}, were obtained by fitting these traces to the general formula *y* = *A*exp(-*k*_{obs}*t*). Second order rate constants were obtained from the gradients of plots of *k*_{obs} vs. [**2**] (Figure 5).

^{7.} Ceroni, P.; Bergamini, G.; Balzani, V. Angew. Chem. Int. Ed. 2009, 48, 8516.



Figure S1. Representative stacked ¹H NMR plots, showing how titration of **2** into a solution of **1-H**⁺ affects the rate of self-exchange, recorded at 295 K on Varian Inova-500 NMR in 0.1 M D_2SO_4/D_2O . The peaks at 8.8 ppm (for cubane **2**) and 9.2 ppm (from cubane **1-H**⁺) are the two in exchange. Recorded spectra are shown in red and shifts are reported relative to the internal DSS standard, which was itself referenced relative to TMS. Simulated spectra are shown as solid black lines.



Figure S2. Representative stacked ¹H NMR plots, showing how titration of **2** into a solution of **1** affects the rate of self-exchange, recorded at 295 K in D_2SO_4/D_2O , pD 4. The peaks at 8.8 ppm (for cubane **2**) and 9.2 ppm (from cubane **1**) are the two in exchange. Recorded spectra are shown in red and shifts are reported relative to the internal DSS standard, which was itself referenced relative to TMS. Simulated spectra are shown as solid black lines.



Figure S3. Representative stacked ¹H NMR plots, showing how temperature affects the rate of self-exchange in an equimolar solution of **2** and **1-H**⁺ in 0.1 M D_2SO_4/D_2O . The peaks at 8.8 ppm (for cubane **2**) and 9.2 ppm (from cubane **1-H**⁺) are the two in exchange. Recorded spectra are shown in red and shifts are reported relative to the internal DSS standard, which was itself referenced relative to TMS. Simulated spectra are shown as solid black lines. All spectra were recorded at 295 K on Varian Inova-500 NMR.



Figure S4. Eyring plots showing $\ln(k_{obs}/T)$ vs. 1/T for the values of k_{SE} found from fitting VT-¹H NMR spectra such as those shown in Figure S2. The three sets of data correspond to three independent repeats of the experiment.



Figure S5. Overlaid of plots of k_{obs} vs. [2] for the values of k_{SE} found from computational fitting of the ¹H NMR spectra acquired at pD 4 (\bullet, \bullet, \star) and pD 1 (\bullet, \bullet, \star) for titrations of 2 into 1 and 1-H⁺ respectively. Values for the rate of self-exchange were obtained by analysis of the gradients of these curves, which are shown as solid lines.



Figure S6. Overlaid of plots of k_{SE}/kD vs. fractional content of H₂O (χ H₂O) for the values of k_{SE} found from computational fitting of the ¹H NMR spectra acquired at (a) pH/D 1 ($\blacksquare, \blacktriangle, \diamondsuit$) for titrations of 0.1 M H₂SO₄/H₂O into equimolar solutions of **2** and **1-H**⁺ in 0.1 M D₂SO₄/D₂O and (b) pH/D 4 ($\bullet, \diamondsuit, \bigstar$) for titrations of 0.1 mM H₂SO₄/H₂O into equimolar solutions of **2** and **1** in 0.1 mM D₂SO₄/D₂O. KIEs were obtained by analysis of the gradients of these curves, which are shown as solid lines.



Figure S7. UV-vis spectra of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (2.5 μ M in 0.1 M H₂SO₄/H₂O, —), cubane 2 (25 μ M in 0.1 M H₂SO₄/H₂O, —•• —), a solution of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (2.5 μ M) and cubane 2 (25 μ M) in 0.1 M H₂SO₄/H₂O immediately after mixing (••••), a mixture of cubane 2 (22.5 μ M) and protonated cubane 1-H⁺ (2.5 μ M) in 0.1 M H₂SO₄/H₂O (— — —), and the calculated spectrum that would be expected in the absence of any redox process between 2 and $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, *i.e.* the sum of the black and red traces (— • —).



Figure S8. Representative stopped-flow kinetic trace (averaged from 30 individual runs) of the decay in absorbance at 450 nm *vs.* time upon mixing $[Ru(bpy)_3]Cl_2$ (final concentration = 2.5 μ M) and cubane **2** (final concentration = 25 μ M) in 0.1 M H₂SO₄/H₂O (left) and 0.1 M D₂SO₄/D₂O (right). Data points are shown in black, and the calculated fit in red (left) and blue (right).