## **Supporting Information**

# Electrochemical investigation of $[Co_4(\mu_3-O)_4(\mu-OAc)_4(py)_4]$ and peroxides by cyclic voltammetry

Edwin B. Clatworthy, Xiaobo Li, Anthony F. Masters and Thomas Maschmeyer\*

Laboratory of Advanced Catalysis for Sustainability, School of Chemistry, The University of Sydney, Sydney, NSW 2006, Australia, E-mail: thomas.maschmeyer@sydney.edu.au; Fax: (+61) 0293513329; Tel: (+61) 93512581.

#### Materials

Na<sub>2</sub>EDTA (AJAX Fine Chem, > 99%), KH<sub>2</sub>PO<sub>4</sub> (Ajax, > 99%), K<sub>2</sub>HPO<sub>4</sub> (Ajax, > 99%), Pyridine (Ajax), potassium bis(oxalate)-oxotitanate(IV) dihydrate (Alfa Aesar), cobalt(II) nitrate hexhydrate (Riedel-de Haën, > 98%), cobalt(II) acetate tetrahydrate (Asia Pacific) and sulphuric acid (Merck, 98 wt%) were used as received. *Tert*-butylhydroperoxide (70 wt%; Sigma) and hydrogen peroxide (30 wt%; Merck) were determined iodometrically.<sup>1</sup> Acetonitrile (HPLC grade; AJAX) was stirred over calcium hydride (Sigma-Aldrich) under nitrogen overnight followed by distillation under nitrogen. Tetraethylammonium perchlorate (TEAP) was prepared by dropwise addition of perchloric acid (70%; Merck) to tetraethylammonium hydroxide (20%; Alfa Aesar), recovered by filtration and recrystallised from ethanol. The material was then dried under vacuum at 70 °C for a minimum of 24 h. Ferrocene (Sigma-Aldrich) was purified by sublimation. Milli-Q water was prepared using Millipore Elix 10.

#### Instrumentation

All cyclic voltammetry experiments were performed using an eDAQ ER466 Integrated Potentiostat System with a three electrode cell configuration. A glassy carbon electrode (ID 1.6 mm, BAS Inc), Pt wire, and a leakless Ag/AgCl electrode (3.4 M aq. KCl, eDAQ) were employed as the working, counter and pseudo-reference electrodes, respectively. All potentials are quoted versus a secondary standard of the ferrocene/ferrocenium couple ( $Fc^{0/+}$ ). The potentials of the  $Fc^{0/+}$  couple *vs* the Ag/AgCl electrode as a function of scan rate are collected in Table S2. A 2 mL sample cell with a stirrer bar and lid designed for a multi-electrode configuration was used.

Before use, the glassy carbon electrode was polished using 0.3  $\mu$ M and then 0.05  $\mu$ M alumina powder (SLS Lapidary) followed by sonication in Milli-Q water and then rinsing with acetone and acetonitrile. Fresh electrochemical solutions were deoxygenated with argon for 5 min before experiments. The solutions were then left saturated under a continuous-flow argon atmosphere at a low rate to minimise solvent evaporation. NMR (300 MHz) spectra were recorded on a Bruker Avance DPX300 spectrometer and referenced internally to residual solvent signals (CD<sub>3</sub>CN,  $\delta$  1.94, 5-multiplet). Data were collected using Bruker TopSpin 3.0 software. ESI MS data were acquired using a Finnican LCQ ion trap spectrometer.

All UV/Vis measurements were performed using an Agilent Technologies Cary 60 UV-Vis Spectrophotometer. Monitoring the decomposition of  $H_2O_2$  was performed by recording the absorbance of a peroxotitanium complex at 390 nm. Samples (100 µL) were taken from a solution of hydrogen peroxide (82 µL, 40 mM) and 1 (0.1 mM) in 0.1 M TEAP in MeCN (20 mL) with constant stirring and then worked up (adapted to scale) from Brandhuber and Korshin.<sup>2</sup> Experiments were also run at lower ratios of hydrogen peroxide (20 mM) to 1 (1 mM). Samples were taken immediately after the addition of  $H_2O_2$  and every minute for 30 minutes. All electrolyte solutions of 1 were prepared fresh.

Oxygen evolution experiments were performed using an Ocean Optics Fluorimeter and HIOXY probe. The probe was positioned in the headspace of a sealed 100 mL round bottom flask equipped with a stirrer bar. Nitrogen and samples were introduced by needle through a side arm with a septum cap. The probe was calibrated by measuring the ambient atmosphere and then a nitrogen-saturated atmosphere in the flask. A baseline was measured by purging the flask with nitrogen until the probe was stable and then a 2 mL solution of 1 (0.1 mM) in 0.1 M TEAP in MeCN was introduced into the flask. The purging needle was removed and the oxygen measured for at least 40 min. For experiments monitoring peroxide decomposition, the flask was purged with nitrogen until the probe was stable and then a 1 mL solution of 1 (0.2 mM) in 0.1 M TEAP in MeCN was introduced into the flask. This was quickly followed by introduction of a 1 mL solution of peroxide (80 mM) to give a solution containing 1 (0.1 mM) and peroxide (40 mM). All electrolyte solutions of 1 were prepared fresh.

#### Preparation of $[Co_4(\mu_3-O)_4(\mu-OAc)_4(py)_4]$ , 1

The following procedure was adapted from Chakrabarty *et. al.*<sup>3</sup> Cobalt(II) acetate tetrahydrate (2.5 g, 10 mmol) and pyridine (0.8 mL, 10 mmol) were dissolved in methanol (30 mL) and water (5 mL). The solution was heated to 70 °C and hydrogen peroxide (30 wt%, 5 mL) was then added slowly. After heating at 70 °C for 4 h the solution was cooled to room temperature and

filtered. Chloroform (100 mL) was added to the filtrate and the organic phase separated from the pink aqueous phase.

The chloroform was allowed to evaporate leaving dark olive green crystals which were redissolved in dichloromethane (20 mL) and the solution dried over Na<sub>2</sub>SO<sub>4</sub>. The organic phase was separated by filtration and green crystals were collected by evaporation of dichloromethane layered with hexane. The green solids were further purified by column chromatography on silica with 10 vol% methanol in dichloromethane. The organic fractions were dried over Na<sub>2</sub>SO<sub>4</sub> before being separated by filtration, layered with hexane, and left to recrystallise. To ensure removal of trace Co(II) ions, the purified material was dissolved in 5 mL of 0.1 M EDTA solution and extracted with dichloromethane (5x50 mL). The solution was dried over Na<sub>2</sub>SO<sub>4</sub>, separated by filtration, and volatiles removed *in vacuo* to afford a green solid. The final yield was 30–50 %.

Selected MS ESI data: m/z (%) = 852.84 (100 [M+H]<sup>+</sup>). <sup>1</sup>H NMR (300 MHz; CD<sub>3</sub>CN):  $\delta$  8.37 (d, 8H), 7.58 (t, 4H), 7.09 (t, 8H), 1.98 (s, 12H) ppm.

#### Preparation of Co-OEC

The procedure followed was a literature method.<sup>4</sup> Co-OEC was prepared by electrodeposition on a glassy carbon electrode (ID 1.6 mm, BAS Inc) at 1.05 V vs (Ag/AgCl) for 40 minutes from fresh solutions of 0.5 mM Co(NO<sub>3</sub>)<sub>2</sub> and 0.1 M potassium phosphate buffer, pH 7.13 (KPi). After the electrode was removed from the cell it was gently rinsed once with de-ionised water then once with acetonitrile, and then used as the working electrode.

### Additional data

All scans in this work began at 0 V vs Ag/AgCl in the anodic direction unless otherwise stated.



**Figure S1.** Dependence of the  $I_p^{ox}$  of the second quasi-reversible oxidation on the square-root of the scan rate.

Table 1 Electrochemical data for the second quasi-reversible oxidation of 1 (1 mM) vs Fc <sup>0/+</sup> .
Background correction of CVs was applied.

v	E <sub>p</sub> ox	I <sub>p</sub> ox	$E_{p}^{red}$	$I_p^{red}$	ΔEp	Ip <sup>ox</sup> /Ip <sup>red</sup>	E <sub>1/2</sub>
(mV/s)	(mV)	(µA)	(mV)	(μA)	(mV)		(mV)
50	1464	4.78	1401	-4.52	64	1.06	1433
100	1474	6.02	1399	-5.60	75	1.07	1436
200	1478	8.76	1398	-7.54	80	1.16	1438
400	1483	11.2	1403	-10.5	80	1.07	1443
800	1490	16.5	1400	-15.3	90	1.08	1445
1000	1494	18.1	1400	-17.5	94	1.03	1447
1600	1495	22.8	1395	-21.8	100	1.05	1445

V	$E_p^{ox}$	I <sub>p</sub> ox	$E_p^red$	$I_p^{red}$	ΔE <sub>p</sub>	Ip <sup>ox</sup> /Ip <sup>red</sup>	E <sub>1/2</sub>
(mV/s)	(mV)	(μA)	(mV)	(µA)	(mV)		(mV)
50	316	4.32	251	-3.88	65	1.11	283
100	326	5.42	256	-5.00	70	1.09	291
200	323	7.74	253	-6.76	70	1.14	288
400	338	9.86	248	-9.66	90	1.02	293
800	345	14.1	255	-14.4	90	0.98	300
1000	344	16.4	256	-16.5	88	0.99	300
1600	345	20.2	255	-20.3	90	0.99	300

**Table S2** Electrochemical data for the first quasi-reversible oxidation of **1** (1 mM) vs Fc<sup>0/+</sup> in 0.1 M TEAP in MeCN. Background correction of CVs was applied.

**Table S3** Electrochemical data for the ferrocene/ferrocenium ( $Fc^{0/+}$ ) couple (1 mM) vs Ag/AgCl in 0.1 M TEAP in MeCN. Background correction of CVs was applied.

V	$E_p^{ox}$	I <sub>p</sub> ox	$E_p^red$	$I_p^{red}$	ΔE <sub>p</sub>	Ip <sup>ox</sup> /Ip <sup>red</sup>	E <sub>1/2</sub>
(mV/s)	(mV)	(μA)	(mV)	(μA)	(mV)		(mV)
50	444	7.49	375	-7.07	69	1.06	409
100	443	9.79	370	-8.96	73	1.09	406
200	445	13.2	370	-12.6	75	1.04	408
400	440	18.5	365	-18.3	75	1.01	403
800	440	27.6	360	-27.6	80	1.00	400
1000	438	30.7	363	-30.0	75	1.02	400
1600	450	38.6	360	-37.5	90	1.03	405



**Figure S2.** Cyclic voltammograms of the supporting electrolyte solution (0.1 M TEAP in MeCN) with (blue) and without (red) water (1 M) present. The peak at *ca*. 0.9 V is the oxidation of water at the GCE. Starting potential = -0.409 V *vs*  $Fc^{0/+}$  in the anodic direction, scan rate = 50 mV/s.



**Figure S3.** Cyclic voltammograms of **1** (5 mM) in 0.1 M TEAP in MeCN with different switching potentials. Starting potential =  $-0.409 \text{ V} vs \text{ Fc}^{0/+}$  in the anodic direction, scan rate = 50 mV/s.



**Figure S4.** Cyclic voltammograms of Co-OEC (blue) and blank GCE (red) in 0.1 M TEAP in MeCN with  $H_2O(1 \text{ M})$ , scan rate = 50 mV/s, starting at -0.409 V vs Fc<sup>0/+</sup> scanning initially in the anodic direction.



**Figure S5.** Peak current *vs* time of the oxidation of  $H_2O_2$  (20 mM) in 0.1 M TEAP in MeCN. Scan rate = 50 mV/s.



**Figure S6.** Log-plot of the peak current (at  $E = 1.7 \text{ V } vs \text{ Fc}^{0/+}$ ) vs time of the oxidation of H<sub>2</sub>O<sub>2</sub> (30 wt%, 20 mM) in 0.1 M TEAP in MeCN. Scan rate = 50 mV/s. Observed rate constant (k) = 0.0164 s<sup>-1</sup>.



**Figure S7.** Cyclic voltammogram of **1** (black, 5 mM) in the presence of  $H_2O_2$  (20 mM) in 0.1 M TEAP in MeCN showing the first quasi-reversible redox process. The reduction process of the first redox couple of **1** is significantly diminished in the presence of  $H_2O_2$ . As  $H_2O_2$  is decomposed over time, the current of the reduction process reaches equivalence with the corresponding oxidative current. Starting potential = -0.309 V vs Fc<sup>0/+</sup> in the anodic direction, scan rate = 50 mV/s.

**Table S4** Electrochemical data for the transient quasi-reversible oxidation of **1** (5 mM) in the presence of  $H_2O_2$  (20 mM) vs Fc<sup>0/+</sup> in 0.1 M TEAP in MeCN. Background correction of CVs was applied.

					Ip <sup>ox</sup> /	
E <sub>p</sub> ox (mV)	I <sub>p</sub> <sup>ox</sup> (μΑ)	E <sub>p</sub> <sup>red</sup> (mV)	I <sub>p</sub> <sup>red</sup> (μΑ)	$\Delta E_p$ (mV)	$I_p^{red}$	E <sub>1/2</sub> (mV)
997	5.96	860	-2.82	138	2.12	929



**Figure S8.** Cyclic voltammogram of **1** (black, 5 mM) in the presence of  $H_2O_2$  (20 mM) showing the first quasi-reversible redox process and transient redox couple (diminishes and finally disappears over successive scans), in 0.1 M TEAP in MeCN. Starting potential = -0.309 V vs Fc<sup>0/+</sup> in the anodic direction, scan rate = 50 mV/s.



**Figure S9.** Cyclic voltammograms of only **1** (red, 5 mM), only  $H_2O_2$  (blue, 20 mM) and **1** (5 mM) in the presence of  $H_2O_2$  (20 mM) (black) in 0.1 M TEAP in MeCN. Starting potential = -0.409 V vs  $Fc^{0/+}$  in the anodic direction, scan rate = 50 mV/s.



**Figure S10.** Plot of peak current vs time for **1** (1 mM) in the presence of  $H_2O_2$  in 0.1 M TEAP in MeCN. Scan rate = 50 mV/s. \*Concentration of **1** was 5 mM. The peak current measured appeared at *ca.* **1**.7 V vs Fc<sup>0/+</sup> but was shifted cathodically as the peak current decreased over successive scans towards **1**.46 V vs Fc<sup>0/+</sup>.

	H2O2	
<b>1</b> (mM)	(mM)	k (μA/s)
1	40	24.3
5	20	15.1
1	20	12.8
1	10	6.35
1	5	6.66

**Table S5.** Considering only the linear portion of the plots in Fig S6., observed rate constants of the change in peak current (measured at  $1.7 \text{ V} \text{ vs Fc}^{0/+}$ ) over time of **1** in the presence of H<sub>2</sub>O<sub>2</sub>.



**Figure S11.** Plot of observed rate constants (k) vs [H<sub>2</sub>O<sub>2</sub>] derived from the natural logarithm of peak potentials of **1** (1 mM) in the presence of H<sub>2</sub>O<sub>2</sub> (5, 10, 20, 40 mM).



**Figure S12.** Linear fit applied to the plot of observed rate constants (k) vs [H<sub>2</sub>O<sub>2</sub>] derived from the natural logarithm of peak potentials of **1** (1 mM) in the presence of H<sub>2</sub>O<sub>2</sub> (10, 20, 40 mM).



**Figure S13A.** Monitoring the decomposition of  $H_2O_2$  (40 mM) in the presence of **1** (0.1 mM) by measuring the absorbance of a peroxotitanium complex at 390 nm. At high ratios of  $H_2O_2$  to **1** (400:1), the kinetic profile of the  $H_2O_2$  decomposition was not reproducible over multiple experiments generating large errors. The sigmoidal shape of the curve and the observation of insoluble precipitates indicate autocatalytic behaviour and complex decomposition.



**Figure S13B.** Decomposition of  $H_2O_2$  (20 mM) in the presence of **1** (1 mM). At lower ratios of  $H_2O_2$  to **1** (20:1), the kinetic profile is reproducible over multiple experiments and no precipitates were detected indicating the complex was not decomposed.



**Figure S14.** Monitoring the evolution of oxygen from electrolyte solutions of **1** (0.1 mM) with  $H_2O_2$  (40 mM) and <sup>t</sup>Bu-O<sub>2</sub>H (40 mM). Ratio of peroxide to **1**, 400:1.



**Figure S15.** Cyclic voltammograms of only **1** (red, 5 mM), only  $H_2O_2$  (blue, 20 mM) and only <sup>t</sup>Bu-O<sub>2</sub>H (black, 20 mM) in in 0.1 M TEAP in MeCN. Starting potential = -0.409 V vs Fc<sup>0/+</sup> in the anodic direction, scan rate = 50 mV/s.



**Figure S16.** Cyclic voltammograms of only  ${}^{t}Bu-O_{2}H$  (red, 20 mM) and **1** (5 mM) in the presence of  ${}^{t}Bu-O_{2}H$  (black, 20 mM) in 0.1 M TEAP in MeCN. Starting potential = -0.409 V vs Fc<sup>0/+</sup> in the anodic direction, scan rate = 50 mV/s.

**Table S6** Electrochemical data for the first quasi-reversible oxidation of **1** (5 mM) in the presence of  ${}^{t}Bu-O_{2}H$  vs Fc/Fc<sup>+</sup> in 0.1 M TEAP in MeCN. Background correction of CVs was applied.  $I_{p}{}^{ox}/I_{np}{}^{ox}$  and  $I_{p}{}^{red}/I_{np}{}^{red}$  are the ratios of the peak currents of CVs with  ${}^{t}Bu-O_{2}H$  and no  ${}^{t}Bu-O_{2}H$  present.

t <sub>Bu</sub> −O₂H	$E_p^{ox}$	I <sub>p</sub> ox	$E_{p}^{red}$	$I_p^{red}$	ΔE <sub>p</sub>	Ip <sup>ox</sup> /	E <sub>1/2</sub>	Ip <sup>ox</sup> /	$I_p^{red}/$
(mM)	(mV)	(µA)	(mV)	(µA)	(mV)	$I_p^{red}$	(mV)	$I_{np}^{ox}$	$I_{np}^{red}$
0	329	18.2	252	-17.5	78	1.04	291	N/A	N/A
2.5	324	18.4	254	-10.9	70	1.69	289	1.0	0.62
5	336	20.8	254	-14.4	82	1.45	295	1.1	0.82
10	337	18.3	256	-15.5	81	1.18	297	1.0	0.88
20	333	17.7	253	-10.8	80	1.64	293	1.0	0.62

**Table S7** Electrochemical data for the second quasi-reversible oxidation of **1** (5 mM) in the presence of <sup>t</sup>Bu-O<sub>2</sub>H vs Fc/Fc<sup>+</sup> in 0.1 M TEAP in MeCN. Background correction of CVs was applied.  $I_p^{ox}/I_{np}^{ox}$  and  $I_p^{red}/I_{np}^{red}$  are the ratios of the peak currents of CVs with <sup>t</sup>Bu-O<sub>2</sub>H and no <sup>t</sup>Bu-O<sub>2</sub>H present. Scan rate = 50 mV/s.

$E_p^{ox}$	Ip <sup>ox</sup>	$E_p^red$	$I_p^{red}$	ΔEp	Ip <sup>ox</sup> /	E <sub>1/2</sub>	Ip <sup>ox</sup> /	$I_p^{red}/$
(mV)	(µA)	(mV)	(µA)	(mV)	$I_p^{red}$	(mV)	$I_{np}^{ox}$	$I_{np}^{red}$
1487	19.5	1407	-16.2	80	1.21	1447	N/A	N/A
1473	29.0	1402	-16.2	71	1.79	1438	1.5	1.0
1493	42.6	1383	-21.0	110	2.03	1438	2.2	1.3
1503	61.7	1333	-44.6	170	1.38	1418	3.2	2.8
1517	108	1318	-47.6	199	2.06	1418	5.5	2.9
	Ep <sup>ox</sup> (mV) 1487 1473 1493 1503 1517	$\begin{array}{c c} E_{\rho}^{\text{ox}} & I_{\rho}^{\text{ox}} \\ \hline (mV) & (\mu A) \\ 1487 & 19.5 \\ 1473 & 29.0 \\ 1493 & 42.6 \\ 1503 & 61.7 \\ 1517 & 108 \end{array}$	$\begin{array}{c c} E_{\rho}{}^{\text{ox}} & I_{\rho}{}^{\text{ox}} & E_{\rho}{}^{\text{red}} \\ \hline (mV) & (\mu A) & (mV) \\ \hline 1487 & 19.5 & 1407 \\ \hline 1473 & 29.0 & 1402 \\ \hline 1493 & 42.6 & 1383 \\ \hline 1503 & 61.7 & 1333 \\ \hline 1517 & 108 & 1318 \\ \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $



**Figure S17.** Linear fit applied to the peak current values of the second oxidation peak of **1** in the presence of  ${}^{t}Bu-O_{2}H$  at different concentrations. Data from Table S7. The linear relationship indicates a first order dependence of the catalytic rate on [ ${}^{t}Bu-O_{2}H$ ].



**Figure S18.** Plot of the peak current values of the second oxidation peak of **1** in the presence of  ${}^{t}$ Bu-O<sub>2</sub>H at different concentrations across different scan rates, in 0.1 M TEAP in MeCN.

Table S8 Electrochemical data for the second quasi-reversible oxidation of 1 (5 mM) in the
presence of <sup>t</sup> Bu-O <sub>2</sub> H (20 mM) vs Fc/Fc <sup>+</sup> in 0.1 M TEAP in MeCN. Background correction of CVs
was applied. $I_p^{ox}/I_{np}^{ox}$ is the ratios of the peak currents of catalytic wave with <sup>t</sup> Bu-O <sub>2</sub> H (20 mM)
present.

V	$E_p^{ox}$	Ip <sup>ox</sup>	$E_{p}^{red}$	$I_p^{red}$	ΔE <sub>p</sub>	Ip <sup>ox</sup> /	E <sub>1/2</sub>	Ip <sup>ox</sup> /
(mV/s)	(mV)	(µA)	(mV)	(μA)	(mV)	$I_p^{red}$	(mV)	I <sub>np</sub> ox
50	1517	108	1318	-47.6	199	2.1	1418	5.5
100	1546	129	1338	-47.5	208	2.7	1442	5.3
200	1583	165	1353	-52.7	230	3.1	1468	5.0
400	1643	204	1363	-62.3	280	3.3	1503	4.7
800	1683	247	1383	-73.1	300	3.4	1533	4.4
1600	1743	295	1383	-72.8	360	4.1	1563	4.0



Figure S19. Plot of the scan rate normalised catalytic current vs scan rate.

#### **Rate Constant Calculation**

Adapted from Du Bois *et al.*, the relationship between the catalytic current,  $I_c$  and the peroxide concentration for a reaction that is second order dependent in peroxide (Fig. S20) is given by Eq. S1 for peroxide concentrations sufficiently high that they are unchanged during the course of the reaction and at potentials sufficiently positive that electron transfer is fast.<sup>5</sup>

$$\frac{i_c}{i_p} = \frac{n}{0.4463} \sqrt{\frac{RTk[\ ^tBu-O_2H]^2}{Fv}} \quad \text{Equation S1} \quad (n = 1)$$

From Eq. S1 it can be seen that ratio of  $I_c/I_p$  should be linear with respect to peroxide concentration (Fig. S20). The slopes of the lines shown in Figure S20 should exhibit a linear dependence on  $(1/v)^{1/2}$  (Fig. S21) from which a rate constant of  $2.1x10^{-3}$  M<sup>-2</sup> s<sup>-1</sup> can be calculated.



**Figure S20.** Plot of  $I_c/I_p$  vs <sup>t</sup>Bu-O<sub>2</sub>H concentration for a concentration of 5 mM of **1** in 0.1 M TEAP in MeCN. The linear plots of  $(I_c/I_p)$  vs peroxide concentration indicate a second-order dependence of the catalytic reaction on peroxide.



**Figure S21.** Plot of the slopes of  $I_c/I_p$  vs [<sup>t</sup>Bu-O<sub>2</sub>H] vs  $1/v^{1/2}$ . From Eq. S1 the slope of this plot is  $0.36k^{1/2}$ , or  $k = 2.1x10^{-3}$  M<sup>-2</sup> s<sup>-1</sup>.

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