Electronic Supplementary Material (ESI) for Dalton Transactions

Supplementary Information

"Double-Pillared Cobalt Pacman Complexes: Synthesis, Structures and Oxygen Reduction Catalysis"

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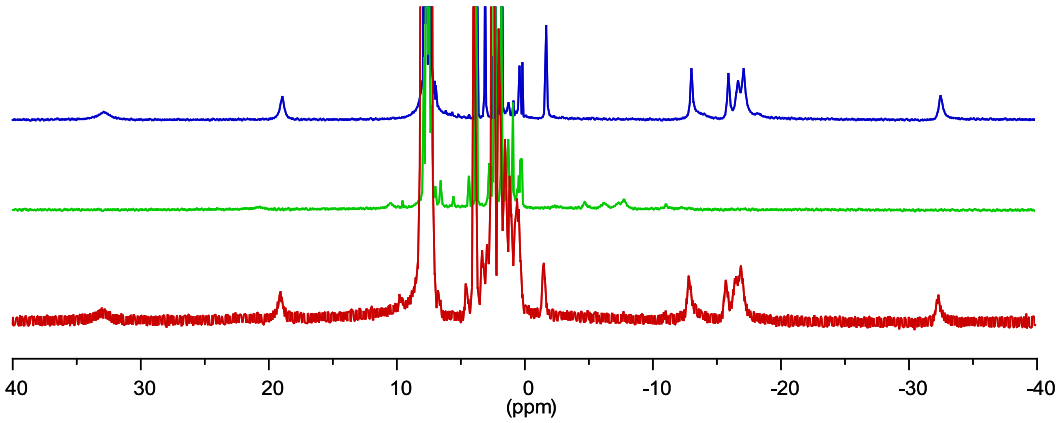

Figure S1: ^{1}H NMR spectra of [Co_2(L)], **1** in PhCN under nitrogen (top, blue spectrum), degassed and placed under oxygen (middle, green spectrum), and degassed again and placed back under nitrogen (bottom, red spectrum). Intensities were scaled to a residual resonance of PhCN.

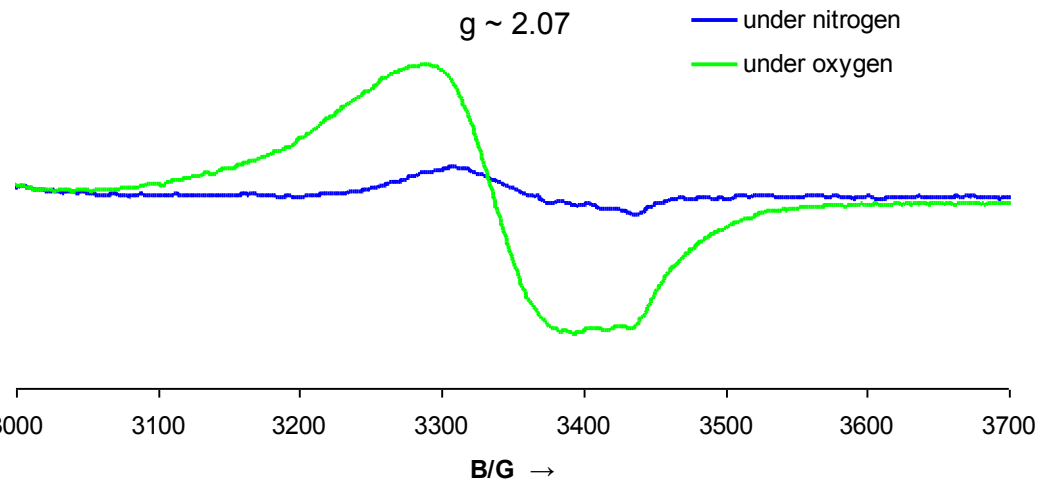

Figure S2: Frozen solution EPR spectra of [Co_2(L)], **1** at 100 K in PhCN under nitrogen (blue line) and under oxygen (green line).

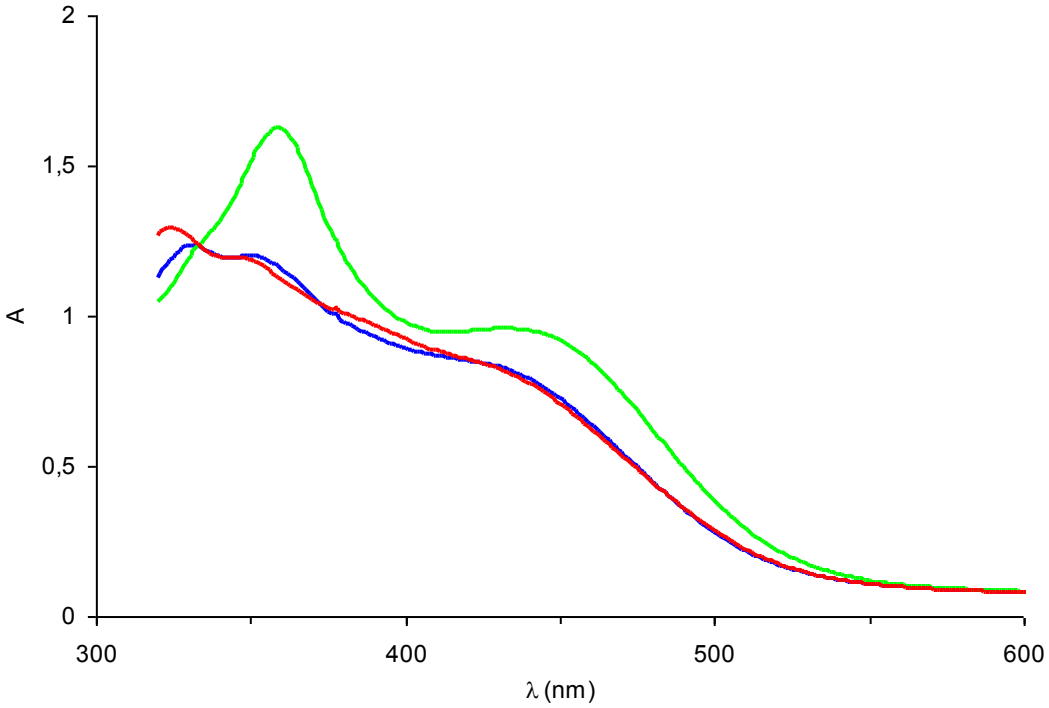

Figure S3: UV-visible spectrum of a 20 µM solution of [Co_2(L)], **1** in PhCN under nitrogen (blue spectrum), degassed and placed under oxygen (green spectrum), degassed again and placed back under nitrogen (red spectrum).

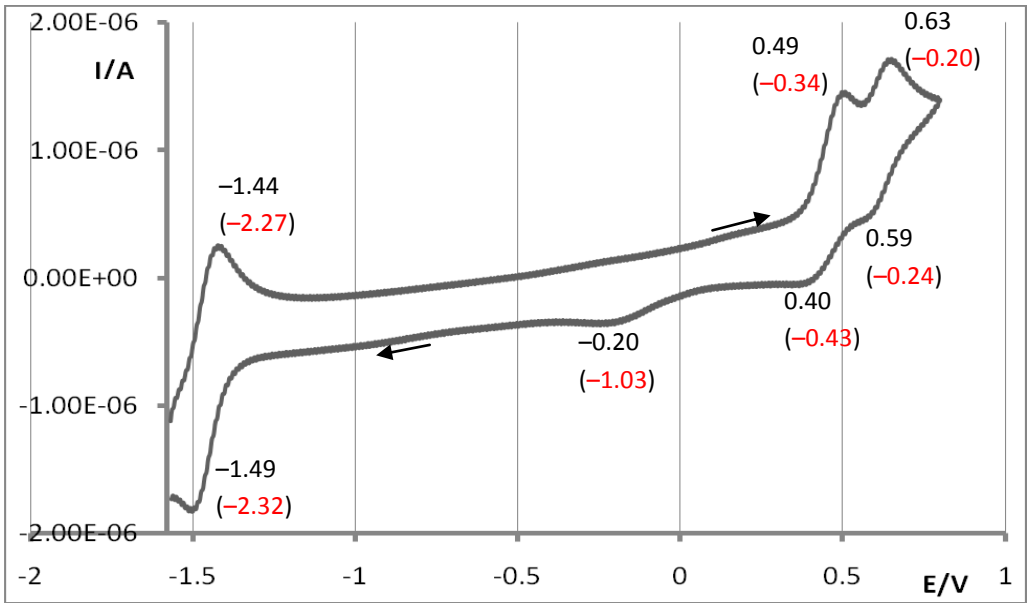

Figure S4: CVs under nitrogen of [Co_2(L)], **1** recorded at 100 mV.s^{-1}. Conditions: 1mM of [Co_2(L)] in dried and distilled PhCN, 0.2 M $^nBu_4NBF_4$ *vs.* Ag^+/Ag (Reference electrode: silver wire; counter electrode: platinum wire; working electrode: platinum). The arrows indicate the direction of scan. Note, the reduction wave seen at –0.20 V is associated with the oxidations that occur at 0.63 V and suggests that a chemical transformation occurs at this potential. Data referenced to Fc^+/Fc shown in parentheses.

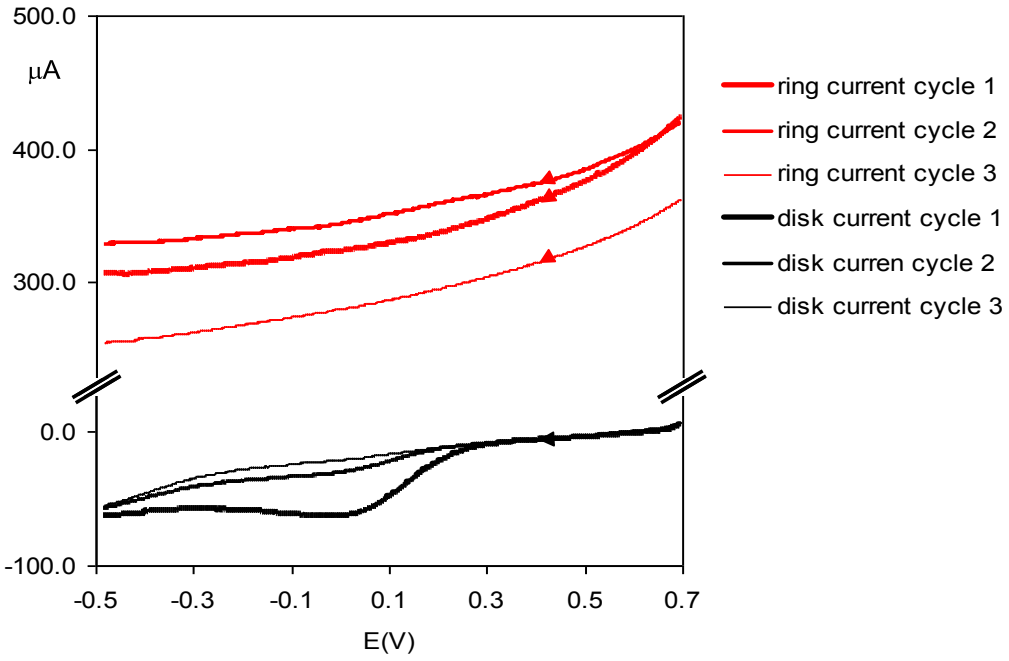

Figure S5: Successive Rotating Ring Disk voltammograms for the reduction of O_2 with [Co_2(L)] coated on a glassy carbon electrode in air-saturated 1.0 M aqueous TFA. The platinum ring was held at +1.00 V *vs.* Ag/AgCl. Rotation rate: 100 rpm (23 % collection efficiency correction factor was applied to the ring current).

Table S1. Crystal data for dicobalt complexes of the Schiff-base pyrrole macrocycle L

	$[Co_2(L)][Co_2(THF)_2(L)]$	$[Co_2(py)_2(L)]$	$[Co_2(H_3O_2)(py)_2(L)][BF_4]$
Crystal data			
Chemical formula	$C_{283}H_{264}Co_8N_{32}O_4$	$C_{84}H_{90}Co_2N_{10}O_4$	$C_{35.25}H_{30.50}B_{0.33}CoF_{1.33}N_{5.25}O$
M_r	4648.70	1421.52	631.53
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$	Hexagonal, $P\bar{3}C1$
Temperature (K)	93	100	100
a, b, c (Å)	15.777 (8), 19.297 (9), 21.128 (11)	14.9616 (3), 16.2706 (3), 28.8075 (6)	27.5796 (4), 27.5796 (4), 15.5052 (3)
α, β, γ (°)	108.942 (8), 110.955 (5), 90.469 (7)	90, 91.944 (2), 90	90, 90, 120
V (Å^3)	5625 (5)	7008.7 (2)	10213.7 (3)
Z	1	4	12
Radiation type	Mo $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	0.65	4.19	4.29
Crystal size (mm)	0.20 × 0.10 × 0.05	0.20 × 0.13 × 0.10	0.26 × 0.14 × 0.07
Data collection			
Diffractometer	Rigaku Saturn70 (2x2 bin mode) diffractometer	SuperNova, Dual, Cu at zero, Atlas diffractometer	SuperNova, Dual, Cu at zero, Atlas diffractometer
Absorption correction	Multi-scan *SADABS* 2007/2	Multi-scan CrysAlisPro, Oxford Diffraction Ltd.	Multi-scan CrysAlisPro, Oxford Diffraction Ltd.
T_{min}, T_{max}	0.723, 1.000	0.616, 1	0.689, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	57646, 20434, 17081	68295, 13901, 9847	50108, 6781, 4322
R_{int}	0.077	0.131	0.054
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.075, 0.215, 1.07	0.082, 0.237, 1.02	0.058, 0.180, 0.75
No. of reflections	20434	13901	6781
No. of parameters	1498	900	393
No. of restraints	54	0	1
H-atom treatment	Riding	Riding	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.98, -0.88	1.28, -0.63	0.81, -0.42
CCDC number	815017	815018	815019

Computer programs: *SMART* (SIEMANS, 1993), *SAINT* (SIEMANS, 1995), SUPERFLIP (Palatinus, 2007), *SHELXL97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 1997), *ORTEP* (FARRUGIA, 1997), *enCIFer* (ALLEN ET AL., 2004).

Table S2. Selected bond lengths and angles for dicobalt complexes of the Schiff-base pyrrole macrocycle L

	$[Co_2(exo\text{-}THF)_2(L)][Co_2(L)]$	$[Co_2(exo\text{-}py)_2(L)]$	$[Co_2(\mu\text{-}H_3O_2)(exo\text{-}py)_2(L)]$
N1-C1	1.329 (5) / 1.331 (5)	1.318 (6)	1.319 (4)
N1-C55	1.433 (6) /1.439 (5)	1.420 (5)	1.431 (4)
C1-C2	1.413 (6) / 1.403 (6)	1.403 (6)	1.403 (5)
C2-C3	1.400 (6) /1.405 (6)	1.395 (6)	1.399 (5)
N2-C2	1.375 (5) / 1.375 (5)	1.376 (5)	1.383 (4)
N2-C5	1.341 (6) / 1.345 (5)	1.340 (5)	1.346 (4)
C3-C4	1.394 (7) / 1.394(6)	1.388 (6)	1.389 (5)
C4-C5	1.427 (6) / 1.415(6)	1.420 (6)	1.407 (5)
Co1-N1	1.998 (4) / 1.976 (4)	2.012 (3)	1.990 (3)
Co1-N2	1.876 (4) / 1.846 (3)	1.881 (4)	1.859 (3)
Co1-N3	1.861 (4) / 1.855 (4)	1.875 (3)	1.865 (3)
Co1-N4	2.001 (3) / 1.967 (3)	2.013 (4)	2.049 (3)
Co2-N5	2.033 (4) / 1.956 (3)	2.009 (4)	-
Co2-N6	1.869 (4) / 1.856 (4)	1.872 (4)	-
Co2-N7	1.867 (4) / 1.841 (3)	1.871 (4)	-
Co2-N8	1.979 (3) / 1.965 (4)	2.008 (4)	-
Co1-S1	2.233 (3) / -	2.145 (4)	1.973 (3)
Co2-S2	2.243 (3) / -	2.142 (4)-	-
Co1-S3	-	-	1.929 (2)
S3-S3′	-	-	2.455 (3)
Co1•••Co2	5.710 (2) / 5.471 (2)	5.8373 (9)	5.5739 (7)
C1-N1-C55	117.3 (4) / 114.9 (3)	117.1(4)	120.4 (3)
N1-Co1-N2	82.51 (15) / 83.17 (15)	81.98(15)	83.40 (12)
N2-Co1-N3	86.81 (15) / 87.27 (15)	86.77(15)	87.77 (13)
N3-Co1-N4	83.04 (15) / 83.17 (15)	82.27(15)	82.52 (12)
N4-Co1-N1	107.45 (14) / 106.37 (14)	107.11(14)	106.14 (11)
	S1 = O1, S2 = O2	S1 = N9, S2 = N10	S1 = N9, S3 = O1