Tailoring dicobalt Pacman complexes of Schiff-base calixpyrroles towards dioxygen reduction catalysis
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General Experimental Details
The synthesis of $\text{Co}_2(L^5)$ was carried out according to literature procedures using standard Schlenk procedures or in a Vacuum Atmospheres Omnilab glovebox and using solvents dried by a Vacuum Atmospheres solvent purification assembly. All other synthetic procedures were carried out using commercial-grade solvents in air. The $^1\text{H}$ NMR spectra were recorded on a Bruker ARX250 spectrometer operating at 250.13 MHz, with residual protic impurities serving as internal standard. Electrospray mass spectra were recorded using a Thermo-Finnigan LCQ Classic ion trap mass spectrometer. UV/Vis spectra were recorded on a Perkin-Elmer Lambda 900 spectrophotometer and IR spectra on a Nicolet Avatar 320 FTIR spectrometer as Nujol mulls. Fluid solution EPR spectra were recorded at 300 K in THF using a Bruker EPX080 spectrometer by Dr. Paul Murray of the University of Edinburgh and were simulated by Prof. Eric McInnes at the University of Manchester. Elemental analyses were carried out by Mr. Stephen Boyer at the London Metropolitan University.

Crystallographic details
X-Ray diffraction data from single crystals of $\text{Co}_2(\text{OH})(\text{py})(L^5)$·4CHCl$_3$ were collected at 93.15 K using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) on a Rigaku MM007 high brilliance RA generator equipped with Saturn 70 CCD detector and data for $\{\text{Co}_2(\text{O}_2)(\text{py})_2(L^5)\}\cdot\{\text{OH}\}$.py·2PhMe were collected at 150 K on a Bruker SMART APEX diffractometer equipped with a CCD detector. Both structures were solved by direct methods and refined using full-matrix least square refinement on $|\mathbf{F}|^2$ using SHELXL-97. All non-hydrogen atoms were refined with anisotropic displacement parameters while hydrogen atoms were placed at calculated positions and included as part of a riding model. In $\{\text{Co}_2(\text{O}_2)(\text{py})_2(L^5)\}\cdot\{\text{OH}\}$, one molecule of PhMe was disordered and was refined using an isotropic model over two sites with 55:45 occupancy. The X-ray data for $\text{Co}_2(\text{OH})(\text{py})(L^5)$ was weak and contained partially-occupied and overlapping CHCl$_3$ groups (C4s, C110, C111, C112; C5s, C113, C114, C115) that were refined using an isotropic model with 60:40 occupancy. The bridging hydroxyl hydrogen atom H1A was located using a 2-site free-variable refinement procedure and refined with fixed thermal parameters.

Oxygen reduction catalysis
The reduction of dioxygen catalysed by oxygenated $\text{Co}_2(L^5)$ was studied in duplicate using a modification of the procedures developed by Fukuzumi, Guilard, and co-workers. In a typical experiment, a mixture of $\{\text{Co}_2(\text{O}_2)(L^5)\}\cdot\{\text{OH}\}/\text{Co}_2(\text{OH})(L^5)$ (9.6 x10$^{-5}$ M) and (C$_5$H$_4$Me)$_2$Fe (0.1 M) in aerated PhCN was transferred into a Teflon-tapped UV-Vis quartz cuvette. The CF$_3$CO$_2$H was added directly to this mixture by microsyringe such that the [CF$_3$CO$_2$H] was 0.4 M, and the measurement started immediately. Data were recorded at 650 nm ($\varepsilon = 290$ M$^{-1}$cm$^{-1}$) until asymptotic behaviour was observed and then the background oxidation of (C$_5$H$_4$Me)$_2$Fe by O$_2$ in the presence of acid under the same experimental conditions was subtracted. The function ln(A$_\infty$-At) was plotted versus time and the pseudo-first order rate constant $k_{obs}$ was obtained as the slope in the first 100s.
**Figure S1:** Sequential reaction of Co$_2$(L$^\text{F}$) in CDCl$_3$ with [D$_5$]-pyridine and O$_2$ (top), and in-situ exchange of pyridine with [D$_5$]-pyridine (bottom).
**Figure S2:** Frozen solution (CHCl₃) *in-situ* X-Band EPR spectra of Co₂(Lᵗ) under N₂ and after reaction with O₂ (inset)

**Figure S3:** Space-fill representations of the X-ray crystal structure of {Co₂(μ-O₂)(py)₂(Lᵗ)}{OH}.py
Figure S4: Inter- and intramolecular hydrogen bonding interactions in Co$_2$(μ-OH)(py)(L$^F$)

Figure S5: Pseudo 1$^{st}$ order plot (left, 0.024 mM catalyst, 0.1 M (C$_5$H$_4$Me)$_2$Fe, 0.4 M CF$_3$CO$_2$H) and determination of k$_{cat}$ for dioxygen reduction catalysed by Co$_2$L$^F$ (right, 0.024 and 0.096 mM).

References:
