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Tailoring dicobalt Pacman complexes of Schiff-base calixpyrroles towards dioxygen reduction catalysis

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Abstract

By modifying the mouth of a macrocyclic dicobalt Pacman complex, it is possible to both isolate new bridging-superoxo and hydroxyl complexes and to tune the reactivity of this system towards catalytic four-electron reduction of dioxygen to water.

Introduction

The reduction of dioxygen is a chemical reaction intrinsic to fuel cells and aerobic organisms and relies on transition metal-based compounds or enzymes to manage the multiple proton and electron inventory during catalysis and ensure the efficient and selective generation of water. Much effort has gone into elucidating a fundamental understanding of this proton-coupled, multi-electron redox reaction,1 in particular to help develop new, base-metal catalysts that are more robust and economical than the Pt-based materials currently used in polymer electrolyte membrane fuel cells.2 In this context, molecular systems such as cofacial or Pacman dicobalt diporphyrins and corroles have proved very effective as catalysts for dioxygen reduction and the spectroscopic, structural, and theoretical analysis of these systems has provided much detail of the mechanism, in particular the identification of the superoxo complex [Co₂(µ-O₂)(diporph)]⁺ as a key director of selectivity.3-6

As an alternative to these porphyrinic complexes that are typically difficult and time-consuming to synthesise, we found that the dicobalt Pacman complex Co₂(L), in which the Schiff-base calixpyrrole ligand L has methyl meso-substituents, reacts with air to form a 90:10 mixture of the peroxo complex Co₂(µ-O₂)(py)₂(L) and the superoxo cation Co₂(µ-O₂)(py)₂(L)⁺; the former peroxo complex was characterised structurally and displayed a zigzag bonding mode of the O₂⁻ unit between the two metals.7 This mixture of compounds acted as a catalyst for the selective four-electron reduction of oxygen to water, albeit slowly and with decomposition, and we proposed that this poor activity profile was due to a combination of the formation of a stable hydroxyl-bridged cation Co₂(µ-OH)(L)⁺ coupled with difficulty in accessing the superoxo cation, the entry point into the catalytic cycle.8 We reasoned that the use of sterically-hindering, aryl meso-groups such as fluorenyl in L°F would both obviate the formation of µ-OH bridged compounds and change subtly the electronic nature of these compounds, features that could promote better catalytic activity. We present here the significance of this ligand modification on the oxygen chemistry of its dicobalt complexes.

The Co⁰Co⁰ complex Co₂(L°F) was prepared as described previously,9 and reacted with air in the presence of pyridine to form a mixture of two new complexes, the Co³⁺Co³⁺ superoxo cation {Co₂(µ-O₂)(py)₂(L°F)}{OH} and the mixed valence Co²⁺Co³⁺ hydroxyl-bridged complex Co₂(µ-OH)(py)(L°F) that are related formally by O₂ loss (Scheme 1).
Scheme 1. Synthesis of dicobalt compounds of the macrocycle $H_4L^F$. Reagents and conditions: (i) 2 [Co(THF){N(SiMe$_3$)$_2$}$_2$], THF; (ii) Air, py, THF.

This reaction was monitored by $^1$H NMR and EPR spectroscopies.† In the $^1$H NMR spectrum (SI, Fig. S1), addition of pyridine to a CDCl$_3$ solution of Co$_2$(L$^F$) causes the well-resolved, but paramagnetically-shifted signals of Co$_2$(L$^F$) to disappear and, on exposure of this mixture to air, new resonances to appear between +40 and -70 ppm that are consistent with the asymmetric environment of the new Co$^{II}$Co$^{III}$ paramagnetic complex Co$_2$(μ-OH)(py)(L$^F$). This formulation is supported further by addition of [D$_5$]-pyridine to the mixture which results in exchange of only one molecule of pyridine (SI, Fig. S1) and also by X-ray crystallography (see below). Significantly, there is no evidence of any diamagnetic peroxo complex Co$_2$(μ-O$_2$)(py)$_2$(L$^F$) in any of these NMR spectra, which contrasts to that seen by us in the oxygenation reactions of Co$_2$(L)$^7$. In the X-band EPR spectrum in frozen CHCl$_3$ (SI, Fig. S2), the broad, featureless resonance for Co$_2$(L$^F$) at $g$ 2.214 is replaced by a less intense (24% by integration), $S = \frac{1}{2}$ signal centred at $g$ 2.016 on exposure to air which is best assigned to the superoxo cation Co$_2$(O$_2$)(L$^F$)$^+$; no signal is seen in fluid solution. Simulation of this resonance in rhombic symmetry suggests that the oxygen radical is bound primarily to one Co centre, with $g_x$ 1.991, $A_x$ 11.5 G, $g_y$ 2.015, $A_y$ 14.0 G, and $g_z$ 2.068, $A_z$ 21.5 G, which contrasts to the 15-line EPR spectra seen normally for superoxo cobalt cofacial diporphyrin complexes and also for Co$_2$(O$_2$)(L)$^+$ in which the O$_2^-$ is bound symmetrically between the two Co$^{III}$ centres. This suggests that the O$_2^-$ is bound either in an asymmetric manner within the cleft or that it coordinates to a single Co outside the cleft.

The superoxo complex {Co$_2$(μ-O$_2$)(py)$_2$(L$^F$)}{OH} was isolated as an analytically-pure material from hot toluene solution.‡ The frozen solution X-band EPR spectrum of this isolated material is identical to that seen in the in-situ experiments, and the IR spectrum displays a broad absorption at 3398 cm$^{-1}$ which supports the
presence of hydrogen-bonded hydroxide; dark red prisms were grown from toluene from which the X-ray crystal structure was determined (Figure 1).†

**Figure 1.** The solid state structures of \{Co₂(µ-O₂)(py)₂(L⁵)\} {OH} (left) and \([Co₂(µ-OH)(py)(L⁵)]\) (right). For clarity, all hydrogen atoms, except on the bridging hydroxyl oxygen and solvent of crystallisation have been omitted (displacement ellipsoids are drawn at 50 % probability).

In the solid state, the O₂ is bound asymmetrically within the Co₂ cleft (Co₁-O₁ 1.907(4), Co₂-O₂ 1.942(3) Å) with an O₁-O₂ bond distance of 1.389(4) Å and a Co₁···Co₂ separation of 4.15 Å. Although the O-O distance is similar to that seen by us in the solid state structure of the peroxo complex Co₂(µ-O₂)(py)₂(L) (1.361(3) Å), DFT calculations carried out by us on this latter peroxo compound and the singly-oxidised superoxo complex Co₂(O₂)(py)₂(L)⁺ showed the O-O bond distances to be identical (difference 0.001 Å) and so a poor measure of the electronic structure. The slightly elongated O-O bond in this case is likely a consequence of the different ligand environment and the strong hydrogen-bonding interaction seen between O₁ and the hydroxide O₁s (O₁•••O₁s 2.801 Å). Analysis of a space-filling model of \{Co₂(µ-O₂)(py)₂(L⁵)\} {OH} (SI, Fig. S3) shows that O₁s is nestled tightly in a cleft formed between the two fluorenyl substituents and the bridging O₂ and that the fluorenyl substituents also display π-stacking interactions with a molecule of pyridine that binds in a cleft adjacent to the hydroxyl group. Intermolecular hydrogen-bonding interactions between metal-coordinated O₂ and a donor such as H₂O or ROH are observed frequently in Ti, V and Mo O₂ complexes in
which the O$_2$ is side-on bound (mean O$_2$···O shortest contact 2.97 Å)$^{10}$ but to a much lesser extent in binuclear Co$_2$(μ-O$_2$) compounds (4 examples, range 3.187-3.653 Å; mean O$_2$···O shortest contact 3.35 Å).$^{11}$ This interaction may suggest that the bound-O$_2$ in {Co$_2$(μ-O$_2$)(py)$_2$(L$^5$)}{OH} is more basic than in previous examples, a feature desirable in oxygen reduction catalysis in which protonation of the superoxo cation is a key mechanistic step that leads to O$_2$ scission and water production.$^5$ The $^1$H NMR spectrum of analytically-pure, crystalline {Co$_2$(μ-O$_2$)(py)$_2$(L$^5$)}{OH} in CDCl$_3$ displays only resonances attributable to Co$_2$(μ-OH)(py)(L$^5$) and implies that the O$_2$ ligand is substituted readily by the OH$^-$ ligand.

The hydroxyl-bridged compound Co$_2$(μ-OH)(py)(L$^5$) is less soluble than the superoxo complex {Co$_2$(μ-O$_2$)(py)$_2$(L$^5$)}{OH}, and a few poorly-diffracting red prisms were isolated from CDCl$_3$ and the X-ray crystal structure determined (Figure 1).$^\dagger$ As with the superoxo cation, a wedged, Pacman structure is seen, in this case with a hydroxyl-group bound asymmetrically between the two cobalt cations (Co1-O1 1.987(5), Co2-O1 1.916(5) Å) which are separated by 3.53 Å. The distorted octahedral coordination sphere of Co2 is completed by a molecule of pyridine, while Co1 adopts a square pyramidal geometry, moving 0.59 Å out of the N$_4$-donor plane into the molecular cleft (c.f. 0.07 Å for Co2). Hydrogen-bonding contacts between the OH$^-$ group and both the fluorenyl group and a molecule of CHCl$_3$ are also seen (SI, Fig. S4) and may provide additional stability to the solid state structure. These geometric features, along with the longer Co-N(pyrrole) and Co-N(imine) bond distances seen for Co1 compared to Co2 and the absence of a counter ion, shows that Co$_2$(μ-OH)(py)(L$^5$) is a rare example of a mixed valence Co$^{II}$Co$^{III}$ hydroxide in which the hydroxyl ligand bridges the two metals asymmetrically.

Preliminary evaluation of the catalytic activity of oxygenated Co$_2$(L$^5$) towards oxygen reduction was carried out using a modification of Fukuzumi and Guilard’s method in which ferrocene derivatives (Fc) act as one-electron reductants in air-saturated PhCN in the presence of acid.$^{12}$ For Co$_2$(L$^5$), the best data were obtained using (C$_9$H$_2$Me)$_2$Fe$^+$ with 9.6x10$^{-5}$ M of catalyst and 0.4 M of CF$_3$CO$_2$H (background production of ferrocenium was subtracted)$^4$ and resulted in the generation of (C$_9$H$_2$Me)$_2$Fe$^+$ that became asymptotic at 6.2 mM concentration after 100 s (Fig. 2); this concentration of (C$_9$H$_2$Me)$_2$Fe$^+$ equates primarily to a four-electron reduction process, i.e. the formation of H$_2$O in preference to H$_2$O$_2$ ([C$_9$H$_2$Me)$_2$Fe$^+$] expected 6.8 x 10$^{-3}$M with [O$_2$] = 1.73 x 10$^{-3}$M).$^\dagger$

Similar data were obtained using the less reducing Cp$_2$Fe as the electron source although in this case asymptotic behaviour was only seen after 600 s (Fig 2, dashed lines). The use of lower concentrations of catalyst results in a decrease in total [Fc$^+$], which may suggest that the catalytically-active species has a moderate turnover. Even so, the catalytic activity of Co$_2$(L$^5$) is enhanced significantly when compared to Co$_2$(L) under the same conditions (Fig. 2, 0.024 mM, Cp$_2$Fe$^+$) and suggests that the ligand modification moving from L to L$^5$ has generated a much more robust catalyst. The rate of formation of (C$_9$H$_2$Me)$_2$Fe$^+$ obeys pseudo-first order kinetics, and $k_{obs}$ obtained from the pseudo-first order plot varies linearly with catalyst concentration with the second order rate constant $k_{cat} = 6.1 \times 10^2 \text{M}^{-1}\text{s}^{-1}$ (SI, Fig. S5). This value of $k_{cat}$ is ca.
600 times less than that of the best cofacial diporphyrin catalyst for four electron O₂ reduction, Co₂(DPX), where \( k_{\text{cat}} = 3.6 \times 10^5 \text{ M}^{-1}\text{s}^{-1} \) (DPX has a xanthene single pillar between the two porphyrins).\(^{12}\)

**Figure 2.** Time profiles for the formation of Fc⁺ (solid lines \((C₅H₄Me)_2Fe⁺\), dashed lines \(Cp₂Fe⁺\)) monitored by UV-vis spectrophotometry in the electron transfer oxidation of Fc by O₂ \((1.73 \times 10^{-3} \text{ M})\) catalysed by Co₂(L²) or Co₂(L) in the presence of 0.4 M CF₃CO₂H in PhCN at 298 K.

It is clear that the presence of the fluorenyl meso-substituents in Co₂(L²) modifies significantly its reactions with O₂, forming the two new compounds \(\{\text{Co}_{2}(\mu-O_2)(\text{py})_2(L^2)\}\{\text{OH}\}\) and Co₂(OH)(py)(L²), and transforming a compound that is a relatively poor catalyst for four-electron dioxygen reduction into one that is considerably more effective. Detailed mechanistic assessments of the dioxygen chemistry of related cobalt cofacial diporphyrin complexes have shown that the entry point into the catalytic cycle for dioxygen reduction is the mixed valence cation Co₂(diporph)⁺ that reacts reversibly with O₂ to form the superoxo cation Co₂(O₂)(diporph)⁺; this latter compound is the key director for the reduction reaction.\(^{1,4,6}\)

In contrast, the oxidation of Co₂(L²) occurs spontaneously on exposure to air to form the mixed valence compound Co₂(OH)(py)(L²) which can react with O₂ to form the key superoxo complex \(\{\text{Co}_{2}(\mu-O_2)(\text{py})_2(L^2)\}\{\text{OH}\}\), so forming a mixture that are effective oxygen reduction catalysts.
Notes and references

‡Syntheses: \{Co_2(O_2)(py)_2(L^5)\} \{OH\} – Solid Co_2(L^5) (0.10 g) was dissolved in air-saturated THF (20 mL), causing an immediate red to dark brown colour change. Pyridine (0.04 mL) was added, and after 3 h, hexane (100 mL) which caused the products to precipitate. The precipitate was collected on a frit and extracted into hot toluene (60 °C, 60 mL), filtered, and reduced in volume. The crude product was precipitated by the addition of hexane and isolated as a brown powder (0.064 g, 54 %). Red brown crystals of \{Co_2(O_2)(py)_2(L^5)\} \{OH\}.py.2PhMe were grown by hexane diffusion into a toluene/pyridine mixture.

Found: C, 70.47; H, 4.50; N, 11.46. C_{27}H_{35}N_{16}O_{2} requires: C, 70.53; H, 4.52; N, 11.42 % \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 360 MHz, 298 K): \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 360 MHz, 298 K): \delta \textsuperscript{1}H 36.7 (s, 1H), 32.5 (s, 2H), 31.3 (s, 2H), 30.5 (s, 2H), 21.6 (s, 6H), 20.6 (s, 2H), 17.5 (s, 1H), 16.8 (s, 2H), 14.5 (s, 1H), 14.4 (s, 1H), 13.7 (s, 1H), 11.9 (s, 1H), 10.0 (s, 1H), 5.5 (s, 1H), 4.8 (s, 1H), 4.4 (s, 2H), 2.1 (s, 1H), 0.9 (s, 1H), 0.8 (s, 2H), -5.0 (s, 1H), -5.8 (s, 1H), -16.4 (s, 6H), -22.3 (s, 1H), -30.4 (s, 1H), -63.1 (s, 2H); IR (KBr, nujol): \nu_\text{max} 332 nm (ln \epsilon 11.12), 257 (11.29), 221 (11.4); ESI-MS (+ve ion): m/z 1052 (M\textsuperscript{+} + H - OH, 100 %). 1036 (M\textsuperscript{+} + H - OH – O, 52), 1019 (M\textsuperscript{+} + H - OH – 2O, 12).

Red crystals of Co\textsubscript{2}(OH)(py)(L\textsuperscript{5}).4CDCl\textsubscript{3} were grown by the slow evaporation of a sample of \{Co\textsubscript{2}(O\textsubscript{2})(py\textsubscript{2})(L\textsuperscript{5})\} \{OH\} in CDCl\textsubscript{3}.

Crystal data \{Co\textsubscript{2}(\mu-O\textsubscript{2})(py\textsubscript{2})(L\textsuperscript{5})\} \{OH\} \textsuperscript{C_{72}H_{63}N_{16}O_{2}Co_{2}(C_{5}H_{2}N)(C-H_{2})_{2}} \textsuperscript{M 1489.49, a 14.4714(4), b 14.8327(4), c 18.8570(6) \AA, \alpha 78.571(2), \beta 75.865(2), \gamma 71.571(2)°, T 150(2) K, triclinic, P-1, Z 2, 43676 reflections}. CCDC 749304; Co\textsubscript{2}(\mu-OH)(py)(L\textsuperscript{5}) \textsuperscript{C_{67}H_{49}N_{16}O_{2}Co_{2}(CHCl\textsubscript{3})_{4}, M 1592.49, a 20.627(2), b 22.087(3), c 30.628(4) \AA, \alpha = \beta = \gamma = 90°, T 150(2) K, orthorhombic, Pbca, Z 8, 85490 reflections}. CCDC 749305.


