

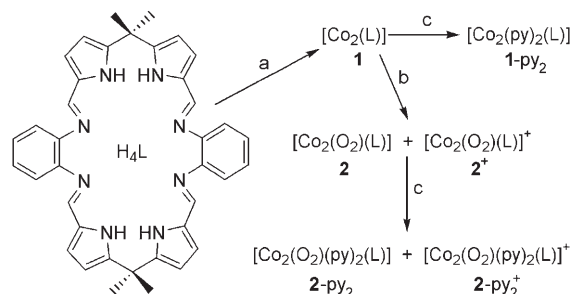
Dioxygen Reduction at Dicobalt Complexes of a Schiff Base Calixpyrrole Ligand**

Gonzalo Givaja, Manuel Volpe, Michael A. Edwards, Alexander J. Blake, Claire Wilson, Martin Schröder, and Jason B. Love*

Cofacial dicobalt diporphyrin and porphyrin–corrole complexes successfully manage the multiple proton and electron inventories essential for the selective catalysis of the four-electron reduction of oxygen to water.^[1–6] The distinctive, face-to-face positioning of the two metal ions within the diporphyrinic cleft helps to circumvent routes to undesired peroxide intermediates, a feature that makes these compounds not only functional models of cytochrome *c* oxidase metalloenzymes,^[7] but also potential non-noble-metal catalysts for fuel cells.^[8] The fundamental role of dioxygen reduction in fuel-cell devices makes these complexes increasingly significant.^[9]

The mechanistic features of dioxygen reduction by dicobalt cofacial diporphyrin complexes have been studied extensively,^[6] and key intermediates such as the superoxido cation $[\text{Co}^{\text{III}}_2(\text{O}_2^*)(\text{diporph})]^+$ (diporph = cofacial or pacman diporphyrin ligands) have been identified spectroscopically and electrochemically.^[4,10,11] Plausible mechanistic pathways for both two- and four-electron reductions of dioxygen have also been elucidated.^[1,2,5] However, the coordination modes of reduced forms of dioxygen within the binuclear cleft have not yet been fully identified. Theoretical calculations present conflicting evidence, and favor both Griffith $\text{Co}_2(\mu^2:\kappa^2:\kappa^2-\text{O}_2)$ and Pauling $\text{Co}_2(\mu^2:\kappa^1:\kappa^1-\text{O}_2)$ coordination modes.^[1,5] Significantly, neither of these modes has been corroborated by solid-state structural data for any dioxygen-containing cobalt diporphyrin complexes or porphyrinic analogues.

We,^[12–15] as well as Sessler and co-workers,^[16,17] recently described a binucleating macrocycle (H_4L , Scheme 1) that is prepared readily in three high-yielding steps from pyrrole and which, upon metal complexation, form rigid structures reminiscent of pacman diporphyrin complexes; significantly, pacman diporphyrin complexes are much more difficult and complicated to synthesize. This structural similarity prompted us to explore the dioxygen reduction chemistry of dicobalt compounds of L^{4-} . We report herein the synthesis and the



Scheme 1. Synthesis of cobalt complexes of L^{4-} : a) $[\text{Co}(\text{thf})\{\text{N}(\text{SiMe}_3)_2\}_2]$, THF, $-2\text{HN}(\text{SiMe}_3)_2$; b) O_2 ; c) pyridine. The ratio of $2/2^+$ is ca. 9:1 and is unchanged upon addition of pyridine.

structural and spectroscopic characterization of unique dicobalt complexes of Schiff base calixpyrroles and their participation in the reduction of oxygen.

The anaerobic transamination reaction between anhydrous H_4L ^[13] and $[\text{Co}(\text{thf})\{\text{N}(\text{SiMe}_3)_2\}_2]$ in THF results in the formation of the toluene-soluble, dark-red, oxygen-free dicobalt complex $[\text{Co}_2(\text{L})]$ (**1**, Scheme 1). The magnetic moment of **1** in CDCl_3 at 300 K is $3.43 \mu_B$ per complex, which is consistent with a ground state of $S = 1$ ($\mu_{\text{so}} = 2.83 \mu_B$) with an orbital contribution, and we tentatively suggest the formation of low-spin, square-planar $\text{Co}^{\text{II}}\text{Co}^{\text{II}}$ cations in **1**. The X-band EPR spectra in fluid and frozen (77 K) solutions and the ^1H NMR spectrum of **1** are featureless. The structure of the bis(pyridine) adduct **1-py**₂ was determined (Figure 1) and clearly demonstrates that a pacman structural motif is

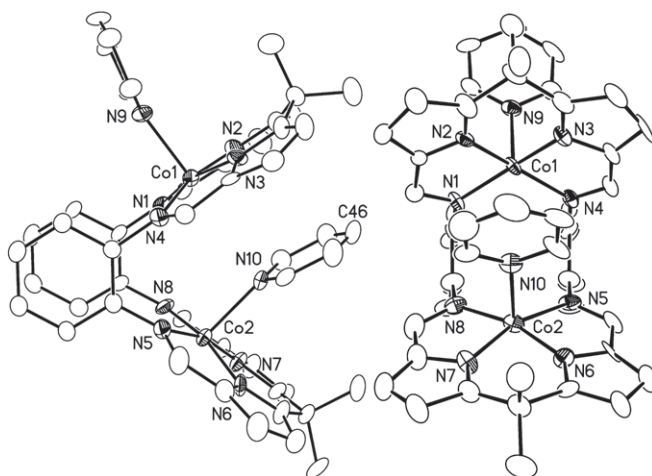


Figure 1. Orthogonal views of **1-py**₂. For clarity, all hydrogen atoms and solvent molecules are omitted; displacement ellipsoids are drawn at 50% probability.

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indeed adopted. Both the cobalt cations are square pyramidal, with Co1 and Co2 displaced out of the N_4 -basal planes by 0.17 and 0.18 Å, respectively, and the apical sites are occupied by pyridine nitrogen atoms that are *exo* and *endo* to the cleft. The canted geometry of the *endo*-pyridine (Co2-N10-C46 161.70°) is similar to that seen by us in $[Cu_2(\textit{endo-py})(L)]$,^[14] and reflects the inability of the binuclear cleft to expand. In contrast, pacman diporphyrin and bis(corrole) complexes have the capacity to undergo considerable vertical expansion.^[18]

The reaction between **1** and O_2 in THF is spontaneous, and the addition of pyridine to the reaction mixture leads to $[Co_2(O_2)(py)_2(L)]$ (**2-py₂**) in moderate yield. The presence of O_2 is supported by elemental analysis, and, in part, by ESMS $[m/z\ 735\ (M-O-2py+H)^+]$, and the 1H NMR spectrum of **2-py₂** supports a pacman structural motif in solution with resonances at 1.52 and 1.21 ppm, which are consistent with *endo*- and *exo-meso*-methyl groups.^[12,13] Furthermore, the diamagnetism of **2-py₂** suggests that it is best described as a $Co^{III}Co^{III}$ bridging peroxide complex.

The X-ray crystal structure of **2-py₂** (Figure 2) confirms that a pacman structural motif is indeed adopted in the solid state and that the peroxido ligand bridges the two cobalt

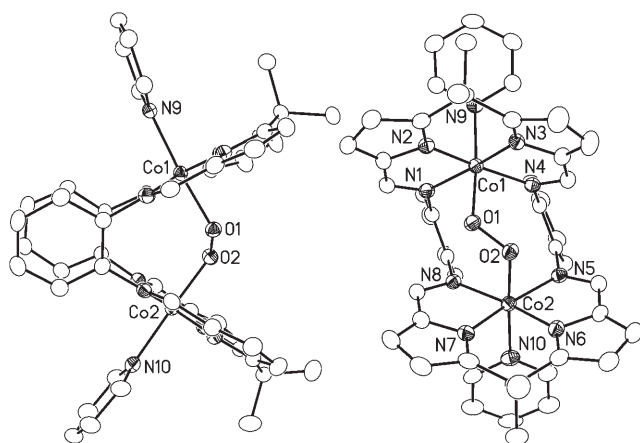


Figure 2. Orthogonal views of **2-py₂**. For clarity, all hydrogen atoms and solvent molecules are omitted; displacement ellipsoids are drawn at 50% probability.

centers. This is, to our knowledge, the first crystallographic characterization of O_2 bound within any dicobalt pacman-like cleft.

The two Co atoms in **2-py₂** adopt octahedral geometries with equatorial macrocyclic N_4 donors and pyridine-N and dioxygen-O donors in the axial sites. The peroxido ligand bridges the two metal centers in a Pauling mode with an O1–O2 bond length of 1.361(3) Å. This value lies at the lower end of the range normally associated with dicobalt peroxido complexes (1.34–1.53 Å, mean 1.45 Å) and could equally be considered as a superoxido bond length (1.29–1.36 Å, mean 1.33 Å).^[19] The O1–O2 bond length is also similar to that calculated for the cationic $Co^{III}Co^{III}$ superoxide complex $[Co_2(\mu-O_2)(dpx)]^+$ (1.35 Å; dpx = diporphyrin xanthene).^[1] It is therefore evident that the O–O bond length in **2-py₂** is not diagnostic of the degree of dioxygen reduction. Comparison

of **2-py₂** with the $Co^{II}Co^{II}$ complex **1-py₂** shows that the average equatorial Co–N(pyrrole) (**1-py₂** 1.870 Å, **2-py₂** 1.870 Å) and Co–N(imine) (**1-py₂** 1.974 Å, **2-py₂** 1.984 Å) bond lengths are similar. However, the average axial Co–N(pyridine) bond in **2-py₂** (2.071 Å) is significantly shorter than in **1-py₂** (2.149 Å) and suggests Co^{III} oxidation states in **2-py₂**. Although the bite angles and Co···Co separation distances for **2-py₂** (62.7°, 4.151 Å) and **1-py₂** (64.8°, 4.301 Å) are similar, the macrocycle is considerably more laterally twisted in **2-py₂** (16.1°) than in **1-py₂** (2.4°), which is commensurate with the zigzag coordination mode of the peroxide ligand.

To gain further insight into the oxygenation of **1**, the reaction between **1** and O_2 was monitored by UV/Vis, EPR, and 1H NMR spectroscopy (see the Supporting Information). It is clear from these reactions that two products are formed on exposure of **1** to O_2 : the $Co^{III}Co^{III}$ peroxide complex $[Co_2(O_2)(L)]$ (**2**) and also the $Co^{III}Co^{III}$ superoxide cation $[Co_2(O_2)(L)]^+$ (**2⁺**; Scheme 1). The cation **2⁺** is a minor component of the mixture, and, furthermore, addition of pyridine to this mixture forms the adducts **2-py₂** and **2-py₂⁺**.

Reaction between **1** and O_2 is associated with the appearance of an absorption band at 500 nm ($\log \epsilon = 4.08\ M^{-1}\ cm^{-1}$) in the UV/Vis spectrum in THF; a similar feature was observed in the UV/Vis spectrum of the diiron oxido complex $[Fe_2(\mu-O)(L)]$.^[17] Degassing the mixture does not regenerate the spectrum of **1**, which indicates that oxygenation is irreversible.

The featureless fluid-solution EPR spectrum of **1** in THF develops into a 15-line signal under O_2 as a result of the formation of the superoxido radical cation **2⁺** (Figure 3). The

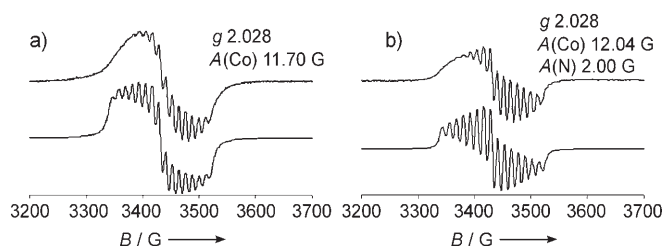


Figure 3. Fluid-solution X-band EPR spectra of a) $[Co_2(O_2)(L)]^+$ (**2⁺**) and b) $[Co_2(O_2)(py)_2(L)]^+$ (**2-py₂⁺**) in THF (top = experiment, bottom = simulation).

isotropic g value and the magnitude of the hyperfine splitting obtained by simulation of the observed spectra are comparable to those of diporphyrinic analogues,^[4,10,11] and the addition of pyridine to the EPR sample results in a spectrum that supports axial pyridine coordination in **2-py₂⁺**. However, quantitative calibration by double integration of the EPR signal of **2⁺** to a $[Cu(acac)_2]$ standard reveals that this former complex is only a minor component of the mixture (< 10%); presumably, **2⁺** is formed by initial oxidation of **1** to **1⁺** followed by dioxygen uptake.^[5]

No significant changes are observed in the 1H NMR spectrum of **1** in $CDCl_3$ upon exposure to O_2 . However, the subsequent addition of $[D_5]$ pyridine results in the observation of an NMR spectrum of the diamagnetic peroxido complex **2-py₂**. This is corroborated by in situ solution magnetic-suscept-

ibility measurements, as, on sequential oxygenation and addition of pyridine, the solution magnetic moment drops from 3.43 μ_B per complex for **1** to 0.76 μ_B ; presumably, the residual magnetic moment is due to the presence of **2-py₂⁺** (see above).

Although the solid-state structure of **2-py₂** provides only limited insight into the degree of dioxygen reduction, it does represent a possible coordination mode of a reduced form of dioxygen within the cleft of cobalt diporphyrin complexes; calculations have shown that these latter complexes display sufficient vertical and lateral flexibility to accommodate O₂ in a Pauling bonding mode.^[1,5] However, the oxygenation chemistry of **1** contrasts subtly with that of [Co₂(diporph)] complexes. Whereas the reaction between **1** and O₂ is spontaneous, irreversible, and yields, primarily, the neutral Co^{III}Co^{III} peroxido complexes **2** and **2-py₂**, the Co^{II}Co^{II} diporphyrinic analogue [Co₂(diporph)] must first be oxidized to the Co^{II}Co^{III} cation [Co₂(diporph)]⁺ before any appreciable dioxygen uptake occurs; this facilitates the reversible generation of the Co^{III}Co^{III} superoxido cation [Co₂(O₂)(diporph)]⁺.^[5] Furthermore, spontaneous dioxygen uptake by [Co₂(diporph)] only occurs in the presence of an imidazole base (NMeIm) and yields the Co^{III}Co^{III} peroxido-bridged cation [Co₂(O₂)(NMeIm)₂(diporph)]⁺.^[5,10]

We have, as yet, been unable to isolate the Co^{III}Co^{III} superoxido cations **2⁺** and **2-py₂⁺**. However, it is clear that facile electron-transfer processes can operate during the oxygenation of **1** and that these resemble the well-studied cobalt diporphyrin complexes; as such, extensive spectroelectrochemical investigation of these new systems is warranted and may provide further insight into the dioxygen reduction reaction.

Experimental Section

1: A solution of [Co(thf)[N(SiMe₃)₂]₂] (2.30 g, 4.96 mmol) in THF (15 mL) was added dropwise to a suspension of H₄L (1.50 g, 2.48 mmol) in THF (50 mL) at room temperature. The resultant deep-red solution was stirred for 16 h, after which the mixture was filtered by cannula and evaporated to dryness under vacuum. The dark solids were extracted into warm toluene (ca. 50 °C, total 50 mL), the mixture was filtered by cannula, and the filtrate was cooled to –20 °C, which resulted in the deposition of **1** (0.89 g, 50%) as dark-red solids, which were isolated and dried under vacuum. Elemental analysis: found C 63.4, H 4.43, N 15.6; C₃₈H₃₂N₈Co₂ requires C 63.5, H 4.49, N 15.6%. Dark-red crystals of **1-py₂** were grown by diffusion of Et₂O into a CH₂Cl₂/pyridine solvent mixture.

2-py₂: A solution of **1** (0.150 g, 0.209 mmol) in dry CHCl₃ (25 mL) was degassed and exposed to air, which resulted in an immediate color change from dark-red to dark-brown. Pyridine (0.5 mL) was added, and the mixture was reduced in volume under vacuum. The addition of Et₂O (25 mL) caused **2-py₂** (0.085 g, 45%) to precipitate as dark-brown solids, which were isolated by filtration, washed with Et₂O (2 × 5 mL), and dried under vacuum. Elemental analysis: found C 63.5, H 4.54, N 15.3; C₄₈H₄₂N₁₀Co₂O₂ requires C 63.4, H 4.66, N 15.4%. ¹H NMR spectroscopy (CDCl₃): δ = 8.20 (brs, 4H, *o/m*-py), 7.98 (s, 4H, N = CH), 7.59 (m, 2H, *p*-py), 7.21 (m, 4H, *o/m*-py), 7.12 (d, 4H, *J* = 3.8 Hz, pyrrole), 6.83 (m, 4H, aryl), 6.38 (brs, m, 4H, aryl), 6.32 (d, 4H, *J* = 3.8 Hz, pyrrole), 1.52 (s, 6H, *meso*-CH₃), 1.21 ppm (s, 6H, *meso*-CH₃); ESMS (positive ion): *m/z* 735 [(*M*–2py–O+H)⁺, 100%]. Crystals of **2-py₂** were grown by diffusion of Et₂O into a CHCl₃/MeOH solvent mixture.

CCDC 617113 (**2-py₂**) and 617114 (**1-py₂**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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