Electrochemical Generation of a New Type of Dioxygen Carrier Complex. Reversible Fixation of Dioxygen by the Highly Electron-deficient Two-electron Oxidized Derivative of a Dicobalt Face-to-face Diporphyrin

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The two-electron oxidized form of the dicobalt(II) face-to-face porphyrin dimer Co_2FTF4, electrogenerated in strictly anhydrous conditions, reversibly binds dioxygen.

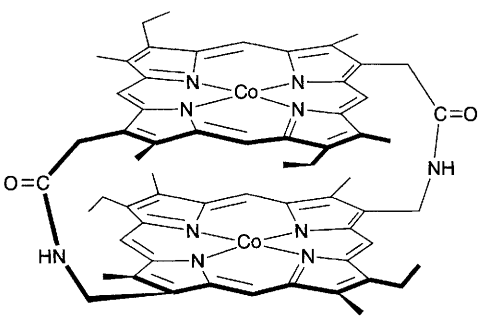
The discovery by Collman and coworkers (confirmed by Chang *et al.*), that dicobalt cofacial diporphyrins are able to promote the direct four-electron reduction of O_2 to H_2O, has stimulated much research.[1,2] Understanding the exact mechanisms by which this catalysis and the O_2 fixation process proceed presents a challenge of relevance to both electrocatalytic and bioinorganic reduction of O_2. In previous articles, we have reported that the dicobalt dimer Co_2FTF4, Fig. 1, does not give rise to reversible oxygen fixation in the neutral redox state $[PCo^{II} Co^{II}P]$ **1**, but that its one-electron oxidized form $[PCo\text{-}CoP]^+$ $\mathbf{1}^+$ gives a remarkably strong complex with O_2;† we suggested that this O_2 complex **2** can be considered to be a μ-superoxo derivative.[2–4]

We now report that under strictly anhydrous conditions the two-electron oxidized form of the Co_2FTF4 dimer $[PCo\ CoP]^{2+}$ $\mathbf{1}^{2+}$ also gives rise to reversible oxygen fixation (Scheme 1). Binding of O_2 to such an electron-deficient dicobalt moiety is unprecedented.

Under N_2, cyclic voltammetry (CV) of the dicobalt cofacial dimer Co_2FTF4 displays two one-electron reversible steps previously ascribed to the oxidation of cobalt(II) to cobalt(III); this illustrates the stability of a mixed-valence intermediate species (Fig. 2).[5] When the solution is saturated with anhydrous O_2, as shown in Fig. 2, the splitting between the two redox steps is enhanced, in accord with the remarkably strong affinity[4] for O_2 of the mixed valence species $\mathbf{1}^+$. However, the first oxidation process becomes electrochemically quasi-reversible under O_2 with a very large peak-to-peak separation ($\Delta E_p = E_{pa} - E_{pc} = 300$ mV at 0.1 V s^{-1}) which is dependent on both the scan rate and on the O_2 partial pressure. Critically, the negative shift and broadening of the cathodic peak for the **2** → **1** process, each increasing with the sweep rate, clearly illustrate that decomplexation of O_2 is required before the reduction to **1**. Consequently, as previously observed,[3,4] **1** does not act as a reversible oxygen carrier Conversely, as is clearly shown by Fig. 2, the second oxidation step, positively shifted under O_2, remains a fully reversible process at $p_{O_2} = 1$ atm, independent of the scan rate, with a $\Delta E_p \approx 60$ mV. Moreover, the variation of the O_2 partial pressure leads to a simple interconversion between the redox systems observed under N_2 and those observed at $p_{O_2} = 1$ atm, with isopotential points for intermediate p_{O_2}. The transformation of the CV is totally reversible and the original trace is restored by bubbling N_2 through the solution. These observations unambiguously show that there is no oxygen uptake/loss during a **2** ↔ **3** electrochemical process and that, therefore, the two electron-oxidized form $\mathbf{1}^{2+}$ gives rise to a reversible oxygen binding reaction leading to complex **3**.

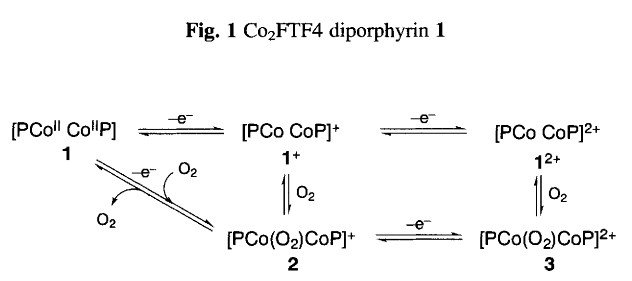
The reversible formation of complex **3** was confirmed by UV–VIS spectrophotometry and EPR measurements. When a solution of the dioxidized species $\mathbf{1}^{2+}$ is saturated with O_2, its UV–VIS spectrum changes totally as shown in Fig. 3; the original spectrum is almost completely restored after purging with N_2 for a short time. Complex $\mathbf{1}^{2+}$ is EPR-silent; the presence of O_2 in the solution generates an intense one-line spectrum at 140 K with $g = 2.003(9)$, typical of a π-cation radical of porphyrin. Again, bubbling N_2 leads back to an almost EPR-silent species.‡ The UV–VIS spectra and the CV indicate that the formation of complex **3** is almost quantitative at $p_{O_2} = 1$.

The present results emphasise an unprecedented reactivity towards O_2 of this family of cofacial dimers. The generally accepted scheme for O_2 interactions with cobalt monoporphyrins and other macrocyclic derivatives involves the binding of dioxygen by neutral cobalt monoporphyrins ($Co^{II}P$).[6] In the present case (Scheme 1), the dimer in its neutral dicobalt(II) form **1** does not bind O_2 whereas the two oxidized forms $\mathbf{1}^+$ and $\mathbf{1}^{2+}$ behave as reversible dioxygen carriers. In terms of electron complement, O_2 fixation by $\mathbf{1}^{2+}$ appears even much more



Co_2FTF4

Fig. 1 Co_2FTF4 diporphyrin **1**



Scheme 1

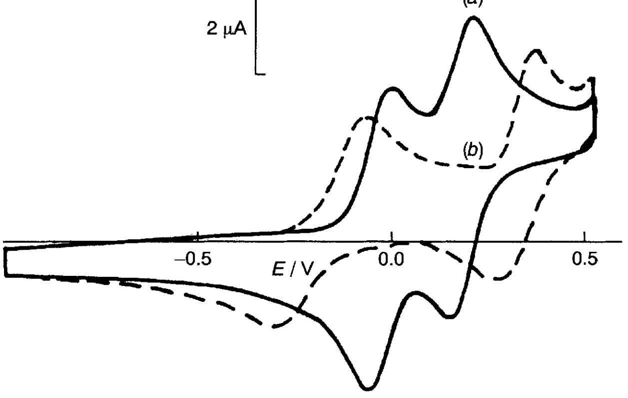


Fig. 2 CV of *ca.* 10^{-3} mol dm^{-3} Co_2FTF4 in PhCN, Bu_4NPF_6 0.2 mol dm^{-3} at a Pt electrode, scan rate 100 mV s^{-1}; (*a*) under N_2 and (*b*) under $p_{O_2} = 1$ atm

puzzling than by $\mathbf{1}^+$,[3,4] in so far as both the two cobalt porphyrin moieties of the dimer are oxidized.

A thorough investigation of the cofacial diporphyrin systems, through experimental evidence rationalised in terms of theoretical considerations, demonstrates that, owing to a so-called 'cofacial effect' of intramolecular interactions (π–π and d–d),[7,8] $\mathbf{1}^{2+}$ must indeed be considered as a dicobalt(II) derivative. This is corroborated by, and also provides a rationale for, the existence of an O_2 fixation process by $\mathbf{1}^{2+}$.

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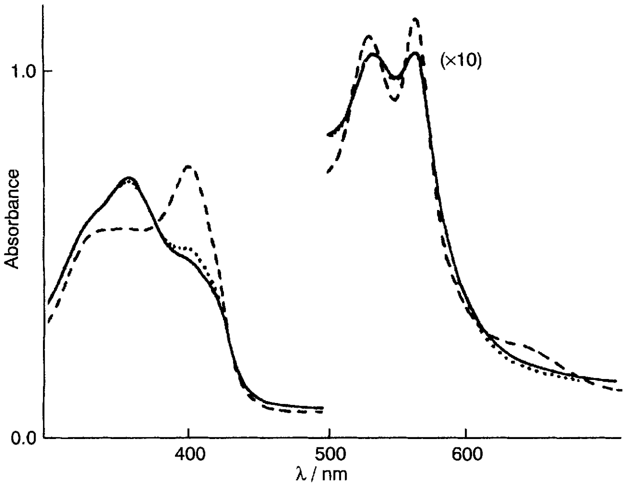

Fig. 3 UV–VIS spectrometry of a *ca.* 4 × 10^{-5} mol dm^{-3} solution of the two-electron oxidized form $\mathbf{2}^+$. (*a*) ——, under N_2; (*b*) - - - -, under p_{O_2} = 1 atm; (*c*) · · · · ·, (*b*) after bubbling N_2.

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Footnotes

† Throughout the present paper the redox states of the cobalt for the different complexes $\mathbf{1}^+$, $\mathbf{1}^{2+}$, **2** and **3** are not indicated: they are the subject of forthcoming discussions.

‡ In both cases the oxy/deoxy cycle can be repeated; however, it is noteworthy that a prolonged bubbling of either N_2 or O_2 through the solution leads to a partial to total loss of activity while the UV–VIS spectrum is converted into that of the hydrated form of $\mathbf{1}^{2+}$.[5] This illustrates the extreme avidity of this redox state for H_2O even at trace levels in the saturating gas.

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