The Role of Lewis Acids in promoting the Electrocatalytic Four-electron Reduction of Dioxygen

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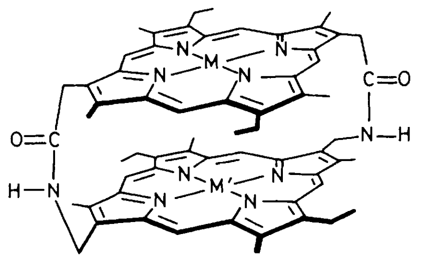
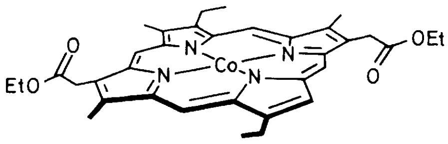
The electrocatalytic reduction of dioxygen by cofacial porphyrins CoMFTF4 (M = H_2, Al, Co, Cu) indicates that a Lewis acid facilitates the four-electron path.

Cobalt derivatives of particular cofacial porphyrin dimers catalyse the overall four-electron reduction of dioxygen while adsorbed on graphite electrodes in aqueous media.[1] The mechanism of this process is poorly understood. At first it was suggested that the fully reduced $Co^{II}Co^{II}$ form of Co_2FTF4, (**1**) (Figure 1) is the active form of the catalyst. This hypothesis was based on an apparent relationship between the more negative surface wave of the adsorbed catalyst and the potential at which the onset of O_2 reduction occurs.[2] This proposed hypothesis has been challenged by the finding that the more positive of the two surface waves involves a porphyrin ring redox process rather than cobalt.[3] We also have discovered that in nonaqueous media the mixed-valence $Co^{II}Co^{III}$ complex, (**1**), exhibits a much greater affinity for O_2 than the $Co^{II}Co^{II}$ form does.[4] The monocobalt derivative of Chang's 'pacman' porphyrin dimer was reported to catalyse the four-electron reduction of O_2 in acid media where the free base porphyrin would be protonated.[5] Taken together these results suggest that the four-electron pathway requires only one redox active cobalt, but that a Lewis acid centre must be present at the oxygen binding site. This hypothesis is further supported by data presented herein.

The present study is based on the Co/Co (**1**), the Co/H_2 (**2**), the Co/Cu (**3a**) and (**3b**), and Co/Al (**4**) derivatives of the FTF4 cofacial porphyrins. These compounds† were tested as catalysts for O_2 reduction while adsorbed on edge plane graphite rotating disk electrodes immersed in O_2-saturated, 0.1 M CF_3CO_2H. The currents were determined potentiostatically as a function of electrode rotation rate at 0.4 V *vs.* a normal hydrogen electrode in a three-electrode cell.‡ Typical linear slopes of Koutecky–Levich plots ($i_{\lim}^{-1}$ *vs.* $\omega^{-1/2}$) derived from data points at 400, 1600, 2500, and 3600 r.p.m. are displayed in Figure 2 along with theoretical dashed lines for n = 2e and n = 4e paths.§ Data from a monomeric cobalt porphyrin, known to be a two-electron O_2 reduction catalyst,



(**1**)-(**4**)



(**5**)

Compound	M	M'	$n \pm 0.2$
(**1**)	Co	Co	3.8
(**2**)	Co	H_2	2.9
(**3a**)	Co	Cu	1.8
(**3b**)	Cu	Co	1.9
(**4**)	Co	Al	3.0
(**5**)	Co	—	2.1

Figure 1. The number of electrons, n, taken from the slopes of Koutecky–Levich plots for O_2 reductions with the catalysts (**1**)—(**5**).

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† These substances were prepared by standard methods[6] and analysed by electron impact and secondary ion mass spectrometry. It is important to note that the complexes (**2**), (**3a**), (**3b**), and (**4**) are free of (**1**) by this criterion.

‡ The reference electrode was Ag/AgCl (saturated KCl) and the counter electrode was a Pt disk. If the electrode is operated at more positive potentials, the catalyst is degraded.

§ The method of Anson[7] using a platinized graphite electrode was used to determine the product $(D_{O_2})^{2/3}(\cdot C_{O_2})$ required for the theoretical plots. Pt is a four-electron catalyst.

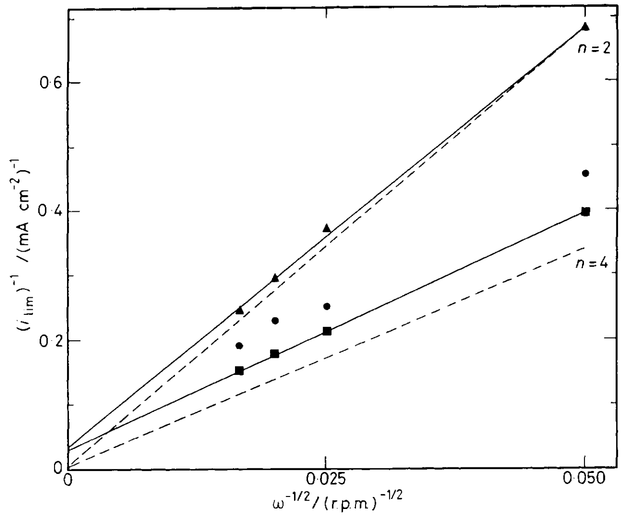

Figure 2. Koutecky–Levich plots for catalysed O_2 reduction by (■) Co_2FTF4 (**1**); (▲) Co monomeric porphyrin (**5**); (●) CoH_2FTF4 (**2**). Dashed lines represent the theoretical values for the diffusion controlled two- and four-electron pathways.

are also shown. With the assumption that a common catalyst site is involved in O_2 reduction paths, the slopes of their linear plots reflect the average *n* values for these catalysts. The estimated composite *n* values are shown in Figure 1.

Control experiments show that introducing Cu into the free-base ring of the mono-Co derivative produces a catalyst which exhibits an *n* value of 1.8 ± 0.2. However, similar treatment of the bis Co derivative (**1**) with Cu^{2+} has no measured effect on its catalytic activity. Thus, Cu does not displace Co. Independently prepared Co/Cu derivatives, (**3a**) and (**3b**), afforded two-electron catalysts, $n = 1.8$ and 1.9. Taken together, these results show that the *n* value for the H_2/Co derivative, (**2**), does not derive from a Co_2FTF4 impurity.†

Copper porphyrins do not exhibit electrocatalytic activity towards O_2 reduction; neither do these exhibit any affinity for axial ligands. Thus, the catalysts which exhibit a significant fraction of an $n = 4$e path have in common a Lewis acid site near the O_2 binding Co^{II} centre: a Co^{III} [in (**1**)], an Al^{III} [in (**4**)], or a protonated free-base porphyrin [in (**2**)]. We speculate such Lewis acids bind the terminal O of Co–O–O in the inner porphyrin cavity, thereby facilitating electron transfer and promoting O–O bond cleavage. It is interesting that the highly acidic aqueous medium itself is not effective in promoting the four-electron reduction of O_2. For example, monomeric cobalt porphyrins such as (**5**) catalyse the two-electron path exclusively. An adjacent Lewis acid site is apparently required to stabilise kinetically the intermediate reduced states. These compounds do catalyse the reduction of free H_2O_2, but at a much slower rate than that observed for O_2 reduction. The rate limiting step in O_2 reduction probably involves O_2 binding to the metal centre. This step may be common to both the four-electron and two-electron paths.

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