Dioxygen Fixation by a Mixed-valence Dicobalt Cofacial Porphyrin

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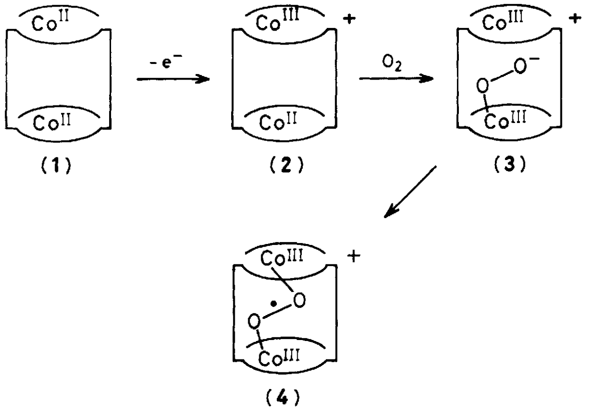
A mixed-valence $Co^{II}Co^{III}$ compound is obtained by electrochemical oxidation of a dicobalt(II) cofacial dimeric porphyrin; unexpectedly, this compound reacts instantaneously with oxygen, even in the absence of an axial ligand on the cobalt(II), leading to a μ-superoxo dicobalt complex.

Recently we described the catalytic properties towards dioxygen electroreduction of a dicobalt porphyrin dimer where the two cofacial rings are linked by four-atom bridges (Co_2FTF_4)† (**1**). This compound catalyses the four-electron reduction of oxygen to water in acidic aqueous media.[1] A rotating ring-disc electrode was used to demonstrate the absence of hydrogen peroxide during the catalytic reduction of oxygen, the catalyst being adsorbed on the graphite disc. Owing to the experimental conditions and to the very low amount of dimeric porphyrin adsorbed at the electrode surface, it is difficult to elucidate the electrode reaction pathway; solutions of the cobalt porphyrin in organic media were therefore studied in order to understand the role played by the catalyst and to characterize some of the intermediates. The use of aprotic solvents permits us to separate the redox, oxygen fixation, and protonation steps.

An important result of the present study reveals an unexpected high oxygen affinity of the mixed valence $Co^{II}Co^{III}$ cofacial porphyrin (**2**).



The electrochemistry of the cofacial porphyrin (**1**) under a nitrogen atmosphere clearly shows that the two cobalt(II) atoms of the molecular form are oxidized separately; the difference between the two Co^{III}/Co^{II} apparent standard potentials is close to 0.2 V.[2] A mixed-valence compound (**2**) in which the cofacial porphyrin contains a cobalt(II) and a cobalt(III) is conveniently produced by electrolysis. Although the mixed-valence binary porphyrin (**2**) seems to be very reactive, its solutions in benzonitrile or methylene chloride are

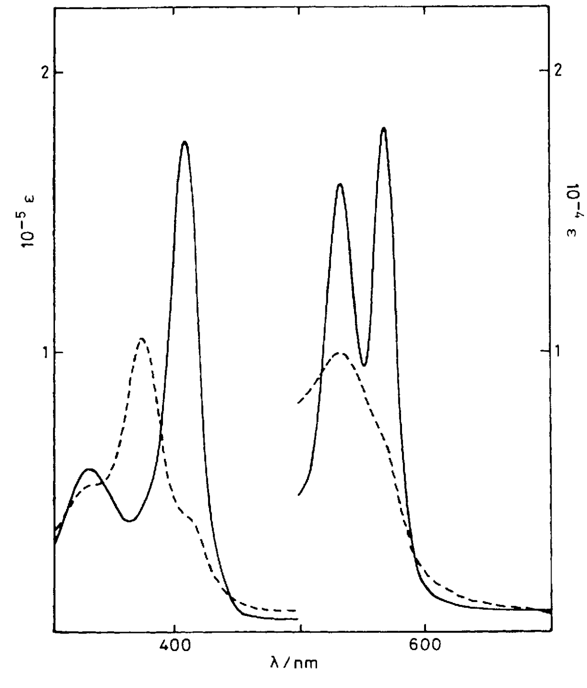


Figure 1. U.v.-visible spectra of the mixed-valence $Co^{II}Co^{III}$ cofacial porphyrin: —— under a nitrogen atmosphere, – – – – in the presence of oxygen.

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† FTF = 'face to face,' ref. 1.

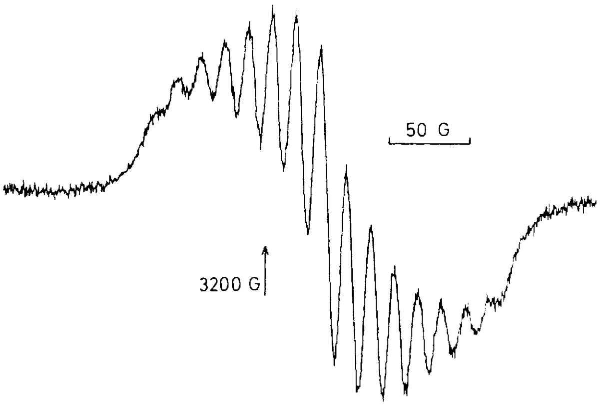

Figure 2. E.s.r. spectrum (room temperature) of the mixed-valence $\mathrm{Co^{II}Co^{III}}$ cofacial porphyrin in the presence of oxygen in methylene chloride.

chemically stable under an inert atmosphere and do not appreciably disproportionate. These solutions of (**2**) were characterized by u.v.–visible and e.s.r. spectroscopy. The stabilization of the two cobalt ions at different redox states, though they are in quasi-identical environments, probably results from interactions between the metal centres held close to each other by the configuration of the biporphyrin ligand.

The binary porphyrins (**2**) and (**1**), bearing respectively one and two cobalt(II) ions, are each potential candidates for dioxygen binding, and so we have examined their reactivity.

In the absence of an axial ligand other than the solvent itself, (**1**) reacted *slowly* with oxygen, giving the putative μ-superoxo complex (**4**); the half-reaction time for a 10^{-4} M solution in oxygen saturated benzonitrile was about one hour. When a nitrogenous base was present the same oxygenated complex was obtained as soon as air or pure oxygen was bubbled through the solution, meaning that oxygen not only binds to the biporphyrin but also behaves as an oxidant. The formation of such μ-superoxo species has previously been reported for the biporphyrin (**1**) and for a closely related compound;[3] these paramagnetic complexes were obtained by chemical oxidation of μ-peroxo, e.s.r. silent, intermediates.

The behaviour of the mixed-valence compound (**2**) is different; in benzonitrile or methylene chloride solutions, in the absence of a potential axial ligand, (**2**) reacted *instantaneously* with oxygen. The u.v.–visible spectrum of a solution of (**2**) prepared under a purified nitrogen atmosphere is represented in Figure 1. The spectral modification was complete as soon as the solution was brought into contact with pure oxygen or air. When in contact with oxygen, the mixed-valence porphyrin (**2**), which is e.s.r. silent at ambient temperature in methylene chloride, exhibited an isotropic, fifteen-line spectrum (Figure 2) [$g_{\mathrm{iso}} = 2.02$, $A_{\mathrm{iso}}^{\mathrm{Co}} = 14.5$ G‡]. This spectrum is typical of a μ-superoxo dicobalt complex (**4**), and was largely unchanged when a nitrogenous ligand (*N*-methylimidazole) was present in solution; there were slight modifications of the e.s.r. spectrum [$g_{\mathrm{iso}} = 2.02$, $A_{\mathrm{iso}}^{\mathrm{Co}} = 10.8$ G‡].

These results clearly establish that the co-ordination of oxygen by (**2**) is fast and complete in the absence of an axial ligand other than the solvent itself. In this case, the μ-superoxo dicobalt complex is the product of a complexation reaction of dioxygen with the $\mathrm{Co^{II}Co^{III}}$ complex, whereas such compounds are generally obtained from dimeric cobalt(II) complexes by an oxidation step which follows the formation of a μ-peroxo complex.[3,4]

The high reactivity of the mixed-valence cofacial porphyrin (**2**) can be understood if one postulates the existence of a superoxo intermediate (3). Previous studies refer to the formation of such compounds from cobalt monomers in the absence of a base.[5] An intermediate such as (3), formally equivalent to a $\mathrm{Co^{III}{-}O_2^{-}\ Co^{III}}$ complex, would spontaneously evolve to the μ-superoxo form (**4**) by interaction of the negative charge located on the O_2 moiety with the very close cobalt(III) centre.

This result demonstrates the participation of the two cobalt centres in the oxygen co-ordination process. The complexation of O_2 by the mixed-valence compound may be an important step in the mechanism of the oxygen electroreduction catalysed by the cobalt cofacial porphyrin on an electrode surface.

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‡ 1 G = 10^{-4} T.