The Four-electron Reduction of Oxygen to Water on a Planar Cobalt Chelate

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In the reduction of oxygen on the planar binuclear cobalt chelate bis-(3,5-di-2-pyridyl-1,2,4-triazole)dicobalt dichloride, adsorbed on pyrolytic graphite, reduction to water occurred in alkaline solution, whereas in acid solution only hydrogen peroxide was formed; the results are compared with those for other binuclear cobalt chelates already reported.

For almost two decades, 3d transition metal chelates have been studied as electrocatalysts for the cathodic reduction of oxygen. The best activities were obtained with the N4-chelates of Fe and Co. It was also shown that mononuclear Co chelates reduce oxygen to hydrogen peroxide; only with Fe as a central metal ion was reduction of oxygen to water observed. In 1979 Collman, Anson, and collaborators, however, reported the reduction of oxygen to water on the cofacial dicobaltporphyrin. The two porphyrin rings are so spaced that bridging absorption of O2 is possible. Clearly, this bridging absorption, requiring the presence of two Co centres at the appropriate distance, is a crucial condition for the occurrence of 4e⁻ reduction. In principle, this condition can also be fulfilled by planar chelates, containing two Co-ions. Indeed, 4e⁻ reduction of oxygen in the planar cobalt complex was reported recently by Yeager and Sarangapani.3

We now report our results with a different planar binuclear Co complex, namely bis-(3,5-di-2-pyridyl-1,2,4-triazole)-dicobalt dichloride (3) [Co2(dpt)2Cl2], kindly provided by Dr. R. Prins, Leiden State University. The electrochemical measurements were performed with a rotating ring (Pt)-pyrolytic graphite disc electrode (S = 0.5 cm²; N = 0.27), in a standard three-compartment electrochemical cell. All potentials are given with respect to the reversible hydrogen electrode (R.H.E.). The ring was slightly platinized to ensure quantitative H₂O₂ detection; the ring potential was set at 1.2 V vs. R.H.E. Before each experiment, the ring was activated by periodic evolution of hydrogen and oxygen for 1 min. The catalyst was applied to the disc (previously polished with 0.3 μm Al₂O₃, Buehler) via irreversible adsorption from a 5 × 10⁻³ M solution of Co₂(dpt)₂Cl² in warm (~40 °C) dimethyl sulphoxide. Since the adsorption appeared to be slow, an adsorption time of 2 h was used. The reduction of O₂ was measured in both alkaline and acidic O₂-saturated solutions (1 M KOH and 0.5 M H₂SO₄, respectively), by scanning the disc potential from 1.0 to 0.2 V vs. R.H.E. at 50 mV s⁻¹. Moreover, an attempt was made to characterize the disc electrode in O₂-free 1 M KOH. The results for the O₂ reduction in alkaline solution are given in Figure 1, the curves for which were taken after ca. 5 scans at 64 s⁻¹. During the first scans, qualitatively the same results were obtained; however, somewhat less H₂O₂ was produced. Since the diffusion-limited current for O₂ to H₂O conversion at 64 s⁻¹ is 3 mA in this electrolyte, it is clear from both disc and ring current that O₂ is reduced to water in two waves; in the first wave, the main product is H₂O₂. During the second wave, the limiting current for the 4e⁻ reduction of water is virtually reached.

The results in acid solution are presented in Figure 2. Since the complex is unstable in acid solution, only the first scans at 16 s⁻¹ are given. The diffusion-limited current for the reduction of O₂ to H₂O at 16 s⁻¹ is 2 mA under these conditions; it is therefore clear that virtually only H₂O₂ is formed. Owing to the lack of stability in acid solution the characterization of the disc electrode was only performed in O₂-free 1 M KOH. In this case the disc potential was varied from 1 to 0 V vs. R.H.E. at 100 mV s⁻¹, and vice versa. The results (Figure 3) show that although the cyclic voltammogram...
of the modified disc electrode significantly differs from that of the unmodified electrode background, no distinct redox couples can be detected, as was also reported by Sarangapani\(^3\) for complex (2). If nevertheless the observed humps are considered to correspond to one-electron redox processes, one can conclude from Figure 2 that the complex is adsorbed on a monolayer level. Summarizing, the conclusion of this study is that Co\(\text{dpt})_2\text{Cl}_2\) is able to reduce O\(_2\) to H\(_2\)O in alkaline solution.

If we now compare the properties of the binuclear cobalt chelates reported so far, two groups can be distinguished: planar complexes, reducing O\(_2\) to H\(_2\)O in alkaline solution, and ‘sandwich’ complexes, either amide,\(^2\) complex (1), or anthracene\(^4\) bridged, complex (4), giving reduction to H\(_2\)O in acid solution. Both groups allow the formation of \(\mu\)-peroxo adducts so this cannot explain the reversed selectivity. In our view this phenomenon is related to the formal redox potentials of the Co centres; 4e\(^-\) reduction seems only to occur if these potentials have values in the range 0.6—0.7 V vs. R.H.E. The sandwich complexes fulfill this condition in acid solution. If it is assumed that the Co\(^{II}\)-Co\(^{III}\) redox processes are pH-independent, the potentials with respect to R.H.E. in the same solution can shift 60 mV in the anodic direction per unit increase in pH. As a consequence, the potentials of the sandwich complexes will be too high in alkaline solution, leading to H\(_2\)O\(_2\) production. Unfortunately, neither we nor Sarangapani and Yeager\(^3\) were able to detect distinct redox peaks at the planar complexes in alkaline solution, but the experimental results indicate that these potentials have the appropriate values in this electrolyte. Likewise, these potentials will be too low in acid solution, leading, again, to H\(_2\)O\(_2\) as end product. If this model is correct, it also implies that it is impossible to develop cobalt-containing catalysts that give 4e\(^-\) reduction both in acid and in alkaline solution since the reduction of O\(_2\) and H\(_2\)O can only occur in a limited pH range.

The observation that the sandwich complexes (1), (4), and (5) produce virtually no H\(_2\)O\(_2\), while the planar complexes (2) and (3) yield considerable amounts, can be explained by the fact that the activity of the corresponding monomeric adducts differ in acid and alkaline solution. If O\(_2\) is attached to one Co atom, the most probable rate-determining step is the formation of superoxide: O\(_2\) + e\(^-\) → O\(_2^\cdot\)^-, leading to H\(_2\)O\(_2\) as end product. This reduction to H\(_2\)O\(_2\) is more reversible in alkaline

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**Figure 1.** Oxygen reduction in 1 m KOH at Co\(\text{dpt})_2\text{Cl}_2\), (3), adsorbed on pyrolytic graphite. Rotation frequencies 4 (i), 16 (ii), 36 (iii), and 64 s\(^-\) (iv).

**Figure 2.** Oxygen reduction in 0.5 m H\(_2\)SO\(_4\) at Co\(\text{dpt})_2\text{Cl}_2\), (3), adsorbed on pyrolytic graphite. Results of the first scans at a rotation frequency of 16 s\(^-\). i, unmodified disc electrode; ii, disc electrode modified with Co\(\text{dpt})_2\text{Cl}_2\), scan 1, iii, scan 4; iv, scan 10.
solution because its rate-determining step is pH-independent. At high pH the monomeric and dimeric pathways proceed at comparable rates, leading to mixed production of \( \text{H}_2\text{O} \) and \( \text{H}_2\text{O}_2 \). The dimeric pathway, however, seems to be pH-dependent. The \( E_4 \) of this pathway with respect to R.H.E. remains therefore unchanged at different pH values. The \( E_1 \) of the monomeric pathway is pH-independent and this \( E_4 \) vs. R.H.E. shifts 60 mV in the anodic direction per unit increase in pH. In acid solution, the dimeric pathway is therefore much more favourable, so at low overpotential, there will be no competition between the two pathways, and only \( \text{H}_2\text{O} \) is formed. At potentials where the monomers also start to reduce oxygen, \( \text{H}_2\text{O}_2 \) can be formed. This indeed is observed experimentally.  

Finally, we discuss a striking result of Liu et al., namely the fact that the anthracene-linked diporphyrin (5), containing only one cobalt atom, was also able to reduce \( \text{O}_2 \) to \( \text{H}_2\text{O} \), but at lower rates than the corresponding dicobalt complex. Although the second porphyrin ring does not contain a Co ion, the potential of the remaining Co has shifted to 0.6 V vs. R.H.E.  

Nevertheless, the formation of an intramolecular adduct seems unlikely since the molecule contains only one catalytic centre. Perhaps in this case intermolecular \( \mu \)-peroxo adducts are formed. The lower activity of the monocobalt diporphyrin (5) is easily explained by a lower number of active sites, since only relatively few dimeric species will be present on the surface. Such a decrease in the number of active sites shifts \( E_4 \) in the cathodic direction, but does not prevent the attainment of the limiting current. This hypothesis could be checked by repeating the experiment on 'stress annealed' pyrolytic graphite. This approximates to a perfectly smooth surface. Assuming that the porphyrin rings of adsorbed molecules lie parallel to the surface, intermolecular Co–O–O–Co binding will be absent on this substrate, and consequently no 4e\(^-\) reduction should occur.

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References