Electrochemically Induced Release of Dioxygen from a Cobalt(II) Complex

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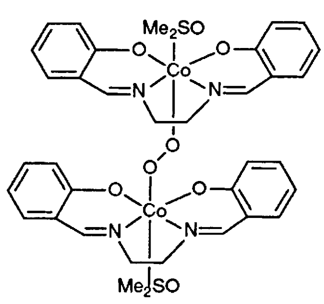
Electrochemical oxidation of the μ-peroxo dimer of Co(salen) [salen = *N,N'*-ethylenebis(salicylideneiminato)] results in dissociation of the dimer to Co^{III}(salen) and molecular oxygen.

Cobalt(II) chelates with Schiff's base ligands have attracted considerable interest due to their ability to bind dioxygen reversibly.[1,2] Complexes with this property have potential in the separation of dioxygen from liquids or gas mixtures. Recently there has been considerable interest in the patent literature in the electrochemically induced release of dioxygen from transition metal complexes.[3,4] In some previous work, we have shown that the results of one of these studies had been wrongly interpreted.[5] Since electrochemical release of bound oxygen could be an important part of an oxygen extraction



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system, particularly from sea water, we have examined the electrochemical behaviour of another dioxygen complex, the μ-peroxo dimer of Co(salen). This complex is of particular interest in that the binding of O_2 in the formation of the dimer is essentially pressure-swing irreversible; hence there is no requirement to have both 'free' oxygen and 'metal ion bound' oxygen present simultaneously in solution.

The complex $[Co(salen)]_2O_2(Me_2SO)_2$ **1** was prepared according to the literature procedure.[6]

Fig. 1*a* shows the cyclic voltammogram of complex **1** (0.005 mol dm^{-3}) at a Pt electrode in Me_2SO solution containing Bu_4NBF_4 (0.1 mol dm^{-3}) as supporting electrolyte. The half-wave potential ($E_{1/2}$) for the Co^{II-III} couple is at −0.08 V *vs.* a standard calomel electrode (SCE) while the less reversible Co^{I-II} couple has $E_{1/2}$ −1.32 V. In Fig. 1*a* the cathodic wave at −0.8 V *vs.* SCE is due to the reduction of dissolved oxygen to superoxide ($O_2^{\bullet -}$).[7] After purging the solution with argon for 10 min, the voltammogram (Fig. 1*b*) showed loss of the peak ascribed to the presence of O_2. Over a period of 60 min there was no evidence for atmospheric oxygen having re-entered the cell. Controlled potential electrolysis at a Pt grid electrode at +0.4 V *vs.* SCE gave rise to the reappearance of a cathodic wave at −0.8 V (Fig. 1*c*) which disappeared after purging the solution with argon. This wave is also ascribed to the reduction of O_2 to $O_2^{\bullet -}$.

The only source of oxygen in the electrochemical cell after the electrolysis step was the dioxygen originally bound up in the μ-peroxo dimer. No oxygen was detected by simply stirring the solution under argon without applying a potential. This leads us to conclude that the electrochemical process shown in equation 1 occurred. This process yields two products, dioxygen and monomeric Co^{III}(salen). However, since reduction of the monomeric species occurs at the same potential as reduction of the dimeric species, only dioxygen reduction emerges as a new wave in the cyclic voltammogram.

$$[Co^{II}(salen)]_2O_2(Me_2SO)_2 \rightarrow 2Co^{III}(salen)Me_2SO + O_2 + 2e^- \quad (1)$$

The Co^{III} complex can be electrochemically re-reduced back to the active Co^{II} form for use in a cyclic system. We believe this is the first evidence in the open literature for the successful release of O_2 from a complex, upon application of an oxidizing potential.

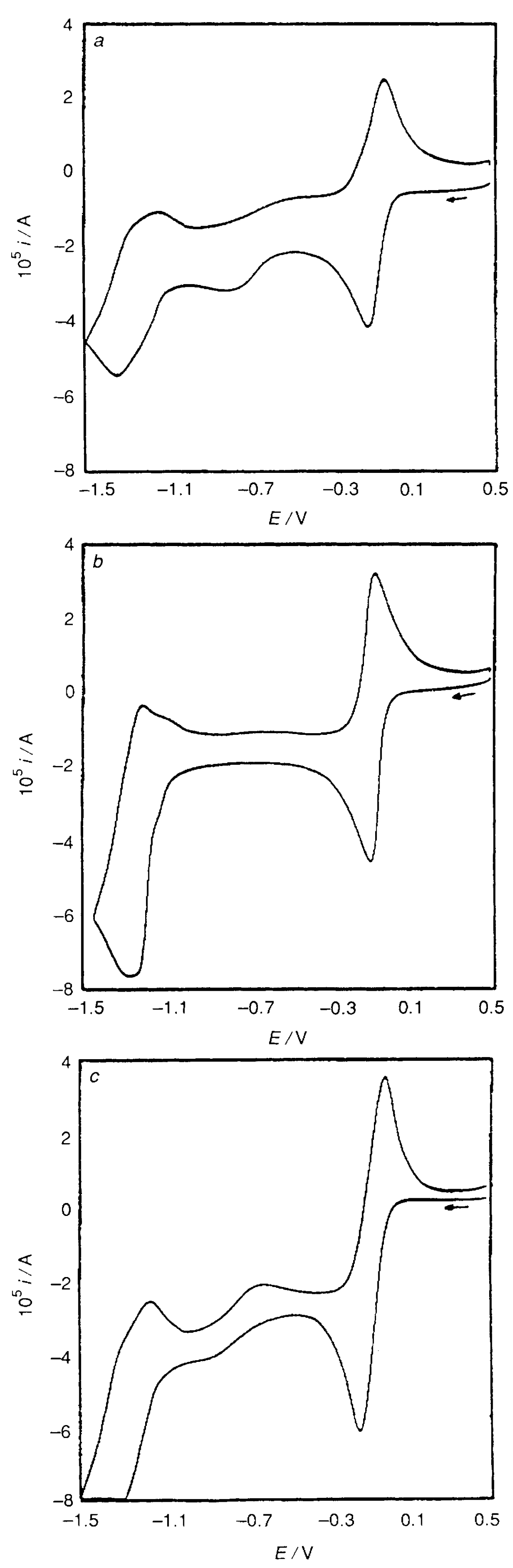

Fig. 1 Cyclic voltammograms of $[Co(salen)]_2O_2(Me_2SO)_2$ (0.005 mol dm^{-3}) in Me_2SO *vs.* SCE. (*a*) Solution exposed to air; (*b*) after, purging with argon; (*c*) after controlled potential electrolysis at a Pt grid at +0.4 V *vs.* SCE.

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