Electrochemically Controlled Dissociation of Dioxygen from a μ-Peroxo Cobalt(III) Dimer†

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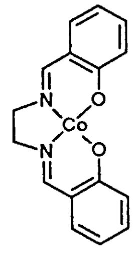
The electrochemistry of the μ-peroxo dimer of a cobalt Schiff-base complex, $[\{Co^{III}(salen)(dmso)\}_2O_2]$ [salen = *N,N'*-ethylenebis(salicylideneiminate), dmso = dimethyl sulfoxide], has been studied in solution in dmso. Controlled-potential oxidative electrolysis of the dimer is a two-electron process and resulted in its dissociation, with release of dioxygen to the solution and formation of $[Co^{III}(salen)(dmso)_2]^+$. Reduction of the cobalt(III) complex produced the corresponding cobalt(II) complex. The various redox and co-ordination states of the process were characterised by spectroelectrochemistry. The results provide conclusive evidence that electrochemical oxidation can be used as a mechanism for release of O_2 from a dioxygen-containing complex.

The chemistry of the cobalt(II) complexes of multidentate Schiff-base ligands has been very widely studied.[1] This is largely because of the well known ability of these complexes to interact with the dioxygen molecule. This has resulted in both the development of reversible O_2 binding agents, where the O_2 molecule forms a co-ordinate bond to the metal centre, and in the production of new oxygenation catalysts, where the cobalt(II) complex activates the O_2 molecule toward reaction with organic substrates.[2] These areas have been extensively reviewed.[1,2]

In recent years there has been great interest in the electrochemical properties of O_2-active complexes. The vast majority of this work has concerned electroreduction of co-ordinatively bound dioxygen.[3] This reaction is of great practical importance in the development of hydrogen–oxygen fuel cells. It is believed that metal complexes may act as catalysts in facilitating rapid four-electron reduction of dioxygen to water at, or near, the standard potential for dioxygen reduction [+1.23 V *vs.* normal hydrogen electrode (NHE)]. To this end, the electrochemistry of many O_2-active complexes has been studied both in bulk solutions and as coatings on electrode surfaces.[4] For example, Collman and co-workers[5] have studied cofacial cobalt porphyrin complexes where the two cobalt(II) ions are capable of jointly binding an oxygen molecule and then supplying the required number of electrons.

An altogether less well studied area concerns the use of an electrochemical method for the release of dioxygen from a kinetically stable dioxygen adduct. The basis of this method lies in the experimental observation that while some complexes of Fe^{II} and Co^{II} have very high affinities for binding of dioxygen, those of Fe^{III} and Co^{III} with the same ligands do not react with the dioxygen molecule. Therefore it was proposed that the oxidation of a complex of M^{II} containing a dioxygen ligand should generate the M^{III} oxidation state and result in the breaking of the $M–O_2$ bond. A few reports have appeared which involve this 'electrochemical release mechanism', mainly confined to the patent literature.

In early work, Bonaventura *et al.*[6] reported a study of haemoglobin suspended in a polyurethane foam. A later patent, by Aquanautics,[7] described the use of other iron(II) porphyrin complexes in the development of a kind of artificial gill, with the absorbed oxygen being recovered by electrochemical oxidation of the $Fe–O_2$ adducts. Another patent, to Roberts and Laine,[8] disclosed a similar type of process, this time involving a cobalt(II) complex of a Schiff-base ligand. In the open literature, Zanello *et al.*,[9] as part of a wider study of the electrochemistry of some cobalt(II) complexes of quinquedentate Schiff-base ligands, ascribed some of their experimental observations as being consistent with the dissociation of the $Co–O_2$ bond following electrochemical oxidation of the monomeric adduct.



Since we have a long-standing interest in the behaviour of the dioxygen molecule as a ligand and were intrigued by the prospect of the electrochemical release mechanism, we undertook a re-examination of the work of Roberts and Laine. Our work showed that the original results had been misinterpreted by the authors and did not lend support to the existence of this mechanism.[10]

In this paper we report the results of a detailed study, including the use of spectroelectrochemistry, of the electrochemical oxidation of a complex containing co-ordinated O_2, the μ-peroxo dimer of a cobalt(II) Schiff-base complex, $[Co^{II}(salen)]$ [salen = *N,N'*-ethylenebis(salicylideneiminate)]. These results give conclusive proof that electrochemical oxidation of a complex containing a dioxygen ligand does result in the release of the dioxygen molecule. Some of these results have been reported in a preliminary communication.[11]

Results and Discussion

$[Co^{II}(salen)]$.—The electrochemistry of $[Co^{II}(salen)]$ and its derivatives has been very well studied, using a variety of solvents and added ligands.[1] For example, a recent report described the substituent effects on the value of the $Co^{III}–Co^{II}$ redox couple for a family of $[Co^{II}(salen)]$ derivatives, in dimethylformamide solution.[12] As part of the present work we re-examined the electrochemistry of $[Co^{II}(salen)]$, using the technique of cyclic

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† *Supplementary data available* (No. SUP 56902, 3 pp.): calculation of diffusion coefficients. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

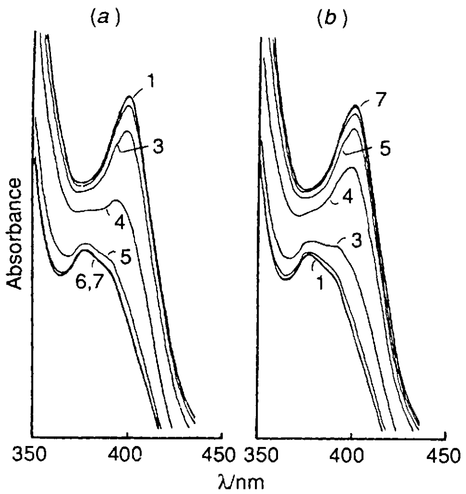


Fig. 1 Electronic spectra run during controlled-potential electrolysis of [Co^{II}(salen)] within the OTTLE cell: (*a*) commencing at −0.4 V *vs.* SCE (curves: 1, −0.4; 2, −0.2; 3, −0.1; 4, −0.05; 5, 0.0; 6, +0.1; 7, +0.2 V) and (*b*) commencing at +0.2 V *vs.* SCE (curves: 1, +0.2; 2, +0.05; 3, 0.0; 4, −0.075; 5, −0.125; 6, −0.2; 7, −0.4 V)

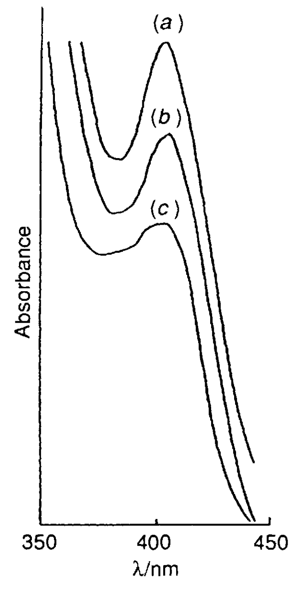


Fig. 2 Electronic spectra of [Co^{II}(salen)]: (*a*) under anaerobic conditions, (*b*) after 4 h under O_2 and (*c*) after 12 h under O_2

voltammetry, in neat dimethyl sulfoxide (dmso) solution and also in the presence of added pyridine (py). In both cases the electron transfer was quasi-reversible, in keeping with the behaviour expected for process (1) where L represents dmso or

$$[\mathrm{Co^{II}(salen)L}] \xrightarrow{L} [\mathrm{Co^{III}(salen)L_2}]^+ + e^- \qquad (1)$$

py co-ordinated to the metal centre. The $E_{\frac{1}{2}}$ values for the Co^{III}–Co^{II} couples were found to be −0.09 and −0.30 V in dmso and dmso–py respectively (*vs.* saturated calomel electrode, SCE). This negative shift is not readily explained by merely considering the ability of the respective ligands to act as donors to the metal ion, since the Gutmann donor numbers of py and dmso are rather similar (33.1 and 29.8, respectively).[13] In fact, this type of negative shift has been observed previously in studies with cobalt(II) 5,10,15,20-tetraphenylporphyrinate and was explained in terms of a change in solvent co-ordination in the presence of pyridine.[14]

The diffusion coefficients (*D*) of the oxidised and reduced forms of [Co(salen)] in pyridine solution were determined from the scan-rate dependency of the cyclic voltammogram using the Randles–Sevcik equation;[15] for [Co^{II}(salen)(py)], *D* was 1.66×10^{-6} cm^2 s^{-1} while for [Co^{III}(salen)(py)$_2$]$^+$, *D* was 1.73×10^{-6} cm^2 s^{-1}.

The heterogeneous electron-transfer rate constant, *k*, for the Co^{III}–Co^{II} couple of [Co(salen)] in solution in neat pyridine was estimated using Nicholson's equation.[16] Evaluation at different scan rates gave an average value of *k* of 1.10×10^{-3} cm s^{-1}. This is of the same order as values reported[9] for a family of quinquedentate cobalt Schiff-base complexes, which lay in the range 2.2×10^{-3}–36×10^{-3} cm s^{-1}.

Spectroelectrochemistry of [Co^{II}(salen)] was carried out using an optically transparent thin-layer electrode (OTTLE), in order to characterise spectroscopically the various oxidation and co-ordination states of [Co(salen)]. Spectra of [Co(salen)] in dmso at successively more negative potentials, from −0.9 to −1.5 V *vs.* SCE, showed the conversion of the spectrum of [Co^{II}(salen)(dmso)] (λ_{max} 410 nm) into that of [Co^{I}(salen)]$^-$ (λ_{max} 710 nm), characterised by a series of isosbestic points. The series of spectra was in excellent agreement with that reported.[17]

A second series of spectra was obtained, starting at −0.4 V and using successively more positive potentials up to +0.2 V. At −0.4 V the spectrum was that of [Co^{II}(salen)(dmso)] (λ_{max} 410 nm). As the potential was swept to more positive values the spectrum changed, consistent with oxidation of Co^{II}, until at +0.2 V it was characteristic of [Co^{III}(salen)(dmso)$_2$]$^+$ (λ_{max} 384 nm) [Fig. 1(*a*)]. Reversing the direction of the potential sweep, from +0.2 to −0.4 V, resulted in the progressive reversal of the spectroscopic change, until, at −0.4 V, the spectrum of [Co^{II}(salen)(dmso)] was completely restored (λ_{max} 410 nm) [Fig. 1(*b*)].

Exposure of the [Co^{II}(salen)(dmso)] solution to the atmosphere over a period of 12 h resulted in a spectroscopic change assigned to the formation of the corresponding μ-peroxo dimer complex, [{Co^{III}(salen)(dmso)}$_2$O$_2$] (Fig. 2). This assignment was confirmed by dissolution of a freshly prepared sample of the genuine μ-peroxo complex, prepared by the literature procedure,[18] which exhibited an identical spectrum (λ_{max} 400 nm).

The cyclic voltammogram of a dmso solution of [Co^{II}(salen)(dmso)], before and after oxygenation, indicated that, although the position of $E_{\frac{1}{2}}$ did not change appreciably upon formation of the dioxygen adduct, the current peak height (i_p) decreased to half its original value. Since i_p is proportional to the concentration, this indicated that [Co(salen)] had indeed dimerised to produce half an equivalent of the μ-peroxo dimer and this dimer underwent a quasi-reversible one-electron transfer during oxidation. Vigorous bubbling of N_2 through the solution resulted in no change in the appearance of the cyclic voltammogram, indicating that the binding of O_2 was essentially irreversible.

Electrochemical Release of Dioxygen from [{Co^{III}(salen)(dmso)}$_2$O$_2$].—As discussed in the preliminary communication,[11] it was decided to study the release of dioxygen from a μ-peroxo dimer complex because the adduct is kinetically stable and the co-ordinated oxygen molecule is not pressure-swing labile. This allows study of the system without the complication of having free O_2 present in solution, in equilibrium with co-ordinated O_2. {In fact dilute solutions of the μ-peroxo dimer do show evidence of very slow dissociation of O_2 over a period of several days, when left stirring in an inert-atmosphere glovebox, but the rate of this process is deemed to be too slow to interfere with the results of the present study.}

The results of a controlled-potential electrolysis study of the μ-peroxo dimer formed the basis of the preliminary communication. The cyclic voltammogram of the dimer is shown in Fig. 3(*a*). The Co^{III}–Co^{II} couple appeared at −0.08 V, with the Co^{II}–Co^{I} at *ca.* −1.32 V. The small cathodic peak at −0.8 V was ascribed to reduction of dissolved O_2. Purging the solution with argon for 10 min resulted in the loss of this peak [Fig. 3(*b*)]. There was no change in the electrochemistry of the

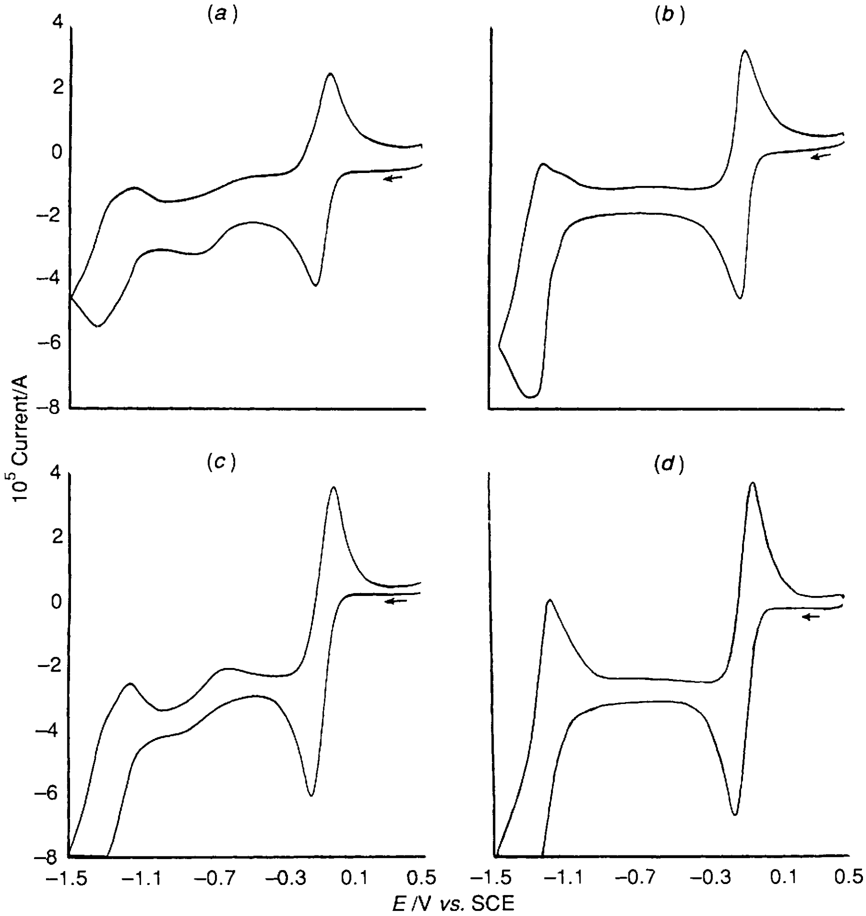


Fig. 3 Cyclic voltammetry scans of a solution containing the μ-peroxo dimer of [Co(salen)]: (*a*) exposed to air; (*b*) after purging with Ar; (*c*) after controlled-potential electrolysis at +0.4 V *vs.* SCE; (*d*) after purging electrolysed solution with Ar

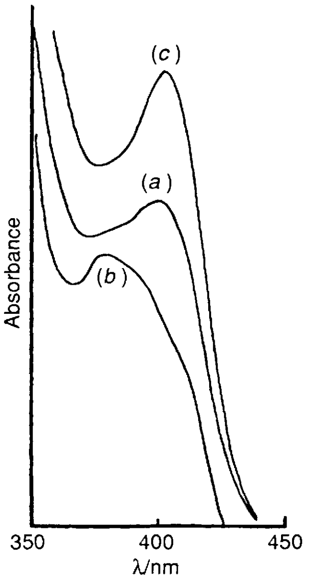


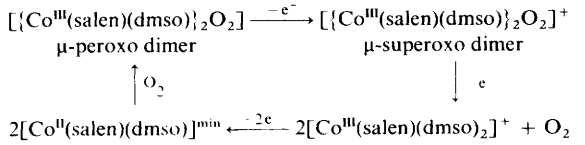
Fig. 4 Electronic spectra of the μ-peroxo dimer solution: (*a*) before electrolysis; (*b*) after electrolysis at +0.4 V *vs.* SCE; (*c*) after electrolysis at −0.4 V *vs.* SCE

system over the period of 1 h, indicating that atmospheric oxygen was unable to enter the cell. Controlled-potential electrolysis of the solution at +0.4 V gave rise to the reappearance of the cathodic wave at −0.8 V [Fig. 3(*c*)] which again disappeared upon purging with argon [Fig. 3(*d*)]. Since the only source of O_2 in the cell was the dimer, these results were taken as good evidence for the electrochemically induced release of O_2 from the complex.

In order to characterise the cobalt species present in the system during the electrochemical experiments, the μ-peroxo dimer was studied by the spectroelectrochemistry technique. During controlled-potential electrolysis at positive potentials within the OTTLE cell, the spectrum of the μ-peroxo dimer (λ_{max} 400 nm) changed to that characteristic of [Co^{III}(salen)(dmso)$_2$]$^+$ (λ_{max} 384 nm) (Fig. 4). Subsequent controlled-potential reduction of the system brought about the appearance of the spectrum characteristic of [Co^{II}(salen)(dmso)], at λ_{max} 410 nm (Fig. 4). Taken together, the voltammetry and spectroelectrochemistry results provide conclusive evidence for the oxidative oxygen-release mechanism illustrated in equation (2).

$$[\{Co^{III}(salen)(dmso)\}_2O_2] \longrightarrow 2[Co^{III}(salen)(dmso)_2]^+ + O_2 \quad (2)$$

Mechanism of Dioxygen Release.—Integration of the current *vs.* time curves obtained during the controlled-potential oxidative-electrolysis experiments indicated that the release of dioxygen came about as the result of a two-electron process, as predicted in equation (2). This is at odds with the results of the cyclic voltammetry experiments which were consistent with the μ-peroxo dimer undergoing a quasi-reversible, one-electron transfer. It is proposed that this apparent anomaly arises as a result of the different time-scales of the experiments. On the relatively short time-scale of the cyclic voltammogram, the μ-peroxo dimer does indeed undergo a one-electron transfer, producing the corresponding μ-superoxo dimer species, while on the much longer time-scale of controlled-potential elec-



Scheme 1

trolysis experiments two electrons are transferred, resulting in the release of dioxygen from the complex. This type of behaviour has been reported previously, in a study of the electroreduction of dimers of iron protoporphyrin IX (3,7,12,17-tetramethyl-8,13-divinylporphyrin-2,18-dipropanoic acid) in aqueous solution.[19]

Based upon the results from cyclic voltammetry and controlled-potential electrolysis it is possible to infer that oxidation of the μ-peroxo dimer takes place in two successive steps, as outlined in Scheme 1. In the first step, a relatively stable μ-superoxo dimer species is formed, which can be reduced back to the peroxo form. Although oxidation of the μ-peroxo dimer removes an electron from what is formally a cobalt–oxygen bonding orbital, it is proposed that this does not lead to dissociation of the dimer. In fact a number of stable, superoxo-bridged cobalt(III) dimers have been reported, with crystal-structure data being given in some cases.[20] Only after the second electron-transfer step has occurred, removing another Co–O bonding electron, the dimer is so destabilised that it fragments, producing dioxygen and 2 equivalents of the cobalt(III) complex. If indeed the μ-superoxo species underwent fragmentation, it would be expected that the cyclic voltammetry experiments would show evidence for a peak assignable to reduction of O_2. As described above, the dioxygen reduction peak was only observed following the oxidative-electrolysis experiments (a two-electron process). Unfortunately, attempts to identify the proposed μ-superoxo species by ESR spectroscopy were unsuccessful.

There is one problem with this interpretation of the results. It would be expected that the system should display an independent peak on the cyclic voltammogram for the oxidation of the superoxo dimer, albeit of an irreversible nature. In fact no such peak is observed. It is proposed that oxidation of the superoxo complex occurs at the same potential as that of the oxidation of the peroxo species. This can be rationalised by proposing that the Schiff-base ligands of the dimers compensate for the loss of the electron during the first oxidation step by acting as better donors to the metal centres, thereby reducing the potential required for the second oxidation step. A similar argument has been used to account for the fact that there is no shift in the cobalt(II) oxidation potential in going from a Schiff-base complex to its corresponding monomeric Co–O_2 adduct.[21]

Conclusion

The results of this study show that electrochemical oxidation of a cobalt complex which has dioxygen as a ligand brings about the release of O_2 into the solution phase. The cobalt-containing product of this electrochemical process is the corresponding cobalt(III) complex, which is oxygen insensitive. Reduction of this complex regenerates the dioxygen-binding cobalt(II) form and so in principle this process could form the basis for a cyclic system for dioxygen separation.

Experimental

The complex [Co^{II}(salen)] and its corresponding μ-peroxo dimer, [{Co^{III}(salen)(dmso)}$_2$O$_2$], were prepared according to the literature procedures.[18] All solvents were dried and distilled using standard techniques. The platinum minigrid (52 mesh) was purchased from Johnson Matthey plc. The electronic spectra were recorded on a Philips Analytical SP1800 spectrophotometer. All electrode potentials are quoted with respect to a saturated calomel reference electrode.

Cyclic voltammetry (CV) experiments were performed using a Thomson E-series potentiostat with a miniscan potential sweep generator. Plots of current *vs.* potential were recorded on a Linseis 18100 *x-y* recorder. The cell consisted of a Metrohm glass cup fitted with an airtight plastic lid which contained five access holes. A Metrohm doublet platinum electrode provided the working and auxiliary electrodes and a Russel SCE was used as the reference. The cell was fitted with a gas-inlet system which allowed oxygen-free nitrogen or argon to be bubbled through the solution or passed over the solution surface. A thermometer and a magnetic stirrer were also included. The cyclic voltammograms were recorded using solutions of dmso (25 cm^3) containing the cobalt complex (0.005 mol dm^{-3}) and NBu_4BF_4 (0.1 mol dm^{-3}) as the supporting electrolyte. The temperature was controlled to 20 ± 0.5 °C.

Controlled-potential electrolyses were carried out using the CV cell fitted with a platinum-grid working electrode (area = 6.45 cm^2). The platinum-wire auxiliary electrode was placed in a separate compartment. Electrical contact with the test solution was *via* a sintered disc. The solutions were electrolysed with rapid stirring for periods of 60 min. Current *vs.* time curves were recorded on the Linseis 18100 *x-y* recorder fitted with a time drive circuit.

Spectroelectrochemistry was performed in a specially designed cell which incorporated an optically transparent electrode. The cell was a modification of one reported by Hawkridge and co-workers[22] and readily allowed work under anaerobic conditions. A platinum wire was used as a pseudo-reference electrode. The cell consisted of two circular plates, of either Perspex or Teflon, held tightly together by six screws and which contained glass or quartz windows for passage of the light beam. The solution volume was defined by a Viton O-ring which also provided the seal between the two plates. The working electrode consisted of a gold or platinum minigrid. Electrical contact to the minigrid was *via* a small brass cylinder, insulated from the test solution by a Viton O-ring, and passing through the top plate of the cell. The reference and auxiliary electrodes were two platinum wires passing through the top plate, sealed with epoxy, then bent at 90° to lie in two grooves on the inner surface of the plate. The top plate also contained two valves for the introduction of the test solution, *via* syringe, once the cell had been assembled. Anaerobic solutions were loaded inside an inert-atmosphere glove-box (Miller-Howe), fitted with O_2-scavenging and drying trains.

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