Spectroelectrochemistry of the Dioxygen Adduct of an Iron(II) C_2-Capped Porphyrin

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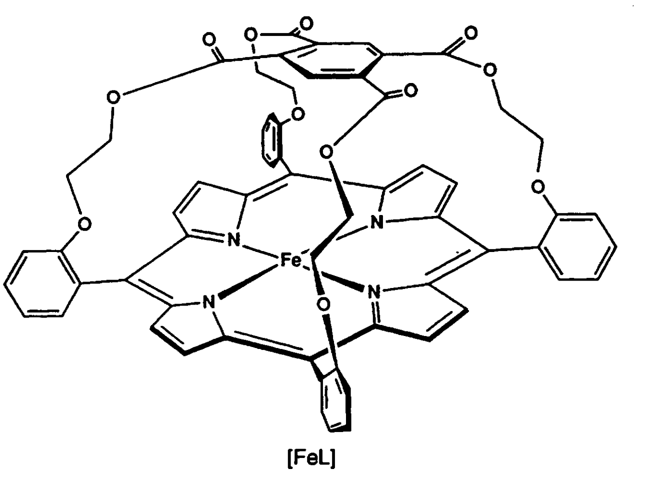
The spectroelectrochemistry of the dioxygen adduct of the iron(II) C_2-capped porphyrin complex [$Fe^{II}L(B)$] {H_2L = 5,10,15,20-tetraphenylporphyrin capped at the *o*-position of each of the phenyl rings by $C_6H_2[C(O)O(CH_2)_2O]_4$-1,2,4,5, B = 1-methylimidazole or pyridine} has been studied in both dimethyl sulfoxide and pyridine solutions. In both cases electrooxidation of the adduct produced an unusual spectrum, assigned to a new type of O_2 adduct, [$Fe^{III}L(B)(O_2)$]$^+$. Subsequent electroreduction of the system regenerated the original O_2 adduct, but not in 100% yield, indicating that some dissociation of O_2 had occurred during the redox cycling. This behaviour is discussed in terms of bonding in the Fe–O_2 adducts.

One of the first examples of a synthetic iron(II) compound which could undergo the reversible binding of dioxygen was the C_2-capped porphyrin complex of Baldwin and co-workers,[1] [$Fe^{II}L$]. The steric protection of one co-ordination site of the iron(II) ion by the capping group prevented all but very small molecules entering the molecular cavity and co-ordinating to the metal centre. A number of reports have since appeared concerning the binding of various small molecules (O_2, CO, NH_3, *n*-propylamine) to this complex and to its analogues.[2]

In previous work we have shown that when [$Fe^{II}L$] is dissolved in dimethyl sulfoxide (dmso) containing 1-methylimidazole (mim), a molecule of solvent is able to enter the cavity of the porphyrin to bind to the metal centre, giving a six-co-ordinate iron(II) complex, [$Fe^{II}L$(mim)(dmso)].[3]

Recently the dioxygen adduct of [$Fe^{II}L$(mim)] was described in the patent literature[4] as releasing the bound O_2, upon electrochemical oxidation of the metal centre, but the results were not reported in any detail. Since we have a general interest in the chemistry of oxygen complexes and have recently reported on the release of O_2 from some cobalt complexes of a Schiff-base ligand, triggered by an electron-transfer step,[5] it was of interest to re-examine the work described in the patent. In this paper we report the results of a spectroelectrochemical study of [FeL(B)(O_2)] [B = mim or pyridine (py)] in two different solvents (dmso or pyridine) and we offer a new interpretation for the effect of electrochemical oxidation of the O_2 adduct.



[FeL]

Results and Discussion

The electronic spectroscopic changes accompanying oxygenation of the iron(II) complex of the C_2-capped porphyrin ligand L in two solvent systems are shown in Fig. 1. In toluene–mim (9:1) the complex exists as the five-co-ordinate species, [$Fe^{II}L$(mim)], reversible oxygenation occurred readily. The spectroscopic changes [Fig. 1(*a*)] were in excellent agreement with those reported in the literature for oxygenation of the same complex in pyridine solution[6] and the process can be described by equation (1).

$$[Fe^{II}L(mim)] + O_2 \xrightleftharpoons{K_{O_2}} [FeL(mim)(O_2)] \qquad (1)$$

The corresponding spectra for the complex in solution in dmso–mim (9:1) were markedly different [Fig. 1(*b*)]. This arises because in this solvent, even in the absence of dioxygen, the iron(II) complex exists as the six-co-ordinate species, [$Fe^{II}L$(mim)(dmso)], with a dmso molecule acting as a ligand and binding to the metal inside the cavity provided by the

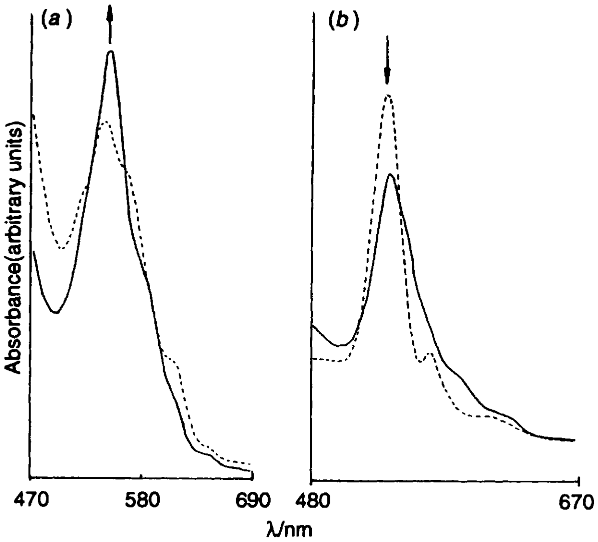


Fig. 1 Electronic spectroscopic changes accompanying oxygenation of [FeL] in (*a*) toluene–mim (9:1) and (*b*) dmso–mim (9:1); (– – –) under N_2, (——) under O_2. Arrow indicates direction of change following O_2 addition

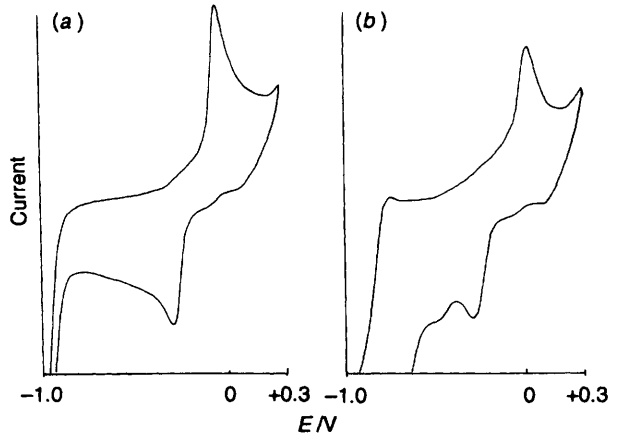


Fig. 2 Cyclic voltammograms of [FeL] in dmso–mim (9:1) solution with NBu_4BF_4 as supporting electrolyte; (*a*) under N_2, (*b*) under O_2

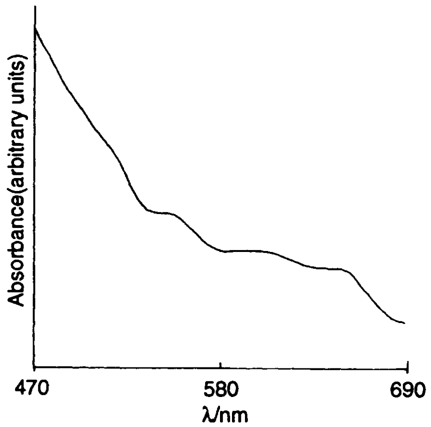


Fig. 3 Electronic spectrum of the product of one-electron oxidation of [FeL(mim)(O_2)] in dmso–mim (9:1) solution, obtained using the OTTLE cell

capping group.[3] Therefore oxygenation in dmso solution is described by equation (2). This behaviour is very similar to that

$$[\mathrm{Fe^{II}L(mim)(dmso)}] + O_2 \rightleftharpoons [\mathrm{FeL(mim)(O_2)}] + \mathrm{dmso} \qquad (2)$$

described by Baldwin and co-workers[7] for the oxygenation of the iron(II) complex of the corresponding C_3-capped porphyrin (L′), in the presence of mim.[7] The greater flexibility of the C_3 cap allows the Fe^{II} to exist as the six co-ordinate species, [Fe^{II}L′(mim)$_2$]. Notably, the electronic spectrum reported for this species is very similar to that observed in this work for [Fe^{II}L(mim)(dmso)]. Although the oxygenation of the C_3-capped species led to the production of a novel seven-co-ordinate dioxygen adduct, in the present work the electronic spectra of the products of oxygenation in both toluene and dmso solutions were so similar that the oxygen adducts were assigned as being six-co-ordinate species of the normal type, with the O_2 molecule binding within the sterically protected cavity. The relative absorbances of the respective solutions are entirely consistent with complete oxygenation of the iron(II) complex in both solvents.

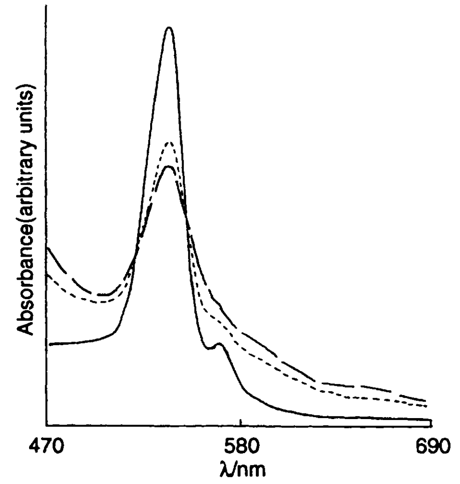


Fig. 4 Electronic spectra obtained using the OTTLE cell during oxygenation, then oxidation/reduction cycling: (——) [Fe^{II}L(mim)(dmso)] under N_2, (– – –) [FeL(mim)(O_2)] under O_2, (· · ·) spectrum following complete electrooxidation at +0.3 V, then electroreduction at −0.5 V, of [FeL(mim)(O_2)]

Electrochemistry of [Fe^{II}L] *in the Presence of Dioxygen.*—The cyclic voltammograms of [Fe^{II}L] in solution in dmso–mim (9:1) were recorded under an atmosphere of N_2 or of O_2 [Fig. 2(*a*) and (*b*), respectively]. The chemical species concerned were therefore [Fe^{II}L(mim)(dmso)] in Fig. 2(*a*) and [FeL(mim)(O_2)] in Fig. 2(*b*). Very little change in the voltammetric response was observed following exposure of the solution to dioxygen. The most dramatic change was the emergence of a large cathodic current at *ca.* −0.7 V, attributed to the reduction of dissolved dioxygen. A slight reduction in the peak currents occurred, but the oxidation and reduction waves, ascribed to $Fe^{II} \rightleftharpoons Fe^{III} + e^-$, remained at the same potentials as under nitrogen. Similar behaviour has been observed with other dioxygen complexes.[5] Since the separation of the anodic and cathodic peaks (255 mV) of the O_2 adduct was substantially greater than the 59 mV predicted for a reversible step, the electron-transfer process (3)

$$[\mathrm{FeL(mim)(O_2)}] \rightleftharpoons [\mathrm{FeL(mim)(O_2)}]^+ + e^- \qquad (3)$$

was regarded as being electrochemically pseudo-reversible.

Electronic spectra were recorded in an optically transparent thin-layer electrode (OTTLE) cell, accompanying exposure of a solution of [FeL] in dmso–mim to the atmosphere and confirmed the formation of the oxygen adduct [*cf.* Fig. 1(*b*)]. Formation of the O_2 adduct took 48 h to reach completion, owing to the slow rate of diffusion of O_2 into the thin layer of the OTTLE cell. A potential of −0.5 V *vs.* SCE (saturated calomel electrode) was applied throughout the oxygenation step, to ensure that the iron remained in the dioxygen-binding Fe^{II} state.

According to the patent literature,[4] electrooxidation of the dioxygen adduct of [FeL] should bring about the release of bound dioxygen, with concomitant formation of the iron(III) complex of the porphyrin ligand, [Fe^{III}L(mim)]$^+$. In this work, the solution of the Fe–O_2 adduct was electrolytically oxidised in the OTTLE cell for 80 min at +0.3 V and the spectrum recorded at the end of that period is shown in Fig. 3. This spectrum did *not* correspond to that of the electrooxidised product, [Fe^{III}L(mim)]$^+$ (λ_{max} *ca.* 513 nm, based upon literature data for a 1,2-dimethylimidazole complex),[8] nor indeed to any other reported iron C_2-capped porphyrin complex of varying oxidation state and axial ligand.

There was some concern that decomposition of the complex may have occurred during the experiment, particularly during the oxygenation stage but this was obviated by carrying out electroreduction of the system at −0.5 V which resulted in regeneration of the spectrum of the dioxygen adduct (Fig. 4). Notably, recovery of the O_2 adduct was not 100% efficient, and this is further discussed below.

Based upon the spectroelectrochemistry results, the spectrum shown in Fig. 3 was assigned to a new type of iron porphyrin complex, previously unreported. Since the product of electrooxidation was not [Fe^{III}L(mim)]$^+$ but a species that could be electroreduced to regenerate the O_2 adduct, it was assigned as the one-electron oxidised product of the O_2 adduct, $[Fe^{III}L(mim)(O_2)]^+$. As stated above, the electroreduction step did not result in 100% recovery of the spectrum of the original oxygen adduct but produced a spectrum intermediate between that of $[Fe^{II}L(mim)(dmso)]$ and $[FeL(mim)(O_2)]$, suggesting that some dioxygen had dissociated during the electrochemical oxidation step (Fig. 4) and diffused away from the complex.

The only interpretation consistent with the observed spectroelectrochemical results was that the new species, $[Fe^{III}L(mim)(O_2)]^+$, established a new equilibrium between oxy- and deoxy-forms [equation (4)]. This is directly analogous to the normal

$$[FeL(mim)]^+ + O_2 \overset{K_{O_2}'}{\rightleftharpoons} [FeL(mim)(O_2)]^+ \qquad (4)$$

equilibrium for O_2 binding [equation (1)], described by the equilibrium constant, K_{O_2}.

At equilibrium, the dominant species is $[Fe^{III}L(mim)(O_2)]^+$ but since $K_{O_2}' < K_{O_2}$, electrochemically generated $[Fe^{III}L(mim)(O_2)]^+$ partially dissociates, producing a higher concentration of the deoxy form after electrooxidation than was the case before the electrolysis. Consequently the spectrum recorded immediately following the reductive electrolysis showed that a lower concentration of oxygen adduct was present than prior to the electrolysis steps.

Although no direct precedent for this behaviour was found in the literature for iron–dioxygen chemistry, work by Mu and Kadish[9] on the binding of NO to iron porphyrin complexes showed analogous results. Electrooxidation of the nitrosyl adduct of $[Fe^{II}(tpp)]$ (tpp = 5,10,15,20-tetraphenylporphyrinate) produced $[Fe(tpp)(NO)]^+$ which was stable for long periods but after a second oxidation, to $[Fe(tpp)(NO)]^{2+}$, the complex dissociated. In related work, involving oxidation of the NO adduct of $[Fe^{II}(oep)]$ (oep = 2,3,7,8,12,13,17,18-octaethylporphyrinate), Mu and Kadish[10] found that $[Fe(oep)(NO)]^+$ transferred NO to [Co(oep)]. Since the affinity of [Fe(oep)] for NO is much higher than that of [Co(oep)], they concluded that the effect of oxidising the system was to dramatically reduce the affinity of the iron complex for NO.

The present work accounts for the observed release of O_2 during electrooxidation of iron–dioxygen adducts reported in the patent literature by Aquanautics,[4] but is not in support of the mechanism produced in the patent [equation (5)]. This

$$[FeL(O_2)] \xrightarrow{-e^-} [Fe^{III}L]^+ + O_2 \qquad (5)$$

mechanism implies complete release of O_2 from the complex, with formation of the corresponding iron(III) complex. If this were the mechanism of release, then the spectrum of the electrooxidation product should be that of $[Fe^{III}L(mim)]^+$ (λ_{max} *ca.* 513 nm), which clearly it was not. Scheme 1 illustrates the proposed behaviour of the [FeL] system in the presence of oxygen and mim in dmso and under conditions of electrochemical oxidation or reduction.

Attempts were made to characterise the novel paramagnetic O_2 adduct, $[FeL(mim)(O_2)]^+$, using ESR spectroscopy on a frozen solution at 77 K, but unfortunately it did not prove possible to observe a signal that could be ascribed to this species. Our efforts in this area are continuing.

Spectroelectrochemistry of [FeL] *in Pyridine Solution.*—It was of interest to determine the effect of dmso on the spectroelectrochemistry results and so the system was studied using pyridine as solvent. On electroreduction of $[Fe^{III}L(Cl)]$ in pyridine solution at −0.5 V *vs.* SCE, under nitrogen, the spectrum changed from λ_{max} 514 nm to 540 nm (Fig. 5), consistent with equation (6). The isosbestic nature of this

$$[Fe^{III}L(Cl)] \xrightarrow{+e^-} [Fe^{II}L(Cl)]^- \longrightarrow [Fe^{II}L] + Cl^- \overset{py}{\rightleftharpoons} [Fe^{II}L(py)] \qquad (6)$$

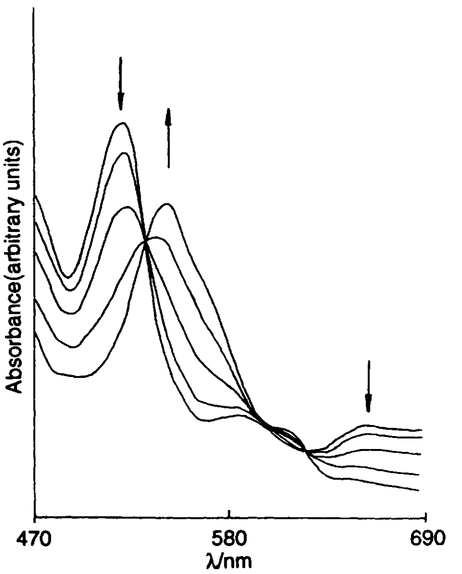


Fig. 5 Time-resolved electronic spectra obtained using the OTTLE cell during controlled-potential reduction of $[Fe^{III}L(Cl)]$ at −0.5 V, in pyridine solution under N_2. Time period *ca.* 5 min; arrows indicate the direction of change during reduction

$$\begin{tikzcd}
{[Fe^{II}L(mim)(dmso)] + O_2} \arrow[r, shift left, "K_{O_2}"] \arrow[d, shift right, "+e^-"'] & {[FeL(mim)(O_2)] + dmso} \arrow[l, shift left] \arrow[d, shift right, "+e^-"'] \\
{[Fe^{III}L(mim)]^+ + O_2} \arrow[r, shift left, "K_{O_2}'"] \arrow[u, shift right, "-e^-"'] & {[FeL(mim)(O_2)]^+} \arrow[l, shift left] \arrow[u, shift right, "-e^-"']
\end{tikzcd}$$

Scheme 1

series of spectra implied that dissociation of Cl^- from Fe^{II} and subsequent pyridine binding are both rapid processes, producing no significant build up of any intermediate complexes, and only two coloured species were present in solution at any significant concentration. Notably the chemical process accompanying this electrochemical step (replacement of Cl^- by pyridine after reduction) was completely reversible upon subsequent reoxidation, since electrooxidation produced $[Fe^{III}L(Cl)]$ and not $[Fe^{III}L(py)]^+$. The high affinity of iron(III) porphyrin complexes for Cl^- has been noted by other workers.[11]

Exposure of the reduced species, $[Fe^{II}L(py)]$, to dry oxygen over 30 min resulted in changes in the spectrum very similar to those shown in Fig. 1(*a*), consistent with literature results for the formation of an oxygen adduct.[6]

Electrooxidation of this adduct at +0.3 V over a period of 5 min gave the spectroscopic changes shown in Fig. 6. The final spectrum was similar to that observed for the electrooxidation of $[FeL(mim)(O_2)]$ in dmso solution (see above).

Re-reduction at −0.5 V produced a spectrum with an absorbance at 540 nm intermediate between that of $[Fe^{II}L(py)]$ and $[FeL(py)(O_2)]$ (Fig. 7), consistent with the results observed in dmso solution, again suggesting that some O_2 had dissociated upon electrooxidation of the dioxygen adduct. It is noteworthy that although oxygenation of $[Fe^{II}L]$ in pyridine solution caused an increase in absorbance at 540 nm while the same reaction in dmso solution caused an absorbance decrease, in both cases electrochemical cycling produced spectra that were intermediate between the spectra of the fully oxygenated and fully deoxygenated complexes. This is consistent with the electrochemical release of some, but not all, of the bound oxygen during the electrochemical oxidation step.

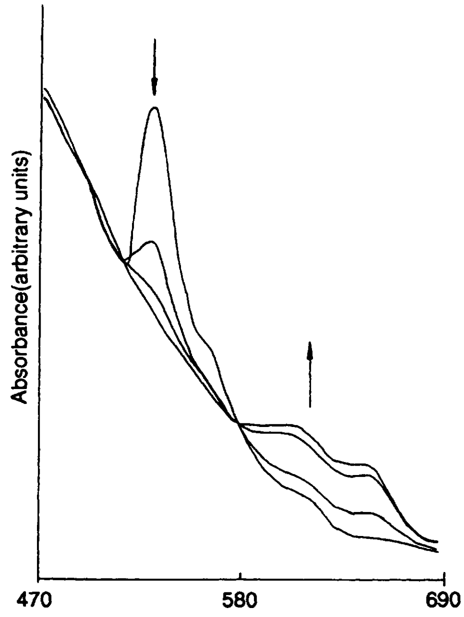


Fig. 6 Time-resolved electronic spectra during electrooxidation of [FeL(py)(O_2)] at +0.3 V, in pyridine solution under O_2. Time period *ca.* 5 min; arrows indicate direction of change

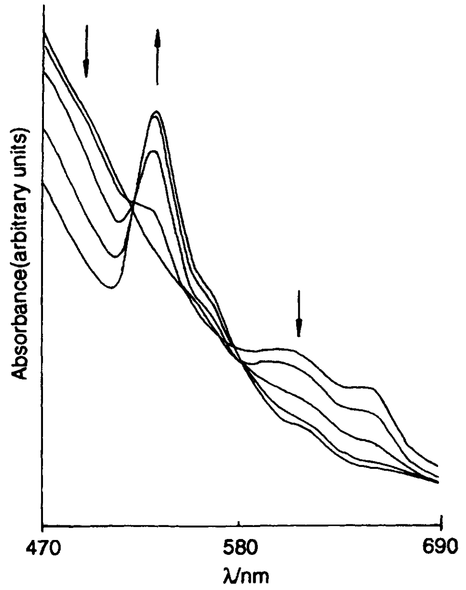


Fig. 7 Time-resolved electronic spectra during electroreduction of [Fe^{III}L(py)(O_2)]$^+$ at −0.5 V, in pyridine solution under O_2. Time period *ca.* 5 min; arrows indicate the direction of change

Bonding in [FeL(mim)(O_2)] *and its Oxidised Product*.—The nature of the bonding in dioxygen adducts has been the subject of numerous reports, using both the valence-bond and the molecular-orbital approach. In this discussion, the results of calculations reported by Newton and Hall[12] will be used. These workers found that the highest occupied molecular orbital of the oxygenated iron complex was the d_{xy} orbital of the metal ion, which was doubly occupied. Therefore one-electron oxidation of the oxygen adduct will remove an electron of essentially non-bonding character from the system and thus it is not surprising that, to a large extent, the O_2 remains bound to the metal centre following oxidation.

However the oxidation reaction does exert an indirect influence on the binding of dioxygen to the metal ion. The calculations of Newton and Hall indicate the occurrence of an important π interaction, between the d_{yz} orbital of the iron and the 1 $\pi_g{}^a$ orbital of O_2, which makes a significant contribution to the stabilisation of the O_2 adduct. They formally likened this π-bonding interaction to back donation from a filled metal orbital to an empty ligand orbital. Oxidation of the metal centre, in this case removing an electron from the d_{xy} orbital, while it will improve the σ-acceptor properties of the metal ion, will reduce the ability of the d_{yz} orbital to participate in this π-bonding process, leading to an overall weakening of the Fe–O_2 bond. This theoretical prediction is in excellent agreement with our spectroelectrochemical observations of the behaviour of the oxygen adduct of [FeL] in both dmso–mim and neat pyridine solution.

Conclusion

In both dmso and pyridine solutions, the dioxygen adduct of [Fe^{II}L(B)] (B = mim or py respectively) undergoes a reversible one-electron oxidation to form a new type of dioxygen adduct, [Fe^{III}L(B)(O_2)]$^+$. Spectroelectrochemistry results indicate that reduction of the new adduct produces the original species, but not in 100% yield. This is because [Fe^{III}L(B)(O_2)]$^+$ undergoes partial dissociation of bound O_2 following its formation in the electrooxidation process. The lower affinity of the iron(III) complex for O_2, relative to the iron(II) complex can be rationalised in terms of the reduced ability of Fe^{III} to π bond to O_2.

Experimental

All solvents and mim were carefully dried using standard literature procedures. Tetrabutylammonium tetrafluoroborate was recrystallised from ethanol and dried under vacuum at 80 °C. The C_2-capped porphyrin ligand was prepared by the method of Baldwin and co-workers.[1] The complex [Fe^{III}L(Cl)] was prepared by a modification of the literature procedure[13] described in our earlier report.[3] The iron(III) complex was reduced to the iron(II) form by treating a toluene solution of the porphyrin complex with aqueous sodium dithionite in a two-limbed reaction vessel, freezing the aqueous layer, decanting the organic layer into the second limb and sealing it off. The toluene was removed by vacuum distillation and the resulting red solid dried under high vacuum at 100 °C.

The solutions for spectroscopic and electrochemical studies were made up in an inert-atmosphere glove-box (Miller-Howe), equipped with an oxygen scrubbing unit and drying train.

The electrochemical apparatus was that described in detail in a previous report.[5] In addition, an OTTLE cell based upon the design of Scherson *et al.*[14] was also used, which allowed the direct incorporation of a SCE reference electrode rather than the Pt wire pseudo-reference of the other system. Qualitatively the results were identical in either cell. All potentials quoted in this work are with respect to the SCE reference. Typically the electrochemical experiments were run on solutions *ca.* 3.3×10^{-3} mol dm^{-3} in porphyrin complex and 0.1 mol dm^{-3} in supporting electrolyte (NBu_4BF_4). The electronic spectra were recorded using either a Shimadzu UV-240 or Philips Analytical SP1800 spectrophotometer.

Acknowledgements

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