Dual Electron-transfer Reactivity of a High-spin Iron(III) Porphyrin Cation Radical Complex

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Easily oxidised nucleophiles, such as iodide, bromide, and 1,8-bis(dimethylamino)naphthalene, react with the diaquotetraphenylporphyrinatoiron(III) cation radical complex, $[Fe(H_2O)_2(tpp\cdot)]^{2+}$, to give the corresponding tetraphenylporphyrin complex, $[Fe(H_2O)_2(tpp)]^+$, while pyridine gives an entirely different product, $[(tpp)FeOFe(tpp\cdot)]^+$; e.s.r. spectra and potentiometric evidence suggest that a base-dependent internal electronic isomerisation, leading to tetraphenylporphyrinato-oxoiron(IV), takes place in the latter reaction.

One-electron oxidation of high-spin iron(III) tetraphenylporphyrin (tpp) complexes is centred on the porphyrin ring, rather than on the metal, and it affords a novel class of complexes which bring together a high-spin iron(III) centre and tetraphenylporphyrin cation radical of A_{2u} symmetry.[1–6] Recently, we have suggested a qualitative explanation of the observed magnetic interactions between metal and macrocyclic ligand within two such complexes, $[Fe^{III}Cl(tpp\cdot)]^+SbCl_6^-$ and $Fe^{III}(ClO_4)_2(tpp\cdot)$, on the basis of their stereochemistry derived from *X*-ray structure analysis.[6] In this communication, we report on the reactivity of $Fe(ClO_4)_2(tpp\cdot)$, which contains two easily displaced axial perchlorato ligands.

Electrochemical measurements suggest that, at millimolar concentrations in dichloromethane solution, $Fe(ClO_4)_2(tpp\cdot)$ undergoes aquation by residual water to give $[Fe^{III}(H_2O)_2(tpp\cdot)]^{2+}2ClO_4^-$. One electron oxidation ($E_{1/2}$ = + 1.12 V *vs.* standard calomel electrode of the well-characterised[7] parent complex, $[Fe^{III}(H_2O)_2(tpp)]^+ClO_4^-$, at a rotating platinum electrode in CH_2Cl_2–Bu_4NClO_4 (10^{-1} M) is clean and reversible, and the peak separation in its cyclic voltammogram (ΔE_p *ca.* 80 mV) indicates close structural similarity between the two components of the redox system [reaction (1)].

$$[Fe^{III}(H_2O)_2(tpp)]^+ - e \rightleftharpoons [Fe^{III}(H_2O)_2(tpp\cdot)]^{2+} \qquad (1)$$

Exhaustive one-electron oxidation results in a u.v.–visible spectrum which is identical to that obtained by mere dissolution of $Fe(ClO_4)_2(tpp\cdot)$, indicating that the same diaquo species is present in both solutions [reaction (2)]. The diperchlorato complex, being the least soluble species, is obtained from these solutions on crystallisation[6] [reverse of reaction (2)].

$$Fe(ClO_4)_2(tpp\cdot) + 2H_2O \rightleftharpoons [Fe(H_2O)_2(tpp\cdot)]^{2+} + 2ClO_4^- \qquad (2)$$

$[Fe(H_2O)_2(tpp\cdot)]^{2+}$ exhibits two distinct patterns of reactivity towards nucleophiles. It reacts readily with easily oxidised bases, such as iodide (one equivalent of Bu_4NI), bromide (excess of solid KBr), and 1,8-bis(dimethylaminonaphthalene) (one equivalent) to give $[Fe(H_2O)_2(tpp)]^+$. This (presumably outer-sphere) electron-transfer process is consistent with the known reactivity of aromatic cation radicals.[8] In striking contrast, the reaction of $[Fe(H_2O)_2(tpp\cdot)]^{2+}$ with pyridine (1.3 equiv.) affords an entirely different product, $[(tpp)FeOFe(tpp\cdot)]^+ClO_4^-$ (identified by its u.v.–visible,[4] i.r.,[3] and e.s.r.[9] spectra), as well as pyridinium perchlorate (identified by its i.r. spectrum). Potentiometry measurements suggest the intermediate formation of a highly oxidising species in this reaction. The equilibrium potential of a nickel electrode immersed in a solution containing 200 mg of $[Fe(ClO_4)_2(tpp\cdot)]$ in 100 ml of dichloromethane is +900 mV *vs.* an aqueous calomel electrode saturated with KCl. Upon addition of 5 µl of neat pyridine, the potential of the solution abruptly jumps to about +1200 mV, then decreases to a stable value of +1100 mV in *ca.* 30 s. Successive pyridine aliquots

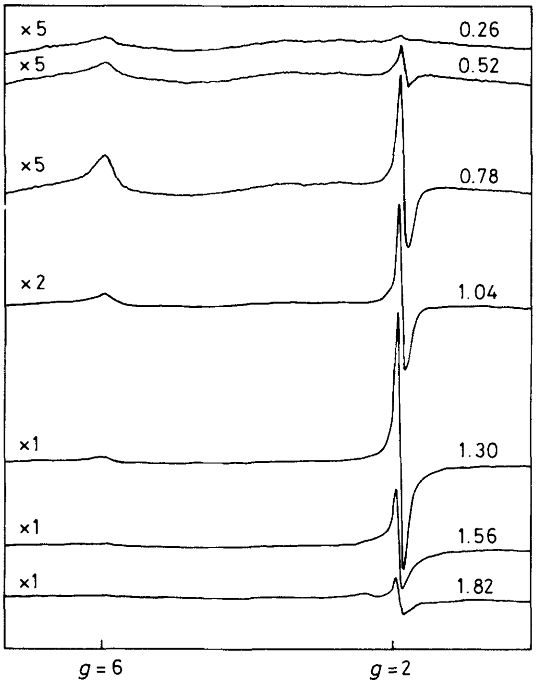

Figure 1. E.s.r. spectra at −180 °C of a solution containing 50 mg of $Fe(ClO_4)_2(tpp\cdot)$ in 30 ml of dichloromethane, during progressive addition of pyridine. The amount of pyridine added (in equiv.) is indicated on the right of each spectrum. Conditions of e.s.r. measurements: scan range 4000 G (1 G = 10^{-4} T); time constant 0.128 s; modulation 25 G; gain 250; microwave power 10 mW; frequency 9.13 GHz. Gain multiplication factors are indicated on the left of each spectrum.

lead to a steady decrease of the equilibrium potential, until the equivalence point is reached at 24 μl (1.3 equiv.) of added pyridine. E.s.r. spectra in frozen solution (−180 °C) at various stages of the reaction (Figure 1) indicate that the end-product, $[(tpp)FeOFe(tpp\cdot)]^+$, accumulates in the solution (see $g = 2$ signal) before one equivalent of pyridine has been added; in addition, a high-spin iron(III) species appears as an intermediate (see $g = 6$ signal). It is thus clear that reduction of the porphyrin ring takes place before formation of the binuclear complex.

The presence of pyridinium perchlorate as a major product suggests that pyridine acts as a Bronsted base in this reaction. A reducing agent must be involved, however, since the porphyrin radical is reduced, and as the reduction is stoicheiometric this cannot be a pyridine impurity. Thus, the question is whether pyridine generates a strongly oxidising species from $[Fe(H_2O)_2(tpp\cdot)]^{2+}$, or an easily oxidised species from the solvent. Potentiometric evidence favours the former hypothesis. Moreover, $[Fe(H_2O)_2(tpp\cdot)]^{2+}$ is probably a stronger acid than any other species present in the solution, and it is likely to react with pyridine in an acid–base reaction (a redox process is unlikely,† as the oxidation potential of pyridine is too high[10]). The results are satisfactorily accounted for by the mechanism outlined in reactions (3)—(6).

$$[Fe(H_2O)_2(tpp\cdot)]^{2+} + py \rightleftharpoons [Fe(OH)(H_2O)(tpp\cdot)]^+ + Hpy^+ \quad (3)$$

$$2[Fe(OH)(H_2O)(tpp\cdot)]^+ \rightleftharpoons [Fe(H_2O)_2(tpp\cdot)]^{2+} + Fe^{IV}(O)(tpp) + H_2O \quad (4)$$

$$Fe^{IV}(O)(tpp) + HA \rightarrow Fe^{III}(OH)(tpp) + A\cdot \quad (5)$$

$$Fe(OH)(tpp) + [Fe(OH)(H_2O)(tpp\cdot)]^+ \rightleftharpoons [(tpp)FeOFe(tpp\cdot)]^+ + 2H_2O \quad (6)$$

In a first step [reaction (3)], deprotonation of the initial diaquoporphyrinato iron(III) radical complex takes place. Hydroxo ligand disproportionation to aquo and oxo species then results in stabilisation of a iron(IV) intermediate, $Fe^{IV}(O)(tpp)$ [reaction (4)]. The latter abstracts a hydrogen atom from the solvent (or more likely from the ethanol added as a stabilising agent) to give a hydroxoiron(III) complex which gives rise to the intermediate $g = 6$ signal [reaction (5)]. In a final step, condensation of this species with a porphyrin radical complex affords the mixed-valence end-product [reaction (6)]. The overall reaction is in reasonable agreement with the observed stoicheiometry of 1.3 pyridine (py) molecules per molecule of the starting complex [reaction (7)].

$$2[Fe(H_2O)_2(tpp\cdot)]^{2+} + 3\,py + HA \rightarrow [(tpp)FeOFe(tpp\cdot)]^+ + 3Hpy^+ + A\cdot + 3H_2O \quad (7)$$

The above experimental evidence, although indirect, indicates for the first time that a porphyrinato-oxoiron(IV) complex can be obtained by base-dependent internal electronic isomerisation of a porphyrinato aquoiron(III) cation radical complex. Moreover, this reaction can be utilised synthetically to give the mixed-valence complex $[(tpp)FeOFe(tpp\cdot)]^+ClO_4^-$ in good yield (80—85%) in a state of analytical purity. Previously, this complex has been obtained by electrochemical oxidation of $[Fe(tpp)]_2O$,[4] but contamination by background electrolyte was difficult to avoid.

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† It can be argued that the easily oxidised 1,8-bis(dimethylamino)naphthalene molecule loses its basic character upon oxidation to its radical cation, explaining why the reaction product is $[Fe(H_2O)_2(tpp)]^+$ rather than $[(tpp)FeOFe(tpp)]$ in this case.