# Oxoiron(IV) Porphyrins Derived from Charged Iron(III) Tetraarylporphyrins and Chemical Oxidants in Aqueous and Methanolic Solutions

**Steven E. J. Bell, Paul R. Cooke, Paul Inchley, Donald R. Leanord, John R. Lindsay Smith * and Angus Robbins**
*Department of Chemistry, University of York, York YO1 5DD, UK*

The oxidation of six charged iron(III) tetraarylporphyrins with chemical oxidants has been investigated. In aqueous solution each can be converted by *tert*-butyl hydroperoxide or monopersulphate into its corresponding oxoiron(IV) porphyrin, whereas in methanol only the iron(III) tetra(*N*-methylpyridyl)porphyrins form detectable ferryl porphyrins at ambient temperatures. On standing, the iron species revert to the parent porphyrin with a small loss due to non-reversible oxidative destruction. That the oxidised porphyrin intermediates are oxoiron(IV) species has been determined using UV–VIS, resonance Raman, $^1$H NMR and EPR spectroscopy.

The mechanism of formation of the ferryl porphyrins and the factors that influence their stability are examined and discussed. In particular steric effects and to a lesser extent electron-withdrawing substituents are shown to be important in stabilising the iron(IV) species. These effects are explained in terms of their influence on the disproportionation of two ferryl species into an iron(III) porphyrin and an iron(IV) porphyrin π radical cation.



Oxoiron(IV) porphyrins are important intermediates in haem-catalysed oxidations. They are well established in the chemistry of peroxidases [1] and have been proposed as transient species in the reactions of catalase,[2] cytochrome P450 [1c,3] and cytochrome oxidase.[4] Models of these intermediates can also be prepared from synthetic iron porphyrins either electrochemically,[5] photochemically,[6] with chemical oxidants [7] or by autoxidation.[8]

The large majority of the studies with model systems have used non-polar iron tetraarylporphyrins, often with *ortho*-substituents on the aryl rings to prevent porphyrin aggregation. The intermediates have been generated in organic solvents at low temperatures ($\leqslant -50$ °C) to slow down their further reactions. Very recently there have been a few reports of the preparation of oxoiron(IV) species from ionic porphyrins in aqueous solution, and some of these intermediates are surprisingly stable even at ambient temperatures.[5d,7d,f,9]

The oxoiron(IV) species fall into two categories analogous to horse radish peroxidase compound I and compound II. The former are oxoiron(IV) porphyrin π radical cations, two oxidation levels above the iron(III) resting enzyme, whilst the latter involve a single electron oxidation of the iron. These species have been characterised by their chemical reactions,[7c] resonance Raman,[6a,7e,8c–e,10] Mossbauer,[7c,11] EPR,[12] EXAF,[7a,13] $^1$H NMR [7b,d,e] and UV–VIS spectroscopy,[5d,7c,e,f,8e] and by electrochemical [5d,7c] and magnetic methods.[7c,d] The data provide information on the factors that stabilise these species and a good comparative framework for identification of new oxoiron(IV) porphyrins.

In this paper we report the results of our studies on the chemical oxidation of some charged iron(III) tetraarylporphyrins in water and in methanol and the characterisation of their corresponding oxoiron(IV) porphyrins. Some of these results have already been presented at conferences.[14]

† The following abbreviations are used: T4MPyP, 5,10,15,20-tetra(4-*N*-methylpyridyl)porphyrin; T2MPyP, 5,10,15,20-tetra(2-*N*-methylpyridyl)porphyrin; TSPP, 5,10,15,20-tetra(4-sulphonatophenyl)porphyrin; TTMAPP, 5,10,15,20-tetra(4-trimethylammoniumphenyl)porphyrin; TDCSPP, 5,10,15,20-tetra(2,6-dichloro-3-sulphonatophenyl)-porphyrin; TCPP, 5,10,15,20-tetra(4-carboxyphenylporphyrin; $Fe^{III}P$, iron(III) porphyrin; $OFe^{IV}P$, oxoiron(IV) or ferryl porphyrin; $OFe^{IV}P^{\cdot+}$, oxoiron(IV) porphyrin π radical cation; 3-CPBA, 3-chloroperoxybenzoic acid; MPS, potassium monopersulphate.

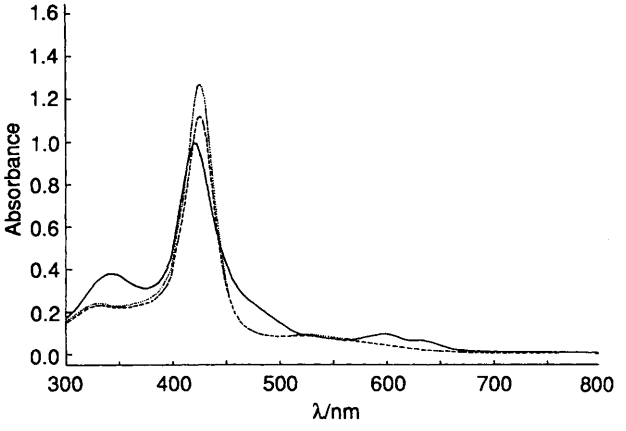



**Fig. 1** UV–VIS spectra of $Fe^{III}$T4MPyP (9.41 × $10^{-6}$ mol $dm^{-3}$) in borate buffer (0.1 mol $dm^{-3}$, pH 9.2) before (——) and after addition of 3 mol equiv. of $Bu^tO_2H$ (· · ·) or MPS (– – – –)

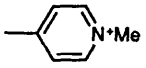
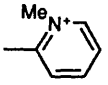
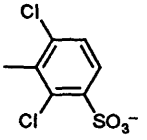
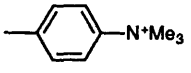
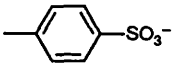
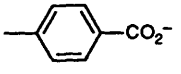
## Results

*UV–VIS Spectroscopic Studies.—The reactions of charged iron(III) tetraarylporphyrins with* tert*-butyl hydroperoxide or potassium monopersulphate in aqueous solution.* The addition of excess $Bu^tO_2H$ to an aqueous solution of $Fe^{III}$T4MPyP † at pH 9.2 leads to a distinct green-brown to red-brown colour change. On standing the red colour is slowly discharged and the solution reverts to its original appearance with a small loss of absorbance. Repeat addition of the oxidant regenerates the intermediate and results in a further bleaching of the iron(III) porphyrin.

UV–VIS spectroscopy shows that the addition of 3 mol equiv. of $Bu^tO_2H$ to $10^{-5}$ mol $dm^{-3}$ $Fe^{III}$T4MPyP leads to a complete conversion, within 1 min, to a new species. The Soret absorbance increases in intensity and shifts from 420 to 426 nm and the α, β bands at 596 and 630 nm are replaced by a new absorbance at 525 nm (Fig. 1).

3 mol equiv. of MPS generate the same spectral changes as $Bu^tO_2H$, although the rate of formation and decay of the red species is greater with the former oxidant (Fig. 1, Table 1). Furthermore, the maximum intensity of the 426 nm absorbance is less than that obtained with $Bu^tO_2H$, indicating that with

**Table 1** Times required for the formation and decay of oxoiron(IV) porphyrins and percentage bleaching on addition of $Bu^tO_2H$ or MPS to iron(III) tetraarylporphyrins in 0.1 mol $dm^{-3}$ borate buffer, pH 9.2 at 30 °C

| Iron(III) tetraarylporphyrin | | | | | | |
|---|---|---|---|---|---|---|
| Aryl group | Concentration/$10^{-6}$ mol $dm^{-3}$ | Oxidant | Molar ratio oxidant: porphyrin | Time/min for $OFe^{IV}P$ Formation | Decay | % Bleaching of $Fe^{III}P$[a] |
|  | 9.4 | $Bu^tO_2H$ | 3 | 0.5 | 240 | 3 |
| | | MPS | 3 | <0.3 | 40 | 35 |
|  | 9.1 | $Bu^tO_2H$ | 3 | 1.0 | 800 | <1 |
| | | MPS | 3 | <0.3 | 180 | 30 |
|  | 6.8 | $Bu^tO_2H$ | 5 | 60 | 1440 | 1.0 |
| | | MPS | 5 | 10 | 600 | 10 |
|  | 7.9 | $Bu^tO_2H$ | 5 | 5 | 120 | 4 |
| | | MPS | 5 | 0.5 | 60 | 39 |
|  | 8.0 | $Bu^tO_2H$ | 5 | 1.0 | 60 | 35 |
| | | MPS | 5 | 0.5 | 60 | 39 |
|  | 9.3 | $Bu^tO_2H$ | 5 | 1.0 | 60 | 50 |
| | | MPS | 5 | 0.5 | 30 | 25 |

[a] Obtained by measuring bleaching of Soret absorption at the end of the reaction.

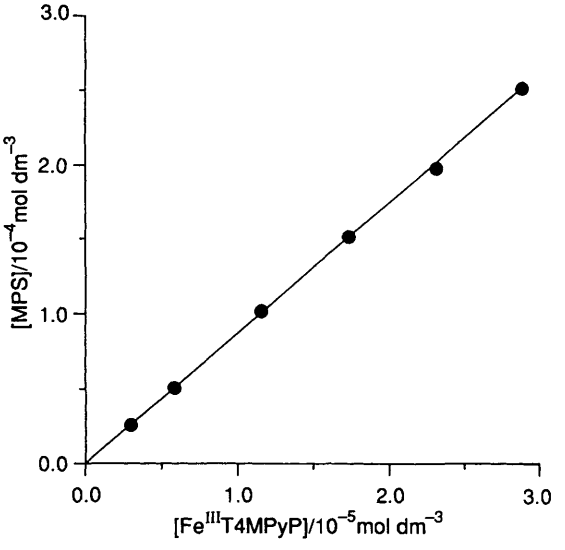



**Fig. 2** The concentration dependence of MPS required to bleach $Fe^{III}T4MPyP$ completely in borate buffer (0.1 mol $dm^{-3}$, pH 9.2)

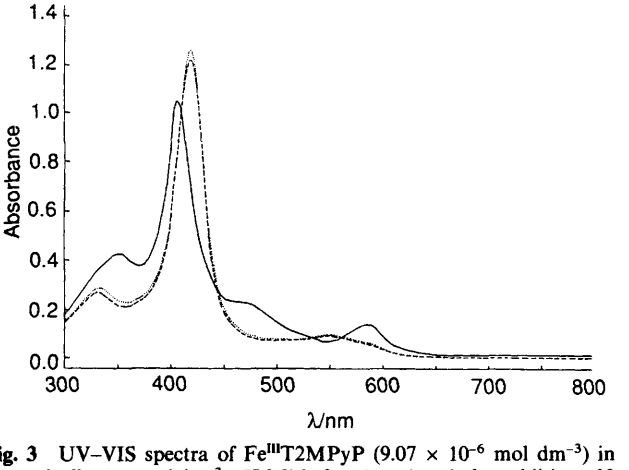


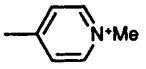
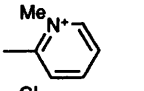
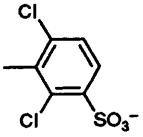
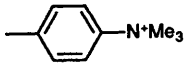
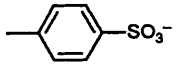
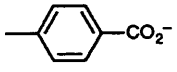

**Fig. 3** UV–VIS spectra of $Fe^{III}T2MPyP$ (9.07 × $10^{-6}$ mol $dm^{-3}$) in borate buffer (0.1 mol $dm^{-3}$, pH 9.2) before (——) and after addition of 3 mol equiv. of $Bu^tO_2H$ (· · · ·) or MPS (– – – –)

MPS substantial porphyrin degradation has occurred. The absorption spectrum at the end of the reaction shows that there has been *ca.* 35% oxidative bleaching of the iron(III) porphyrin. Spectrophotometric measurement of the $Fe^{III}T4MPyP$ concentration following repeated additions of MPS shows that the extent of bleaching is directly porportional to the concentration of the oxidant (Fig. 2). In the catalyst concentration range 2.8–28 × $10^{-6}$ mol $dm^{-3}$, *ca.* 9 mol equiv. of oxidant are required for complete catalyst bleaching.

$Fe^{III}T2MPyP$ behaves in an analogous way to its 4-isomer. Addition of 3 equiv. of either oxidant to a $10^{-5}$ mol $dm^{-3}$ aqueous solution at pH 9.2 leads to new absorptions at 412 and 549 nm (Fig. 3, Table 2). Since $Fe^{III}T2MPyP$ is a mixture of atropisomers, the spectral changes must correspond to the formation of a stereoisomeric mixture of red species. By comparison with $Fe^{III}T4MPyP$, the intermediates from $Fe^{III}T2MPyP$ are longer lived and the porphyrin ring is more stable towards oxidation (Table 1).

The addition of 5 mol equiv. of $Bu^tO_2H$ or of MPS to aqueous solutions of four charged iron(III) tetra(substituted-phenyl)porphyrins at pH 9.2 results in similar spectral changes to those described above (a typical example is given in Fig. 4). The Soret absorption shifts to longer wavelength (*ca.* 420 nm) and a new band appears near 525 nm (Table 2). The approximate times taken for each intermediate to form and to revert back to the parent iron(III) porphyrin are recorded in Table 1. These data reveal that the most stable intermediates are formed by the dichlorosulphonatophenyl- and the two *N*-methylpyridyl-porphyrins. With all the iron(III) porphyrins, except $Fe^{III}TCPP$, the intermediate is more stable and the porphyrin degradation is less extensive with $Bu^tO_2H$ as the oxidant rather than MPS (Table 1).

**Table 2** UV–VIS absorption maxima for oxoiron(IV) porphyrins formed by addition of oxidant to solutions of charged iron(III) tetraaryl porphyrins

| Iron(III) tetraaryl porphyrin | | | | |
|---|---|---|---|---|
| Aryl group | Concentration/$10^{-6}$ mol dm$^{-3}$ | Oxidant | Solvent[a] | $\lambda_{max}$/nm ($\varepsilon$/$10^3$ m$^2$ mol$^{-1}$) |
|  | 9.4 | $Bu^tO_2H$ or MPS | Water | 426 (12.46) 525 |
| | | PhIO | MeOH | 427 (11.87) 556 |
| | | $Bu^tO_2H$ or 3-CPBA | MeOH | 426 556 |
|  | 9.1 | $Bu^tO_2H$ or MPS | Water | 418 (10.40) 549 |
| | | PhIO | MeOH | 417 (10.34) 557 |
| | | $Bu^tO_2H$ or 3-CPBA | MeOH | 416 553 |
|  | 6.8 | $Bu^tO_2H$ or MPS | Water | 420 525 |
|  | 7.9 | $Bu^tO_2H$ or MPS | Water | 419 525 |
|  | 8.0 | $Bu^tO_2H$ or MPS | Water | 421 525 |
|  | 9.3 | $Bu^tO_2H$ or MPS | Water | 420 525 |

[a] Water = 0.1 mol dm$^{-3}$ borate buffer, pH 9.2.

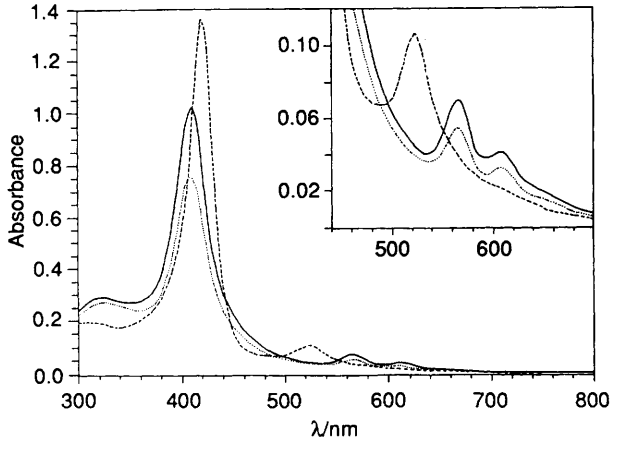



**Fig. 4** UV–VIS spectra of $Fe^{III}$TSPP (8.0 × $10^{-6}$ mol dm$^{-3}$) in borate buffer solution (0.1 mol dm$^{-3}$, pH 9.2) before (——), 30 s (– – – –) and 60 min (· · · ·) after the addition of 5 mol equiv. of MPS

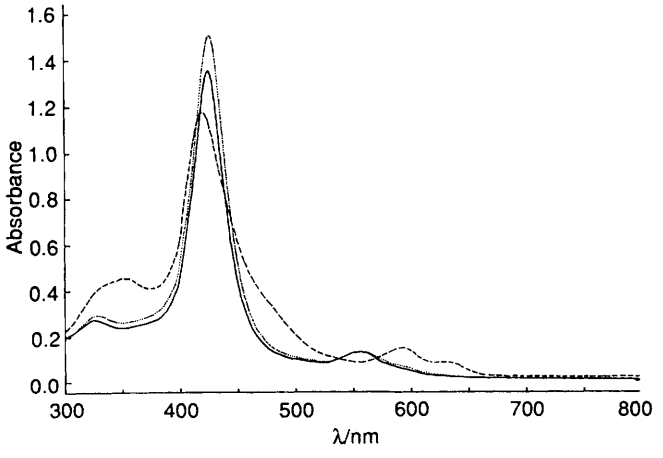



**Fig. 5** UV–VIS spectra of $Fe^{III}$T4MPyP (1.35 × $10^{-5}$ mol dm$^{-3}$) in methanol before (– – – –) and after the addition of 100 mol equiv. of $Bu^tO_2H$ (· · · ·) or 40 mol equiv. of 3-CPBA (——)

*The reactions of charged iron*(III) *tetraarylporphyrins with tert-butyl hydroperoxide, 3-chloroperoxybenzoic acid and iodosylbenzene in methanolic solution.* The addition of excess of $Bu^tO_2H$ to methanolic solutions of $Fe^{III}$T4MPyP or $Fe^{III}$T2MPyP gives very similar colour changes to those from the corresponding reactions in water. UV–VIS spectroscopy indicates that the same reaction occurs in both solvents (Fig. 5). On standing the iron porphyrin reverts to the starting iron(III) state. The main differences between the reactions in water and in methanol (Tables 1 and 3) are that in the latter solvent the build-up of the red species takes longer and requires a much larger excess of oxidant to bring about complete conversion. Furthermore, the extent of porphyrin degradation is significantly less for the reactions in methanol. As is observed in aqueous solution, $Fe^{III}$T2MPyP reacts more slowly and shows more resistance towards bleaching.

When $Fe^{III}$T4MPyP or its 2-isomer in methanol is treated with iodosylbenzene the red species are again formed. With 2.4 × $10^{-5}$ mol dm$^{-3}$ $Fe^{III}$T4MPyP repeated additions of 48 equiv. of iodosylbenzene (based on the initial concentration of catalyst) result in *ca.* 12% bleaching of the porphyrin per aliquot of oxidant. This and experiments with a large excess of oxidant indicate that *ca.* 500 equiv. of PhIO are required for complete destruction of $Fe^{III}$T4MPyP (Table 4).

$Fe^{III}$T2MPyP is more stable and requires *ca.* 3000 equiv. of PhIO. These numbers represent the maximum turnovers of catalyst in the oxidation of methanol to formaldehyde. Table 4 shows that the oxidant accountability as formaldehyde and unreacted PhIO is close to 100%, demonstrating that methanol oxidation and catalyst bleaching are the only significant reactions.

The oxidations of the iron(III) tetra(*N*-methylpyridyl)porphyrins with 3-CPBA in methanol also give the red species. These reactions, which are faster than the corresponding reactions of $Bu^tO_2H$ or PhIO (Table 3), again show that $Fe^{III}$T2MPyP is more stable towards oxidative degradation and is less readily converted to the intermediate. This greater stability of the $Fe^{III}$T2MPyP towards oxidative bleaching can be measured by spectrophotometric titration of each iron(III)

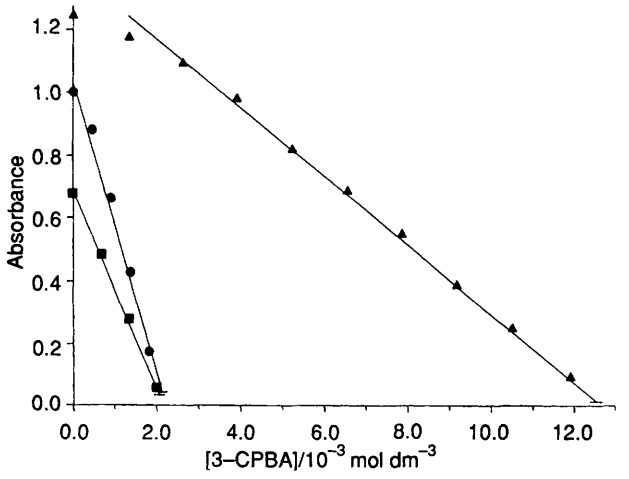



**Fig. 6** Spectrophotometric titration of the bleaching of iron(III) tetra(*N*-methylpyridyl)porphyrins by 3-CPBA in methanol. (●) $Fe^{III}$T4MPyP (initial concentration 1.16 × $10^{-5}$ mol dm$^{-3}$) monitored at 420 nm; (■) $Fe^{III}$T4MPyP (initial concentration 7.78 × $10^{-6}$ mol dm$^{-3}$) monitored at 420 nm; and (▲) $Fe^{III}$T2MPyP (initial concentration 1.05 × $10^{-5}$ mol dm$^{-3}$) in the presence of 600 mol equiv. of 3-chlorobenzoic acid monitored at 414.5 nm.

porphyrin with aliquots of 3-CPBA (Fig. 6). These data demonstrate the linear dependence of the porphyrin degradation on the concentration of the added oxidant, and they also show that more concentrated solutions of $Fe^{III}$T4MPyP are more readily bleached. Complete bleaching of 1.05 × $10^{-5}$ mol dm$^{-3}$ $Fe^{III}$T2MPyP requires 1300 equiv. of 3-CPBA, whereas 1.15 × $10^{-5}$ and 7.78 × $10^{-6}$ mol dm$^{-3}$ $Fe^{III}$T4MPyP require 190 and 270, respectively.

UV–VIS spectroscopy reveals another difference between the two iron(III) tetra(*N*-methylpyridyl)porphyrins, for whereas $Fe^{III}$T4MPyP is regenerated at the end of its reaction with 40 mol equiv. of 3-CPBA, with the 2-isomer a new species is obtained. The origin of this difference lies in the observation that the UV–VIS spectrum of $Fe^{III}$T2MPyP is more sensitive to the presence of acid in the methanol (Fig. 7) than is that of $Fe^{III}$T4MPyP. The final spectrum from the reaction of $Fe^{III}$T2MPyP is of the acid form of the catalyst. This is confirmed by the observation that the reaction of each iron(III) tetra(*N*-methylpyridyl)porphyrin with 3-CPBA in the presence of a large excess of 3-chlorobenzoic acid, generates the red species which at the end of the reaction revert to the partially bleached acid forms of the catalysts.

Attempts to make the transient species from the charged iron(III) tetra(substituted-phenyl)porphyrins in methanol were

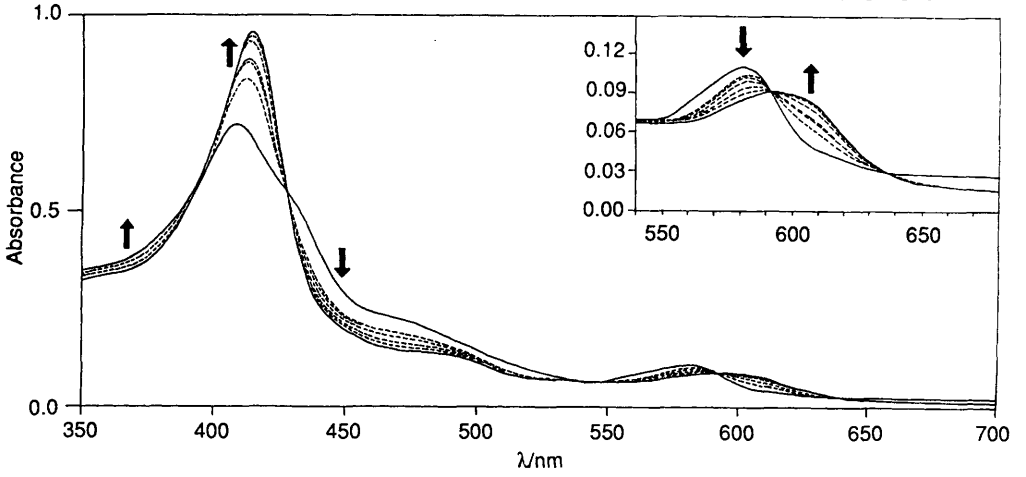



**Fig. 7** UV-VIS spectral changes on addition of 3-CPBA to $Fe^{III}$T2MPyP (8.32 × $10^{-6}$ mol dm$^{-3}$) in methanol. [3-CPBA] = 0, 2.61, 5.22, 6.52, 13.05, 52.18, 78.27 × $10^{-4}$ mol dm$^{-3}$.

**Table 3** Times required for the formation and decay of oxoiron(IV) porphyrins and percentage bleaching on addition of oxidants to iron(III) tetra(*N*-methylpyridyl)porphyrins in methanol at 30 °C

| Iron(III) porphyrin | Concentration/$10^{-5}$ mol dm$^{-3}$ | Oxidant | Molar ratio oxidant: porphyrin | Time/min for $OFe^{IV}P$ | | % Bleaching of $Fe^{III}P$[a] |
|---|---|---|---|---|---|---|
| | | | | Formation | Decay | |
| $Fe^{III}$T4MPyP | 1.35 | $Bu^tO_2H$ | 100 | 30 | >360[b] | 5 |
| $Fe^{III}$T4MPyP | 1.16 | 3-CPBA | 40 | <0.5 | 30 | 20 |
| $Fe^{III}$T2MPyP | 1.00 | $Bu^tO_2H$ | 200 | 180 | >720[b] | 2 |
| $Fe^{III}$T2MPyP[c] | 1.05 | 3-CPBA | 100 | 5 | 30 | 9 |

[a] Obtained by measuring bleaching of Soret absorption at the end of the reaction. [b] Complete decay within 24 h. [c] In the presence of 6.3 × $10^{-3}$ mol dm$^{-3}$ 3-chlorobenzoic acid.

**Table 4** The yield of formaldehyde and the oxidant balance in the reaction of iodosylbenzene with iron(III) tetra(*N*-methylpyridyl)porphyrins in methanol. [$Fe^{III}$T4MPyP], 2.14 × $10^{-5}$ mol dm$^{-3}$; [$Fe^{III}$T2MPyP], 8.9 × $10^{-6}$ mol dm$^{-3}$

| Iron(III) porphyrin | [Oxidant]/ mmol dm$^{-3}$ | [Formaldehyde]/ mmol dm$^{-3}$ | Unreacted PhIO/ mmol dm$^{-3}$ | Oxidant balance[a]/ mmol dm$^{-3}$ | Catalyst turnover[b] |
|---|---|---|---|---|---|
| $Fe^{III}$T4MPyP | 16.1 | 11.0 | 5.1 | 16.1 | 514 |
| | 21.4 | 10.7 | 10.2 | 20.9 | 500 |
| $Fe^{III}$T2MPyP | 53.5 | 26.3 | 28.1 | 54.4 | 2955 |
| | 71.3 | 28.7 | 38.3 | 67.0 | 3224 |

[a] Sum of formaldehyde and unreacted oxidant concentrations. [b] Molar yield of formaldehyde per mole of catalyst.

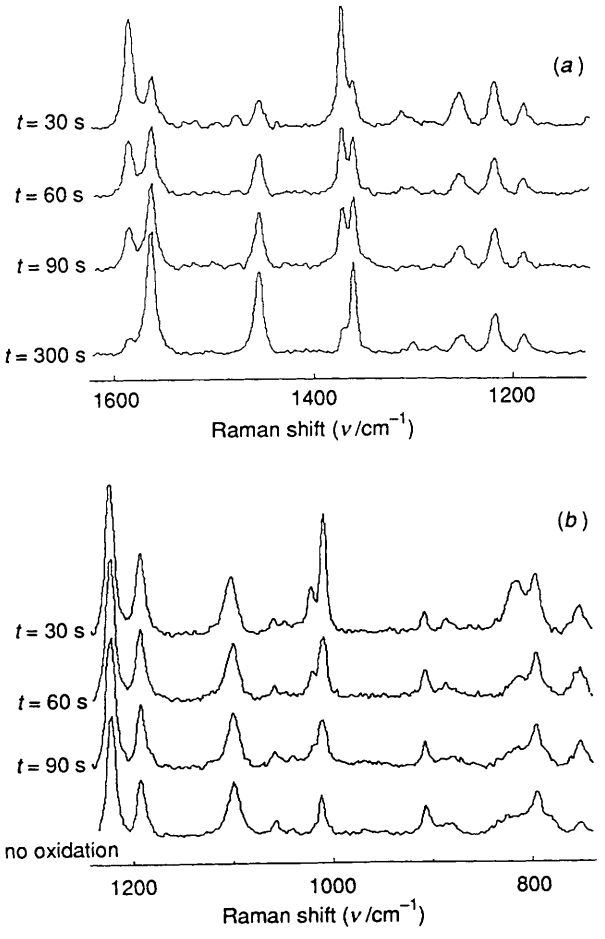



**Fig. 8** Time-resolved resonance Raman spectra of $Fe^{III}$T4MPyP ($10^{-4}$ mol $dm^{-3}$) in aqueous solution following the addition of 3 mol equiv. of $Bu^tO_2H$. (*a*) High-frequency spectrum (pH 9.2); (*b*) low-frequency spectrum (pH 9.4).

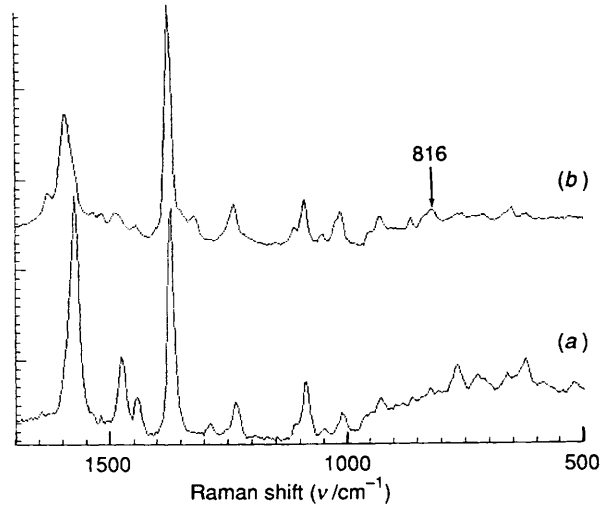



**Fig. 9** Resonance Raman spectrum of $Fe^{III}$TDCSPP in borate buffer (0.1 mol $dm^{-3}$, pH 9.2) before (*a*) and after (*b*) the addition of 3 mol equiv. of $Bu^tO_2H$

unsuccessful. For each porphyrin the addition of either $Bu^tO_2H$ or 3-CPBA results in bleaching without detectable intermediates. As observed above for the *N*-methylpyridylporphyrins the rate of reaction and extent of bleaching are greater with the peroxy acid than with the hydroperoxide.

*Resonance Raman Spectroscopic Studies.—The reaction of* $Fe^{III}$T4MPyP *and* $Fe^{III}$TDCSPP *with* tert-*butyl hydroperoxide*

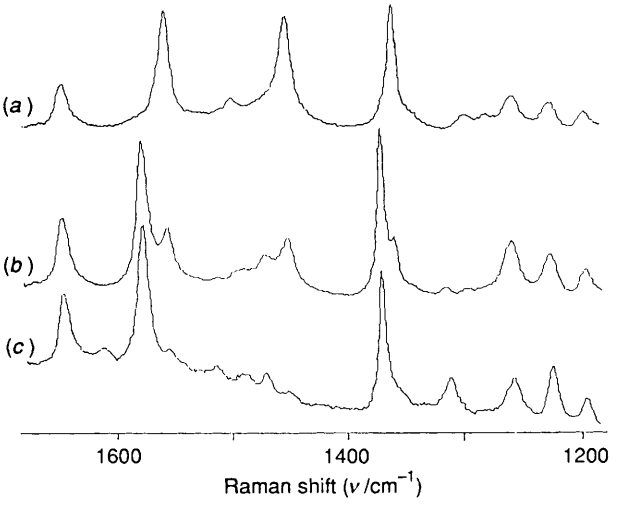



**Fig. 10** High-frequency resonance Raman spectra of $Fe^{III}$T4MPyP ($10^{-4}$ mol $dm^{-3}$) in methanol before (*a*) and after (*b*) the addition of 100 mol equiv. of $Bu^tO_2H$. Spectrum (*c*) is the same reaction in water (pH 9.2) with 3 mol equiv. of $Bu^tO_2H$.

*in aqueous solution.* Resonance Raman spectroscopy (413.1 nm excitation) shows that the addition of three mol equiv. of $Bu^tO_2H$ to $10^{-4}$ mol $dm^{-3}$ $Fe^{III}$T4MPyP in aqueous solution rapidly generates a new species which decays back over 10 min to the original porphyrin (Fig. 8). The life-time of the species at the porphyrin concentrations used for resonance Raman studies is significantly less than those in the more dilute solutions used for UV–VIS spectroscopy. Repeating the reaction with $10^{-4}$ mol $dm^{-3}$ $Fe^{III}$TDCSPP in aqueous borate buffer (pH 9.2) also generates a new species (Fig. 9). However, this intermediate is significantly more stable than that from $Fe^{III}$T4MPyP and the spectrum shows little change after 1 h.

The principal spectral changes that occur between 1600 and 1200 $cm^{-1}$, following addition of $Bu^tO_2H$ to $Fe^{III}$T4MPyP are the replacement of the bands at 1554 and 1359 $cm^{-1}$ in the parent iron(III) porphyrin by bands at 1576 and 1371 $cm^{-1}$, respectively. The other main band at 1450 $cm^{-1}$ decreases in intensity but in common with the bands at 1255, 1220 and 1191 $cm^{-1}$ does not shift on oxidation of the porphyrin. Similar spectral changes occur on reaction of $Bu^tO_2H$ with $Fe^{III}$TDCSPP.

In the region 1200–800 $cm^{-1}$ the most significant new bands in the spectra of the intermediates are at 818 and 816 $cm^{-1}$ for oxidised $Fe^{III}$T4MPyP and $Fe^{III}$TDCSPP, respectively. Carrying out the reactions in $H_2{}^{18}O$ (90 g atom%) gives new bands at 779 and 776 $cm^{-1}$ in place of those at 818 and 816 $cm^{-1}$, respectively. By comparison, replacing the solvent in the reaction of $Fe^{III}$T4MPyP with $D_2O$ causes no discernible shift in the 818 $cm^{-1}$ band, although it becomes sharper.

*The reaction of* $Fe^{III}$T4MPyP *with* tert-*butyl hydroperoxide and iodosylbenzene in methanol.* The resonance Raman spectrum of the transient intermediate from the reaction of $Fe^{III}$T4MPyP with 100 mol equiv. of $Bu^tO_2H$ in methanol was also recorded, and the high frequency region (1600–1200 $cm^{-1}$) is almost identical to that obtained from the reaction in water (Fig. 10). However, the changes that occur $< 1200$ $cm^{-1}$ are less clear. A strong methanol band at 1034 $cm^{-1}$ obscures the 1012 $cm^{-1}$ band observed in water and its subsequent split into 1021 and 1009 $cm^{-1}$ bands on oxidation. The important 818 $cm^{-1}$ band is not present in the methanolic solution. It is possible that this is shifted to 826 $cm^{-1}$ although no $^{18}O$ labelling experiments were carried out to confirm the identity of this band.

The red species prepared from PhIO oxidation of $Fe^{III}$T4MPyP in methanol was also examined by resonance Raman spectroscopy. A wide range of porphyrin and oxidant

**Table 5** The dependence on pH, ionic strength and buffer concentration of the relative amounts of monomer and μ-oxo-dimer in aqueous solutions of $Fe^{III}T4MPyP$ ($7.4 \times 10^{-3}$ mol $dm^{-3}$)

| Buffer | Concentration/$10^{-2}$ mol $dm^{-3}$ | pH | Ionic strength[a] | Percentage | |
|---|---|---|---|---|---|
| | | | | Monomer | μ-oxo-Dimer |
| Hydroxide/KCl | 10 | 13.0 | 0.08 | <5 | >95 |
| Bicarbonate | 2.5 | 10.0 | 0.05 | 28 | 72 |
| Borate | 2.5 | 9.2 | 0.05 | 44 | 56 |
| Phosphate | 2.5 | 7.0 | 0.05 | 61 | 39[b] |
| Phosphate | 10 | 6.0 | 0.06 | 90 | 10[b] |
| Acetate | 10 | 5.8 | 0.09 | 85 | 15 |
| Acetate | 20 | 5.8 | 0.18 | 90 | 10 |
| Acetate | 40 | 5.8 | 0.37 | 93 | 7 |
| Acetate | 10 | 5.8 | 0.19 | 24 | 76 |
| Acetate | 10 | 5.8 | 0.29 | 13 | 87 |
| Acetate | 10 | 5.8 | 0.49 | 8 | 92 |
| Acetate | 20 | 5.0 | 0.14 | *ca.* 100 | trace |
| Acetate | 20 | 4.0 | 0.04 | 100 | 0 |
| HCl | 10 | 1.0 | — | 100 | 0 |

[a] Ionic strength adjusted with $KNO_3$. [b] Two β-pyrrole resonances observed.

**Table 6** The temperature dependence of the $^1H$ NMR resonances of $Fe^{III}T4MPyP$ in $CD_3OD$. [$Fe^{III}T4MPyP$], $6.4 \times 10^{-3}$ mol $dm^{-3}$

| T/°C | Chemical shifts/ppm[a] | | | |
|---|---|---|---|---|
| | $\overset{+}{N}Me$ | 2-pyridyl | 3-pyridyl | β-pyrrole |
| 27 | 5.9 | 11.0 | 12.2 | 79.4 |
| 10 | 6.0 | 11.2 | 12.8 | 85.4 |
| 0 | 6.1 | 11.3 | 13.1 | 88.8 |
| −10 | 6.1 | 11.4 | 13.5 | 92.4 |
| −20 | 6.2 | 11.6 | 14.0 | 97.4 |
| −30 | 6.3 | 11.9 | 14.5 | 102.4 |

[a] Relative to TMS standard.

concentrations was examined but complete conversion to the intermediate was not achieved. The best conditions used were $10^{-4}$ mol $dm^{-3}$ $Fe^{III}T4MPyP$ and a 1000-fold excess of PhIO. The spectrum from this experiment resembles one from $Fe^{III}T4MPyP$ partially oxidised by $Bu^tO_2H$ in water. As noted above for the resonance Raman spectrum of the reaction with $Bu^tO_2H$ in methanol, there is no evidence of the 818 $cm^{-1}$ band in the reaction of $Fe^{III}T4MPyP$ with PhIO.

*$^1H$ NMR Spectroscopic Studies.—Monomers and dimers of* $Fe^{III}T4MPyP$ *in aqueous solution.* $^1H$ NMR studies of the reactions of $Fe^{III}T4MPyP$ in water require porphyrin solutions that are *ca.* 700 times more concentrated than those used in the UV–VIS investigations. For this reason the NMR spectra of the solutions are complicated, at all pHs > 4, by the presence of μ-oxo-dimers. Table 5 shows the dependence of the relative proportions of the two species on the pH, ionic strength and buffer concentration. The μ-oxo-dimer is favoured by increasing pH and ionic strength.

*The reaction of* $Fe^{III}T4MPyP$ *with* tert*-butyl hydroperoxide in aqueous solution.* The optimum temperature for following the reactions in aqueous solution is 10 °C since below this value the increased viscosity of the water broadens the absorbances and at higher temperatures the lifetime of the transient species becomes too short. The time required to accumulate sufficient data to obtain a reliable $^1H$ NMR spectrum was typically 30 min (*ca.* 400 scans) although for some oxidations fewer scans were used to obtain information about the initial phase of the reaction.

The addition of 10 mol equiv. of $Bu^tO_2H$ to $7.4 \times 10^{-3}$ mol $dm^{-3}$ solutions of $Fe^{III}T4MPyP$ in $D_2O$ at 10 °C generates the red species at all pHs between 4 and 13. The resonances of the parent porphyrin are replaced by new resonances of the red intermediate at 9.5 and 9.9 ppm. The *N*-methyl resonance is lost due to the presaturation of the solvent ($D_2O$).

There is no clear distinction between the reactivity of the monomer and the μ-oxo-dimer with $Bu^tO_2H$, both are consumed to make the transient intermediate. Under all the conditions studied NMR spectroscopy shows that on standing the intermediate reverts to the parent porphyrin monomer or a mixture of monomer and μ-oxo-dimer. However, the presence of μ-oxo-dimer complicates the analysis of the NMR spectra of the reaction mixtures because the dimer has a broad resonance with a similar chemical shift to the downfield peaks of the intermediate. This problem cannot be overcome by running the reaction in acidic solution (pH ⩽ 4), where the parent porphyrin exists entirely as the monomer, since the lifetime of the intermediate decreases with the pH of the solution and under these conditions is very short-lived.

Even at pH 5.8, with added acetate to favour the monomer, 10 mol equiv. of $Bu^tO_2H$ give only a partial conversion (*ca.* 25%) to the intermediate.

At pH 7.0, an accumulation of the initial 16 NMR scans (1 min) shows that the conversion to the intermediate is complete. However, within 1 h it has almost totally reverted to a mixture of the monomer and dimer of the parent porphyrin. By contrast, at pH 10 *ca.* 60% of the intermediate is still present after 1.5 h.

*The reaction of* $Fe^{III}T4MPyP$ *with* tert*-butyl hydroperoxide or* 3*-chloroperoxybenzoic acid in methanol.* The $^1H$ NMR spectrum of $Fe^{III}T4MPyP$ in methanol exhibits four resonances, one of which is the very broad low field peak from the β-pyrrole hydrogens that confirms the species is a monomer. All the resonances display a typical dependence on temperature for a high-spin iron(III) tetraarylporphyrin, moving to lower field as the temperature decreases [15] (Table 6).

Addition of 1.3 mol equiv. of 3-CPBA to a $6.4 \times 10^{-3}$ mol $dm^{-3}$ solution of $Fe^{III}T4MPyP$ in methanol at −30 °C gives a deep red coloured solution. $^1H$ NMR spectroscopy of this solution shows that *ca.* 10% of the parent porphyrin has been converted to a new species with resonances at 5.0, 9.5, 9.7 and 10.3 ppm and a complex multiplet centred at 7.8 ppm. The last resonance arises from 3-chlorobenzoic acid. The addition of a further 1.9 equiv. of 3-CPBA gives a further reduction in the resonances from the parent porphyrin and a concomitant increase in those from the red species (*ca.* 50% conversion) (Fig. 11). Warming the solution to −10 °C results in a significant loss of the red species and at 10 °C the $^1H$ NMR spectrum of the parent iron(III) porphyrin is restored.

Attempts to record the $^1H$ NMR spectrum of the oxidised

**Table 7** UV–VIS spectral data of oxoiron(IV) tetraarylporphyrins ($OFe^{IV}TArP$)

| Aryl group | Solvent | $T$/°C | $\lambda_{max}$/nm ($\varepsilon/10^3$ m$^2$ mol$^{-1}$) | Ref. |
|---|---|---|---|---|
| Phenyl | $PhCH_3$[a] | −90 | 427, 555, 563, 597 | 8(*e*) |
| 2,6-Dichlorophenyl | THF | −50 | 417(16.95), 551, 622, 653 | 7(*e*) |
| 2,6-Dichlorophenyl | DMF | −50 | 419(15.76), 554, 632 | 7(*e*) |
| 2,6-Dichlorophenyl | $CH_2Cl_2$/EtOH | −66 | 416(13.84), 552 | 7(*e*) |
| 2,6-Dimethyl-3-sulphonatophenyl | $H_2O$ | 22 | 421(9.97) 551 | 7(*f*) |
| 4-*N*-Methylpyridyl | MeOH | 23 | 427(11.87), 556 | this study |
| 4-*N*-Methylpyridyl | $H_2O$ (pH 9.2) | 30 | 426(12.46), 525 | this study |
| 4-*N*-Methylpyridyl | $H_2O$ (pH 9.0) | | 426, 524, 547 | 5(*d*) |
| 2-*N*-Methylpyridyl | MeOH | 23 | 417(10.34), 557 | this study |
| 2-*N*-Methylpyridyl | $H_2O$ (pH 9.2) | 30 | 418(10.40), 549 | this study |

[a] Containing 1-methylimidazole.

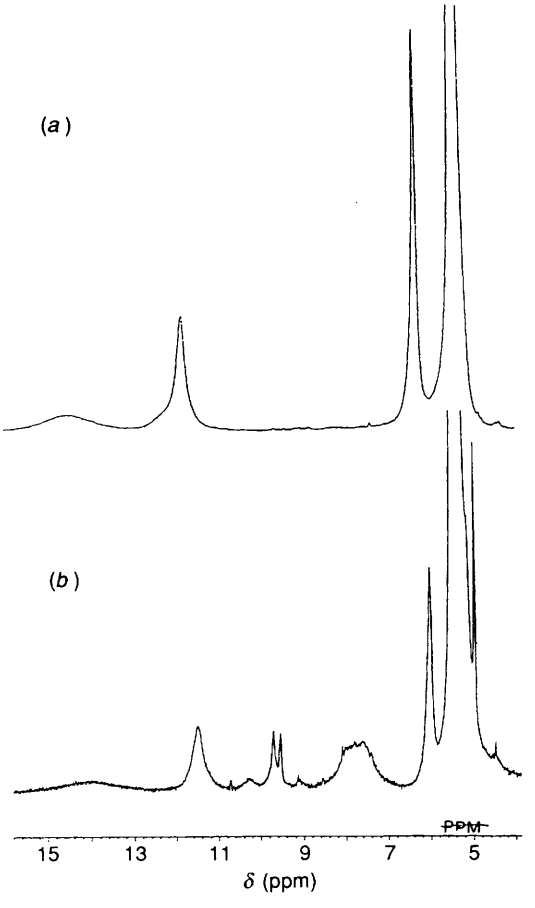



**Fig. 11** $^1$H NMR spectrum of $Fe^{III}T4MPyP$ ($6.4 \times 10^{-3}$ mol dm$^{-3}$) in $CD_3OD$ before (*a*) and after (*b*) the addition of 1.6 mol equiv. of 3-CPBA at −30 °C

porphyrin free of $Fe^{III}T4MPyP$ using 6–10 equiv. of 3-CPBA were hampered by interference from the large resonances from 3-chlorobenzoic acid.

Treatment of a $7.4 \times 10^{-3}$ mol dm$^{-3}$ methanolic solution of $Fe^{III}T4MPyP$ with a ten-fold excess of $Bu^tO_2H$ at −30 °C gives a 40% conversion to the same species as observed with 3-CPBA. Resonances attributable to $Bu^tO_2H$, acetone and *tert*-butylmethyl peroxide, products from the $Bu^tO_2H$, are also detected. Warming to −20 °C leads to a complete reversion to the spectrum of the starting porphyrin.

*EPR Spectroscopic Studies.*—1 or 5 mol equiv. of $Bu^tO_2H$ were added to $10^{-4}$ mol dm$^{-3}$ solutions of $Fe^{III}T4MPyP$ in aqueous borate buffer (pH 9.03) and the mixtures were rapidly cooled to 150, 100 or 90 K. EPR studies on these frozen reaction mixtures gave no observable signals between 5 and 5005 G.

## Discussion

Of the reactions of charged iron(III) porphyrins with oxidants examined in this study, those of $Fe^{III}T4MPyP$ have been investigated in the most detail. The spectroscopic studies show that for this porphyrin all the oxidants generate the same intermediate. This effectively eliminates oxidant–porphyrin complexes analogous to the species reported by Hill and his co-workers for the reactions of iodosylbenzene with manganese(III) porphyrins,[16] as possible structures.

The similarity of the UV–VIS characteristics of the red species from $Fe^{III}T4MPyP$ to those reported for oxoiron(IV) porphyrins (Table 7) suggests that the intermediate is oxoiron(IV) tetra(4-*N*-methylpyridyl)porphyrin ($OFe^{IV}T4MPyP$). A very recent study of the electrochemical oxidation of $Fe^{III}T4MPyP$ in water reaches the same conclusion about the structure of the intermediate.[5d]

The identities of the intermediates from $Fe^{III}T4MPyP$ and $Fe^{III}TDCSPP$ as ferryl porphyrins are unambiguously confirmed by the resonance Raman bands at 818 and 816 cm$^{-1}$, respectively which we assign to the $Fe^{IV}$=O stretch in the two porphyrins. Not only do these bands lie in the range of values reported for the $Fe^{IV}$=O bond of other ferryl porphyrins (Table 8) but with $^{18}O$ labelling they shift to lower frequency by 39 and 40 cm$^{-1}$, respectively. These differences in stretching frequencies of $Fe^{IV}$=O and $Fe^{IV}$=$^{18}$O are in excellent agreement with some very recent values of Babcock and his co-workers for some non-ionic ferryl porphyrins in toluene[8e] and with the predicted isotopic shift of 36 cm$^{-1}$ for an isolated oxoiron(IV) unit. The sharpening of the 818 cm$^{-1}$ band in spectra of $D_2O$ solutions of $OFe^{IV}T4MPyP$ is also expected from the slower rate of oxygen exchange in $D_2O$ than in $H_2O$.[18b]

It has been argued[7e,8e] that in dipolar solvents, or in the presence of suitable donor ligands, the ferryl porphyrins are hexacoordinated and that this results in a lowering of the $Fe^{IV}$=O stretching frequency from the value of the pentacoordinate species. This weakening of the $Fe^{IV}$=O bonding arises either by a *trans* effect or by causing the iron to move towards the plane of the porphyrin ring.[7e,8c,e,17,19] Hydrogen bonding to the oxygen of the ferryl porphyrin also weakens the $Fe^{IV}$=O bonding.[8e] In this respect the shift in the resonance Raman $Fe^{IV}$=O stretch of horse radish peroxidase compound II from 787 to 775 cm$^{-1}$ on changing from high pH to neutral solution has been interpreted in terms of H-bonding to a distal imidazole.[18] Further evidence for the influence of H-bonding on oxometal bonds in porphyrins has been obtained by Spiro and co-workers[20] in a systematic resonance Raman study on stable oxovanadyl porphyrins which showed that water is particularly effective in lowering the oxometal stretching frequency. The 818 cm$^{-1}$ value obtained in this study, although it is not as low as that found in peroxidase compound II[18] (where there is both H-bonding to distal and ligation to proximal histidines), indicates that a probable structure for the ferryl porphyrins in water is **1**; R = H. The structural information from the resonance Raman

**Table 8** Resonance Raman $Fe^{IV}$=O stretching frequencies of oxoiron(IV) tetraarylporphyrins ($OFe^{IV}TArP$)

| Aryl group | Solvent | Sixth ligand | $T$/°C | $Fe^{IV}$=O stretching frequency/$cm^{-1}$ | Ref. |
|---|---|---|---|---|---|
| Phenyl | $O_2$ matrix | — | −258 | 852 | 17 |
| Mesityl | $PhCH_3$ | — | −46 | 845 | 8(*d*) |
| 2,6-Dichlorophenyl | THF | THF | −50 | 841 | 7(*e*) |
| 2,6-Dichlorophenyl | DMF | DMF | −50 | 828 | 7(*e*) |
| 2,6-Dichlorophenyl | $PhCH_3$ | 1-methylimidazole | −50 | 818 | 7(*e*) |
| Phenyl | $PhCH_3$ | 1-methylimidazole | −120 | 820 | 8(*e*) |
| 4-*N*-Methylpyridyl | $H_2O$ | $H_2O$ | RT[a] | 818 | this study |
| 2,6-Dichloro-3-sulphonatophenyl | $H_2O$ | $H_2O$ | RT[a] | 816 | this study |
| HRP compound II | $H_2O$ high pH | imidazole | RT[a] | 787 | 18 |
| HRP compound II | $H_2O$ neutral pH | imidazole | RT[a] | 775 | 18 |

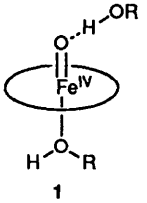
[a] Room temperature.

**Table 9** $^1H$ NMR chemical shifts of oxoiron(IV) tetraarylporphyrins ($OFe^{IV}TArP$)

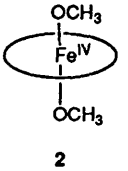
| | | | Chemical shifts/ppm[a] | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Aryl | | | | |
| Aryl group | Solvent | $T$/°C | β-pyrrole | 2 | 3 | 4 | ArMe | Ref. |
| Mesityl | [$^2H_8$]toluene | −70 | 8.4 | — | 6.4<br>6.0 | — | 3.3<br>2.6 | 8(*a*), 21 |
| 2-Pivalamidophenyl | [$^2H_8$]THF | −50 | 7.2 | 12.9 | 9.3<br>8.7 | 7.7 | — | 8(*b*) |
| 2,6-Dichlorophenyl | [$^2H_7$]DMF | −50 | 14.1 | — | 4.0 | 4.0 | — | 7(*e*) |
| 4-*N*-Methylpyridyl | [$^2H_4$]MeOH | −30 | 10.0 | 9.7 | 9.5 | — | 5.0 | this study |
| 4-*N*-Methylpyridyl | [$^2H_2$]water | 10 | 9.9 | 9.5 | 9.5 | — | *b* | this study |

[a] Relative to TMS or DSS. [b] Not detectable due to presaturation of water resonance.

spectra of the oxidised porphyrin in methanol is not as clear cut as that from the aqueous solutions, since without $^{18}O$ labelling experiments the $Fe^{IV}$=O stretching cannot be unequivocally identified. However, the similarity of the high frequency region of the resonance Raman spectra of the species generated by $Bu^tO_2H$ and by PhIO in methanol to that of $OFe^{IV}T4MPyP$ in water suggests strongly that the intermediate has structure **1**, R = Me. An alternative dimethoxyiron(IV) porphyrin, structure **2**, similar to that proposed by Groves *et al.*[12] for the species formed by reaction of iron(III) tetramesitylporphyrin perchlorate with iron(III) perchlorate followed by sodium methoxide, seems less likely. $^1H$ NMR spectroscopy of the species in methanol supports this conclusion.




**1**




**2**

R = H or $CH_3$

= porphyrin dianion

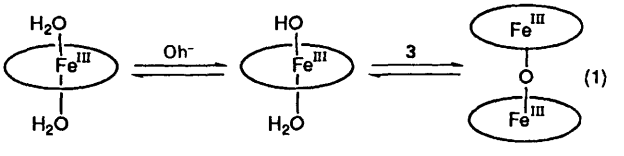
The $^1H$ NMR spectra from oxidised $Fe^{III}T4MPyP$ in methanol are more informative than those from aqueous solutions. In the former solvent the parent porphyrin is a monomer and it reacts cleanly with either $Bu^tO_2H$ or with 3-CPBA to give a new species. This work requires the use of low temperatures because, at the porphyrin concentrations needed for the NMR studies, the lifetime of the intermediate above −30 °C is too short to allow its spectrum to be recorded.

The most striking change in the $^1H$ NMR spectrum of $Fe^{III}T4MPyP$ on addition of the oxidant is the decrease in the intensities of the resonances of the parent porphyrin and non-appearance of any new resonances <11 ppm. Taken in conjunction with the absence of EPR signals from the oxidised porphyrin, these data are in accord with the high spin $Fe^{III}T4MPyP$ ($S$ = 5/2) being converted into an oxoiron(IV) species ($S$ = 1). The upfield shift of all the NMR resonances, and in particular that of the β-pyrrole hydrogens, coupled with the sharpening of these resonances in the oxidised species would be expected from the smaller interaction between the porphyrin ring and the unpaired electrons on the paramagnetic iron. A tentative assignment of the resonances of the oxidised porphyrin, which is in agreement with those of other ferryl porphyrins, is given in Table 9.

The $^1H$ NMR spectra also rule out structure **2** for the intermediate since the β-pyrrole resonances from such iron(IV) porphyrins occur at characteristically high fields, *e.g.* at −37.5 ppm for dimethoxyiron(IV) tetramesitylporphyrin.[12]

In aqueous solution, the ferryl porphyrin is more stable than in methanol and this allows NMR spectra to be obtained at 10 °C. However, the spectra show less structure than those from methanolic solutions since the pyridyl resonances are unresolved (9.5 ppm) and are superimposed on the broader β-pyrrole peak (9.9 ppm).

Apart from structural information on $OFe^{IV}T4MPyP$, the $^1H$ NMR studies on squeous solutions also provide information on the parent porphyrin. Several recent investigations[22] have led to the conclusion that in the pH range 1–10 $Fe^{III}T4MPyP$ undergoes a pH dependent equilibrium between two monomers (**3** and **4**), and, in basic solution, there is also a concentration dependent equilibrium between monomer and μ-oxo-dimer (**5**) [reaction (1)].




**3** **4** **5**

The results from the present study are in agreement with these equilibria, showing clearly that mixtures of monomer and μ-oxo-dimer in basic solutions of $Fe^{III}$T4MPyP are converted to a single monomeric species at pHs ⩽ 4. They also reveal, as observed by Goff and Morgan,[23] that increasing the ionic strength of the solution with a non-ligating salt favours the μ-oxo-dimer. Interestingly, at pH 5.8, increasing the concentration of the buffer favours the monomer. Clearly under the latter conditions, the ligating ability of acetate, which favours the monomer, outweighs the ionic strength effect.

The addition of $Bu^tO_2H$ to aqueous solutions of $Fe^{III}$T4MPyP converts both the monomer and the μ-oxo-dimer into the ferryl porphyrin. We suggest that this arises through oxidation of the monomer, and that the dimer reacts by first forming the monomer. However, we cannot rule out the possibility that the oxidant reacts with the dimer directly.

*Formation, Destruction and Stability of Oxoiron*(IV) *Porphyrins.*—The initial reaction of iron(III) porphyrins with PhIO or with a peroxy acid generates the oxoiron(IV) porphyrin π radical cation in a two-electron oxidation [reaction (2)].

$$Fe^{III}P + OX \longrightarrow OFe^{IV}P^{\bullet+} + X \quad (2)$$

$$OX = \text{3-CPBA, MPS or PhIO}$$

In methanolic solution there are two important competing reactions leading to the removal of this active oxidant; solvent oxidation to regenerate the catalyst and comproportionation with iron(III) porphyrin to give the ferryl porphyrin [reactions (3) and (4), respectively]. In aqueous solution, solvent oxidation

$$OFe^{IV}P^{\bullet+} + CH_3OH \longrightarrow HCHO + H_2O + Fe^{III}P \quad (3)$$

$$OFe^{IV}P^{\bullet+} + Fe^{III}P \xrightarrow{H_2O} 2OFe^{IV}P \quad (4)$$

is unimportant and the competitive process [reaction (4)] predominates. This explains why aqueous solutions of the iron(III) tetra(*N*-methylpyridyl)porphyrins require significantly less oxidant than methanolic ones to give complete conversion to the oxoiron(IV) porphyrin. Indeed, solvent oxidation probably accounts for our inability to detect any oxoiron(IV) porphyrins in oxidations of methanolic solutions of charged iron(III) tetra(substituted-phenyl)porphyrins. It is noteworthy that all previous reports of ferryl porphyrins that are long-lived at ambient temperature have used aqueous solutions.[5d,7d,f,9]

The mechanism of oxidation of iron(III) porphyrins with $Bu^tO_2H$ is in dispute. Investigations by Traylor and his co-workers[24] have been used to support a two-electron process analogous to reaction (2) with peroxy acids. However, there is strong evidence from other work that the initial reaction involves a one-electron transfer [reaction (5)].[7e,25] Whether or

$$Fe^{III}P + Bu^tO_2H \longrightarrow OFe^{IV}P + Bu^tO^{\bullet} \quad (5)$$

not the reaction of $Bu^tO_2H$ with iron(III) porphyrins is a one- or a two-electron process, our recent studies with $Fe^{III}$T4MPyP in aqueous solution have shown that the initial step is followed by a complex sequence of interrelated reactions involving dioxygen, alkyl peroxyl, alkoxyl and methyl radicals.[25d]

The mechanisms of reduction of ferryl porphyrins back to the iron(III) state, particularly in the absence of an oxidisable substrate, are uncertain. Oxoiron(IV) porphyrins, unlike oxoiron(IV) porphyrins π radical cations, are not potent oxidants, particularly when stabilised with a good donor ligand.[26] However, the marked decrease in the stability of $OFe^{IV}$T4MPyP in more concentrated solutions suggests that an important mechanism involves the self-reaction of ferryl porphyrins. This could be disproportionation [reverse of reaction (4)] followed by porphyrin degradation by the oxoiron(IV) porphyrin π radical cation [reaction (6)]

$$2OFe^{IV}P \longrightarrow [Fe^{III}P\ OFe^{IV}P^{\bullet+}] \longrightarrow Fe^{III}P_{ox} + Fe^{III}P \quad (6)$$

where $Fe^{III}P_{ox}$ contains an oxidised porphyrin ring.

If, in aqueous solution, this is the sole route back to the iron(III) porphyrin our results show that with $1.15 \times 10^{-5}$ mol $dm^{-3}$ $Fe^{III}$T4MPyP, 9 equiv. of MPS are required to bring about complete bleaching. It is, however, also possible that the oxoiron(IV)porphyrin π radical cation can oxidise the MPS, and that this competing reaction leads to removal of oxidant without destruction of the porphyrin. In methanol, any oxoiron(IV) porphyrin π radical cation formed by the reverse of reaction (4) is also able to oxidise the solvent to formaldehyde [reaction (3)] and consequently the extent of porphyrin degradation is significantly less than in water. The good oxidant balance in the reactions of PhIO in methanol show that solvent oxidation accounts for virtually all the oxidant. In the reactions with $Bu^tO_2H$, the oxidant and products from the oxidant serve as substrates for the oxoiron(IV) porphyrin. Our current investigations are aimed at defining more fully the reactions of ferryl porphyrins.

The results from the present study demonstrate that the aryl group on the porphyrin has a marked influence on the lifetime of the oxoiron(IV) species and on the stability of the porphyrin towards oxidative bleaching (Table 1). As has been observed previously, steric effects and electron-withdrawing substituents make iron(III) tetraarylporphyrins more resistant to oxidative degradation.[27] Interestingly, these affects also stabilise the ferryl porphyrins. The same explanations can be used to account for both observations. Thus, steric and electron-withdrawing effects make $OFe^{IV}$T2MPyP more stable than $OFe^{IV}$T4MPyP, and $OFe^{IV}$TDCSPP the most stable of the ferryl porphyrins in the present study. This is particularly apparent in more concentrated solutions which encourage reaction (6) in unhindered ferryl porphyrins. For example, changing the concentration of the ferryl porphyrin from $10^{-5}$–$10^{-4}$ mol $dm^{-3}$ has little effect on the lifetime of $OFe^{IV}$TDCSPP, however, it reduces that of $OFe^{IV}$T4MPyP from several hours to a few minutes. No differences in behaviour attributable to the individual atropisomers of $OFe^{IV}$T2MPyP were detected.

With the *N*-methylpyridylporphyrins, the 2-isomer is more resistant to oxidative destruction and has the more stable ferryl porphyrin. This is due to a combination of the steric effect of the methyl group and electron-withdrawing effect of the positive nitrogen. In the 2-position these have a greater influence in discouraging oxidation of the porphyrin ring.

The greater stability of the cationic ferryl porphyrins than the corresponding anionic species can also be accounted for by reaction (6), since electron-withdrawing *N*-methylpyridyl and trimethylanilinium groups will discourage oxidation of the porphyrin ring to the π radical cation. For the sulphonatophenyl and carboxyphenyl ferryl porphyrins, the electron-transfer will be relatively more favoured.

## Experimental

*Materials.*—All materials were commercially available from Aldrich Chemical Co. Ltd. or Fisons Scientific Apparatus Ltd. unless otherwise stated.

The preparation of the following iron(III) porphyrins have been previously reported;[28] 5,10,15,20-tetra(4-*N*-methyl-

pyridyl)porphyrinatoiron(III) pentachloride, 5,10,15,20-tetra(2-*N*-methylpyridyl)porphyrinatoiron(III) pentachloride, 5,10,15,-20-tetra(2,6-dichloro-3-sulphonatophenyl)porphyrinatoiron-(III) tetrasodium salt. 5,10,15,20-Tetra(4-carboxyphenyl)porphyrinatoiron(III) chloride was prepared by metallation of the free base (Nentech Ltd.) with iron(II) chloride following the method of Adler *et al.*[29] and purified by ion-exchange chromatography using Dowex 50-WX8. 5,10,15,20-Tetra(4-sulphonatophenyl)porphyrinatoiron(III) tetrasodium salt and 5,10,15,20-tetra(4-trimethylammoniumphenyl)porphyrinatoiron(III) pentachloride were obtained from Nentech Ltd. and used without further purification. Iodosylbenzene was prepared as described previously.[28] $H_2{}^{18}O$ 90 atom% was from Alpha Products.

*Methods.*—UV–VIS spectra were recorded on a Shimadzu UV-260 scanning spectrometer and on Hewlett Packard 8450 and 8452A diode array spectrometers.

Raman spectra were obtained with either a Spex 1401 double spectrograph or a Jobin-Yvon HR640 single spectrograph and a Wright Instruments liquid nitrogen cooled CCD camera. Indene and 1,4-dioxane were used for routine calibration; the peak positions of well defined bands are accurate to $\pm 3$ cm$^{-1}$. An excitation wavelength of 413.1 nm was used throughout since it lies within the Soret absorptions of both the iron(III) and oxoiron(IV) porphyrins investigated. Samples were contained in a spinning quartz cell at room temperature and the oxidations were carried out *in situ*. In a typical experiment a small aliquot of oxidant (*ca.* 25 mm$^3$) was added as rapidly as possible to the porphyrin solution (1 cm$^3$) in the cell. The mixture was agitated and data acquisition initiated in $< 30$ s. Spectra were acquired at 30 s intervals following the addition of oxidant. In solvent isotope substitution experiments the iron(III) porphyrin solutions were made up in $H_2{}^{18}O$ or [$^2H_2$]water.

$^1$H NMR spectra were recorded on a Bruker MSL 300 spectrometer (300 MHz). All $Fe^{III}$T4MPyP solutions were $7.4 \times 10^{-3}$ mol dm$^{-3}$. For reactions in [$^2H_4$]methanol the porphyrin solution, in an NMR tube, was cooled in a dry ice–acetone bath and the required excess of oxidant was added by syringe. The tube was shaken, placed in the spectrometer and data acquisition begun *ca.* 5 min after oxidant addition. Chemical shifts were measured relative to TMS as an internal standard.

Reactions in [$^2H_2$]water were carried out as above, except that the porphyrin solution was first cooled to 10 °C and the oxidant was added while the mixture was held in an ice-water bath. Chemical shifts were measured relative to the internal standard, DSS. The signal from the small amount of non-deuteriated water in the solvent was suppressed with a 50 μs presaturation pulse.

EPR experiments used a Bruker ESP 300 spectrometer equipped with an X band microwave bridge and 100 kHz modulation. 1 mol equiv. of *tert*-butyl hydroperoxide was added to 0.1 mmol dm$^{-3}$ $Fe^{III}$T4MPyP in 50 mmol dm$^{-3}$ borate buffer (pH 9.03). This mixture was rapidly frozen in liquid nitrogen and spectra were run at 100 and 150 K. The experiment was repeated with 5 mol equiv. of oxidant and at 90 K.

*Measurement of Oxidant Accountability in the Reaction of* $Fe^{III}$T2MPyP *with Iodosylbenzene.*—The iodosylbenzene dissolved in methanol (2 cm$^3$) was added to the methanolic solution of the iron(III) porphyrin (1 cm$^3$). After 72 h an aliquot of the reaction mixture was removed and the formaldehyde estimated spectrophotometrically using Nash's method.[30] The unreacted iodosylbenzene was quantified titrimetrically.[28]

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## References

1 (*a*) H. B. Dunford and J. S. Stillman, *Coord. Chem. Rev.*, 1976, **19**, 187; (*b*) G. N. LaMar, J. S. de Ropp, L. Latos-Grazynski, A. L. Balch, R. B. Johnson, K. M. Smith, D. W. Parish and R. Chen, *J. Am. Chem. Soc.*, 1983, **105**, 782; (*c*) J. H. Dawson, *Science*, 1988, **240**, 433.
2 (*a*) H. B. Dunford, *Adv. Inorg. Biochem.*, 1982, **4**, 41; (*b*) J. E. Few and P. Jones, *Adv. Inorg. Bioinorg. Mech.*, 1984, **3**, 175.
3 (*a*) R. E. White and M. J. Coon, *Annu. Rev. Biochem.*, 1980, **49**, 315; (*b*) J. T. Groves, in *Cytochrome P450: Structure, Mechanism and Biochemistry*, ed. P. Ortiz de Montellano, Plenum, New York, 1985, ch. 1.
4 D. F. Blair, C. T. Martin, J. Gelles, H. Wang, G. W. Brudvig, T. H. Stevens and S. I. Chan, *Chem. Scr.*, 1983, **21**, 43.
5 (*a*) T. S. Calderwood, W. A. Lee and T. C. Bruice, *J. Am. Chem. Soc.*, 1985, **107**, 8272; (*b*) J. T. Groves and J. A. Gilbert, *Inorg. Chem.*, 1986, **25**, 123; (*c*) T. S. Calderwood and T. C. Bruice, *Inorg. Chem.*, 1986, **25**, 3722; (*d*) S.-M. Chen and Y. O. Su, *J. Chem. Soc., Chem. Commun.*, 1990, 491.
6 (*a*) K. Bajdor and K. Nakamoto, *J. Am. Chem. Soc.*, 1984, **106**, 3045; (*b*) M. W. Peterson, D. S. Rivers and R. M. Richman, *J. Am. Chem. Soc.*, 1985, **107**, 2907.
7 (*a*) J. E. Penner-Halm, K. S. Elbe, T. J. McMurray, M. Renner, A. L. Balch, J. T. Groves, J. H. Dawson and K. D. Hodgson, *J. Am. Chem. Soc.*, 1986, **108**, 7819; (*b*) K. Shin and H. M. Goff, *J. Am. Chem. Soc.*, 1987, **109**, 3140; (*c*) H. Sugimoto, H.-C. Tung and D. T. Sawyer, *J. Am. Chem. Soc.*, 1988, **110**, 2465; (*d*) V. P. Shedbalkar, S. Modi and S. Mitra, *J. Chem. Soc., Chem. Commun.*, 1988, 1238; (*e*) A. Gold, K. Jayaraj, P. Doppelt, R. Weiss, G. Chottard, E. Bill, X. Ding and A. X. Trautwein, *J. Am. Chem. Soc.*, 1988, **110**, 5756; (*f*) P. N. Balasubramanian, J. R. Lindsay Smith, M. J. Davies, T. W. Kaaret and T. C. Bruice, *J. Am. Chem. Soc.*, 1989, **111**, 1477.
8 (*a*) A. L. Balch, Y.-W. Chan, R.-J. Cheng, G. N. La Mar, L. Latos-Grazynski and M. W. Renner, *J. Am. Chem. Soc.*, 1984, **106**, 7779; (*b*) M. Schappacher, R. Weiss, R. Monteil-Montoya, A. Trautwein and A. Tabard, *J. Am. Chem. Soc.*, 1985, **107**, 3736; (*c*) M. Schappacher, G. Chottard and R. Weiss, *J. Chem. Soc., Chem. Commun.*, 1986, 93; (*d*) I. R. Paeng, H. Shiwaku and K. Nakamoto, *J. Am. Chem. Soc.*, 1988, **110**, 1995; (*e*) W. A. Oertling, R. T. Kean, R. Weaver and G. T. Babcock, *Inorg. Chem.*, 1990, **29**, 2633.
9 R. Panicucci and T. C. Bruice, *J. Am. Chem. Soc.*, 1990, **112**, 6023.
10 (*a*) J. R. Kincaid, A. J. Schneider and K.-J. Paeng, *J. Am. Chem. Soc.*, 1989, **111**, 735; (*b*) P. M. Champion, *J. Am. Chem. Soc.*, 1989, **111**, 3433.
11 B. Boso, G. Lang, T. J. McMurray and J. T. Groves, *J. Chem. Phys.*, 1983, **79**, 1172.
12 J. T. Groves, R. Quinn, T. J. McMurray, M. Nakamura, G. Lang and B. Boso, *J. Am. Chem. Soc.*, 1985, **107**, 354.
13 J. E. Penner-Hahn, T. J. McMurray, M. Renner, L. Latos-Grazynski, K. S. Elbe, I. M. Davies, A. L. Balch, J. T. Groves, J. H. Dawson and K. O. Hodgson, *J. Biol. Chem.*, 1983, **258**, 12761.
14 S. E. J. Bell, R. E. Hester and J. R. Lindsay Smith, in *Proceedings of the Fourth International Conference on Time-resolved Vibrational Spectroscopy*, ed. T. G. Spiro, Princeton, New Jersey, 1989, p. 26; S. E. J. Bell, P. R. Cooke, P. Inchley, D. R. Leanord, J. R. Lindsay Smith, R. J. Lower and A. Robbins, presented at the European Conference on Homogeneous Catalysis, Arles, September 1989.
15 G. N. La Mar, G. R. Eaton, R. H. Holm and F. A. Walker, *J. Am. Chem. Soc.*, 1973, **95**, 63.
16 J. A. Smegal and C. L. Hill, *J. Am. Chem. Soc.*, 1983, **105**, 2920; J. A. Smegal, B. C. Schardt and C. L. Hill, *J. Am. Chem. Soc.*, 1983, **105**, 3510.
17 J. M. Proniewicz, K. Bajdor and K. J. Nakamoto, *J. Phys. Chem.*, 1986, **90**, 1760.
18 (*a*) J. Terner, A. J. Sitter and C. M. Reczek, *Biochim. Biophys. Acta*, 1985, **828**, 229; (*b*) S. Hashimoto, Y. Tatsuno and T. Kitagawa, *Proc. Natl. Acad. Sci. USA*, 1986, **83**, 2417.
19 R. T. Kean, W. A. Oertling and G. T. Babcock, *J. Am. Chem. Soc.*, 1987, **109**, 2185.
20 Y. O. Su, R. S. Czernuszewicz, L. A. Miller and T. G. Spiro, *J. Am. Chem. Soc.*, 1988, **110**, 4150.

21 A. L. Balch, L. Latos-Grazynski and M. W. Renner, *J. Am. Chem. Soc.*, 1985, **107**, 2983.
22 (*a*) F. L. Harris and D. L. Toppen, *Inorg. Chem.*, 1978, **17**, 71; (*b*) N. Kobayashi, M. Koshiyama, T. Osa and T. Kuwana, *Inorg. Chem.*, 1983, **22**, 3608; (*c*) G. A. Trondeau and R. G. Wilkins, *Inorg. Chem.*, 1986, **25**, 2745; (*d*) G. M. Miskelly, W. S. Webley, C. R. Clark and D. A. Buckingham, *Inorg. Chem.*, 1988, **27**, 3773; (*e*) S. E. J. Bell, J. N. Hill, R. E. Hester, D. R. Shawcross and J. R. Lindsay Smith, *J. Chem. Soc., Faraday Trans.*, 1990, 4017.
23 H. Goff and L. O. Morgan, *Inorg. Chem.*, 1976, **15**, 2062.
24 (*a*) T. G. Traylor, W.-P. Fann and D. Bandyopadhyay, *J. Am. Chem. Soc.*, 1989, **111**, 8009; (*b*) T. G. Traylor and F. Xu, *J. Am. Chem. Soc.*, 1990, **112**, 178 and earlier papers.
25 (*a*) J. R. Lindsay Smith, P. N. Balasubramanian and T. C. Bruice, *J. Am. Chem. Soc.*, 1988, **110**, 7411; (*b*) R. Labeque and L. J. Marnett, *J. Am. Chem. Soc.*, 1989, **111**, 6621; (*c*) R. D. Arasasingham, C. R. Cornman and A. L. Balch, *J. Am. Chem. Soc.*, 1989, **111**, 7800; (*d*) J. R. Lindsay Smith and R. J. Lower, *J. Chem. Soc., Perkin Trans. 2*, 1991, 31.
26 H. Hennig, D. Rehorek, R. Stich and L. Weber, *Pure Appl. Chem.*, 1990, **62**, 1489; L. Weber, personal communication.
27 (*a*) P. S. Traylor, D. Dolphin and T. G. Traylor, *J. Chem. Soc., Chem. Commun.*, 1984, 279; (*b*) M. J. Nappa and C. A. Tolman, *Inorg. Chem.*, 1985, **24**, 4711; (*c*) T. G. Traylor and S. Tsuchiya, *Inorg. Chem.*, 1987, **26**, 1338; (*d*) S. Banfi, F. Montanari and S. Quici, *J. Org. Chem.*, 1988, **53**, 2863.
28 D. R. Leanord and J. R. Lindsay Smith, *J. Chem. Soc., Perkin Trans. 2*, 1991, 25.
29 A. D. Adler, F. R. Longo, F. Kampas and J. Kim, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2443.
30 T. Nash, *J. Biochem.*, 1953, **55**, 416.

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