

Preparation and Characterization of an Oxo-Iron(v)-Porphyrin Complex†

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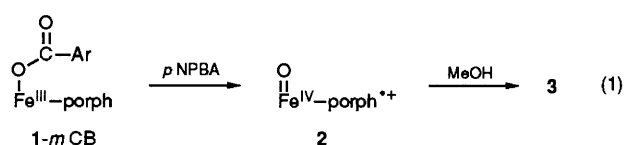
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The novel complex $\text{O}=\text{Fe}^{\text{V}}(\text{tdcpp})$ **3**, which is prepared by the addition of methanol to a methylene chloride solution of the corresponding $\text{O}=\text{Fe}^{\text{IV}}(\text{tdcpp})$ cation radical in CH_2Cl_2 at -90°C , has been characterized on the basis of UV-VIS, ESR, and deuterium NMR spectroscopy.

High-valent oxo-iron porphyrin complexes, formally two-electron oxidized from the iron(III) state, are of interest, because of their important roles in oxidative metabolism by haem enzymes such as P-450 and peroxidases.¹ The structures of high-valent iron porphyrins have been reported: oxo-ferryl porphyrin cation radicals,² iron(III) porphyrin *N*-oxides,³ and iron(III) porphyrin dications.⁴ Here, we report a novel oxo-perferryl ($\text{O}=\text{Fe}^{\text{V}}$) porphyrin complex which is stable only at low temperatures and oxidizes alkenes even at -90°C .

† Abbreviations used in this communication: tdcpp = 5,10,15,20-tetrakis-2,6-dichlorophenylporphyrin; *m*-CB = *m*-chlorobenzoate; *m*-CBA = *m*-chlorobenzoic acid; *p*-NPBA = *p*-nitroperbenzoic acid.

Oxidation of $\text{Fe}^{\text{III}}(\text{tdcpp})$ *m*-chlorobenzoate, **1**-*m*-CB ($2.2 \times 10^{-5} \text{ mol dm}^{-3}$), with 1.8 equiv. of *p*-nitroperbenzoic acid in dry methylene chloride‡ in the presence of 9 equiv. of



‡ Methylene chloride was distilled under argon from calcium hydride.

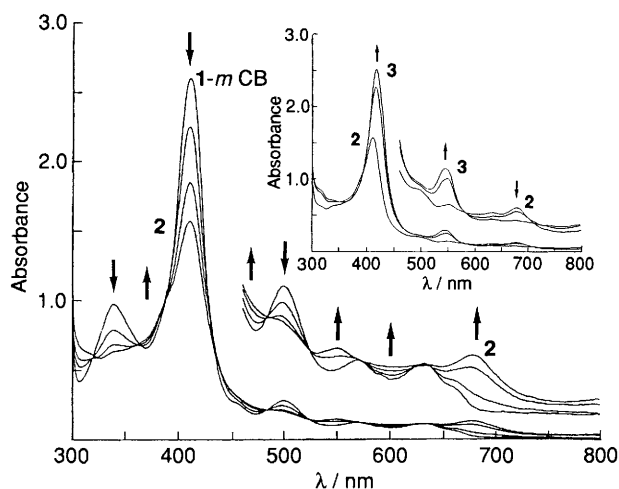


Fig. 1 Spectral changes in the reaction of 1-*m*-CB (2.2×10^{-5} mol dm $^{-3}$) with *p*-NPBA in CH $_2$ Cl $_2$ at -90°C . Inset: spectral changes upon the addition of 4 equiv. of MeOH to the solution of **2** at -90°C .

m-chlorobenzoic acid (*m*-CBA) \S at -90°C produced an oxo-ferryl porphyrin cation radical **2** as shown by the spectral changes in Fig. 1. 5 The addition of 4 equiv. of methanol to the solution afforded a red species **3** with the loss of the characteristic broad band (600–750 nm) for a porphyrin cation radical [Fig. 1 (inset), λ_{max} : 418 and 546 nm]. The spectrum of **3** is similar to that of oxo-ferryl (O=Fe $^{\text{IV}}$) porphyrin species **4** \parallel but very different from those of iron(III) porphyrin dication 4 and iron(III) porphyrin *N*-oxides. 3 Whereas **4** is stable at -5°C , the absorption spectrum of **3** changed to that of the iron(III) high-spin porphyrin **1** even at -70°C after several hours. The addition of norbornene to a methylene chloride solution of **3** caused its absorption spectrum to change to that of **1** at -90°C , whereas **4** does not react with this alkene under similar conditions. 6 In a separate large-scale experiment, norbornene oxide was obtained as the oxidation product in 51% yield. Titration of **2** and **3** with iodide ion was carried out to confirm the oxidation state of **3**. That both **2** and **3** were reduced by 2 equiv. of tetra-*n*-butylammonium iodide is a clear indication that **3** is isoelectronic with oxo-ferryl porphyrin cation radical. On the basis of spectroscopic characteristics, alkene epoxidation and iodometric titration, we have assigned the structure of **3** as an oxo-perferryl porphyrin having methanol as the sixth ligand. The following spectroscopic observations are also in agreement with this assignment.

Fig. 2 shows the deuterium NMR spectra of [$^2\text{H}_8$]pyrrole-1-*m*-CB and its oxidized products. Upon addition of *p*-NPBA to a CH $_2$ Cl $_2$ solution of 1-*m*-CB, the pyrrole deuterium resonance of 1-*m*-CB at δ 130 [signal i, Fig. 2(a)] 7 shifted to δ -46.2 [signal ii, Fig. 2(b)], as **2** was formed at -95°C . 2a,2b,5c,8 Addition of methanol to the solution of **2** at -95°C resulted in replacement of the pyrrole deuterium NMR signal by a new signal for **3** at δ -35.1 [signal iii, Fig. 2(c)] which is in the region associated with unpaired electron occupation in d_{xy} , d_{xz} and d_{yz} orbitals. 9 Signal iii shows Curie law behaviour from

\S Fe $^{\text{III}}$ (tdcpp) is known to react with peracids to give the corresponding oxo-ferryl porphyrin cation radical (**2**), but the rate is very slow. 5d Carboxylic acids are known to accelerate the formation of oxo-ferryl porphyrin cation radical. 2b Thus, we employed 9 equiv. of *m*-CBA to facilitate the preparation of **2**.

\parallel Authentic oxo-ferryl tdcpp complex, prepared from Fe $^{\text{III}}$ (tdcpp)-(*m*-CB) with 5 equiv. of iodosobenzene at -20°C , shows a UV-VIS spectrum (λ_{max} 419 and 543 nm) identical to those reported. 6,13

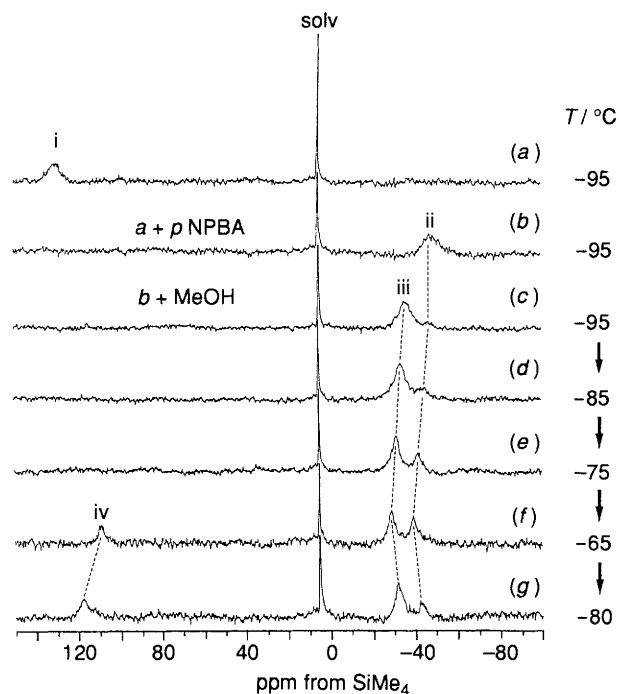
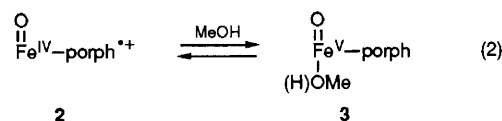


Fig. 2 Deuterium NMR spectra of (a) [$^2\text{H}_8$]pyrrole-1-*m*-CB (3.0×10^{-3} mol dm $^{-3}$); (b) **2** prepared by the addition of 1.8 equiv. of *p*-NPBA to 1-*m*-CB; (c) **3** formed by the addition of 2 equiv. of methanol to **2** in CH $_2$ Cl $_2$ at -95°C ; (d)–(f) temperature dependence of deuterium NMR spectra of solution (c) at -85 , -75 and -65°C ; (g) NMR spectrum of solution (f) at -80°C



-95 to -40°C .|| During the ^2H NMR measurements, we found a reversible appearance of signal ii upon raising the temperature [Fig. 2(c–g)]. That the change is dependent on the temperature and is reversible supports the formation of an oxo-perferryl complex on addition of methanol to **2** [eqn. (2)]. The coordination of methanol to **3** was confirmed by the observation of the deuterium resonance at δ 25.6 for CD $_3$ OH. When the solution was warmed to -65°C , **3** was reduced to **1** [signal iv, Fig. 2(f) after several hours.

While **2** is ESR silent, **3** exhibits an ESR spectrum with $g = 4.33, 3.69$ and 1.99 at 4.2 K in frozen methylene chloride. The ESR spectrum of **3** corresponds to an $S = 3/2$ system 10 with a large value for the zero-field splitting parameter (D) and $E/D = 0.04$. The magnetic susceptibility of **3** was determined by the Evans method to be $4.0 \pm 0.2 \mu_{\text{B}}$, which is close to the spin-only value expected for an $S = 3/2$ system and consistent with the ESR data.

We attempted to compare the reactivity of **2** and **3** for the epoxidation of norbornene. The reaction of 500 equiv. of norbornene with a methylene chloride solution of **2** and **3** (2.0×10^{-5} mol dm $^{-3}$) to afford **1** was directly observed at -90°C from absorption spectral changes and was found to be first-order both in [alkene] and in [**2**] (or [**3**]). The rate constants for **2** and **3** were 1.2×10^{-2} and $1.3 \times 10^{-3} \text{ s}^{-1}$, respectively. Accordingly, **3** is about 10 times less reactive than **2** in the epoxidation of norbornene. Furthermore, competitive epoxidation of norbornene and α -methylstyrene by **2** and **3** was examined. The selectivities (norbornylene:

|| When the sample was warmed to -40°C , species **2** and **3** were unstable and partially decomposed to **1** within several minutes, while signals ii and iii were detected.

α -methylstyrene) of **2** and **3** determined by gas chromatography were 100:30 and 100:35, respectively. These results suggest that the transition-state structures of **2** and **3** in epoxidation are similar.¹¹

Recently, Nanthakumar and Goff have suggested possible formation of a perferryl porphyrin complex.¹² While the UV-VIS spectrum and magnetic properties of the reported species and **3** are similar, the former complex is relatively stable even at ambient temperature. The different stability of the complexes could be caused by ligation of two fluoride anions instead of the oxo ligand in the former species.

In conclusion, we have reported the first example of an oxo-perferryl high-spin porphyrin, which is less reactive than the corresponding oxo-ferryl porphyrin cation radical in alkene epoxidation.**

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** Note added in proof. We have measured ²H NMR of meta-phenyl deuterium of **2** and **3** at -95 °C and observed the resonance at δ 4.4 for **2** and at δ 8.0 for **3**, respectively. These results support that **3** is not a porphyrin π -cation radical species.