Iron(IV) Porphyrins from Iron(III) Porphyrin Cation Radicals

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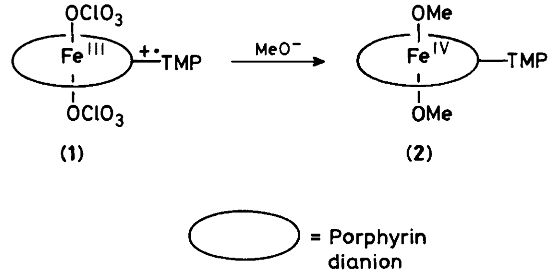
The preparation and spectroscopic data of FeTMP$(ClO_4)_2$ [(**1**), TMP = 5,10,15,20-tetramesitylporphyrinato] are reported; the reaction of (**1**) with NaOMe–MeOH gave a new red species, (**2**), which is indicated to exist (a) as a symmetrically ligated complex with a vacant $d_{x^2-y^2}$ iron orbital (^{1}H n.m.r.) and (b) in the iron(IV) state (Mössbauer spectroscopy).

The importance of oxidized iron–porphyrin complexes in heme-containing enzymes is now fully appreciated.[1—3] However, the electronic structures and mechanistic interrelationships of such species have remained obscure owing to the lack of simple chemical examples. Recently, at least three types of iron(III) porphyrin cation radical complexes have been recognized.[4—8] Further, an oxo-iron(IV)[9] and an oxo-iron(IV)[10] porphyrin cation radical[10,11] have been characterized. Only the oxo-,[12] nitrido-, and carbido-[13] ligands are known to stabilize the iron(IV) state with respect to the iron(III) porphyrin cation radical.[14] We report here the first direct conversion of an iron(III) porphyrin cation radical into an iron(IV) porphyrin by ligand metathesis.

The treatment of perchlorato-5,10,15,20-tetramesitylporphyrinatoiron(III) [FeTMP(ClO_4)] with an excess of iron(III) perchlorate in methylene chloride at room temperature resulted in the formation of a bright green solution. Removal of the solvent and recrystallization of the resulting solid from toluene–hexane afforded crystalline material which gave a satisfactory elemental analysis for FeTMP$(ClO_4)_2$, (**1**). Solutions of (**1**) in toluene or methylene chloride were stable for short periods at room temperature; however, immediate reduction of (**1**) occurred in methanol or acetone at room temperature. The spectroscopic properties of (**1**) were similar to other iron(III) porphyrin cation radical complexes.[5—7] The visible spectrum of (**1**) displayed a broad absorbance at 800 nm and other absorbances as shown in Figure 1(a). The infrared spectrum of (**1**) showed an intense band at 1270 cm^{-1}[15] and there were no apparent e.s.r. signals for (**1**) at 110 K. The ^{1}H n.m.r. spectrum of (**1**) at 25 °C in CD_2Cl_2 was similar to that of Fe^{III}TPP$(ClO_4)_2$[5,7] (TPP = tetraphenylporphyrinato) (pyrrole H, δ 18.7; *meta* H, 55; *o*-methyl, 20; *p*-methyl, 12.5). The assignment of the pyrrole and *meta* protons was confirmed by comparison of the spectra of the corresponding deuteriated porphyrins. The titration of (**1**) with one equivalent of tetrabutylammonium iodide regenerated FeTMP(ClO_4). This result and the spectroscopic data are consistent with a one-electron oxidation of the porphyrin ring.

The addition of two equivalents of sodium methoxide in methanol to CD_2Cl_2 solutions of (**1**) at −50 °C caused the immediate production of a bright red species (**2**) with a visible spectrum dramatically different from that of (**1**) [Figure 1(b)]. The oxidation of FeTMP(OH)[10] with iodosylmesitylene (Mes-IO) in methylene chloride–methanol also produced (**2**) but the addition of methanol to (**1**) did not. The 360 MHz ^{1}H n.m.r. spectrum of (**2**) in CD_2Cl_2 at −78 °C shows a pyrrole resonance at very high field (δ −37.5) and other resonances near the expected diamagnetic positions (*meta* H, 7.72, s; *p*-methyl, 2.86, s; *o*-methyl, 2.4, br.). A broad resonance in the spectrum of (**2**) prepared in methanol at δ 3.6 which was absent in samples prepared from CD_3OD was assigned to co-ordinated methoxide. The general features of this spectrum are similar to those reported recently for low spin, six-co-ordinate manganese(III) porphyrin complexes.[16]

The e.s.r. spectrum of (**2**) shows only weak signals due to high-spin iron(III). The Mössbauer spectrum of ^{57}Fe-(**2**) (δ_{Fe} −0.025 mm/s, ΔE_Q 2.1 mm/s) is unlike those reported for



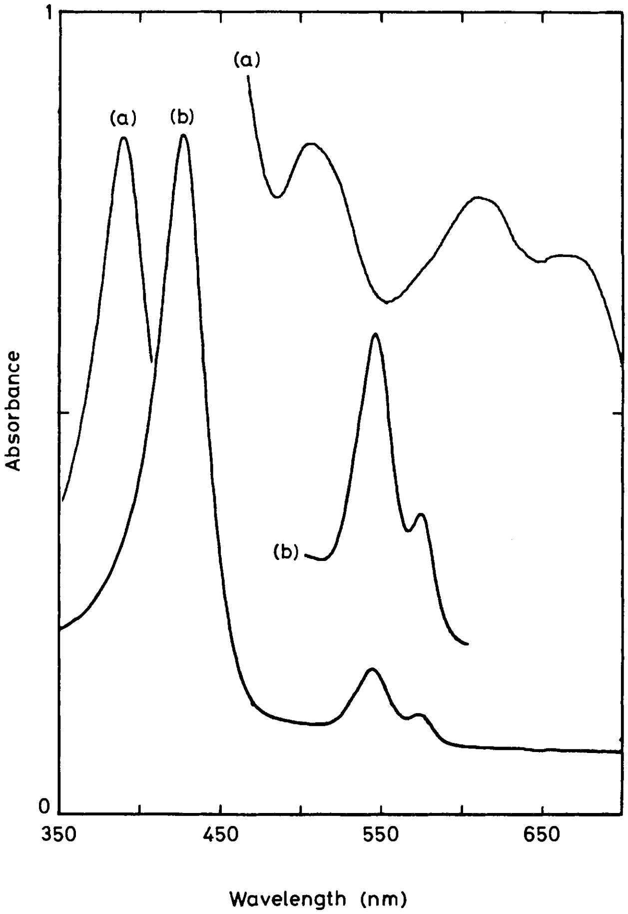


Figure 1. (a) Visible absorption spectrum for (**1**) in CH_2Cl_2 at 25 °C; (b) visible absorption spectrum of (**2**), 1.28 × 10^{-5} M in CH_2Cl_2–methanol at −40 °C.

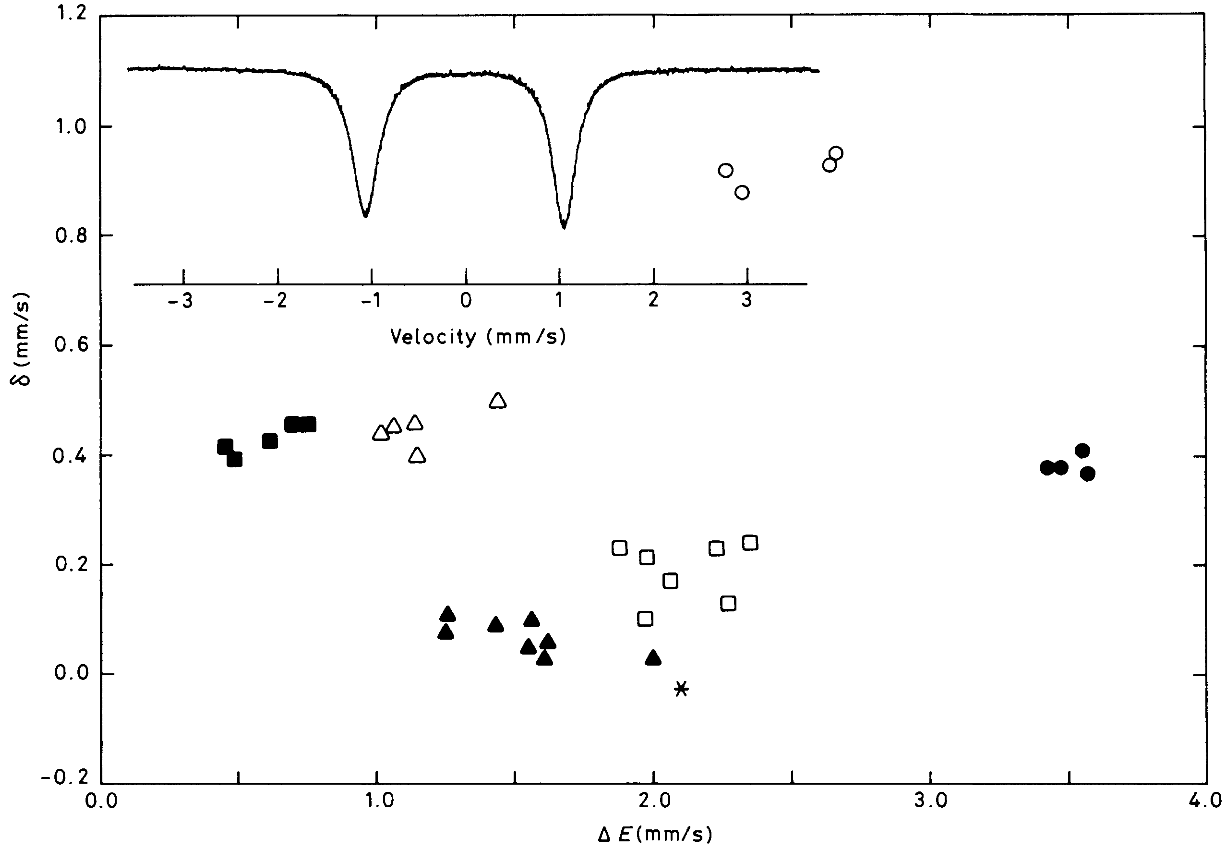


Figure 2. Comparative Mössbauer data for iron porphyrins; ■ high-spin Fe^{III}, □ low-spin Fe^{III}, ● intermediate spin (admixed) Fe^{III}, ○ high spin Fe^{II}, △ low-spin Fe^{II}, ▲ oxo- and imido-Fe^{IV}, * (**2**). *Cf.* refs. 11, 17, and 18. Inset shows the zero field Mössbauer spectrum of ^{57}Fe-(**2**) at 4.2 K.

iron(III) porphyrins and similar to the relatively few known iron(IV) species (Figure 2).[11,17,18] The sharp quadrupole doublet for (**2**) (Figure 2 inset) was unaffected by changes in temperature or a small transverse magnetic field indicating a non-Kramers spin system.

Taken together these results indicate that the co-ordination of methoxide, a strong π-donating ligand, has shifted the site of oxidation from the porphyrin ring in (**1**) to the iron in (**2**).

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