Studies of the Chemical Oxidation of the Iron(II) Complex of *N*-Methyltetraphenylporphyrin to form the Corresponding Symmetrical and Unsymmetrical μ-Oxo Di-iron Complexes

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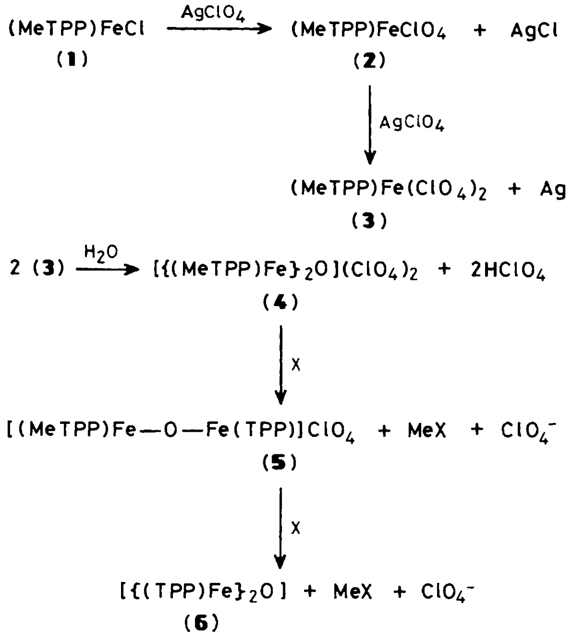
New μ-oxo di-iron *N*-methyltetraphenylporphyrin (MeTPP) species of formula $[\{(\mathrm{MeTPP})\mathrm{Fe}\}_2\mathrm{O}](\mathrm{ClO_4})_2$ and $[(\mathrm{MeTPP})\mathrm{Fe{-}O{-}Fe}(\mathrm{TPP})]\mathrm{ClO_4}$ have been prepared by the reaction of (MeTPP)FeCl with silver perchlorate and characterized by i.r., visible, n.m.r., and Mössbauer spectroscopy and electrochemical measurements; the mechanism of formation of the di-iron complexes is briefly discussed.

Iron *N*-substituted porphyrins have received considerable attention because of the discovery that *N*-alkylporphyrins are formed from the interaction of cytochrome P-450 with a variety of substrates.[1—5]

We now report the oxidation of (MeTPP)FeCl with the mild oxidizing agent[6] $\mathrm{AgClO_4{\cdot}3MeCN}$ to produce stable μ-oxo di-iron(III) *N*-methylporphyrin complexes. Chemical oxidation of (MeTPP)FeCl (**1**) was performed in CH_2Cl_2. The course of the reaction could be monitored by u.v.–visible spectroscopy (Figure 1). Addition of 1 equiv. of $AgClO_4$ resulted in metathesis involving the substrate (**1**) to give $(\mathrm{MeTPP})\mathrm{FeClO_4}$ (**2**) and this was followed by one-electron oxidation (2 equiv. of $AgClO_4$ added). An excess of oxidizing agent did not change the spectrum of the product which is characteristic of $(\mathrm{MeTPP})\mathrm{Fe}(\mathrm{ClO_4})_2$ (**3**).[3,7] Under the condition used, *i.e.* in the presence of water and nucleophiles (*e.g.* pyridine) the complex formed, (**3**), is unstable. During its decomposition three μ-oxo bridged di-iron(III) species could be detected: (**4**), (**5**), and the well known (**6**). These experiment observations allow us to formulate the mechanism in Scheme 1 for the conversion (X = nucleophile).

These reactions offer a general route for the synthesis of new μ-oxo di-iron complexes of types (**4**) and (**5**). The oxidation of (**1**) with $AgClO_4$ in CH_2Cl_2 (1:2 molar ratio) followed by addition of 2,4,6-collidine and CH_2Cl_2 saturated with water gave a mixture of compounds (**4**), (**5**), (**6**), and MeTPPH. The products were chromatographed on a silica gel column. Complexes (**4**) and (**5**) were successively eluted with CH_2Cl_2/MeOH (1:10 to 1:5 vv) and precipitated from CH_2Cl_2/hexane [$\lambda_{\mathrm{max.}}$ ($C_2Cl_2H_4$) (log ε) (**4**): 430 (5.07), 568 (3.95), 632 (3.99), and 670 (4.00) nm; (**5**): 414 (5.35), 455 sh (4.94), 568 (4.18), and 663 (3.94) nm]. The i.r. spectra of (**4**) and (**5**) provide evidence for a bridging μ-oxo ligand (medium intensity band at 850—870 $\mathrm{cm^{-1}}$; asymmetric Fe–O–Fe stretching).[8]

Solution magnetic susceptibility measurements using the Evans method[9] ($CDCl_3$, 303 K) gave magnetic moments of 2.3 μ_B for (**4**) and 2.2 μ_B for (**5**) per dimer molecule, both of which agree well with values expected[10] for a strongly antiferromagnetically coupled $\mathrm{Fe^{III}}$ ($S = 5/2$)–$\mathrm{Fe^{III}}$ ($S = 5/2$) pair. The antiferromagnetic behaviour is reflected also in the n.m.r. spectra by a characteristic isotropic shift of the pyrrole resonances [(100 MHz; $SiMe_4$ reference, solvent $CDCl_3$, 303 K): (**4**), δ 12.35 (2H), 13.85 (2H), 14.65 (2H) (each pyrrole) and *ca.* 7.5 (25H, pyrrole-NMe, and Ph); (**5**) 12.05 (2H), 13.75 (10H), 14.40 (2H) (each pyrrole), and *ca.* 7.5 (25H, pyrrole-NMe and Ph)] and an increase in the isotropic shift on warming.[11] The n.m.r. spectra clearly display characteristics revealing the structure of the complexes (**4**) and (**5**). The spectral pattern for (**4**) corresponds to two identical MeTPPFe subunits whereas two different units are required to account for the n.m.r. spectrum of (**5**) as the n.m.r. pattern arising



Scheme 1

from the paramagnetically shifted pyrroles results from the superposition of singlets [(TPP)Fe] and triplets [(MeTPP)Fe], *i.e.* the combination of spectra observed for the symmetrical analogues (**4**) and (**6**). The structure is in agreement with the preliminary *X*-ray data.[†]

The Mössbauer parameters of the new di-iron complexes are symptomatic of high spin iron(III): isomer shift *vs.* α-Fe (quadrupole splitting), 298 K, (**4**): 0.29 (1.27); (**5**) 0.31 (1.40) and 0.25 (0.30).[12] The μ-oxo di-iron complex (**5**) exhibits two doublets, the outer one assigned to the (MeTPP)Fe moiety, confirming the proposed structure.

The electrochemical reduction behaviour is quite different from that recorded for the dimer (**6**) (not reducible on iron[13] in the 1 to −1 V range) under identical conditions ($C_2H_4Cl_2$, 1 M $Bu^{(n)}{}_4ClO_4$); one-electron reverislbe reduction of (**4**) ($E_{\frac{1}{2}}$ 0.10 V *vs.* standard calomel electrode, S.C.E.) and (**5**) ($E_{\frac{1}{2}}$ −0.44 V *vs.* S.C.E.) occurs. It is proposed that these iron-centred reductions correspond to the formation of mixed-oxidation state Fe^{III}–Fe^{II} μ-oxo di-iron complexes, *i.e.* [(MeTPP)Fe^{III}–O–Fe^{II} (MeTPP)]$^+$, and [(MeTPP)Fe^{II}–O–Fe^{III}(TPP)] respectively.

In conclusion, the present studies have clearly demonstrated that *N*-methyltetraphenylporphyrins form μ-oxo di-iron complexes. The properties of the unsymmetrical species

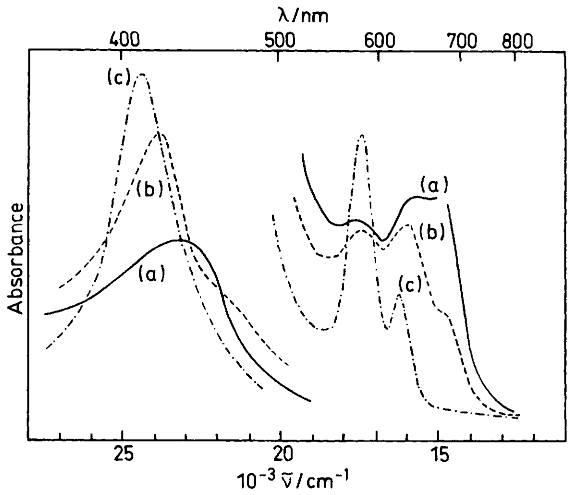


Figure 1. Electronic spectra of the μ-oxo di-iron complexes: (a), (**4**); (b), (**5**); (c), (**6**).

(**5**) are of particular interest as to the best to our knowledge this species belongs to the the unusual class of biological and nonbiological μ-oxo bridged di-iron species[14] in which the stereochemistry about the two iron atoms is significantly different.

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[†] A preliminary *X*-ray diffraction study of the complex (**5**) has defined the gross structural features of the molecule, in particular showing that two different ligands are joined by the Fe–O–Fe moiety. The Fe–O–Fe linkage is slightly bent (167°). The porphyrin rings are rotated with respect to each other (*ca.* 45°). The present state of refinement (R = 14.34%) has not provided sufficiently accurate bond distances but the overall Fe–Fe distance (3.33 Å) is close to those observed for typical μ-oxo dimers.[14]