Coordination Patterns for Oxophlorin Ligands. Pyridine-Induced Cleavage of Dimeric Manganese(III) and Iron(III) Octaethyloxophlorin Complexes

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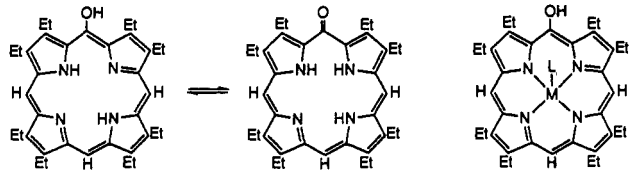
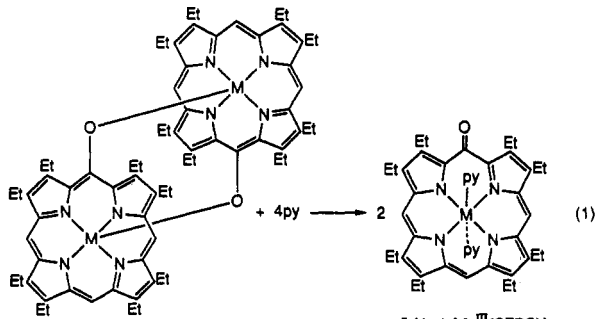
Heme degradation is initiated by regiospecific hydroxylation of the porphyrin.[1] The product of this step is an oxophlorin (or *meso*-hydroxyporphyrin).[2] This laboratory has undertaken a systematic study of the chemical behavior of complexes of octaethyloxophlorin, **1** ($OEPOH_3$), in order to understand the



1a **1b** **2** {(py)Zn^{II}(OEPOH)} {Ni^{II}(OEPOH)}

factors that control its further oxidation. Two tautomeric forms, **1a** and **1b**, are possible for the octaethyloxophlorin ligand. Recently it has been shown that divalent metal ions (Ni^{II}, Zn^{II}) bind to $OEPOH_3$ to form complexes, **2**, with a peripheral hydroxyl group.[3,4] These complexes are readily oxidized in pyridine solution with the loss of a proton to form stable radicals, {(py)Zn(OEPO•)} and {$(py)_2$Ni(OEPO•)}, that have been characterized crystallographically.[3,4] Less is known about the behavior of trivalent ions, although it is known that iron(III) forms the dimeric complex {Fe(OEPO)}$_2$, **3**.[5,6] Here we identify the dimeric nature of the manganese(III) complex of $OEPOH_3$[7] and demonstrate that {Mn^{III}(OEPO)}$_2$ undergoes cleavage into monomers in pyridine solution as shown in eq 1.



3 {Fe^{III}(OEPO)}$_2$
4 {Mn^{III}(OEPO)}$_2$
5 {$(py)_2Mn^{III}$(OEPO)}
6 {$(py)_2Fe^{III}$(OEPO)}

(1)

Metalation of $OEPOH_3$ by manganese(II) acetate followed the original procedure and gave a black complex, **4**, whose

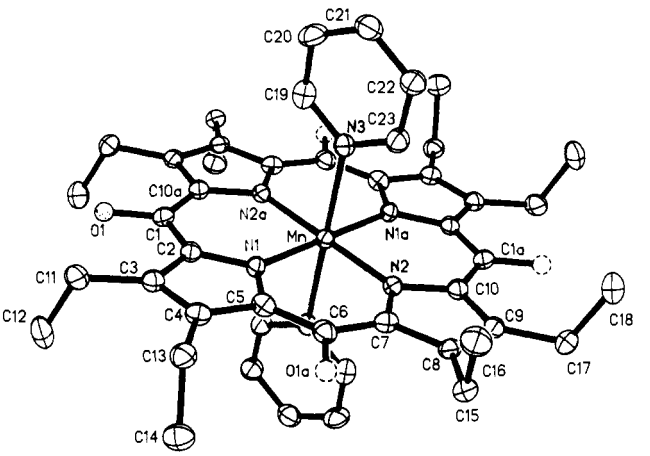


Figure 1. Perspective view of {$(py)_2Mn^{III}$(OEPO)} with 50% thermal contours. Selected bond distances (Å): Mn–N(1), 2.022(4), Mn–N(2), 2.018(3); Mn–N(3), 2.376(4); C(1)–O(1), 1.266(8); C(6)–O(1A), 1.20(2). Bond angles (deg): N(1)–Mn–N(2), 90.6(1); N(1)–Mn–N(3), 88.6(1); N(2)–Mn–N(3), 88.2(1); N(2)–Mn–N(1A), 89.4(1); N(3)–Mn–N(1A), 91.4(1); N(3)–Mn–N(2A), 91.8(1).

composition was previously established as {Mn^{III}(OEPO)}$_x$.[7] The electron impact mass spectrum of **4** shows a parent ion peak at 1204 amu, which suggests that this is the dimer, {Mn^{III}(OEPO)}$_2$.[8] The magnetic susceptibility of **4** in chloroform solution is 3.0(1) μ_B (per Mn) at 298 K. This is below that expected for a high-spin d^4 system but is reasonably explained by the presence of an antiferromagnetically coupled, dimeric complex.

Dissolution of {Mn^{III}(OEPO)}$_2$ in pyridine produces a greenish solution from which dark orange crystals of {$(py)_2Mn^{III}$(OEPO)}, **5**, were obtained through the addition of ethanol. The electronic absorption spectrum of **5** in pyridine is the same as reported earlier for **4** in chloroform/pyridine.[7] The magnetic susceptibility of **5** in pyridine solution is 5.2(2) μB at 297 K. This is consistent with the presence of a monomeric, high-spin ($S = 2$) species.

The structure of {$(py)_2Mn^{III}$(OEPO)} has been determined by X-ray crystallography.[9] Figure 1 shows a perspective view of the complex. It crystallizes with the manganese ion at a center of symmetry. The manganese ion is six-coordinate. The Mn–N distances to the porphyrin nitrogens, 2.022(4) and 2.018(3) Å, are significantly shorter than the distance to the pyridine nitrogen, 2.376(4) Å. These distances and particularly the elongation of the bonds to the axial ligands are consistent with the presence of high-spin Mn(III) in the complex.[10] Because of the crystal

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(7) Bonnet, R.; Dimsdale, M. J. *J. Chem. Soc., Perkin Trans.* **1972**, 2540. The electronic spectrum of **4** matches that in trace (a) (i) and that of **5** matches that in trace (b) (i) of Figure 3 of this article.
(8) We cannot completely rule out a higher oligomeric structure for the manganese complex, since larger ions might not survive in the gas phase as a referee noted.
(9) Orange plates of **5**, $C_{46}H_{53}MnN_6O$, crystallize in the triclinic space group $P\bar{1}$ with $a = 9.870(1)$ Å, $b = 10.252(1)$ Å, $c = 10.458(1)$ Å, $\alpha = 99.264(6)°$, $\beta = 90.267(5)°$, and $\gamma = 114.006(5)°$ at 120 K with $Z = 1$. Refinement of 1810 reflections with $F > 4.0\sigma(F)$ and 249 parameters gave $R = 0.050$; $R_w = 0.053$.
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symmetry, the two pyridine ligands lie in the same plane. That plane makes an angle of 13.8° to the N(1)–Mn–N(1a) axis and an angle of 77.3° to the N(2)–Mn–N(2a) axis. There is disorder in the positions of the oxygen atoms. The major form has the oxygen atom at sites O(1) with 36% occupancy and the centrosymmetrically related O(1b) also with 36% occupancy. The minor forms have 14% occupancy of sites O(1a) and the symmetry related site O(1aa). The C–O bond lengths (1.266(8) Å, major form; 1.20(2) Å, minor form) are consistent with the presence of a keto group in **5**. These data indicate that the Mn(III) ion in **5** coordinates to the deprotonated oxophlorin ligand in a form which corresponds to the tautomeric structure **1b**. This contrasts to the situation in Ni^{II}(OEPOH), (py)Zn(OEPOH), and {Fe(OEPO)}$_2$ where the ligand is present in a deprotonated version of tautomeric structure **1a**.

The behavior of these manganese complexes forms a model for the related iron complexes, which are involved in heme degradation. Treatment of {Fe^{III}(OEPO)}$_2$ with pyridine solution also results in its cleavage to form **6**, {$(py)_2Fe^{III}$(OEPO)} ↔ {$(py)_2$-Fe^{II}(OEPO•)}. This cleavage has previously been inferred from studies of the UV/vis spectra.[5] Figure 2 shows ^{1}H NMR spectral data that confirm this reaction. Trace A shows the spectrum of a chloroform-*d* solution of {Fe^{III}(OEPO)}$_2$ with its characteristic eight methylene resonances,[6] while trace B shows the spectrum of this dimer dissolved in pyridine where **6**, with its higher symmetry, is present. The spectrum shown in trace B has previously been observed from the hydrolysis of a *meso*-benzoyloxyoctaethylporphyrin complex.[11,12] The electronic structure of the low-spin ($S = {}^1/_2$) **6** has been variously characterized as containing iron(I) oxymesoporphyrin or iron(II) oxophlorin radical, {$(py)_2Fe^{II}$(OEPO•)}.[5,11,12] However an electronic structure {$(py)_2Fe^{III}$(OEPO)} analogous to **5** but with low-spin ($S = {}^1/_2$) iron(III) is also worthy of consideration. Previously, the anomalous axial EPR spectrum of **6** (g = 2.30, 1.76) had no counterpart in characterized iron(III) complexes, but recent studies have revealed the existence of a class of low-spin iron(III) porphyrins with axial EPR spectra.[13] It is interesting to note that the electronic structure of the macrocycle allows {Fe^{III}-(OEPO)}$_2$ to be more readily cleaved by bases than are the (μ-oxo)iron complexes. For example, {(OEP)Fe^{III}OFe^{III}(OEP)} and {(TTP)Fe^{III}OFe^{III}(TTP)} (TTP is the tetra(*p*-tolyl)porphyrin dianion) dissolve in pyridine without change. Hypothetical cleavage of such a μ-oxo dimer, PFe^{III}OFe^{III}P (P is a generic porphyrin dianion), would produce two ionic complexes, [PFe^{III}-$(py)_x]^+$ and $[(py)_yPFe^{III}O]^-$. No example of a porphyrin iron(III) oxo species is currently known. The closest known derivatives are the hydroxy complexes, PFe^{III}OH, which would require a proton source to form.[14] In contrast, cleavage of {Fe^{III}(OEPO)}$_2$ produces two neutral species, and the macrocycle incorporates the oxygen atoms into keto groups upon fragmentation.

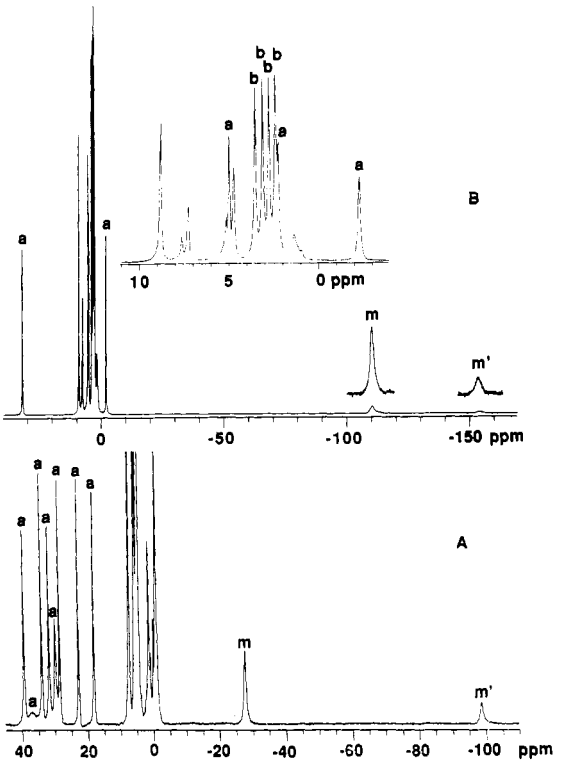

Figure 2. ^{1}H NMR spectra (A) {Fe^{III}(OEPO)}$_2$ in chloroform-*d* at 28 °C; (B) **6** obtained by dissolving {Fe^{III}(OEPO)}$_2$ in dioxygen-free pyridine-d_5. Resonance assignments are m and m′, meso protons; a, methylene protons; b, methyl protons.

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Supplementary Material Available: Tables of atomic parameters, bond lengths, bond angles, anisotropic thermal parameters, hydrogen atom positions, and data collection parameters for {$(py)_2Mn^{III}$(OEPO)} (9 pages). Ordering information is given on any current masthead page.

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