

Chemistry of iron oxophlorins. 2. Oxidation of the iron(III) octaethyloxophlorin dimer and observation of stepwise, two-electron oxidation of the oxophlorin macrocycle.

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The oxidation of iron oxophlorin (zneso-hydroxyporphyrin) complexes has been studied in order to understand the basic chemical reactivity which may contribute to the heme destruction that is catalyzed by heme oxygenase. Reaction of the iron(III) octaethyloxophlorin dimer $[\text{Fem}(\text{OEPO})]_2$ with molecular bromine results in the formation of two new, highly oxidized complexes, $\text{BrFe}^{11}(\text{OEPO}')_2$ and $\text{Br}_2\text{Fem}^{\text{I}}(\text{OEPOx})_2$ (where OEPO' and OEPOx are the octaethyloxophlorin dianion radical and the oxidized octaethyloxophlorin monoanion, respectively), in which the experimental data suggest that it is the ligand rather than the iron that has undergone oxidation. $\text{BrFem}^{\text{I}}(\text{OEPO}')_2 \cdot \text{CHCl}_3$ has been crystallized and subjected to a structure determination by X-ray crystallography. The iron is five-

coordinate with structural parameters consistent with the presence of high-spin ($S = 5/2$) $\text{Fe}(\text{III})$. The magnetic moment ($4.9(2) \mu_B$ at 23°C) for $\text{BrFem}(\text{OEPO})_2$ suggests that there is strong antiferromagnetic coupling between the iron and ligand spins. $\text{Br}_2\text{Fem}(\text{OEPOx})_2$ has a magnetic moment of $5.7(2) \mu_B$ at 23°C and displays an EPR spectrum typical of an axially symmetric, high-spin iron(III) complex with hyperfine splitting due to the two axial ligands clearly resolved. Electronic absorption and NMR spectra for both oxidation products are presented and interpreted. The NMR spectrum of $\text{BrFem}(\text{OEPO})_2$ with some methylene resonances with upfield hyperfine shifts and others with downfield hyperfine shifts and very large downfield meso shifts indicates that this complex possesses a remarkable electronic structure.

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