Chemistry of iron oxophlorins. 1.^{1}H NMR and structural studies of five-coordinate iron(III) complexes.

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As part of a series of studies to understand the role of iron oxophlorin complexes in oxidative heme destruction, the spectroscopic,chemical, and structural features of a group of dioxygen-stable iron(III) complexes of octaethyloxophlorin are reported. Protonation or coordination of the meso oxygen of the oxophlorin ligand appears to stabilize these iron complexes and prevents their conversion to verdoheme through oxidation by molecular oxygen. The 'H NMR spectrum of dimeric [Fem(OEPO)]2 (where OEPO is the trianion of octaethyloxophlorin, 1), is presented and analyzed. The presence of two paramagnetic centers produce marked variation in line widths and 7,'s for the methylene protons. [Fem(OEPO)]2 is cleaved by protic acids (HX) to form high-spin, five-coordinate [XFem(OEPOH)], whose NMR and electron paramagnetic resonance spectra are analyzed. As a model for [XFem(OEPOH)], the complex [ClFe"(OEPOAc)] (where the meso hydroxyl group has been acetylated) has been prepared and characterized by its NMR spectrum. The X-ray crystal structure of [ClFeMI(OEPOAc)-CH2Cl2 shows that the iron is five-coordinate with structural parameters consistent with high-spin (5 = s/2) electronic structure. Crystals of C39H48Cl3FeN402 form in the triclinic

space group Pi with a = 10.238 (2) A, b = 13.301 (2) A, c = 15.088 (3) A, a = 77.610 (2)°, ß = 71.820 (2)°, and y = 75.430 (2)°, at 130 K with Z = 2. Refinement of 4577 reflections with 456 parameters yielded R = 0.051 and Rw = 0.053. The environment about the acetoxy substituent is crowded, and restricted rotation at that site produces two isomers that are observed in solution.

Adres publiczny

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