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# Chemistry of iron oxophlorins. 3. Reversible, one electron oxidation of the iron(III) octaethyloxophlorin dimer.

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Streszczenie

The oxidative behavior of the dimeric octaethyloxophlorin (OEPOH3) complex, {Fem(OEPO)}2,1, has been studied in regard to its relevance toward heme catabolism and the effects of — overlap as seen in the chlorophyll special pair. Electrochemical studies show that {FenI(OEPO)}2,1, undergoes a reversible, one-electron oxidation that is readily accomplished chemically by silver perchlorate or silver tetrafluoroborate. The oxidation occurs 0.26 V more readily than oxidation of the μ-dimer, (OEP)Fe* 111111—O—FeIH(OEP), and 0.66 V more readily thanthe monomeric, meso-methoxy-substituted complex, ClFem(OEPOMe). This ease of oxidation is attributed at least in part to the effect of direct overlap between the two tetrapyrrole planes in 1. The NMR spectrum of the oxidized cation, 1+, shows a number of features, particularly the variation in line widths for the eight methylene resonances, that are consistent with its formulation as a dimer. The pattern of NMR resonances and the UV/vis spectrum of 1+ indicate that a ligand-based oxidation has occurred but that the ligand hole is delocalized

over both macrocycles. The stability of 1+ depends upon the availability of axial ligands. For example 1+ reacts with bromide ion to form 1 and Fein(OEPO‘)Br in a stoichiometric fashion.

Adres publiczny

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