Structural characterization of verdoheme analogs : iron complexes of octaethyloxoporphyrin.

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Streszczenie

The verdohemes are shown to contain the planar, tetradentate oxoporphyrin structure. Structural studies of paramagnetic l(OEOP)FemCl2l, where is the monoanion of octaethyloxoporphyrin, by NMR spectroscopy and X-ray crystallography reveal that the iron is six-coordinate and high-spin (5 = 5/2). The iron resides in the plane of the oxoporphyrin and is coordinated by two equivalent axial chloride ligands. Paramagnetic |(OEOP)Fe"Cl| contains a five-coordinate iron which is also high-spin (5 = 2). The iron is 0.69 Á out of the porphyrin plane and bound to a single axial chloride. The average Fe-N distance increases from 1.964 Á in the iron(III) complex to 2.094 Á in the iron(II) complex. |(OEOP)FemCl2) was obtained by treatment of (OEP)Fe(py)2 (OEP is the dianion of octaethylporphyrin) with dioxygen in the presence of ascorbic acid to form the verdohemochrome [(OEOP)FeM(py)2]Cl, which was subsequently reacted with hydrogen chloride in air. Reduction of l(OEOP)FemCl2| with sodium dithionite yields air-sensitive |(OEOP)Fe"Cl). When |(OEOP)Fe"Cl| is dissolved in pyridine,[(OEOP)Fe"(py)2]Cl is reformed.

Adres publiczny

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