

Models for verdoheme hydrolysis. Paramagnetic products from the ring opening of verdohemes, 5-oxaporphyrin complexes of iron(II), with methoxide ion.

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Streszczenie

Studies of the reaction of 5-oxaporphyrin iron complexes (verdohemes) with methoxide ion have been undertaken to provide models for the initial step in hydrolysis of verdohemes. Treatment of both low-spin $[(py)_2Fe^{II}(OEOP)]Cl$ and high-spin $\{ClFe^{II}(OEOP)\}$ (OEOP is the monoanion of octaethyl-5-oxaporphyrin) with methoxide ion in either pyridine or methanol solution is shown to cause ring opening and addition of methoxide to one end of the tetrapyrrole. Black $\{Fe^{II}(OEBOMe)\}_2$ has been isolated in crystalline form from the reaction of $\{ClFe^{II}(OEOP)\}$ with methoxide in methanol and studied by single-crystal X-ray diffraction. The molecule has a centrosymmetric dimeric structure composed of two helical $Fe(OEBOMe)$ units with FeN_4 coordination which are connected by a pair of $Fe-O$ bonds. Each iron ion has approximately trigonal bipyramidal geometry. Evidence is presented which suggests that $\{Fe^{II}(OEBOMe)\}_2$ dissolves in dichloromethane in the presence of methanol or pyridine to form high-spin $\{(MeOH)_nFe^{II}(OEBOMe)\}$ or $\{(py)_nFe^{II}(OEBOMe)\}$ ($n = 1$ or 2) through rupture of the $Fe-O$ bonds in the dimer. The electronic absorption spectra of these open chain complexes show characteristic low-energy features at ca. 720 and 810 nm. The 1H NMR spectrum of $\{Fe^{II}(OEBOMe)\}_2$ at 23 °C shows a characteristic upfield methoxy resonance, 16 methylene resonances in the 47 to 5 ppm region, and meso resonances in the 51 to 29 ppm region. The temperature dependence of these spectra shows marked deviations from the Curie law, which are consistent with a dimeric structure.

Słowa kluczowe

Alcohols, Iron, Oxidation, Pyridines, pyrroles

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