Iron(II) vacataporphyrins : a variable annulene conformation inside a regular porphyrin frame.

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Streszczenie

5,10,15,20-Tetraaryl-21-vacataporphyrin (**1**), an annulene–porphyrin hybrid containing a butadiene fragment in the macrocycle perimeter, gives paramagnetic iron(II) complexes **2**. The porphyrin **1** is devoid of one donor atom of the coordination core; hence, metal ion is bound in the macrocyclic cavity by only three pyrrolic nitrogen atoms. The coordination sphere in **2-X** (where X = Cl, Br, I) is completed by a halide anion. The butadiene fragment flexibility and constraints of coordination lead to two stereoisomers with the chain oriented inward (**2-i-X**) or outward (**2-o-X**) of the macrocyclic center. Axial halide subtraction ($AgBF_4$ addition) leads to two new forms differing in the butadiene chain configuration. The ^{1}H NMR spectra of all complexes show characteristics typical for high-spin iron(II) complexes of porphyrinoids. The dependence of the relaxation times T_1 versus $Fe^{II}\cdots H$ distances (estimated by MM+ models) for three of the isomers is in accordance with the **in**, **out**, and/or **zigzag** geometries. The **2-o-X** complex is more reactive than **2-i-X** and reacts at room temperature with dioxygen to form the iron(II) 21-oxaporphyrin complex, conserving the iron(II) oxidation state. After the addition of imidazole or excess of methanol to a mixture of **2-o-X** and **2-i-X**, single five-coordinate complexes with **out** annulene configuration and two axial ligands are formed.

Adres publiczny

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https://www.acs.org/content/acs/en.html