

Core-modified porphyrin incorporating a phenolate donor. Characterization of Pd(II), Ni(II), Zn(II), Cd(II), and Fe(III) complexes.

Autorzy

Marcin Stępień

Lechosław Latos-Grażyński

Rok wydania

2003

Czasopismo

Inorganic Chemistry

Numer woluminu

42

Strony

6183-6193

DOI

10.1021/ic0345121

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

Coordinating properties of acetoxybenzporphyrin, (TPBPOAc)H, have been investigated for a number of metal ions. Insertion of Ni, Pd, and Fe results in the cleavage of the acetoxy group leading to complexes (TPBPO)Ni^{II}, (TPBPO)Pd^{II}, and (TPBPO)Fe^{III}X containing a M–O bond. No cleavage is observed with Zn(II) and Cd(II), which form complexes (TPBPOAc)M^{II}Cl, where M = Zn, Cd. (TPBPO)Ni^{II} can also be obtained from the dication of hydroxybenzporphyrin, [(TPBPOH)H₃]Cl₂, which is prepared by acid hydrolysis of the acetoxy compound. The diamagnetic (TPBPO)Ni^{II} can be transformed into the paramagnetic (TPBPOAc)Ni^{II}Cl in a reaction with acetyl chloride. X-ray structures have been determined for (TPBPO)Pd^{II} and (TPBPOAc)Zn^{II}Cl. In the palladium species, the phenolate moiety forms a strong bond to the Pd ion and an unusual interaction geometry is observed, enforced by the macrocyclic environment. Association of a TFA molecule to the phenolic oxygen does not cause significant structural changes in the (TPBPO)Pd^{II} molecule. In (TPBPOAc)Zn^{II}Cl, the metal ion weakly interacts with the phenolic fragment. The paramagnetic Fe(III) complexes, (TPBPO)Fe^{III}X, have been investigated with ¹H NMR spectroscopy. The observed spectral patterns are consistent with the presence of a high-spin Fe(III) center and π delocalization of spin density onto the phenoxide fragment. Each of the compounds (TPBPO)Fe^{III}X exists in solution as a mixture of two isomers, which for X = I are shown to remain in a temperature-dependent equilibrium. The observed isomerism results from two nonequivalent orientations of the axial halide with respect to the puckered macrocyclic ring.

Adres publiczny

<https://doi.org/10.1021/ic0345121>

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

Plik został wygenerowany dnia 2026-10-05 05:06:59

Adres w repozytorium <https://old.chem.uni.wroc.pl/pl/repozytorium/GHSXtFr>.