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Plik pochodzi z repozytorium Wydziału Chemii Uniwersytetu Wrocławskiego

Iron complexes of 5,10,15,20-tetraphenyl-21-oxaporphyrin.

Autorzy

Miłosz Pawlicki

Lechosław Latos-Grażyński

Rok wydania

2002

Czasopismo

Inorganic Chemistry

Numer woluminu

41

Strony

5866-5873

DOI

10.1021/ic025718p

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

The iron complexes of 5,10,15,20-tetraphenyl-21-oxaporphyrin (OTPP)H have been investigated. Insertion of iron(II) followed by one-electron oxidation yielded a high-spin, six-coordinate (OTPP)$Fe^{III}Cl_2$ complex. The reduction of (OTPP)$Fe^{III}Cl_2$ has been accomplished by means of moderate reducing reagents producing high-spin five-coordinate (OTPP)$Fe^{II}Cl$. The molecular structure of (OTPP)$Fe^{III}Cl_2$ has been determined by X-ray diffraction. The iron(III) 21-oxaporphyrin skeleton is essentially planar. The furan ring coordinates in the η^1 fashion through the oxygen atom, which acquires trigonal geometry. The iron(III) apically coordinates two chloride ligands. Addition of potassium cyanide to a solution of (OTPP)$Fe^{III}Cl_2$ in methanol-d_4 results in its conversion to a six-coordinate, low-spin complex [OTPP)$Fe^{III}(CN)_2$] which is spontaneously reduced to [OTPP)$Fe^{II}(CN)_2]^-$ by excess cyanide. The spectroscopic features of [OTPP)$Fe^{III}(CN)_2$] correspond to the common low-spin iron(III) porphyrin $(d_{xy})^2(d_{xz}d_{yz})^3$ electronic configuration. Titration of (OTPP)$Fe^{III}Cl_2$ or (OTPP)$Fe^{II}Cl$ with *n*-BuLi (toluene-d_8, 205 K) resulted in the formation of (OTPP)$Fe^{II}(CH_2CH_2CH_2CH_3)$. (OTPP)$Fe^{II}$(*n*-Bu) decomposes via homolytic cleavage of the iron−carbon bond to produce (OTPP)Fe^{I}. The EPR spectrum (toluene-d_8, 77 K) is consistent with a $(d_{xy})^2(d_{xz})^2(d_{yz})^2(d_{z^2})^1(d_{x^2-y^2})^0$ ground electronic state of iron(I) oxaporphyrin (g_1 = 2.234, g_2 = 2.032, g_3 = 1.990). The ^{1}H NMR spectra of (OTPP)$Fe^{III}Cl_2$, (OTPP)$Fe^{III}(CN)_2$, $\{[(OTPP)Fe^{III})]_2O\}^{2+}$, and (OTPP)$Fe^{II}Cl$ have been analyzed. There are considerable similarities in ^{1}H NMR properties within each iron(*n*) oxaporphyrin−iron(*n*) regular porphyrin or *N*-methylporphyrin pair (*n* = 2, 3). Contrary to this observation, the pattern of downfield positions of pyrrole resonances at 156.2, 126.5, 76.3 ppm and furan resonance at 161.4 ppm (273 K) detected for the two-electron reduction product of (OTPP)$Fe^{III}Cl_2$ is unprecedented in the group of iron(I) porphyrins.

Słowa kluczowe

Iron, Ligands, Nuclear magnetic resonance spectroscopy, Pyrroles, Redox reactions

Adres publiczny

https://doi.org/10.1021/ic025718p

Strona internetowa wydawcy

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

Plik został wygenerowany dnia 2026-07-31 15:38:22

Adres w repozytorium https://old.chem.uni.wroc.pl/pl/repozytorium/m9QgLZ7.