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Plik pochodzi z repozytorium Wydziału Chemii Uniwersytetu Wrocławskiego

Copper(II) and Copper(III) complexes of pyrrole-appended oxacarbaporphyrin.

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Rok wydania

2007

Czasopismo

Inorganic Chemistry

Numer woluminu

46

Strony

6575-6584

DOI

10.1021/ic700631t

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

The reaction of an *O*-confused porphyrin with a pendant pyrrole **4** and copper(II) acetate yields an organocopper(III) diamagnetic complex **4**-Cu(III) substituted at the C(3) position by the pyrrole and H. The transformation of **4**-Cu(III), performed in aerobic conditions, gave a rare copper(II) organometallic compound **6**-Cu(II). In the course of this process, the tetrahedral−trigonal rearrangement originated at the C(3) atom but effects the whole structure. The electron paramagnetic resonance spectroscopic features correspond to a copper(II) oxidation state. A crystallographic analysis of **6**-Cu(II) confirmed the formation of a direct metal−C bond [Cu(II)−C 1.939(4) Å]. It was found that the Cu(II) complex of *O*-confused oxaporphyrin is sensitive to oxidative conditions. The degradation of **6**-Cu(II) to yield copper(II) tripyrrinone complexes has been observed, which was considered as a peculiar case of dioxygen activation in a porphyrin-like environment. This process is accompanied by regioselective oxygenation at the inner C to form the 2-oxa-3-(2‘-pyrrolyl)-21-hydroxycarbaporphyrinatocopper(II) complex ((pyrr)OCP*O*)Cu^{II} (**8**). The reaction of **6**-Cu(II) with hydrogen peroxide, performed under heterophasic conditions, resulted in quantitative regioselective hydroxylation centered at the internal C(21) atom, also producing **8**. Treatment of **8** with acid results in demetalation to form the nonaromatic 21-hydroxy *O*-confused porphyrin derivative ((pyrr)OCP*OH*)H (**9**).

Słowa kluczowe

Degradation, Ions, Macrocycles, Metals, Pyrroles

Adres publiczny

https://doi.org/10.1021/ic700631t

Strona internetowa wydawcy

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

Plik został wygenerowany dnia 2026-11-03 17:45:46

Adres w repozytorium https://old.chem.uni.wroc.pl/pl/repozytorium/8T1DXjU.