

Peroxo and ferryl intermediates detected by ^1H NMR spectroscopy during the oxygenation of iron(II) porphycene.

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Rok wydania

2000

Czasopismo

Inorganic Chemistry

Numer woluminu

39

Strony

3247-3251

DOI

10.1021/ic991417c

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

The iron(III) 2,7,12,17-tetra-*n*-propylporphycene (TPrPc)Fe^{III}Cl is reduced using aqueous sodium dithionite or zinc amalgam to produce (TPrPc)Fe^{II}. The ^1H NMR spectrum of (TPrPc)Fe^{II} (293 K; δ (ppm): pyrrole, -37.52; meso, 71.56; α -CH₂, 27.47; β -CH₂, 8.92; γ -CH₃, 5.55) can be accounted for by the planar unligated iron(II) porphycene with an $S = 1$ ground electronic state. Introduction of dioxygen into a toluene-*d*₈ solution of (TPrPc)Fe^{II} at 203 K results in the formation of the (μ -peroxo)diiron(III) porphycene (TPrPc)Fe^{III}-O-O-Fe^{III}(TPrPc). The value of the chemical shift of the pyrrole resonances (17.99 ppm at 203 K) of this species and its distinct non-Curie behavior imply strong antiferromagnetic iron(III)-iron(III) coupling via a μ -peroxo bridge. The (TPrPc)Fe^{III}-O-O-Fe^{III}(TPrPc) intermediate is stable at 203 K, but it converts into the (μ -oxo)diiron complex (TPrPc)Fe^{III}-O-Fe^{III}(TPrPc) upon warming above 203 K. Reaction of (TPrPc)Fe^{III}-O-O-Fe^{III}(TPrPc) with a nitrogen bases (B: pyridine-*d*₅, 1-methylimidazole) results in a homolytic cleavage of the μ -peroxo bridge to form the ferryl porphycene complex B(TPrPc)Fe^{IV}O (^1H NMR (223 K), δ (ppm): pyrrole, -1.32; meso, 11.80). B(TPrPc)Fe^{IV}O reacts with triphenylphosphine at 223 K to yield triphenylphosphine oxide.

Słowa kluczowe

Nuclear magnetic resonance spectroscopy, Oxides, Pyrroles, Redox reactions, Resonance structures

Adres publiczny

<https://doi.org/10.1021/ic991417c>

Strona internetowa wydawcy

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

