Syntheis, stucture, and redox properties of N-confused bis(porphyrinatonickel(II)) linked byoxylene.

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Rok wydania

2007

Czasopismo

Inorganic Chemistry

Numer woluminu

46

Strony

1617-1626

DOI

10.1021/ic061793e

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

In a reaction of 5,10,15,20-tetraaryl-2-aza-21-carbaporphyrinato nickel(II) 2 with alpha,alpha'-dibromo-o-xylene, three different complexes containing a xylene moiety were obtained in the presence of a proton scavenger. The products were characterized by mass spectrometry, UV-vis, NMR, and, in the case of the dimeric complex 3, X-ray crystallographic analysis (space group P, a =16.455(3) A, b = 16.776(3) A, c = 18.400(4) A, alpha = 77.43(3) degrees , beta = 75.31(3) degrees , gamma = 66.20(3) degrees , V = 4457.1(19) A3, Z = 2). The monomeric species, diamagnetic 4 and paramagnetic 5, contain one and two bromoxylene residues, respectively, while in 3, the xylene bridge links two macrocyclic subunits, involving their internal carbons (C21) coordinated to diamagnetic nickel(II). Cyclovoltammetric measurements for o-xylene-linked bis(carbaporphyrinoid) 3 indicate cooperative effects resulting from an interaction between the subunits despite the isolation of their aromatic pi-bond systems. An EPR-controlled titration of 3 with bromine allows consecutive detection of the mono- and bis-oxidized species (3Br, 3Br2). The spectral patterns and spin-Hamiltonian parameters indicate metal-centered oxidation in 3Br (gx = 2.358, gy = 2.150, gz = 2.062, A(Br)x = 15, A(Br)y = 35, A(Br)z = 129 G) and interaction of two electron spins of nickel(III) ions in 3Br2 (gx = 2.328, gy = 2.195, gz = 2.065, D = 0.0173 cm(-)1, E = -0.0018 cm(-1), A(Br)z = 63 G). A product of the chemical reduction of a protonated form of the dimer was also detected by means of EPR (g1 = 2.298, g2 = 2.218, g3 = 2.192), although no interaction between the nickel(I) centers can be observed for the reduced species.

Adres publiczny

https://doi.org/10.1021/ic061793e