Nickel complexes of 21-oxaporphyrin and 21,23-dioxaporphyrin.

Autorzy

Piotr J. Chmielewski

Lechosław Latos-Grażyński

Marylin M. Olmstead

Alan L. Balch

Rok wydania

1997

Czasopismo

Chemistry-A European Journal

Numer woluminu

3

Strony

268-278

DOI

10.1002/chem.19970030216

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

The nickel(I) and nickel(II) complexes of 5,20-bis(p-tolyl)-10, 15-diphenyl-21-oxaporphyrin (ODTDPPH) and 5,10,15,20-tetraphenyl-21, 23-dioxaporphyrin (O2 TPP) have been investigated. These oxa analogues of 5,10,15,20-tetraarylporphyrin, where one or two pyrrole rings are replaced by a furan moiety, have been synthesized by condensation of the respective precursors, namely 2,5-bis(arylhydroxymethyl)furan, pyrrole, and arylaldehyde. Insertion of nickel(II) into ODTDPPH or O2 TPP yielded high-spin five- and six-coordinate ([(ODTDPP)Ni(II) Cl] and [(O2 TPP)NiIICl2]) complexes, which can be reduced with moderate reducing reagents. The EPR spectra of [(ODTDPP)Ni(I)] and [(O2 TPP)Ni(I) Cl] revealed the Ni(I) oxa(dioxa)porphyrin rather than a Ni(I) anion radical electronic structure. In the structures of [(ODTDPP)Ni(II) Cl], [(O2 TPP)Ni(IICl) 2], and [(ODTDPP)Ni(I)], determined by X-ray diffraction, the furan ring is planar and coordinates in the η(1) fashion through the trigonal oxygen atom; the nickel ion lies in the furan plane for the latter two complexes, but slightly outside it in [(ODTDPP)Ni(II) Cl]. The Ni-N and Ni-O bond lengths decrease upon reduction of high-spin five-coordinate [(ODTDPP)Ni(II) Cl] to four-coordinate [(ODTDPP)Ni(I)]. The pattern of downfield pyrrole resonances in (1) H NMR spectra of [(ODTDPP)Ni(IICl)] and [(O2 TPP)-Ni(II) Cl2] has been established. The downfield positions of furan resonances are unusual for Ni(II) heteroporphyrins; they have been accounted for by the nearly in-plane coordination of the furan moiety as opposed to the side-on coordination found for thiophene- or selenophene-containing heteroporphyrins. An example of ion-pair formation, [(O2 TPPH)2][Ni(II) Cl4], was produced from [(O2 TPP)Ni(II) Cl2] by acidification with HCl.

Słowa kluczowe

heterocycles, heteroporphyrins, nickel, porphyrinoid