Low-valent nickel thiaporphyrins. Nuclear magnetic resonance and electron paramagnetic resonance studies.

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Streszczenie

The /sup 2/H NMR spectra of one-electron reduction product of nickel(II) tetraphenyl-21-thiaporphyrin have been recorded. The following selectively deuterated thiaporphyrins have been used: 5,20-diphenyl-10,15-bis(phenyl-d5)-21-thiaporphyrin (STPPH-d/sub 10/),5,10,15,20-tetraphenyl-21-thiaporphyrin (STPPH-d/sub 6/) deuterated at pyrrole .betha.-positions, 5,20-diphenyl-10,15-bis(p-tolyl)-21-thiaporphyrin (SDPDTPH-d/sub 2/) deuterated at the thiophene .betha.-position. Two characteristic patterns of chemical shifts for one-electron-reduced species have been established as exemplified by Ni(STPP-d/sub 6/) (pyrrole, -52.3, 25.6, 21.0 ppm; 363 K), Ni(SDPDTP-d/sub 2/) (thiophene; 41 ppm; 293 K) and Ni(STPP-d/sub 6/)(1-MeIm) (pyrrole, 61.3, 42.3, 20.8 ppm; 298 K). The coordination of pyridine, methyldiphenylphosphine, and 1-methylimidazole resulted in similar spectral patterns. The /sub 2/H NMR spectra of Cu/sup II/(STPP-d/sub 6/) established a standard pattern for the well-defined d/sup 9/ electronic structure (pyrrole, 49.9, 38.5, 29.6 ppm; thiophene, -9.0 ppm). The isotropic shift of nickel thiaporphyrins have been discussed in terms of the contribution of two canonical forms: nickel(I) thiaporphyrin-Ni(II) and thiaporphyrin anion radical. The .sigma.- and .pi.-delocalization mechanisms of the spin density have been considered to account for the isotropic shift pattern. /sup 61/Ni hyperfine coupling constants have been measured by means of EPR spectroscopy for the series of nickel thiaporphyrins enriched in the /sup 61/Ni isotope. The typical hyperfine coupling constants (A/10/sup -4/ cm/sup -1/) are as follows: /sup 61/Ni(STPP), A/sub 1/ = 6.5, A/sub 2/ = 32.2, A/sub 3/ = 3.2; /sup 61/Ni(STPP)(SO/sub 2/), A/sub 1/ = 49.3, A/sub 2/ = 15.0, A/sub 3/ = 18.5; Ni(STPP)(1-MeIm), A/sub 1/ = 6.9, A/sub 2/ = 4.6, A/sub 3/ = 16; /sup 61/Ni(STPP)(py)/sub 2/, A/sub 1/ = 18.3, A/sub 2/ = 11.1, A/sub 3/ = 15.5. The coordination of P(OEt)/sub 3/ by Ni(STPP) has been confirmed by the characteristic superhyperfine splitting (A/sup p//sub 1/ =124, A/sup p//sub 2/ = 133, A/sup p//sub 3/ = 127). A parallel analysis of /sup 61/Ni hyperfine coupling constants and /sup 2/H NMR isotropic shifts provided direct insight into the electron and spin density distribution in one-electron-reduced nickel tetraphenylthiaporphyrin complexes.

Adres publiczny

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