Nickel(II) and palladium(II) thiaethyneporphyrins. Intramolecular metal(II)–η^2-CC interaction inside a porphyrinoid frame.

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Streszczenie

3,18-Diphenyl-8,13-di-*p*-tolyl-20-thiaethyneporphyrin ([18]thiatriphyrin(4.1.1)), which formally contains an C1–C2 ethyne moiety instead of pyrrole embedded in the macrocyclic framework of 21-thiaporphyrin, was obtained in a modification of the “3 + 1” approach using the ethyne analogue of tripyrrane (1,4-diphenyl-1,4-di(pyrrol-2-yl)but-2-yne) and 2,5-bis(*p*-tolylhydroxymethyl)thiophene. The spectroscopic and structural properties of 20-thiaethyneporphyrin reflect its macrocyclic aromaticity, revealing a combination of the acetylene (≥C–C≡C–C≤) and cumulene (>C═C═C═C<) character of the C18–C1–C2–C3 linker. The magnetic manifestations of aromaticity and antiaromaticity of thiaethyneporphyrin and its two-electron-oxidized derivative were observed using ^{1}H NMR spectroscopy and were confirmed by density functional theory calculations involving chemical shifts and nucleus-independent chemical shift analysis. Protonation of 20-thiaethyneporphyrin yielded a nonaromatic tautomer of *iso*-20-thiaethyneporphyrin, locating the saturated meso carbon adjacent to thiophene. Insertion of palladium(II) and nickel(II) into 20-thiaethyneporphyrin afforded planar palladium(II) thiaethyneporphyrin and low-spin diamagnetic nickel(II) 20-thiaethyneporphyrin as determined by X-ray crystallography. 20-Thiaethyneporphyrin acts as a dianionic ligand that coordinates through the two nitrogen and one sulfur donors. Metal(II) ions are uniquely exposed to form an intramolecular metal(II)−η^2-CC bond, whereas the organometallic fragment is coplanar with the whole macrocycle. Coordination of pyridine converts diamagnetic nickel(II) thiaethyneporphyrin into its paramagnetic counterpart as determined by ^{1}H NMR.

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