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5,20-diphenyl-10,15-bis(*p*-tolyl)-21-selenaporphyrin and its nickel(II) complexes.

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Streszczenie

The synthesis of a new monoheteroporphyrin, 5,20-diphenyl-10,15-bis(*p*-tolyl)-21-selenaporphyrin (SeDPDTPH), is reported. The 21-selenaporphyrin has been characterized by ^{1}H NMR, ^{13}C NMR, mass spectrometry, and UV−visible spectra and an X-ray structural analysis. The free base selenaporphyrin SeDPDTPH crystallizes in the monoclinic space group $P2_1/n$ with a =19.848(3) Å, b = 8.8410(14) Å, c = 20.503(4) Å, β = 103.375(12)° at 125 K with Z = 4. Refinement of all 4577 unique reflections and 453 parameters yielded R_1 = 0.096 (based on F^2). The presence of selenium atom elongates the macrocycle along the N(1)−N(3) axis when compared to a regular porphyrin. The π delocalization pattern is altered in the selenophene moiety in relation to the free selenophene. SeDPDTPH undergoes a two-step proton addition in solution. Mono- and dication formation results in distortion of the planar 21-selenaporphyrin structure. The monocation structure is solvent dependent as shown by the ^{1}H NMR titration experiments. Insertion of Ni(II) into 21-selenaporphyrin yields Ni^{II}(SeDPDTP)Cl (S = 1, μ_{eff} = 3.3 μ_B). The electronic spectrum of this complex is porphyrin-like with a strong Soret band at 433 nm. The ^{1}H NMR spectra of the high-spin nickel(II) complexes of 21-selenaporphyrin have been recorded and assigned by means of the selective deuteration, line width considerations, and a 2D COSY experiment. The characteristic pattern of pyrrole (downfield) and selenophene (upfield) resonances has been established. Direct σ-π spin density transfer has been proposed to explain the upfield shift of the selenophene protons. Imidazole replaces the chloride ligand to form five- and six-coordinate complexes. The spectroscopic and chemical properties of Ni^{II}(SeDPDTP)Cl resemble those of nickel(II) complexes with 21-thiaporphyrin. To account for these similarities, we suggest that the selenophene moiety is bent out of the porphyrin plane in Ni^{II}(SeDPDTP)Cl. Such a geometry allows metal ion to interact with selenium of selenophene in a side-on fashion.

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