

Nickel(II) complexes of 21-C-alkylated inverted porphyrins: synthesis, protonation, and redox properties.

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Streszczenie

Reaction of the nickel(II) complex of an inverted porphyrin, (5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrinato)nickel(II) (**1**), with haloalkanes in the presence of proton scavengers yields 21-C-alkylated complexes. The products are separated and characterized spectroscopically. Chirality of the formed substituted metalloporphyrins is discussed on the basis of the ^1H NMR spectra. Diastereomers are observed for the complexes containing chiral substituents. Protonation of the external nitrogen of the inverted pyrrole is combined with coordination of the apical ligand that leads to paramagnetic nickel(II) complexes. Very strong differentiation of the isotropic shift for diastereotopic methylene protons is observed in ^1H NMR spectra of the protonated paramagnetic species. For the systems containing benzyl, allyl, and ethoxymethyl substituents a mild dealkylation in solution of protonated complexes is observed in the presence of oxygen. Redox properties of the alkylated complexes are studied by means of cyclic voltammetry. Oxidation of the nickel center in 21-alkylated systems takes place at the potentials comparable to that of unsubstituted complex **1**. Protonation introduces small changes to the potential of the $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$ redox couple, but it stabilizes nickel(I) species. Products of chemical oxidation and reduction of the alkylated complexes are detected by means of the EPR spectroscopy indicating in both cases metal-centered redox processes.

Słowa kluczowe

Ligands, Molecular structure, Pyrroles, Reaction mechanisms, Substituents

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