Nitration of norcorrolatonickel(II): first observation of a diatropic current in a system comprising a norcorrole ring.

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Streszczenie

A one-pot reaction of 5,14-bis(mesityl)-norcorrolatonickel(II) with isoamyl nitrite under mild reaction conditions resulted in the consecutive formation of 3-nitro-, 3,12-dinitro- and 3,16-dinitro-, 3,7,12-trinitro-, and 3,7,12,16-tetranitro-norcorrolatonickel(II) in 50–80 % yield. The substituted macrocycles retained their antiaromatic character. The observed regioselectivity of the substitution was analyzed by comparing the relative energies of the DFT energy-optimized models of the radical or arenium cationic intermediates that can be formed upon reaction with NO_2. The nitrated systems were characterized by high-resolution mass spectrometry, NMR and UV/Vis spectroscopy, X-ray diffraction analysis, cyclic voltammetry, and DFT calculations. A significant and systematic cathodic shift of the redox couples was observed to correlate with an increasing number of the NO_2 group. A decrease of the LUMO energies in the tri- and tetra-nitrated products stabilizes mono- and bis-reduced complexes of these ligands. The reduction takes place on the macrocycle rather than on the metal ion leading to the consecutive formation of stable paramagnetic monoanion radicals and water-soluble diamagnetic dianions with an aromatic character, which were revealed by ESR and ^1H NMR measurements, respectively. The electronic structures of the reduced forms were analyzed by extensive TD-DFT calculations.

Adres publiczny

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