Novel reactions of iron(III) tetraphenylporphyrin π-cation radicals with pyridine.

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The reactivity of iron(III) tetraphenylporphyrin -cation radical complexes [(TPP,)FeraCl][SbCl6] (1-1) and [(TPP*)-Fem(C104)2] (1-2) with pyridine has been examined by and 2H NMR spectroscopy in dichloromethane solutionat low temperatures. Evidence for the reaction of the porphyrin ring with pyridine with formation of stable/8-pyridiniumyltetraphenylporphyrin (2) and unstable 5-pyridiniumylisotetraphenylporphyrin (3) and 5,10-dipyridiniumyltetraphenylporphodimethene (4) complexes of iron is presented. Forms 3 and 4 may be directlyobserved over the temperature range —80 to —40 °C. They are new forms of highly oxidized, highly positivelycharged species that are related to the iron porphyrins. The characteristic patterns of paramagnetically shifted pyrrole resonances (i.e., seven for the ^-substituted form, four for isoporphyrin, and two for porphodimetheneiron complexes) are correlated with the symmetry of species and have been used as a definitive indication of porphyrin structural modification. The simultaneous formation of pyridine-substituted iron porphyrins in different oxidation/electronic/spin states has been found. A mechanism of their formation, which involves meso- or /(-substituted -intermediates, has been proposed. The NMR spectra of the stable, high-spin [(y9-py-TPP)- FemCl2 and low-spin [(/?-py-TPP)Fem(py)2]Cl2 products are presented and analyzed. A strong dependency of the NMR spectra on the counteranion for the low-spin form ([(/J-py-TPP)Fem]2+) has been found and isexplained by the formation of a tightly bonded, ionic pair because the complex bears two positive charges.

Adres publiczny

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https://www.acs.org/content/acs/en.html