Metal complexes of *meso*-amino-octaethylporphyrin and the oxidation of Ni^{II}(*meso*-amino-octaethylporphyrin).

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The crystal structures of *meso*-NH_2−$OEPH_2$, Ni^{II}(*meso*-NH_2−OEP), and Cu^{II}(*meso*-NH_2−OEP) (where OEP is the dianion of *meso*-amino-octaethylporphyrin) have been determined to examine the effects of the *meso*-substituent on the geometry of the ligand. Cu^{II}(*meso*-NH_2−OEP) has a nearly planar geometry while the free ligand itself and Ni^{II}(*meso*-NH_2−OEP) have *ruf* conformations. Ni^{II}(*meso*-NH_2−OEP) is much less reactive toward oxidation than are $(py)_2Fe^{II}$(*meso*-NH_2−OEP), $ClFe^{III}$(*meso*-NH_2−OEP), or Ni^{II}(*meso*-HO−OEP), which all undergo oxidation in pyridine solution when exposed to dioxygen. Treatment of Ni^{II}(*meso*-NH_2−OEP) with iron(III) chloride in chloroform solution does result in oxidation of the ligand in two separate processes. One involves oxygenation at the *trans*-meso position, while the other results in ring cleavage and removal of the amino function. The open-chain tetrapyrrole complex, Ni^{II}(OEB−CO_2Et), has been characterized by single-crystal X-ray diffraction and shown to contain a helical ligand with a four-coordinate nickel ion.

Adres publiczny

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