

Monomeric and trimeric manganese(III) complexes of 2-hydroxy-5,10,15,20-tetraphenylporphyrin. Synthesis and characterization.

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Rok wydania

1996

Czasopismo

Inorganic Chemistry

Numer woluminu

35

Strony

4812-4818

DOI

10.1021/ic951663y

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

The hydrolysis of the monomeric five-coordinate (2-BzO-TPP)Mn^{III}Cl complex has been investigated.¹ Evidence for the formation of the cyclic trimeric complex [(2-O-TPP)Mn^{III}]₃ is presented. The ¹H NMR spectroscopic evidence indicates that the trimeric manganese(III) complex has a head-to-tail cyclic trimeric structure with the pyrrolic alkoxide groups forming bridges from one macrocycle to the manganese(III) ion in the adjacent macrocycle PMn-O-PMn-O-PMn-O. The three manganese(III) porphyrin subunits are not equivalent. The characteristic upfield shift of the 3-H pyrrole resonance (−111.5 ppm at 291 K) was determined and considered as the diagnostic feature for the high-spin d⁴ manganese(III)–pyrrole alkoxide coordination. The strong upfield shift of the 3-H resonance has been accounted for by the donation of the electron density from the filled orbital of the 2-O atom on the half-occupied d_{z²} orbital of the external manganese(III) ion. The other pyrrole resonances produce the complex multiplet at the typical −5 to −40 ppm region. The ¹H NMR spectra of the series of monomeric 2-substituted manganese(III) 5,10,15,20-tetraphenylporphyrin complexes (2-X-TPP)Mn^{III}Cl have been obtained and analyzed. The pattern of the assigned seven pyrrole resonances reflects the asymmetry imposed by 2-substitution and has been used as a ¹H NMR spectroscopic probe to map the spin density distribution. The electronic effect is strongly localized at the β-substituted pyrrole. The upfield shift of the 3-H resonance increases in the order (2-NO₂-TPP)Mn^{III}Cl < (2-BzO-TPP)Mn^{III}Cl < (2-OCH₃-TPP)Mn^{III}Cl < (2-OH-TPP)Mn^{III}Cl < (2-NH₂-TPP)Mn^{III}Cl < [(2-O-TPP)Mn^{III}(OH)][−] following the increasing electron-donating properties of the β-substituent

Słowa kluczowe

Pyrroles, Ions, Transition metals, Nuclear magnetic resonance spectroscopy, Resonance structures

Adres publiczny

<https://doi.org/10.1021/ic951663y>

Strona internetowa wydawcy

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

Plik został wygenerowany dnia 2026-10-03 20:04:14

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