Characterization of high-spin and low-spin iron(III) quinoxalinotetraphenylporphyrin.

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The ^{1}H NMR spectra of iron(III) quinoxalinotetraphenylporphyrin ($(\mathrm{QTPP})\mathrm{Fe}^{\mathrm{III}}\mathrm{X}_n$), iron(III) (methylquinoxalino)tetraphenylporphyrin ($(\mathrm{MQTPP})\mathrm{Fe}^{\mathrm{III}}\mathrm{X}_n$), and iron(III) pyrazinotetraphenylporphyrin ($(\mathrm{PTPP})\mathrm{Fe}^{\mathrm{III}}\mathrm{X}_n$) have been studied to elucidate the impact of an aromatic extension of a single pyrrole ring on the electronic structure of the corresponding high- and low-spin iron(III) porphyrins. The ^{1}H NMR spectra of the complexes with the following axial ligands have been reported: chloride, iodide, cyanide, pyridine-d_5 (py-d_5), 4-aminopyridine (4-$\mathrm{NH_2}$py), and imidazole (ImH). Modification of the tetraphenylporphyrin by addition of the quinoxaline (pyrazine) fragment results in stabilization of the rare low-spin iron(III) $(d_{xz}d_{yz})^4(d_{xy})^1$ electronic ground state in the presence of axial cyanide or pyridine ligands. The more common $(d_{xy})^2(d_{xz}d_{yz})^3$ electronic ground state has been established for $[(\mathrm{QTPP})\mathrm{Fe}^{\mathrm{III}}(4\text{-}\mathrm{NH_2py})_2]^+$ and $[(\mathrm{QTPP})\mathrm{Fe}^{\mathrm{III}}(\mathrm{ImH})_2]^+$ species. To account for the substituent contribution, the Hückel linear combination of atomic orbitals (LCAO) method has been used to determine the molecular orbitals involved in the spin density delocalization. The deviation from Curie law observed for $[(\mathrm{QTPP})\mathrm{Fe}^{\mathrm{III}}(\mathrm{CN})_2]^-$ suggests Boltzmann equilibrium $\{(d_{xz})^2(d_{yz})^2(d_{xy})^2(\Psi_{-1})^1 \leftrightarrow (d_{xz})^2(d_{yz})^2(d_{xy})^1(\Psi_{-1})^2\} \rightleftharpoons (d_{xz})^1(d_{yz})^2(d_{xy})^2(\Psi_{-1})^2 \rightleftharpoons (d_{xz})^2(d_{yz})^1(d_{xy})^2(\Psi_{-1})^2$ where Ψ_{-1} is related to the a_{2u} orbital of a regular porphyrin. For the first time in the group of low-spin iron(III) tetraarylporphyrins, the sign reversal of the isotropic shift was directly observed for pyrrole-proton resonances. The structure of $(\mathrm{QTPP})\mathrm{Fe}^{\mathrm{III}}\mathrm{Cl}$ was determined by X-ray crystallography. $(\mathrm{QTPP})\mathrm{Fe}^{\mathrm{III}}\mathrm{Cl}$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 18.016(5)$ Å, $b = 11.399(3)$ Å, $c = 21.996(5)$ Å, $\beta = 112.22(5)°$, and $Z = 4$. The refinement of 548 parameters and 2696 reflections yields $R_1 = 0.0654$, $R_{w2} = 0.1717$. The $(\mathrm{QTPP})\mathrm{Fe}^{\mathrm{III}}\mathrm{Cl}$ presents features of the high-spin five-coordinate iron(III) tetraphenylporphyrin. The quinoxalinotetraphenylporphyrin macrocycle assumes a saddle-shape geometry.

Adres publiczny

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Strona internetowa wydawcy

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