New insight into the electronic structure of iron(IV)-oxo porphyrin compound I. A quantum chemical topological analysis.

Autorzy

Ignacio Viciano

Sławomir Berski

Sérgio Martí

Juan Andrés

Rok wydania

2013

Czasopismo

Journal of Computational Chemistry

Numer woluminu

34

Strony

780-789

DOI

10.1002/jcc.23201

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

The electronic structure of iron-oxo porphyrin π-cation radical complex $Por^{\cdot+}Fe^{IV}$O (S=H) has been studied for doublet and quartet electronic states by means of two methods of the quantum chemical topology analysis: electron localization function (ELF) η(*r*) and electron density ρ(*r*). The formation of this complex leads to essential perturbation of the topological structure of the carbon–carbon bonds in porphyrin moiety. The double C=C bonds in the pyrrole anion subunits, represented by pair of bonding disynaptic basins $V_{i=1,2}$(C,C) in isolated porphyrin, are replaced by single attractor $V(C,C)_{i=1–20}$ after complexation with the Fe cation. The iron–nitrogen bonds are covalent dative bonds, N→Fe, described by the disynaptic bonding basins $V(Fe,N)_{i=1–4}$, where electron density is almost formed by the lone pairs of the N atoms. The nature of the iron–oxygen bond predicted by the ELF topological analysis, shows a main contribution of the electrostatic interaction, $Fe^{\delta+}\cdots O^{\delta-}$, as long as no attractors between the C(Fe) and C(O) core basins were found, although there are common surfaces between the iron and oxygen basines and coupling between iron and oxygen lone pairs, that could be interpreted as a charge-shift bond. The Fe=S bond, characterized by the disynaptic bonding basin V(Fe,S), is partially a dative bond with the lone pair donated from sulfur atom. The change of electronic state from the doublet (*M* = 2) to quartet (*M* = 4) leads to reorganization of spin polarization, which is observed only for the porphyrin skeleton (−0.43e to 0.50e) and S=H bond (−0.55e to 0.52e).

Słowa kluczowe

quantum chemical topology, electron localization function, electron density, chemical bond, compound I, cytochrome P450, porphyrin pyrrole