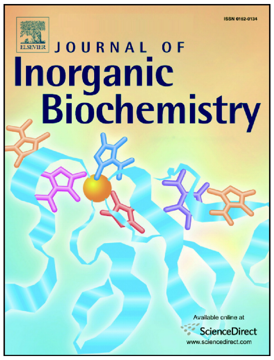

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Modeling the Hydrogen Sulfide Binding to Heme

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Abstract

The binding of hydrogen sulfide to a model heme compound is investigated by coupled-cluster singles-doubles augmented by a perturbative triple excitations, CCSD(T), and density functional theory, DFT. The minimum energy path for the H_2S addition to an isolated heme center of the heme protein is evaluated by adopting as a model the heme compound FeP(Im) (P=porphyrin; Im=imidazole). The FeP(Im)-H_2S aduct is bound by 13.7 kcal/mol at the CCSD(T) level of theory. Relaxed potential energy curves for the lowest lying spin states of the H_2S to FeP(Im) binding using DFT reveal that the binding process is associated with a "double spin-crossover" reaction with the existence of long-distance van der Waals minima only 5-7 kcal/mol above the FeP(Im)-H_2S ground state. The fact that the energy of the singlet ground state of FeP(Im)-H_2S is so close in energy to the dissociation products FeP(Im)+H_2S points towards the reversibility of the H_2S adsorption/desorption process in biochemical reactions.

Keywords: heme; imidazole; H_2S binding; electronic states; density functional theory; coupled cluster theory.

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