

A DFT Study of the Properties of Two Diiron(II) Synthetic Model Compounds

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Abstract

Density functional theory calculations have been conducted on two diiron(II) synthetic model compounds and on the diiron(III) complexes they form with O₂. The model compounds have been synthesized to mimic the diiron O₂ binding centers of proteins such as ribonucleotide reductase. The iron(II) complexes have both been crystallographically well characterized and offer excellent opportunities to compare calculated and experimental geometries in bridged diferrous complexes. Raman spectra are available for the oxygenated iron(III) complexes, and these are compared with harmonic frequencies obtained in the calculations. The calculations employ the BPW91 density functional with numerical basis sets. The study compares the effects on optimized geometries and harmonic vibrational frequencies of spin-paired high-spin and broken symmetry antiferromagnetically coupled singlet representations of the spin density distribution. The geometries around the diiron centers in the high-spin and broken symmetry representations are found to be similar. Small differences between the high-spin and broken symmetry results are seen in bond lengths, angles, Raman frequencies and spin densities associated with oxo and peroxy bridges between the irons.