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A Theoretical Study on Single-electron Reduction of a Thiolate-Bridged Diiron Diazene Complex

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Abstract

The single-electron reduction of the thiolate-bridged diiron diazene complex $[\text{Cp}^*\text{Fe}(\mu\text{-SEt})_2(\mu\text{-}\eta^1:\eta^1\text{-HN=NH})\text{FeCp}^*]^+$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_4\text{H}$, $\mathbf{1}^+$) to $[\text{Cp}^*\text{Fe}(\mu\text{-SEt})_2(\mu\text{-}\eta^1:\eta^1\text{-HN=NH})\text{FeCp}^*]$ ($\mathbf{2}$) has been computationally found to be a metal-based reduction process. Such a reduction event decreased the acidity of N–H bond and increased the basicity of N atoms of the diazene moiety. The results derived from broken-symmetry calculations suggest that the electronic ground state of $\mathbf{1}^+$ is better described as antiferromagnetic BS(2,1) and both BS(1,1) and RKS states could coexist in the case of $\mathbf{2}$. Both the charge decomposition and atom-in-molecule analysis indicate a donor-acceptor interaction between the Fe centers and the diazene ligand.

Keywords: Electronic structure, Thiolate-bridged diiron diazene complexes, Single-electron reduction, DFT

1. Introduction

The active site of the nitrogenase is generally considered to be the FeMo-cofactor, which contains Fe–S–Fe bridging connections and produces ammonia from dinitrogen at ambient temperature and pressure. In view of the complexity of the process of biological nitrogen fixation, a variety of organometallic model complexes, especially iron–sulfur clusters [1-4], have been examined to mimic the behavior of nitrogenase and the related mechanism. During such a process, except for the reduction of nitrogenase substrate such as dinitrogen and diazene (HN=NH), the redox

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