How NO Interacts with Fe(II)? A Density Functional and Multireference Ab Initio Study.

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The CASSCF/CASPT2 approach along with various functionals of Density Functional Theory (PBE0, B3LYP, B3LYP*, O3LYP, OLYP, BP86, PBE) is applied to selected iron(II)-nitrosyl (or, more precisely, {FeNO}⁷) complexes. These are: (1) FePNO, (2) FePImNO, (3) FePNH₃NO, (4) Fe(salen)NO, (5) FeTNO⁻, and (6) Fe(H₂O)₅NO²⁺, where P=porphyrine, Im=imidazole, salen=N,N'-ethylenebis(salicylimine), T=tris(carbamoylmethyl)amine. So far many DFT calculations have been reported for these challenging and biologically relevant systems (e.g., 2,3 are simple models of the myoglobin active site), but they were often inconclusive with respect to the spin density distribution [1], spin state energetics [1], and NO binding energies [2]. This motivates the present ab initio investigation [3].

CASPT2 correctly predicts a doublet ground state for 1–3, with the excited quartet state about 4–5 kcal/mol higher in energy (the energy and character of the quartet state is important for the NO binding dynamics). However, calculations of the quartet-doublet gap for the spin crossover complex 4 indicate that CASPT2 might overstabilize the quartet state in these systems by several kcal/mol. The binding energies of NO obtained from the CASPT2 calculations (about 32 kcal/mol for the five coordinate complex 1 and about 22 kcal/mol for the six coordinate complex 2) are in good agreement with experimental estimates [2] (similar holds true for the CO and O₂ binding). Among the tested DFT methods only OLYP and B3LYP* yield results of comparable quality.

We also present the CASSCF spin densities of complexes 1-4 (S = 1/2 and S = 3/2) and 5,6 (only S = 3/2) with hope to shade some light on their DFT spin densities, which are very sensitive to the choice of exchange functional [1]. Comparison with CASSCF is in favor of the spin densities from the non hybrid functionals (BP86, OLYP). We note that the CASSCF spin densities are consistent with Magnetic Circular Dichroism [4] and Electron Spin Resonance [5] experiments on complexes similar to 1–3. An analysis of the CAS CI expansion upon localisation of the strongly interacting Fe 3d and NO π^* orbitals points to a mixture of Fe(III)–NO⁻ and Fe(II)–NO⁰ resonance structures. Both have a comparable contribution for the complexes 1–5 (and are also very similar for both spin states), while complex 6 has more Fe(II)–NO⁰ character.

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