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Electronic Structure Analysis of the Oxygen-Activation Mechanism by Fe^{II}- and α -Ketoglutarate (α KG)-Dependent Dioxygenases

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Geometric and electronic structures of O₂ adducts

The molecular orbital diagram for the septet {FeO₂}⁸ species (Figure S1) displays that of five metal d-based MOs four are singly occupied, and one is doubly occupied. The last two spin-up SOMOs are essentially O₂ π*-orbitals. By inspection, the bonding MO referred to as Fe-d_{xz} in Figure 5 contains nearly equal contributions from the O₂-π_{ip}* and the Fe-d_{xz} fragment orbitals (60% Fe vs 34% O₂), and so does its singly occupied antibonding partner denoted as O₂-π_{ip}*. Therefore, the bonding pattern is best rationalized by two resonance electronic structures, both of which are BS(6,0) solutions: a) a HS Fe^{II} center (S_{Fe} = 2) ferromagnetically coupled to a triplet O₂ (S_{O2} = 1) and b) a HS Fe^{III} ion (S_{Fe} = 5/2) bound to an O₂^{-•} radical ligand with S_{O2} = 1/2 in a ferromagnetic fashion. Relative to the resting state, it becomes evident that the bound O₂ group is partially reduced upon binding to the iron center. The calculated isomer shift for the septet {FeO₂}⁸ species is 0.83 mm/s, which is between typical values of HS Fe^{II} and HS Fe^{III}, supporting our interpretation that the electronic structure is best described by the above two resonance structures.

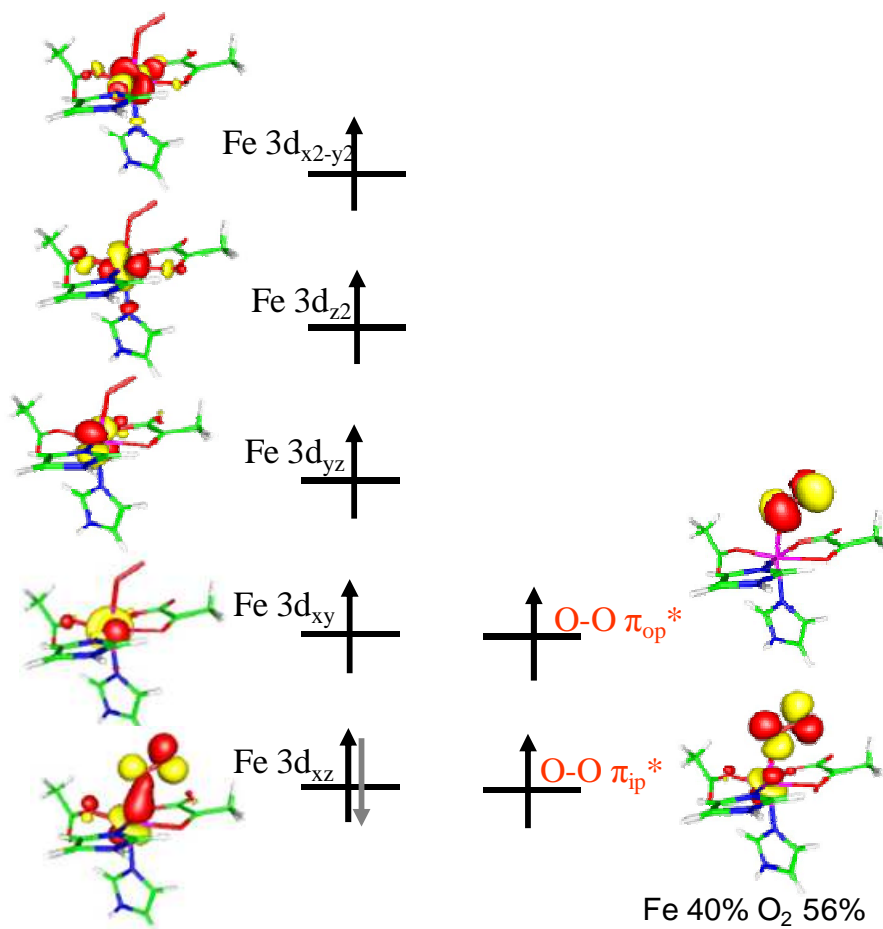


Figure S1. Schematic MO diagram for the septet O_2 adduct, quasi-restricted orbitals were employed.

The electronic structure of the quintet $\{\text{FeO}_2\}^8$ species may be best interpreted either as a HS ferric ion ($S_{\text{Fe}} = 5/2$) antiferromagnetically coupled to a superoxo anion radical ($S_{\text{O}_2} = 1/2$) referred to as a BS(5,1) solution; or as a HS Fe^{II} ($S_{\text{Fe}} = 2$) center coordinated to a neutral $^1\text{O}_2$ approached by a BS(4,0) calculation. Both initial guesses eventually converged to the same BS(5,1) state. As depicted in Figure S2, five SOMOs in the spin-up manifold have predominantly Fe-3d character. In the spin-down set one unpaired electron resides in the π_{op}^* -orbital of the O_2 -fragment, thereby yielding an overall quintet state. The other O_2 π^* -orbital is doubly occupied. Thus, the bonding situation defines a

HS Fe^{III} center ($S_{\text{Fe}} = 5/2$) that is antiferromagnetically coupled to a $^2\text{O}_2^{-\bullet}$ ($S_{\text{O}_2} = 1/2$) π -radical. Consistent with this description, the calculated Fe isomer shift of 0.56 mm/s is typical of HS Fe^{III}. Inspection of the doubly occupied $\text{O}_2 \pi_{\text{ip}}^*$ -orbital reveals that there is a weak bonding interaction between the uncoordinated O-atom in O_2 and the C2 atom in αKG . However, this weak bonding is absent in the corresponding septet species, which explains the shorter C-O distance in the quintet species relative to that in the septet analogue.

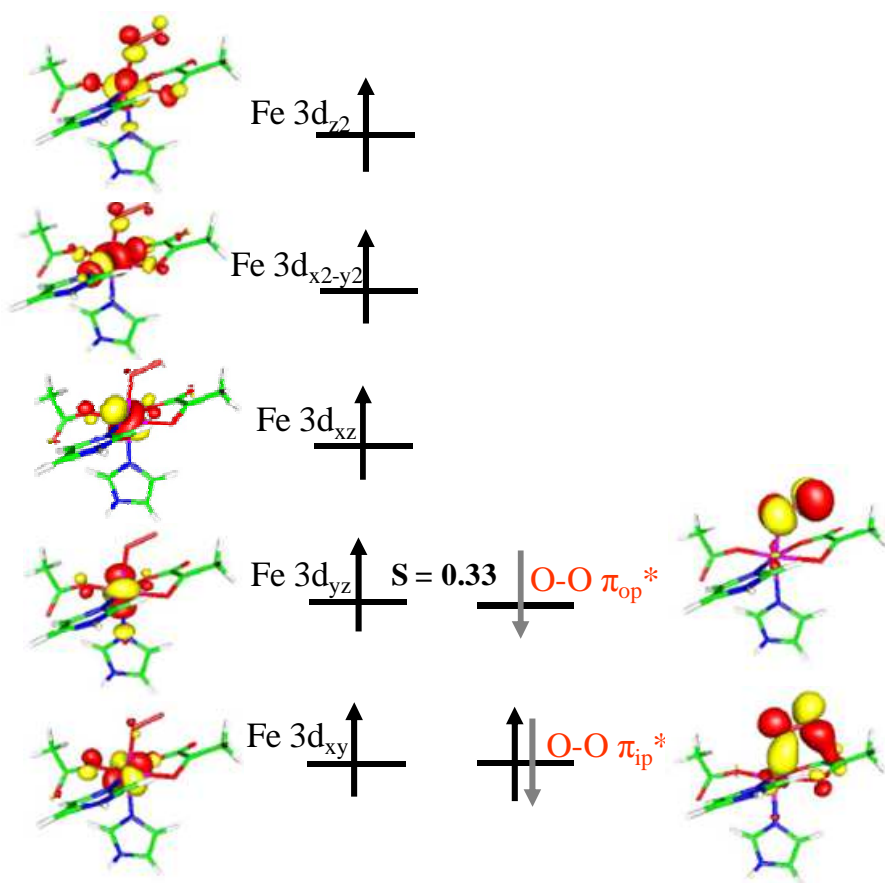


Figure S2. Schematic MO diagram for the quintet O_2 adduct, the spin coupled pair represents unrestricted corresponding orbitals, whereas for the remaining orbitals quasi-restricted orbitals were employed.

The electronic structure of the triplet $\{\text{FeO}_2\}^8$ species was calculated using the three different initial guesses, namely, BS(2,0), BS(3,1) and BS(4,2). The BS(2,0) solution may be used to describe an intermediate-spin (IS) Fe^{II} ion ($S_{\text{Fe}} = 1$) bound to a singlet O_2 ligand with $S_{\text{O}_2} = 0$ or a low-spin (LS) ferrous center ($S_{\text{Fe}} = 0$) coordinated to a triplet O_2 ligand with $S_{\text{O}_2} = 1$. The BS(3,1) state is thought to correspond to antiferromagnetic coupling between an IS ferric center ($S_{\text{Fe}} = 3/2$) and an O_2^{\bullet} radical ligand ($S_{\text{O}_2} = 1/2$). By contrast, a HS Fe^{II} ion ($S_{\text{Fe}} = 2$) that is antiferromagnetically coupled to a ground state O_2 ligand ($S_{\text{O}_2} = 1$) is approached by the BS(4,2) calculation. However, the calculations with the guesses BS(2,0) and BS(3,1) always converged to the same BS(4,2) solution. A molecular orbital diagram obtained from the optimized structure of the triplet $\{\text{FeO}_2\}^8$ species is presented in Figure 7. In the upper valence region one can identify one doubly occupied and four singly occupied metal-based 3d orbitals in the spin-up set and two singly occupied O_2 π^* -orbitals in the spin-down manifold. Two pathways of spin coupling are evident: a π -pathway involving the Fe d_{yz} - and the O_2 π_{op}^* -orbitals and a σ -pathway consisting of the Fe d_{z^2} - and O_2 π_{ip}^* -orbitals. As anticipated, this orbital occupation pattern is best rationalized by a HS ferrous center ($S_{\text{Fe}} = 2$) interacting with a neutral triplet O_2 ligand ($S_{\text{O}_2} = 1$) in an antiferromagnetic manner. Accordingly, the calculated Fe isomer shift of 1.02 mm/s is typical of HS Fe^{II} .

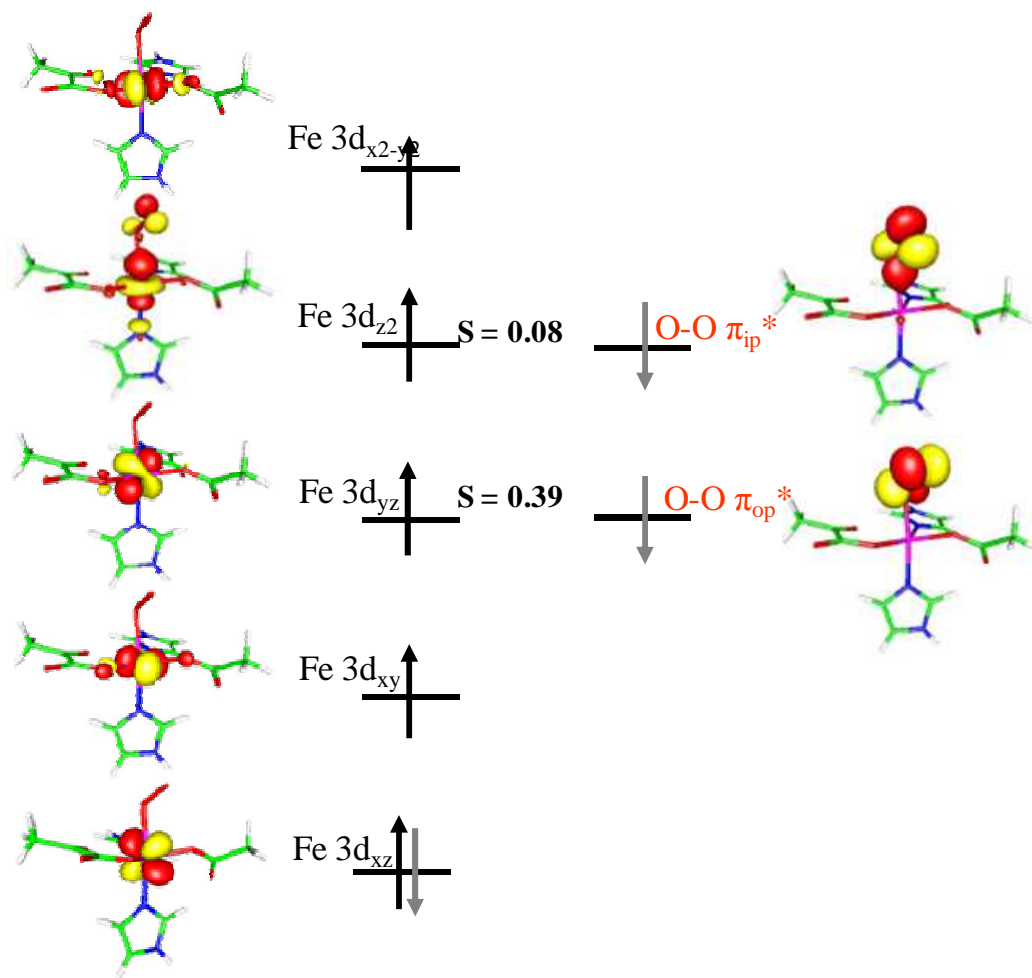


Figure S3. Schematic MO diagram for the triplet O_2 adduct, the spin coupled pair represents unrestricted corresponding orbitals, whereas for the remaining orbitals quasi-restricted orbitals were employed.

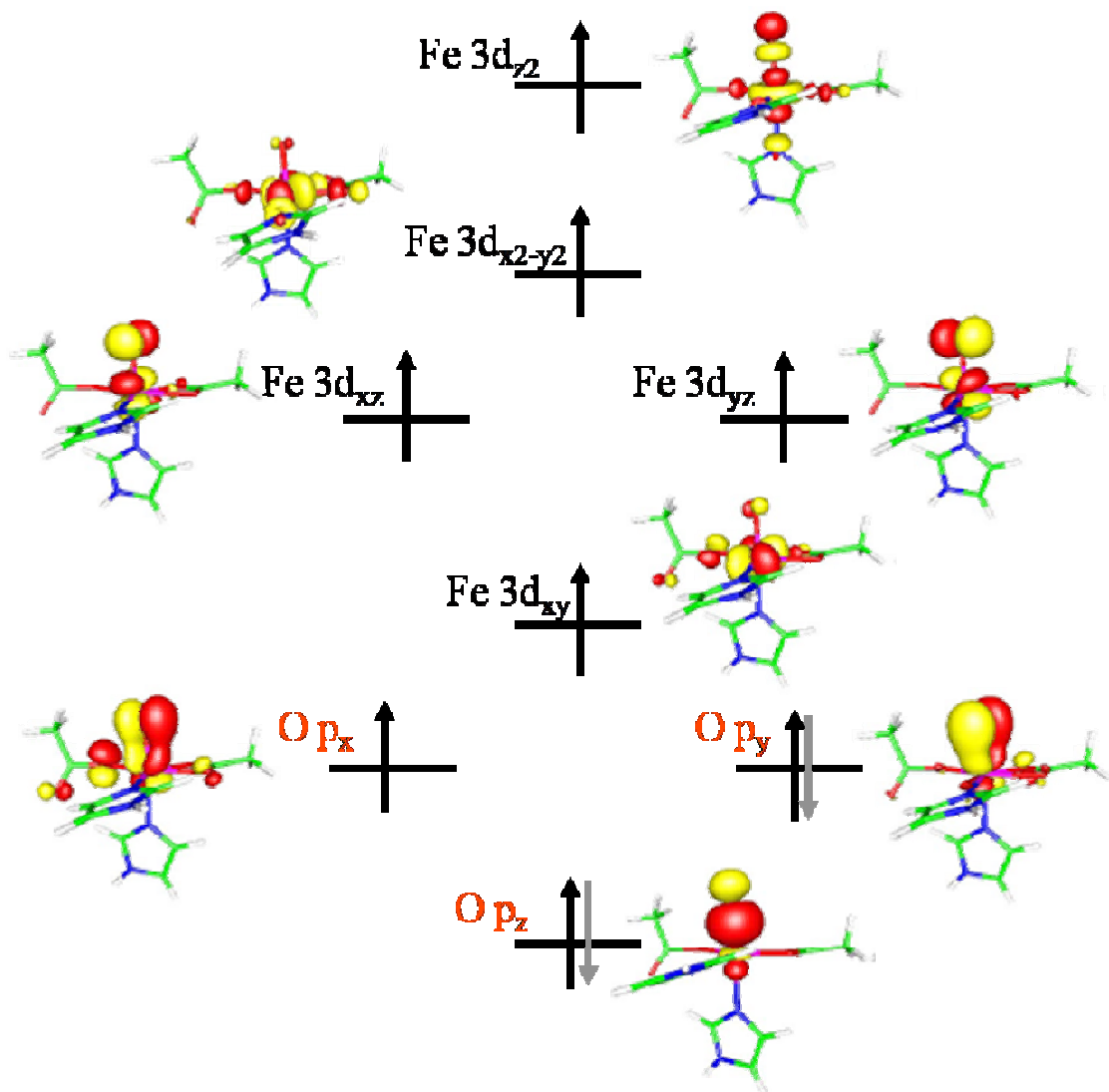


Figure S4. Schematic MO diagram for the septet Fe^{III} -oxyl species, quasi-restricted orbitals were employed.

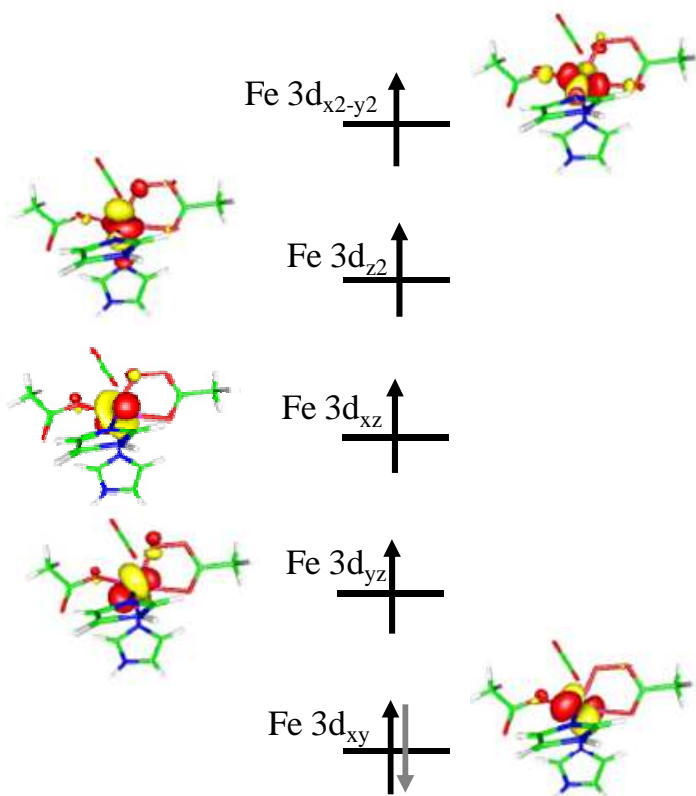


Figure S5. Schematic MO diagram for the peroxo-succinate ferrous complex, quasi-restricted orbitals were employed.

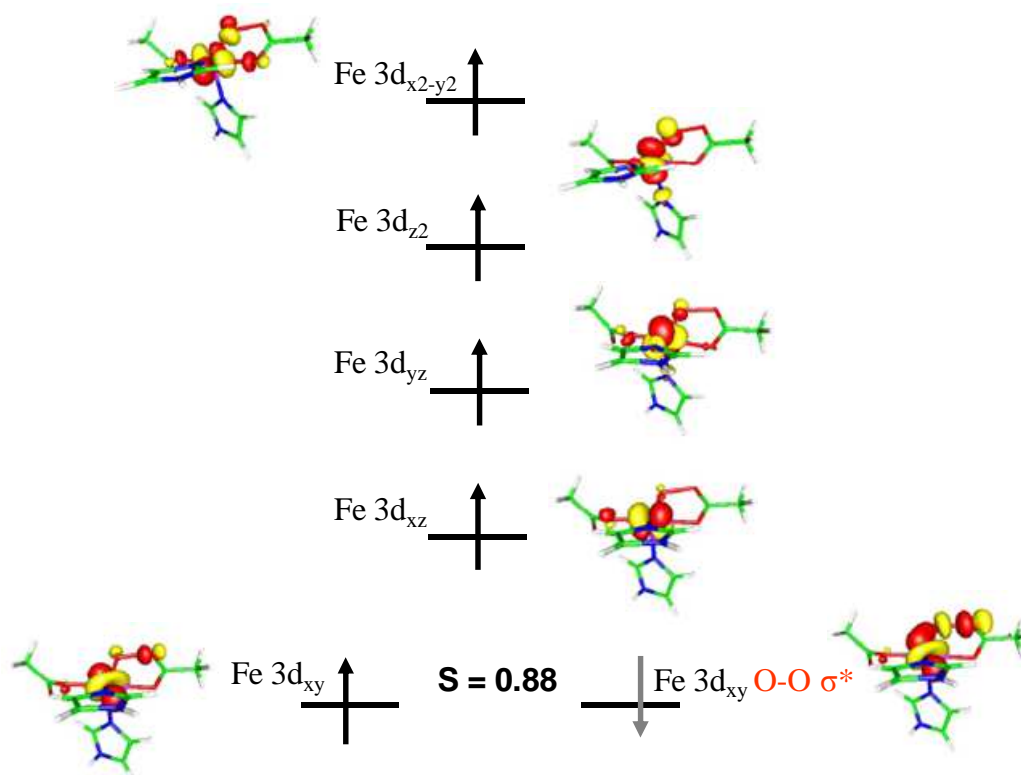


Figure S6. Schematic MO diagram for $^5\text{TS2}$, the spin coupled pair represents unrestricted corresponding orbitals, whereas for the remaining orbitals quasi-restricted orbitals were employed.

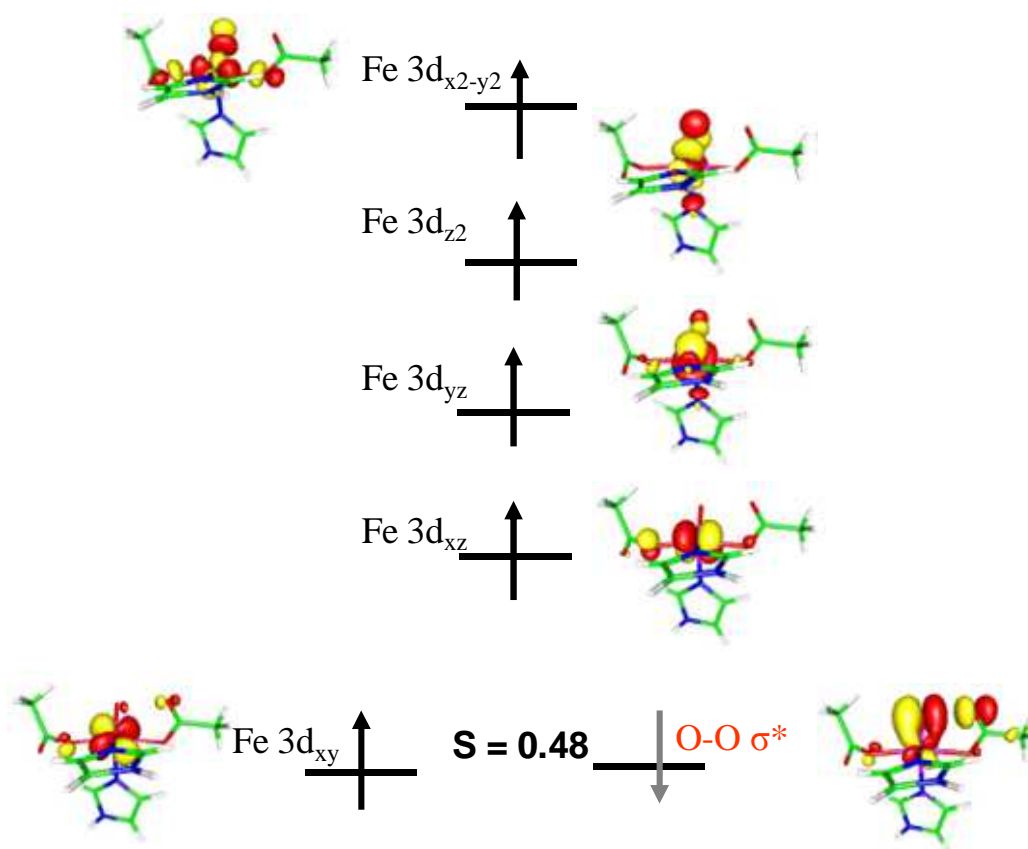


Figure S7. Schematic MO diagram for the half-bond intermediate, the spin coupled pair represents unrestricted corresponding orbitals, whereas for the remaining orbitals quasi-restricted orbitals were employed.

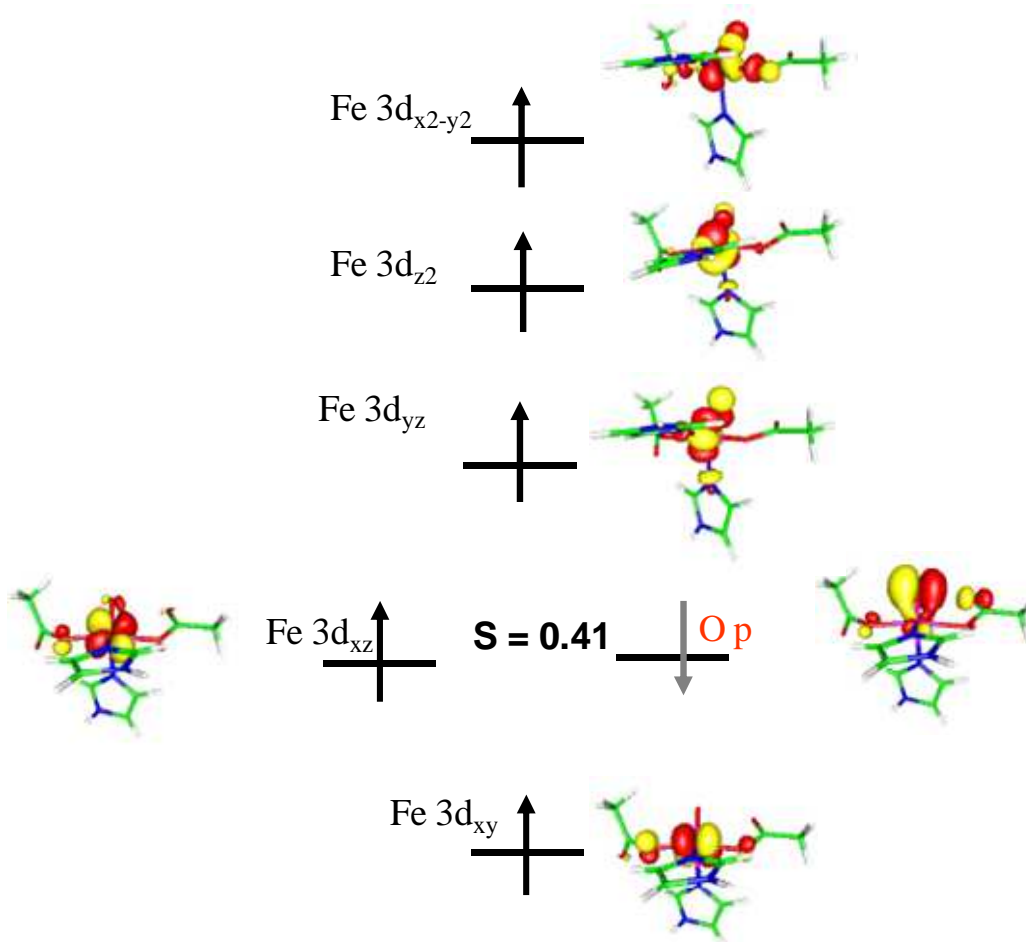


Figure S8. Schematic MO diagram for ${}^5\text{TS3}$, the spin coupled pair represents unrestricted corresponding orbitals, whereas for the remaining orbitals quasi-restricted orbitals were employed.

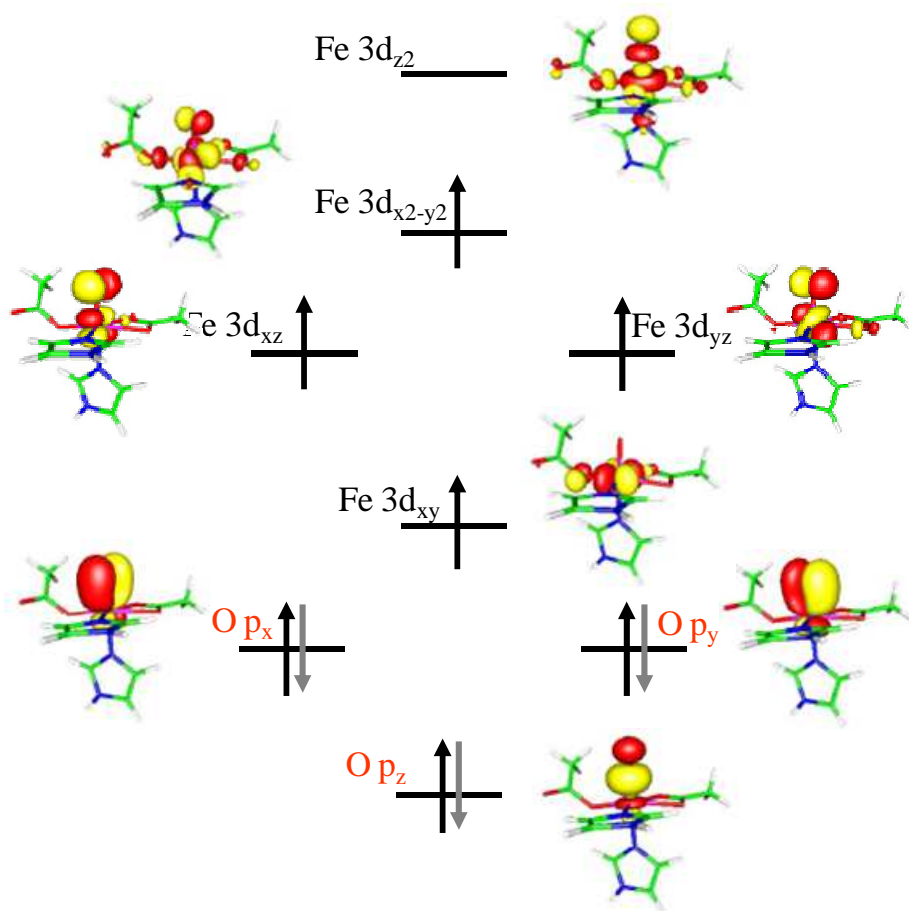


Figure S9. Schematic MO diagram for the quintet Fe^{IV}-oxo complex, quasi-restricted orbitals were employed.