Mössbauer and DFT Studies of Non-heme Iron(IV) Complexes

Audria Stubna[1], Emile L. Bominaar[1], Lawrence Que, Jr.[2] and Eckard Münck[1]

[1]*Department of Chemistry, Carnegie Mellon University,* [2]*Department of Chemistry, University of Minnesota*

It has been proposed that dioxygen activation by non-heme, mono-iron enzymes involves an S = 1 Fe(IV)=O intermediate that is responsible for the substrate oxidation step. Here we present the Mössbauer results for a number of model complexes for this intermediate. The analysis shows that the substitution of the axial, non-oxo ligand as well as the replacement of the equatorial amines with pyridines has a discernable effect on the hyperfine parameters and zero-field splitting. DFT reproduces the trends in these data and gives insight into the influence of the ligands on the electronic structure of the iron. The DFT optimized geometries of the crystallographically characterized Fe(IV)=O complexes are remarkably accurate. We also present the optimized geometries of complexes, including a ^{t}Bu-peroxo species, for which the crystal structures have not yet been determined. The reliability of the predicted structures is assessed on the basis of a comparison between calculated and observed values for the hyperfine parameters.

To estimate the energies of excited triplet and quintet states of the non-heme Fe(IV)=O species, (TD)DFT calculations were carried out for the model $[Fe (O) (NCCH_3) (NH_3)_4]^{2+}$. By treating the spin-orbit coupling between the ground and excited states with second-order perturbation theory, we evaluated the zero-field splitting for the ground state. The resulting value D~30 cm^{-1} derives from nearly equal spin triplet and quintet contributions. The excitation energies for the d-d transitions generated by (TD)DFT were fit with a crystal field model to obtain the Racah parameters and 3d orbital energies. The values for the Racah parameters are considerably reduced when compared to the free ion values, which we ascribe to donation of electronic ligand charge into the virtual d-orbitals.