High-Valent Iron Complexes: Characterization of Fe(V) in Model Systems and a QM/MM Study of the Spectroscopic Properties of Cytochrome $P450_{CAM}$

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High-valent iron intermediates are ubiquitous in heme- and nonheme iron systems.[1] Understanding and predicting their properties is therefore an important line of research. We have recently been engaged in the two ways in the characterization of such systems. The first study to be presented deals with the experimental preparation and characterization of a genuine Fe(V) complex in a nonheme environment.[2] This oxidation state has been very often invoked in the chemistry of iron but the properties of Fe(V) have been largely unknown due to a lack of suitable model complexes which feature this oxidation state. We have pursued the route to generate Fe(V) photochemically in complexes of "innocent" cyclam-based amine ligands.[3] Fe(V) is generated through photolysis of the Fe(III)-N_3^- precursor and has been characterized by Mössbauer, XAS/EXAFS, ABS, MCD and IR spectroscopies as well as by magnetic susceptibility and electronic structure calculations at the correlated *ab initio* and density functional theory (DFT) levels. Our data strongly indicates that Fe(V) has really been formed and that the system features a S=1/2 ground state.[2]
The second study deals with the properties of the as yet unobserved central compound I intermediate in the reaction cycle of cytochrome $P450_{CAM}$.[4] The study is aimed at predicting a set of experimentally calibrated theoretical spectroscopic parameters for compound I in the presence of the protein matrix. Comparison is made to known heme- and nonheme iron-oxo complexes[5] which were studied using DFT and correlated *ab initio* methods.

[1] (a) Ortiz de Montellano, P.R. Ed., *Cytochrome P450: Structure, Mechanisms and Biochemistry,* 2nd ed.; Plenum Press, New York, 1995; Vol. 2 (b) Solomon, E.I.; Brunold, T.C.; Davis, M.I.; Kemsley, J.N.; Lee, S.K.; Lehnert, N.; Neese, F.; Skulan, A.J.; Yang, Y.S.; Zhou, J. *Chem. Rev.*, **2000**, *100*, 235 [2] Aliaga-Alcade, N.; DeBeer George, S.; Mienert, B.; Bill, E.; Wieghardt, K.; Neese, F. *Angew. Chemie. Int. Ed.*, **2005**, in press [3] (a) Rohde, J.-U.; In, J.-H.; Lim, M. H.; Brennessel, W.; Bukowski, M. R.; Stubna, A.; Münck, E.; Nam, W.; Que Jr., L. *Science* **2003**, *299*, 1037 (b) Meyer, K.; Bill, E.; Weyhermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **1999**, *121*, 4859 [4] Schöneboom, J.; Thiel, W.; Neese, F. *J. Am. Chem. Soc.*, **2005**, in press [5] (a) Mandon, D.; Weiss, R.; Jayaraj, K.; Gold, A.; Terner, J.; Bill, E.; Trautwein, A.X. *Inorg. Chem.* **1992**, *31*, 4404 (b) Schulz, C. E.; Devaney, P. W.; Winkler, H.; Debrunner, P. G.; Doan, N.; Chiang, R.; Rutter, R.; Hager, L. P. *FEBS Letters* **1979**, *103*, 102