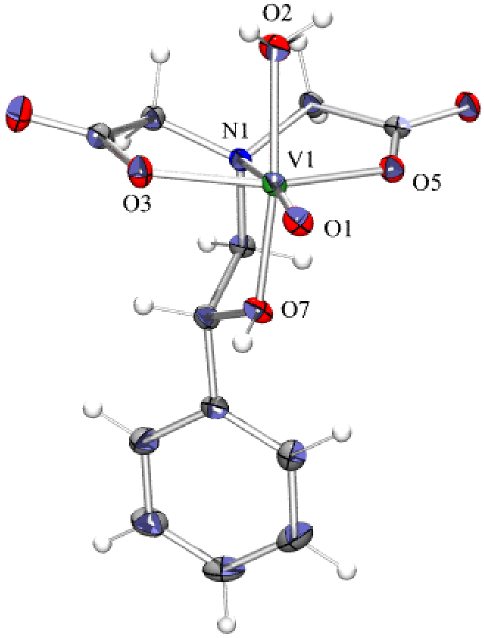
Development of Asymmetric Sulfoxidation Catalysts based on Functional Models of Vanadium Depedent Haloperoxidases

Curtis J. Schneider,[a] Jeff Kampf,[a] Luca De Gioia,[c] and Vincent L. Pecoraro[a,b]

[a]*Department of Chemistry, University of Michigan, Ann Arbor, MI, USA*
[b]*Biophysics Research Division, University of Michigan, Ann Arbor, MI, USA*
[c]*Department of Biotechnology and Biosciences, University of Milano-Bicocca, Milano, Italy*

Vanadium dependent haloperoxidases (VHPO) are a class of enzymes capable of oxidizing both halides and organic sulfides. The oxidation of organic sulfides proceeds stereoselectively, yielding chiral sulfoxides. Previously the Pecoraro group developed a set of tripodal amine complexes capable of oxidizing both halides and organic sulfides. To further develop the modeling chemistry of VHPO, two sterically hindered O_3N tripodal amine including (1*S*)-N-(1-phenyl-1-hydroxyethyl) iminodiacetic acid (H_3pheida) and N,N-(diacetic acid)-(1*S*,2*R*)-norephedrine (H_3pheida$^{2\text{-}Me}$). The oxovanadium(IV) complex of H_3pheida has been crystallographically characterized and shows a coordination mode identical to the vanadium(IV) analogue of an established functional model K[VO(O_2)Hheida]. A set of N_2O_2 tripodal amine complexes based on N-(2-aminoethyl)iminodiacetic acid have also been synthesized to explore the factors influencing the stability of protonated monoperoxo-oxovanadium(V) complexes. Additionally we will report on recent density functional calculations on these systems.



CJS acknowledges the Chemical Biology Interface Training Grant for support.