Axial Coordination of Pseudohalides Modulates the Physical Properties of a Non-Heme Fe^{IV}=O Unit

Timothy A. Jackson,‡ Chivukula V. Sastri,§ Mi Joo Park,§ Jinheung Kim,§ Wonwoo Nam,§ and Lawrence Que Jr.‡

‡Department of Chemistry and Center for Metals in Biocatalysis, University of Minnesota, and
§Department of Chemistry and Center for Biomimetic Systems, Ewha Womans University
(e-mail: jackson@chem.umn.edu)

High valent non-heme iron-oxygen species, such as Fe^{IV}=O adducts, have been proposed as key intermediates for numerous non-heme iron enzymes. However, only one such Fe^{IV}=O adduct has been detected in an enzyme system. In contrast, synthetic complexes containing non-heme Fe^{IV}=O units have been generated using a variety of supporting ligands, and these studies have already demonstrated that the coordination environment of Fe^{IV}=O complexes influences spectroscopic and reactivity properties. The best characterized of these non-heme Fe^{IV}=O adducts is [Fe^{IV}(O)(TMC)(NCCH₃)]^{2+} (1-NCCH₃), where TMC is 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane. Recently it has been shown that the axially coordinated NCCH₃ ligand that is trans to the oxo ligand may be substituted by trifluoroacetate (CF₃CO₂⁻), yielding a new complex, [Fe^{IV}(O)(TMC){OC(O)CF₃}]^{+}, that is a more reactive one-electron oxidant.

To further explore the effects of axial ligation on the spectroscopic and reactivity properties of Fe^{IV}=O adducts supported by TMC, the abilities of the pseudohalides azide (N₃⁻) and thiocyanate (NCS⁻) to displace NCCH₃ were examined. Treatment of 1-NCCH₃ with one equivalent of N₃⁻ or NCS⁻ yielded [Fe^{IV}(O)(TMC)(N₃)]⁺ (1-N₃) and [Fe^{IV}(O)(TMC)(NCS)]⁺ (1-NCS), respectively. These complexes both have altered electronic absorption spectra relative to 1-NCCH₃, particularly in regards to the near-UV spectral region (~410 nm) where the 1-N₃ and 1-NCS complexes exhibit moderately intense features that likely arise from ligand-to-metal charge transfer transitions. 1-N₃ and 1-NCS were further characterized using X-ray absorption spectroscopy, and an extended X-ray absorption fine structure (EXAFS) analysis of the corresponding X-ray absorption spectra yielded metal-ligand bond lengths for these species. In regards to stability, both 1-N₃ and 1-NCS display shorter half-lives than 1-NCCH₃. The reactivities of these complexes towards substrates are discussed.

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