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

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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 $[Fe^{IV}(O)(TMC)(NCCH_3)]^{2+}$ (**1-NCCH$_3$**), where TMC is 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane. Recently it has been shown that the axially coordinated $NCCH_3$ ligand that is *trans* to the oxo ligand may be substituted by trifluoroacetate ($CF_3CO_2^-$), yielding a new complex, $[Fe^{IV}(O)(TMC)\{OC(O)CF_3\}]^+$, 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 (N_3^-) and thiocyanate (NCS^-) to displace $NCCH_3$ were examined. Treatment of **1-NCCH$_3$** with one equivalent of N_3^- or NCS^- yielded $[Fe^{IV}(O)(TMC)(N_3)]^+$ (**1-N$_3$**) and $[Fe^{IV}(O)(TMC)(NCS)]^+$ (**1-NCS**), respectively. These complexes both have altered electronic absorption spectra relative to **1-NCCH$_3$**, particularly in regards to the near-UV spectral region (~410 nm) where the **1-N$_3$** and **1-NCS** complexes exhibit moderately intense features that likely arise from ligand-to-metal charge transfer transitions. **1-N$_3$** 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-N$_3$** and **1-NCS** display shorter half-lives than **1-NCCH$_3$**. The reactivities of these complexes towards substrates are discussed.

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