

TITLE: Fe K-edge XAS of C-H bond activating halogenase structural mimics
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Herein we investigated a series of high valent Fe complexes with cis-oxo labile sites having a tacn ligand backbone $[\text{Fe}^{\text{IV}}(\text{O})(\text{X})(\text{RPytacn})]^{n+}$ (**1Fe**) ($n = 1, \text{X} = \text{Cl}$); Figure 1). These competent C-H activating complexes are structural and functional mimics of non-heme iron halogenases where a high spin $\text{Cl-Fe}^{\text{IV}}=\text{O}$ center is proposed as a reactive intermediate. Data was collected for 2 families of **1Fe** complexes ($\text{R} = -\text{Me}, -\text{H}$; $\text{X} = -\text{Cl}$) in the +2, +3 and +4 formal oxidation state. Currently EXAFS analysis is being performed to provide insight into the geometric structure, ligand speciation and bond metrics of the metal center. The data is expected to help elucidate the nature of the "oxo" species ($-\text{OH}, =\text{O}$) and serve as an experimentally verifiable starting point for theoretical modeling.

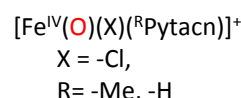
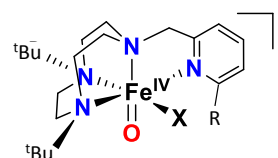


Figure 1: The $[\text{Fe}^{\text{IV}}(\text{O})(\text{X})(\text{RPytacn})]^{n+}$ (**1Fe**) framework.

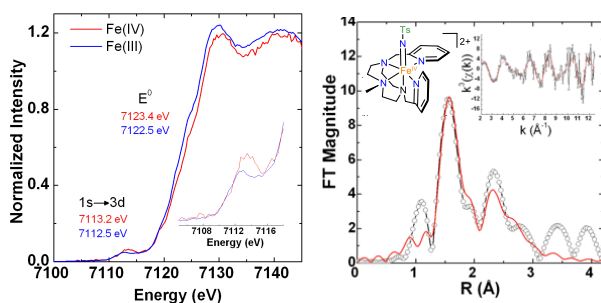


Figure 2: (left) Fe K-edge XANES of $[\text{Fe}(\text{NTs})(\text{MePy}_2\text{tacn})]^{n+}$ (**2Fe**) with +3 and +4 Fe oxidation state; (right) non-phase shift corrected Fourier transforms for 2Fe^{IV} with insets showing the k -space data and fits. Experimental data are shown in black and fits in red.

intermediate spin $S=1$ electronic configuration at the metal centre consistent with a $\delta(\text{Fed}_{xy})^2\pi^*(\text{Fed}_{xz,yz})^2\sigma^*(\text{Fed}_{x^2-y^2})^0\sigma^*(\text{Fed}_{z^2})^0$ arrangement. A manuscript is currently under preparation for this study:

G. Sabenya, L. Gómez, M. Clémancey, I. Gamba, Martin-Diaconescu V., J.-M. Latour, J. Lloret-Fillol, M. Costas. **Preparation, Spectroscopic Characterization and Reactivity of Iron (IV) Tosylimido Complexes with TACN - based N5 - pentadentate Ligands.**

Lastly data was collected on a high-valent highly reactive Ni-oxygen species capable of rapid hydrogen and oxygen atom transfer. The electronic and coordination environment of this highly reactive nickel-oxygen intermediate was trapped following reaction of the Ni(II) precursor with sodium hypochlorite. Using XAS the geometric structure and oxidation state for the intermediate was determined and it was found to be consistent with theoretical calculations which predicted a $\text{Ni}(\text{III})(\text{L})(\text{OCI})$ species having partial ligand radical character. This work was published as:

Corona T., Draksharapu A., Padamati S. K., Gamba I., Martin-Diaconescu V., Acuña-Parés F., Browne W. R., Company A., **J. Am. Chem. Soc.** 2016 **138**(39), 12987-12996