



Manipulating the ferryl tilt in a non-heme oxoiron(IV) complex that makes the complex a better oxidant



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Oxoiron(IV) complexes are often thought to be intermediates in mechanistic cycles of many enzymes, including the non-heme iron oxygenases. Their reactivity varies depending on the molecular geometry which can be altered by substituting ligands attached to the core of the complex. This user collaboration explored chemical properties of a series of oxoiron(IV) complexes differing by modifications at the sites shown in magenta in Fig. 1, some of which affected the angle of the ferryl unit $[\text{Fe}=\text{O}]^{2+}$. *This ferryl tilt changed the spectroscopic and magnetic properties of the complex, and most importantly, increased the chemical reactivity of the complex with oxygen.*

Experiments at the MagLab involved High-Frequency and High-Field Electron Paramagnetic Resonance (HF-EPR) as well as Far-Infrared Magnetic Spectroscopy (FIRMS) (Fig. 2). These experiments measured parameters of the spin Hamiltonian describing the ground $S = 1$ spin state of the complexes.

Magnetic properties of the reported series of oxoiron(IV) complexes were linked to their geometric and electronic structure, as well as their catalytic activity towards C-H bond activation. Such studies will allow a better understanding of catalytic mechanisms of these complexes and potentially develop useful synthetic catalysts for many chemical reactions.

Facilities/instrumentation: EMR Facility (15/17T SC magnet and spectrometer) and DC Facility (SCM3 and FTIR spectrometer)

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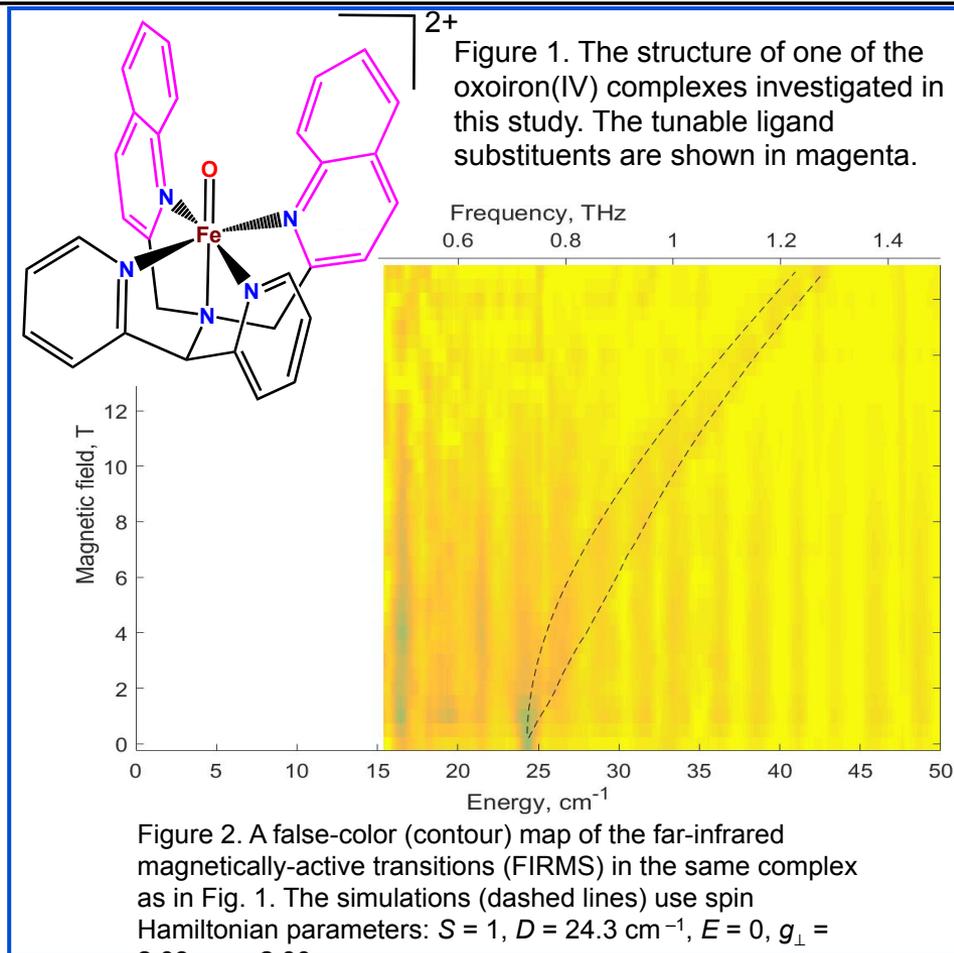


Figure 2. A false-color (contour) map of the far-infrared magnetically-active transitions (FIRMS) in the same complex as in Fig. 1. The simulations (dashed lines) use spin Hamiltonian parameters: $S = 1$, $D = 24.3 \text{ cm}^{-1}$, $E = 0$, $g_{\parallel} = 2.08$, $g_{\perp} = 2.00$.