OXYGEN ACTIVATION AT NONHEME IRON.
NEW FEATURES OF THE OXOIRON(IV) LANDSCAPE

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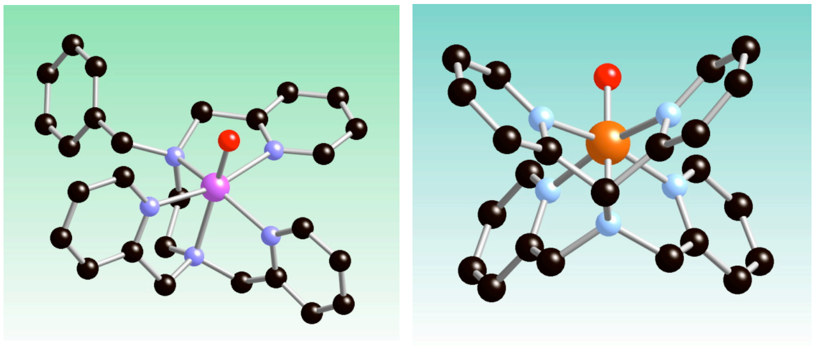
The mechanisms of dioxygen activation at iron centers typically invoke the participation of iron(IV)-oxo species as oxidant. While ample evidence can be found for such intermediates in heme systems, experimental support for corresponding nonheme intermediates is less plentiful. For example, high-valent species have only been observed for three nonheme enzymes, namely methane monooxygenase, ribonucleotide reductase, and the α-ketoglutarate-dependent TauD. In our biomimetic efforts, we have obtained the first examples of well characterized synthetic nonheme oxoiron(IV) species, both mononuclear and dinuclear, from the reactions of iron(II) or iron(III) precursors with peroxides and other oxidants. The exploration of this fascinating oxoiron(IV) reaction landscape has uncovered unexpected features that appear at first glance to be counterintuitive. How ligand environment and topology, as well as metal nuclearity, affect the stability of the oxoiron(IV) center and its reactivity towards hydrocarbon substrates will be discussed.



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