

{FeNO}⁷ Complexes of Mononuclear Non-Heme Fe Enzymes: Exploring Reaction Pathways in α KG-Dependent and Related Enzymes

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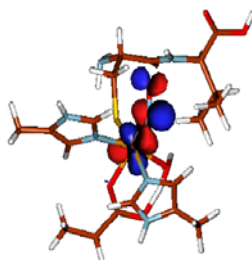
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Nitric oxide reacts with the ferrous site of many mononuclear non-heme iron enzymes to form a stable, reversible analog of possible iron-oxygen intermediates in catalysis. Through spectroscopic methods and Density Functional Theory studies of model complexes, the electronic structure of the {FeNO}⁷ unit has been well defined for a set of redox innocent ligands.[1,2]

During catalysis, α -ketoglutarate (α KG)-dependent enzymes bind the α KG co-factor and subsequent decarboxylation of this co-factor supplies two electrons to the active site. Other α KG-related enzymes including Isopenicillin N-synthase (IPNS) bind other redox active substrates that contribute to reactivity.

Stable enzyme-substrate-NO (ES-NO) complexes of α KG-dependent and related enzymes have been prepared. Through spectroscopic methods and Density Functional Theory studies, the electronic structures of these ES-NO complexes have been defined. We contrast the electronic structures of these complexes to that of previously studied model complexes to elucidate the contributions of the redox active substrates to the reaction pathways of these enzymes.



IPNS-ACV-NO Complex

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