Synthesis and Characterization of a Novel DihydroxamatoDinitrosylIron(II) Complex: A Model for NO reduction to N_2O by Ferrioxamine B

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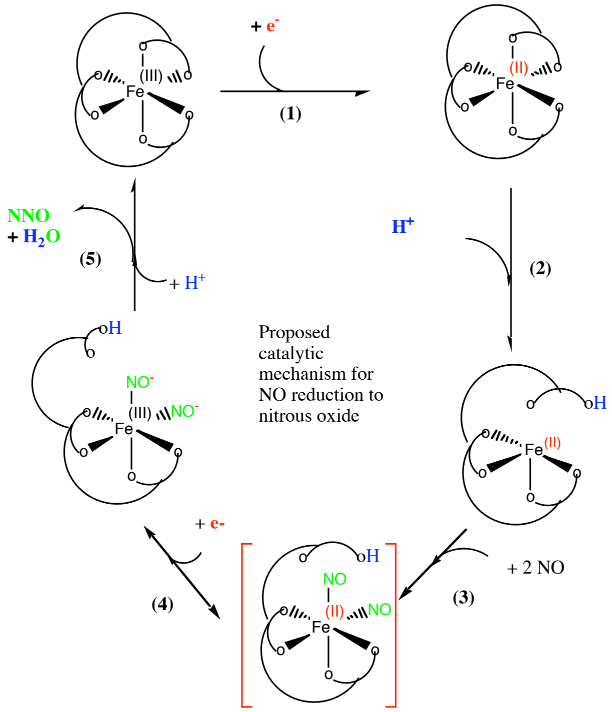
The siderophore complex ferrioxamine B catalyzes the reduction of nitric oxide to nitrous oxide in a reaction that has been shown to have both biomedical and environmental applications. A mechanism has been proposed which requires the formation of a ferrous dinitrosyl species with one of ferrioxamine B's three hydroxamate arms detached from the metal. In order to model this intermediate species, we have synthesized novel nitrosyldihydroxamatoferrous complexes, $FeL(NO)_x$, using simple dihydroxamic acids. These complexes have been characterized by elemental analysis, MS, IR, and UV-vis. Magnetic studies, including EPR and magnetic susceptibility, have been performed to characterize the electronic distribution in the ground state. Ab initio calculations indicate that the complex should favor a formal L(NO)Fe(III)(NO-) state with the complex stabilized by the shifting of electron density from the ferrous center onto *one* of the nitrosyl ligands. This redistribution of charge accounts for the ability of the proposed intermediate to form the N-N bond in N_2O in situ, as well as for the stabilization of a ferrous species with four oxygenic ligands. In the case of the ferrioxamine B complex, the driving force to reattach the third hydroxamate arm to the "ferric" iron, drives ejection of the reduced substrate (in the form of N_2O) and leads to recovery of the catalyst. Reduction of the model complex in aqueous solution yields stoichimetric quantities of N_2O. This



Proposed catalytic mechanism for NO reduction to nitrous oxide complex may also serve as a model for N_2O formation from NO at the non-heme iron site in NO reductase.