Synthesis and Characterization of a Novel DihydroxamatoDinitrosylIron(II) Complex: A Model for NO reduction to N₂O 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 nitrosydihydroxamatoferrous 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 N₂O 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 N₂O) and leads to recovery of the catalyst. Reduction of the model complex in aqueous solution yields stoichiometric quantities of N₂O. This
complex may also serve as a model for \( \text{N}_2\text{O} \) formation from NO at the non-heme iron site in NO reductase.