An Iron-Based Molecular Redox Switch as a Model for Iron Release from Enterobactin via the Salicylate Binding Mode

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The iron release mechanism from protonated ferric enterobactin [FeIII(enterobactinH3)] via the salicylate binding mode was probed. For this purpose, a tripodal dodecadentate ligand incorporating three salicylamide (OO) and three bipyridine (NN) binding sites was synthesized as well as iron complexes thereof. It was shown that a ferric ion coordinates selectively to the hard salicylamides and a ferrous ion binds to the softer bipyridines. Upon reduction or oxidation, the iron translocates reversibly and intramolecularly from one site to the other, thus displaying switchlike properties. Both states were characterized by cyclic voltammetry and visible and Mössbauer spectroscopy. The Mössbauer spectrum for the ferric complex is fully consistent with that obtained by Pecoraro et al. upon lowering the pH of [FeIII(enterobactin)]3- solutions (Pecoraro, V. L., et al. J. Am. Chem. Soc. 1983, 105, 4617), thus supporting the alternative iron release mechanism from enterobactin via the salicylate binding mode.
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