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Abstract

**Biomimetic Models of the Active Site of the Metalloenzyme
Nitrile Hydratase**

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An Fe(III)-NO-bound model compound, $[\text{Fe(III)S}_2^{\text{Me}_2}\text{N}_3(\text{Pr,Pr})(\text{NO})]\text{PF}_6$ (**1-NO**), is prepared. Its electronic properties are nearly identical to those of the active site in NO-inactivated NHase. Therefore, the assignment of the active site in NO-inactivated NHase as being $\{\text{FeNO}\}^6$ is supported. The stability of **1-NO** demonstrates that the ‘claw’ structure observed in NHase is not necessary to stabilize an Fe(III)-NO species.

To examine how small structural changes influence the reactivity of metal complexes, a series of related Fe(III) thiolate complexes was synthesized and characterized. A hexacoordinated Fe(III) complex containing an η^2 -coordinated persulfide is described, $[\text{Fe(III)}(\text{S}_2^{\text{Me}_2}\text{N}_3(\text{Et,Pr}))\text{-S}^{\text{pers}}]\text{PF}_6$ (**4**). It is the first structurally characterized, first row transition metal- η^2 -persulfide complex. This complex is a model for the possible interaction between cysteine persulfide (thiocysteine, cysteine perthiolate) and Fe(III) in biological systems. The extra persulfide sulfur can be removed to afford a pentacoordinated compound, $[\text{Fe(III)S}_2^{\text{Me}_2}\text{N}_3(\text{Et,Pr})]\text{PF}_6$ (**5**), which possesses a more open binding site than the

previously reported, pentacoordinated model compound $[\text{Fe(III)S}_2^{\text{Me}_2}\text{N}_3(\text{Pr,Pr})]\text{PF}_6$ (**1**). A comparison of the reaction of **1** and **5** with azide provides a model system for the concept of entatic state.

Further, the Fe(III) coordination chemistry of N,N'-1,2-ethanediylbis[2-mercapto-2-methyl-propanamide] was investigated. Thereby, two compounds, $(\text{NMe}_4)_2[(\text{Fe(III)S}_2^{\text{Me}_2}\text{N}_2^{\text{amide}}(\text{Et}))_2]$ (**6**) and $(\text{NMe}_4)[\text{Fe(III)S}_2^{\text{Me}_2}\text{N}_2^{\text{amide}}(\text{Et})(\text{Py})]$ (**7**), were isolated that contain deprotonated carboxamide nitrogens coordinated to Fe(III). The deprotonated carboxamide nitrogens provide significant stabilization to the + 3 oxidation state of the Fe(III) ion, as indicated by the reduction potential. A comparison of pentacoordinated, carboxamide nitrogen-coordinated **7** with another pentacoordinated, imine nitrogen-coordinated model compound provides evidence that an imine group is a valid structural and electronic model for a carboxamide.

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