The Mixed-valent $\{Fe^{IV}(\mu\text{-}O)(\mu\text{-carboxylato})_2Fe^{III}\}^{3+}$ Core: Structure and Reactivity

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In 1983 – exactly 20 years ago – two groups independently published the synthesis, structures and spectroscopic features of two non-heme model complexes containing the (μ-oxo)bis(μ-carboxylato)diiron(III) core.[1,2] We have now discovered that the compounds undergo a reversible one-electron oxidation yielding the mixed-valent $\{Fe^{IV}(\mu\text{-}O)(\mu\text{-carboxylato})_2Fe^{III}\}^{3+}$ core with either an $S_t=3/2$ or an $S_t=1/2$ ground state, which are attained via intramolecular antiferromagnetic coupling of a low spin ($S_{Fe}=1$) or high spin ($S_{Fe}=2$) Fe(IV) ion with a high spin ferric ion ($S_{Fe}=5/2$), respectively. Spectroscopic features (UV-vis, EPR, Mössbauer) of this class II core are discussed as well as DFT calculations. The reactivity of this core has been examined and hydrogen abstraction reactions from weak C-H bonds occur in solution.

1) W.H. Armstrong, S.J. Lippard J. Am. Chem. Soc. (1983) 105, 4837.
2) K. Wieghardt, K. Pohl, W. Gebert Angew. Chem., Int. Ed. Engl. (1983) 22, 727.

Intracellular Coordination Chemistry of Zinc Receptors in Metal Trafficking and Zn(II) Sensing

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Zinc is frequently referred to as a trace element in biology; however this designation is misleading: Whether we consider the zinc quota for bacteria such as *E.coli*, yeast or mammalian cells, total zinc concentration falls in a narrow range centered around 0.1 millimolar. Clearly zinc is abundant but how is its speciation controlled in the cell? How much of this zinc is bound by biopolymers and how much is available in the putative 'free zinc pool'? In the recent calibration of two zinc-sensing metalloregulatory proteins, factors which control metal homeostasis genes in response to metal concentration changes, it has been proposed that in *E.coli*, $[Zn(II)]_{free}$ is optimal in femtomolar range (Outten and O'Halloran, Science, 292, 2488, 2001). This is 6 orders of magnitude less than one free zinc ion per cell, consistent with an extraordinary chelation capacity for the intracellular milieu. We propose that availability of free Zn(II) ions in the cytoplasm is significantly limited.

How then does the correct metal find the correct site within the cell? In the case of copper, this apparently dilemma is resolved by metallochaperones, factors that escort the metal and control the kinetics of metal ion transfer reactions. Unfortunately similar factors are not yet known for zinc. This talk will address the cytoplasmic chemistry of the cytoplasmic N-terminal domain of ZntA. This domain exhibits a variation on the structural scaffold of the copper chaperone Atx1, and the Menkes disease proteins, a variation that allows ZntA to mediate Zn(II) trafficking hemistry. The function and coordination chemistry of this domain can be contrasted with the recent structural characterization of the zinc-binding domain of the ZntR metalloregulatory protein. The spectroscopy, energetics and structure of this metal-responsive switch provide new insights into how the cell monitors changes in zinc chemistry. Finally, to test emerging models for the zinc chemistry of the cell, a family of new fluorescent zinc probes will be reported. These fluorescent compounds can permiate the cell wall and are being used to delineate cytoplasmic and vesicular zinc chemistry in eukaryotic single cell organisms as well as neuronal tissues.