Bivalent and Trivalent Iron Complexes of varying Nuclearity with Pyridine/Pyrazine Amide Ligands. Inorganic and Bioinorganic Perspectives

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There has been continued interest in the design of new amide ligands to develop their coordination chemistry in the deprotonated form toward Fe(II)/Fe(III). The identification of deprotonated carboxamido N coordination in (i) anti-tumor drug bleomycins, (ii) iron centers in the P cluster of nitrogenase, and (iii) nitrile hydratases has raised the more interest in the area of bio-inorganic model studies. Interestingly, the number of Fe(III) complexes with coordinated carboxamido nitrogens is steadily increasing. Quite in contrast, only a few examples are known in which coordination of deprotonated carboxamido nitrogens to Fe(II) centers has been authenticated by X-ray crystallography. To enhance stability we decided to provide thioether (a weak σ-donor-cum-π-acceptor) coordination to such Fe(II) environment. We have synthesized and characterized (magnetic, spectroscopic, and redox properties) of a family of Fe(II)/Fe(III) complexes of hexadentate pyridine amide ligands. Structural characterization of Fe(II) complexes provides the first measure of the Fe^{II}-S(thioether) bond in deprotonated pyridyl/pyrazine amide coordination environment. This work provides an opportunity for comparing the structural and redox properties of pseudooctahedral Fe(II)/Fe(III) complexes having MN_2(pyridine/pyrazine)N'_2(amide)S_2(thioether) coordination with that of the corresponding MN_2(pyridine)N'_2(amide)S_2(thiolate) coordination environment.

Oxo-bridged diiron(III) complexes find its importance both from coordination chemistry and bioinorganic chemistry. In fact, synthesis of soluble iron clusters with oxo-/hydroxo- bridges is very challenging, given the propensity of iron(III) for hydrolytic polymerization. Using a bis-(pyridine amide) ligand we have synthesized and characterized (structure, magnetism, and Mössbauer) a soluble form of tetra-iron(III) core $\{Fe^{III}_4(OH)_2(OHO)\}^{7+}$, having biological relevance to ferritin core formation, supported by pyridine N and amide O terminal coordination.

In this presentation, the results from our laboratory on these systems will be highlighted.