Lessons from Nature: Utilizing Hydrogen Bonds to Regulate Metal Mediated Dioxygen Activation

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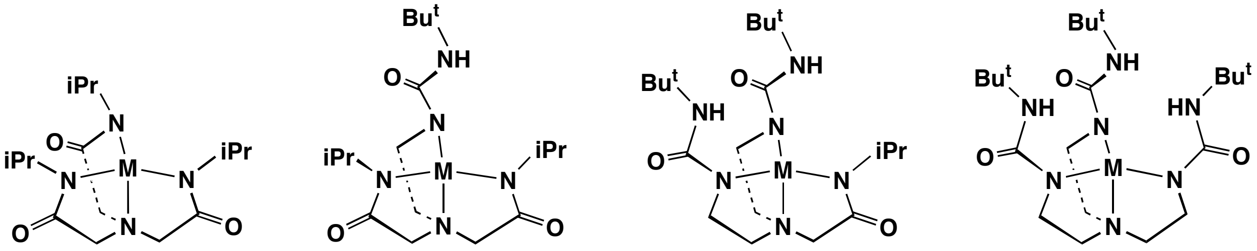
Spectroscopic and structural results on metalloproteins show that non-covalent interactions within the secondary coordination sphere influences the function of active-site metal ions. Hydrogen bonds (H-bonds) are the most common interactions and have essential regulatory roles in a range of proteins, including those whose function is the binding and activation of dioxygen. Duplicating these secondary sphere interactions in synthetic systems has proven difficult and contributes to the scarcity of functional mimics for metalloproteins. We have introduced systems that utilize urea groups to both bind metal ions and provide H-bond donors to other coordinated ligands. For instance, we have used a urea-based tripodal ligand to isolate monomeric Fe(III) and Mn(III) complexes with terminal oxo and hydroxo ligands derived from the activation of dioxygen. Each terminal ligand is surround by a network of three intramolecular H-bonds. To further examine the effects of H-bond networks, we have designed and prepared series of complexes having variable H-bond networks (Figure 1). The complexes contain hybrid urea/amide ligands that produce complexes with similar primary coordination spheres but differing number of H-bond donors within the secondary coordination spheres of coordinatively unsaturated metal ions.



[M**0**] [MH**1**] [MH$_2$**2**] [MH$_3$**3**]

Figure 1. Complexes with varied H-bond networks.

This presentation will describe the preparation of these complexes, their structural and physical properties, and their reactivity with dioxygen.