

Control of Metal-Ion Coordination through Outer-Sphere Ligand Interactions

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A biomimetic approach to the problem of anion monitoring and remediation using inner-sphere and outer-sphere coordination is presented. In Nature, recognition of substrate and control of metal-ion reactivity is accomplished through inner- and outer-sphere coordination chemistry. Inner-sphere coordination is provided through the few amino acids and cofactors capable of binding a metal and outer-sphere influences are a result of protein secondary and tertiary structure. We have designed novel supramolecular hosts based on cyclodextrins as surrogates for protein architecture and function. These hosts are tailored for a variety of substrates including simple anions and those with more complex structures. A prototypical guest is uranyl carbonate, which is an important environmental pollutant, and a highly mobile form of uranium. Guest recognition is tailored to the unique geometric features of the uranyl complex, and modulated by topography, hydrogen bonding and coulombic interactions. The synthesis, structures, and solution thermodynamics of these ligands will be described.