

HIGH VALENT URANIUM DIOXO AND IMIDO COMPLEXES: SYNTHESIS AND STRUCTURE

Anthony E. Vaughn

Dr. Paul B. Duval, Dissertation Advisor

ABSTRACT

Early actinide elements have attracted considerable attention in recent years due to the need for rigorous advancements in spent nuclear fuel recycling and remediation technologies, and for their emerging versatility in organometallic chemistry. Whereas high oxidation state ions dominate environmental speciation, the corresponding high-valent organometallics are rare. These hexa- and pentavalent ions are often stabilized by the isoelectronic oxo or imido ligands, which result in robust molecular properties due to 5f/6d orbital involvement in multiple covalent bonding. The research discussed in this dissertation surveys the synthesis, isolation, and molecular and electronic structural characterization of uranyl(VI) and uranium(V)-imide complexes, and uncovers the influences imparted by a variety of functional ligand designs. In the opening report, salicylidene derived Schiff base chelates adapt to equatorial coordination and control uranyl(VI) photo- and electrochemical activity. In the second study, a ferrocenylcarboxylate ligand undergoes a transformation that renders an unprecedented bent uranyl(VI) moiety supported in a reversible coordination polymer. The final segment focuses on the rare uranium(V) oxidation state supported by pentamethylcyclopentadienyl and imido ancillary ligands in mono- and bimetallic complexes geared to elucidate the effects of ligand substitution and metal-metal communication on the 5f¹ electronic configuration. Future directions and applications for each area are summarized.