Glenn T. Seaborg Center Seminar

Redox chemistry of uranium in controlled conditions: a route to molecular clusters and rare oxidation states

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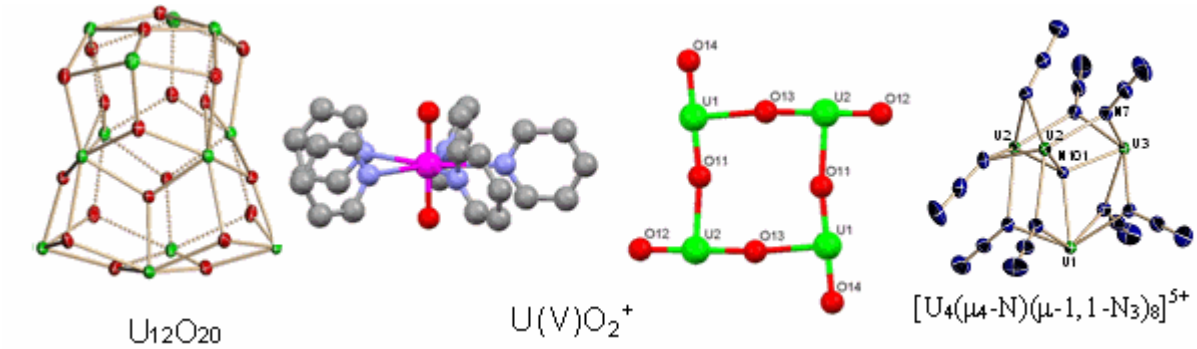
Wednesday, August 12, 2009
4:00 - 5:00 pm
Building 70A, Room 3377

The redox chemistry of actinides plays a crucial role in many aspects of nuclear technology including nuclear fuel reprocessing and safe disposal and in determining the mobility of actinides in the environment. Notably the disproportionation reaction and the hydrolysis are major aspects of actinide chemistry leading to complex systems in aqueous solutions. Accordingly we are interested in studying the redox reactivity of low-valent uranium compounds with different substrates including water, azides and oxygen in non-aqueous conditions. The use of controlled conditions allows the stabilization of the uranium in unusual oxidation states and the isolation of large polymetallic clusters.

Notably, the hydrolysis of trivalent uranium in non-aqueous conditions leads to mixed valence (U(IV)/U(V)) discrete clusters with the U_6O_8 core and with the unprecedented $U_{12}O_{20}$ core. The oxidation reaction of trivalent uranium with uranium tetraazide can promote the assembly of polymetallic azido/nitrido uranium cluster containing an interstitial nitride. Moreover, the oxidation of trivalent uranium in non-aqueous conditions led to the development of a unique and facile synthetic method to produce pure pentavalent uranyl iodide under mild conditions. The isolation of the UO_2^+ species is particularly challenging due to its high tendency to disproportionate yielding An(IV) and AnO_2^{2+}. We will present how taking advantage of the starting product $[UO_2(Py)_5]^+$ and by a careful ligand tuning we have been able to shed light on the mechanism of disproportionation of pentavalent uranyl and to isolate probable polymetallic intermediates presenting cation-cation interaction between UO_2^+ groups .



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