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Polyoxometalates for Radioactive Waste Treatment

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Research Objective

This research is directed towards the use of polyoxoanions of the early transition metals (primarily tungsten) as possible sequestrants and storage matrices for lanthanide, actinide, and technetium species. The latter substances are important radioactive components of tank wastes from spent commercial nuclear fuel, but are present in low proportion by mass. Technetium is a particularly troublesome component because it is highly mobile in groundwater and is volatilized in vitrification processes currently under examination for long-term storage. Scientific goals: synthesis and characterization of new and selective polyoxotungstate complexes of Ln^{3+}, An^{4+}, UO_2^{2+}; exploration of stable polyoxoanions containing Tc (using, in the first instance, Re as a nonradioactive surrogate); thermal conversion of polytungstate complexes to tungsten bronze materials for their evaluation as inert storage matrices.

Research Progress and Implications

This report summarizes the results after 20 months of a 3-year project.

1. *Selective sequestration of Ln^{3+} and U^{4+} by $[NaP_5W_{30}O_{110}]^{14-}$ (I).* Replacement of the central sodium cation in **I** (a doughnut-shaped anion with approximate D_{5h} symmetry) by Ln^{3+} and U^{4+}under hydrothermal conditions has been conditions has been shown to be highly selective for the multivalent cations in neutral or weakly acidic solutions. For example, Nd^{3+} is incorporated with ~60% yield in the presence of a 200-fold molar excess of Na^+, which is a major component of tank wastes. Other major components, such as Fe^{3+} and Al^{3+} are not complexed by **I** and do not interfere with lanthanide incorporation. Structural studies of the complexes with central Na^+, Ca^{2+}, Eu^{3+}, and U^{4+} reveal an axially-coordinated water molecule, the protons of which undergo very slow exchange with solvent water in neutral solution. All three isotopomers (with coordinated HOH, HOD, and DOD) are distinguishable by P-nmr of the paramagnetic complexes.
2. *Diastereomers of 1:2 complexes of An^{4+} with ÿ l -$[P_2W_{17}O_{61}]^{10-}$(**II**).* Anion **II** has a structure of C_1 symmetry and in principle should yield chiral syn and anti isomers of $[An(P_2W_{17}O_{61})_2]^{16-}$, based on a nominal square antiprism coordination polyhedron for An^{4+}. P-nmr spectra of the U^{4+} and Th^{4+}complexes display multiple sets of resonances consistent with the presence of several diastereomers. Single crystal X-ray investigation of U and Th complexes show an anti conformation for the former and a syn conformation for the latter.
3. *New giant heteropolytungstate complexes of Ln^{3+}.* Several new complexes incorporating the tungstoarsenate(III) building block, $[AsW^9O^{33}]^{9-}$ (**III**), are formed in good yields in neutral aqueous solution from appropriate mixtures of the Ln^{3+}, AsO_2ÿ, and WO_4^{2-}. In addition to structurally-characterized As $^3Ce2W_{29}$ and $As_5Ce_4W^{39}$ polyoxoanions, the new species include the largest known discrete polytungstate anions, $[As_{12}Ln_{16}(H_2O)_{36}W_{184}O_{524}]^{76-}$,(**IV**); Ln = La, Ce, Nd, Sm. The structure of **IV** is disk-shaped with a diameter of 4 nm, and the anion has a molar mass of ca 40,000. According to W-NMR the anion structure is stable in aqueous solution, and the ammonium salts of these anions are recrystallizable in the presence of Na+. Among other large complexes are species with $[As_4W_{40}O_{140}]^{28-}$ building blocks.
4. *Heteropolytungstates containing UO_2^{2+}.* The first examples of polytungstate complexes which incorporate the uranyl cation have been prepared and characterized. In every case the uranium atom adopts a pentagonal bipyramidal coordination geometry. Complexes incorporating anion **III** as building blocks include [(UO2)3(H2O)6As3W30O105]15- with C3v symmetry. Other species include novel cation-dependent structures based on the two building blocks

[PW9O34]9- or [SiW9O34]10-, and a W40 structure based on four ÿ-[SiW10O36]8- units. All new complexes are formed in good yield from neutral or weakly acidic solutions.

5. *Thermal conversions of complexes*. Based upon TGA data, the ammonium-sodium [(NH4)70Na6] salt of **IV** was heated in hydrogen atmosphere to 550?C followed by a 3-h isothermal treatment in argon at 920°. The product was the cubic bronze Na0.04Ce0.108WO3 according to X-ray powder diffraction and elemental analysis. Formation of the cerium tungsten bronze has therefore occurred at a much lower temperature than has been previously reported. At somewhat lower temperatures, the hexagonal bronzes are generated
6. *Polyoxoanion complexes of Re (Tc).* Most attention has been focused on the tetravalent (d3) oxidation state of Re since this is known to yield inert octahedral complexes. Several heteropolyanions incorporating isoelectronic Mn4+ are well characterized, and the initial target species were the Anderson anions [ReM6O24]8- (M = Mo,W). It has proved difficult to identify these species, and we have recently moved to evaluate possible niobate complexes (analogues of [M(Nb6O19)2]12-, M = tetravalent Mn and Ni). Very recently we have obtained encouraging results from this approach.

Planned Activities

The synthesis/characterization phase of the lanthanide and actinide complexes (sections 1 - 4 above) is now virtually complete, and has been published or is in preparation for publication. Attention is now directed towards sub-projects 5 and 6 above.

TGA examination of the several tungstolanthanates described in section 3 indicates that they, like **IV**, should be convertible to bronzes at relatively low temperatures. The uranyl derivatives (section 4) will also be subjected to TGA and reductive thermal degradation to bronzes will be developed. Long term hydrolytic/oxidative stability of the bronzes will be explored.

Characterization of the recently discovered nioborhenate complexes (section 6) will assume high priority. These species are particularly attractive since they are stable in alkaline solutions - conditions which prevail in the Hanford tank wastes. Parallel synthetic and characterization procedures involving Tc are to be carried out in collaboration with Dr. Jeffrey Bryan at Oak Ridge National Laboratory.

Other Access To Information

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