Polyoxometalate Chemistry as a Route to Potential Waste Forms and for Immobilization of Technetium

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Introduction

Lanthanides (Ln), actinides (An), and technetium (Tc) are among the long-lived radioactive components of high level wastes in storage tanks at DOE sites such as Hanford. The efficient separation of these isotopes from a heterogeneous matrix (highly alkaline solution plus insoluble sludge) that contains high concentrations of sodium nitrate and a variety of other non-radioactive metal cations, presents a major challenge. Further problems arise with the design of appropriate waste forms for the separated materials. This is especially acute for technetium wastes, since oxidation to the highly soluble and mobile pertechnetate anion TcO_4^- occurs readily, a property that precludes high-temperature vitrification procedures that are contemplated for other radioactive materials.

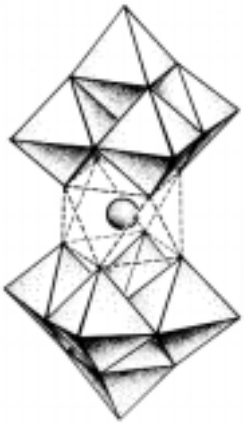
Inorganic polyoxometalate anions (Pope, M. T., *Heteropoly and Isopoly Oxometalates*, Springer Verlag, New York, 1983) are easily synthesized, are robust and radiation-resistant, and exhibit properties that inspire new ways of attacking problems of separation and storage of high-level Ln, An, and Tc wastes.

Part A: Incorporation of lanthanides and actinides into polyoxometalate anions. Facile thermal conversion to tungsten bronzes.

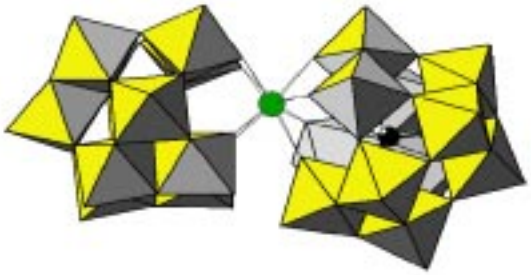
Trivalent lanthanide and tetravalent actinide cations have similar radii and coordination requirements. Formation of polytungstate derivatives of Ln/An occurs spontaneously under appropriate pH conditions in aqueous solution.

Examples include

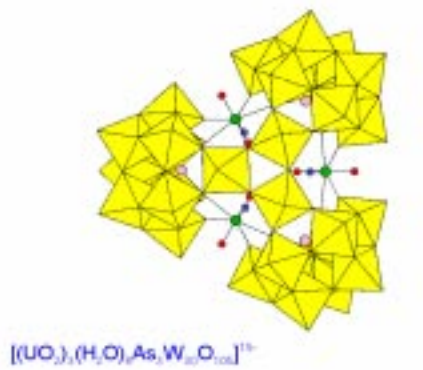
a $Ce^{3+} + 10\ WO_4^{2-} + 8\ H^+ \rightarrow [Ce(W_5O_{18})_2]^{9-}$ (**1**) + $4H_2O$



b $Th^{4+} + 2\ PW_{11}O_{39}^{7-} \rightarrow [Th(PW_{11}O_{39})_2]^{10-}$ (**2**)

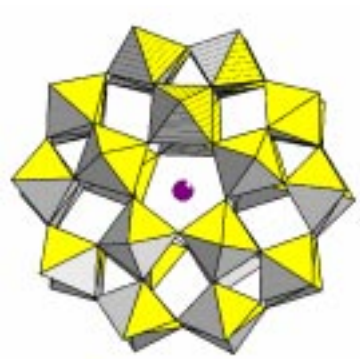


c UO_2^{2+}, $[As_4W_{40}O_{140}]^{28-}$ → $[(UO_2)_3(H_2O)_6(As_3W_{30}O_{105}]^{15-}$ (**3**)



d U^{4+} + $[Na(H_2O)P_5W_{30}O_{110}]^{14-}$ → $[U(H_2O)P_5W_{30}O_{110}]^{12-}$ (**4**) + Na^+

"Preyssler" anion, M = Na^+



$[M^{n+}P_5W_{30}O_{110}]^{(15-n)-}$

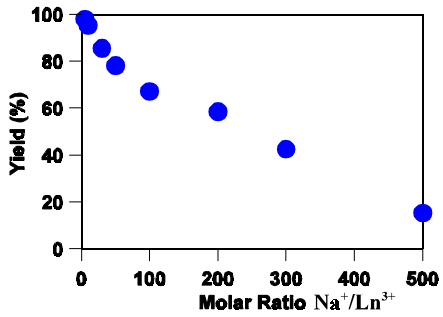


Figure 1

Reaction **d** is *highly selective* for Ln^{3+} and An^{4+} and proceeds with high yield even in the presence of a large excess of Na^+ (*vide* composition of Hanford tank wastes). Figure 1 shows the formation of the Nd^{3+} derivative in the presence of up to a 500-fold excess of Na^+.

Thermal treatment of the ammonium salts of the lanthanide/actinide-containing polytungstates leads to the clean formation of the inert cubic tungsten bronzes. [Wassermann, K.; Pope, M.T.; Salmen, M.; Dann, J.N.; Lunk, H.-J., *J.Solid State Chem.*,**149**, 378-383 (2000)]

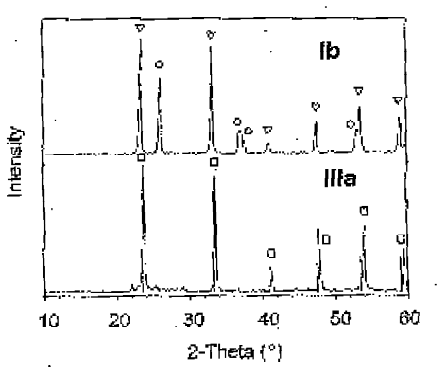


Figure 2. Examples of powder diffractograms of thermally-treated ammonium salts of heteropolytungstates.
Ib: $Ce_{0.17}WO_3$ (triangles) with traces of WO_2 (open circles);
IIIa: $U_{0.1}WO_3$ (squares) with reference diffractogram of $Na_{0.39}WO_3$ (sticks).

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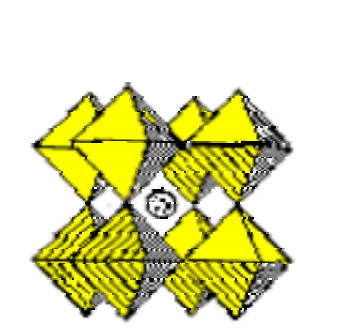
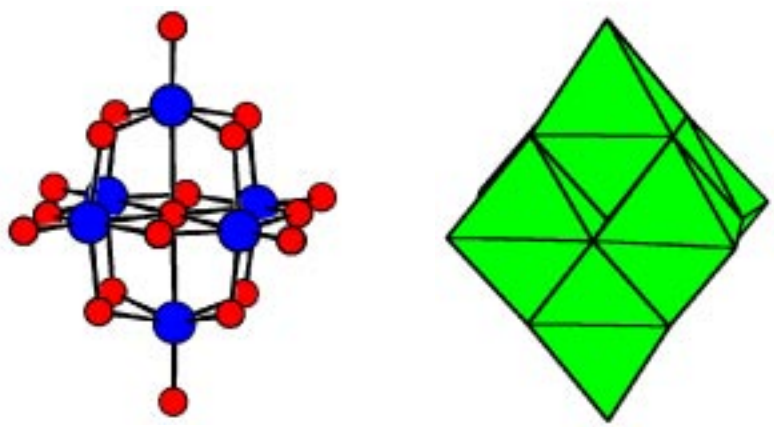


Cubic M_xWO_3 structure

Part B: Robust, alkali-stable hexaniobate complexes of manganese(I), and rhenium(I). Relevance for separation and immobilization of technetium.

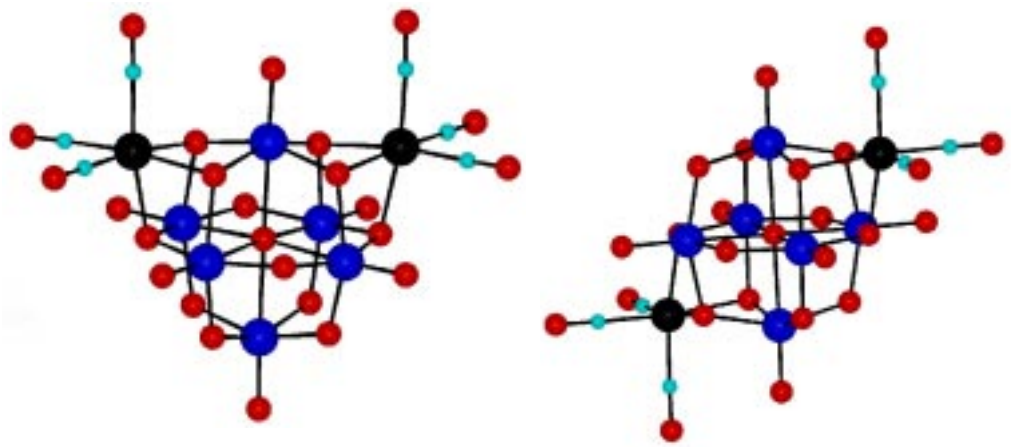
The hexaniobate anion, $[Nb_6O_{19}]^{8-}$, (**5**), is an example of a polyoxometalate anion that is hydrolytically stable in alkaline media. A solution of the potassium salt in water has a pH of *ca* 10.



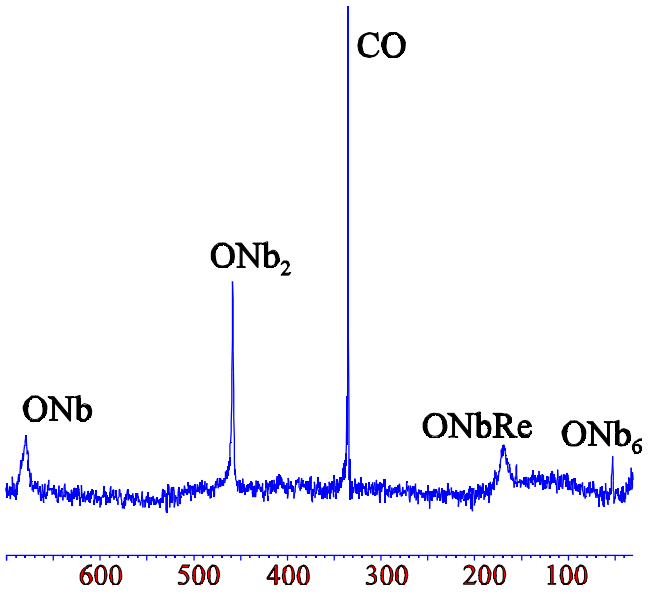
Structure of **5** in ball-and-stick and polyhedral representations

Aqueous solutions containing **5** react with manganese and rhenium carbonyl complexes ($[Mn(CO)_3(CH_3CN)_3]^+$, $Re(CO)_5Br$,...) under reflux or hydrothermal conditions to yield robust complexes in which one or two $M(CO)_3^+$ groups are attached to bridging oxygen atoms on the surface of **5**.

Two isomers (cis and trans) of the 1:2 complexes have been isolated and characterized.



cis and *trans* isomers of $[Nb_6O_{19}\{Re(CO)_3\}_2]^{6-}$



Natural abundance ^{17}O NMR spectrum of *trans*-$[Nb_6O_{19}\{Re(CO)_3\}_2]^{6-}$

The new complexes have high thermal, hydrolytic, and redox stabilities. In the solid state no decomposition occurs until CO is lost at 400ºC.

Numerous routes exist for the conversion of the pertechnetate anion to water- and redox-stable $[Tc(CO)_3(H_2O)_3]^+$. There is little doubt that Tc analogues of the Re and Mn hexaniobate complexes can be readily prepared, and that other nucleophilic polyoxometalates can be employed. We are currently investigating this chemistry as a route to separation and immobilization of Tc in waste solutions.

Besserguenev, A.; Pope, M.T., Manuscript in preparation.

Pope, M.T.; Besserguenev, A., Provisional Patent Application, 02/25/2000