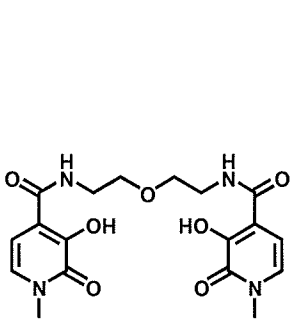
Sequestration of Plutonium in the Body and the Environment

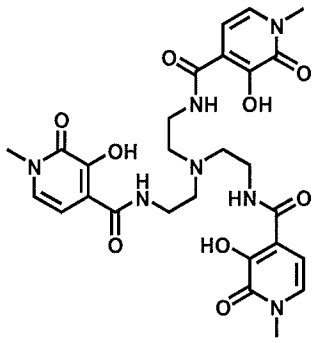
C. Matthew Whaley Inorganic Literature Seminar September 20, 2004

The sequestration of plutonium is an issue of continuing interest, especially for applications in the areas of medicine and nuclear waste management. Each year, the use of nuclear reactions as a source of power generates an estimated 9,000–10,000 tons of radioactive spent fuel, containing approximate 75 tons of plutonium.[1] The processing of plutonium for nuclear weapons production has left behind an additional 345 million liters of high-level radioactive waste.[1] At certain sites, such as Hanford, WA, containment vessels have leaked, allowing high-level waste to enter the soil and contaminate the groundwater.[2] This raises the potential for human exposure to plutonium and other toxic radionuclides. Thus, there is a necessity for sequestering ligands for both biological decorporation and solvent extraction.

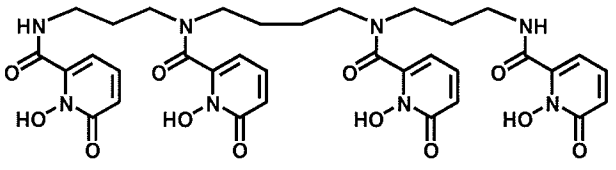
Plutonium(IV) is transported in the body in the same way as Fe(III).[3] Based on microbial siderophores, naturally-occurring Fe(III) chelates, these multi-dentate ligands feature catechoylamide (CAM), hydroxamate, and hydroxypyridinonate (HOPO) binding units. They have been synthesized and tested *in vitro* and *in vivo* for efficacy and toxicity. Ligands featuring these binding units have been synthesized and solution thermodynamic studies have shown that the ligands form extremely stable complexes. Assessment of efficacy and toxicity has been conducted through testing in mice. Of the ligands synthesized and tested, three HOPO ligands exceeded all others in amount of plutonium excreted: 5LIO(Me-3,2-HOPO), TREN(Me-3,2-HOPO), and 3,4,3-LI(1,2-HOPO) (Figure 1).[4,5,6]



A) 5LIO(Me-3,2-HOPO)



B) TREN(Me-3,2-HOPO)



C) 3,4,3-LI(1,2-HOPO)

Figure 1: A) Structure of 5LIO(Me-3,2-HOPO). B) Structure of TREN(Me-3,2-HOPO). C) Structure of 3,4,3-LI(1,2-HOPO).

In each case, the amount of plutonium excreted was in excess of that removed by chelation therapy with the FDA-approved therapeutic agent, calcium trisodium diethylenetriamine N,N,N′,N″,N″-pentaacetate (DTPA).[3] Experiments to determine the toxicity of these ligands have shown that 5LIO(Me-3,2-HOPO) and TREN(Me-3,2-HOPO) cause no deaths or tissue damage, while 3,4,3-LI(1,2-HOPO) caused some kidney damage that was completely reversed after 21 days.[7]

To prevent the most likely scenario for biological incorporation of plutonium through the spread of high level waste through the environment, improved remediation processes are needed that can more efficiently separate radionuclides from waste streams. Currently, the Plutonium Uranium Recovery by Extraction process (PUREX) uses tributylphosphate to separate plutonium and uranium from fission products in spent nuclear fuel. This process, however, requires several cycles to sufficiently extract the plutonium and uranium. New ligand designs could provide extraction agents that strongly bind to plutonium and allow for extraction in one cycle, reducing the amount of solvents used while concentrating the radioactive waste.

Neu and coworkers have applied a set of phosphinopyridine ligands, first synthesized by Paine, to the task of binding plutonium.[8] These ligands combine phosphine oxide and nitrogen oxide donor groups to bind to the highly Lewis acidic metal. Plutonium complexes with NOPO (2-[(diphenylphosphino)methyl]pyridine *N,P*-dioxide) and NOPOPO (2,6-bis[(diphenylphosphino)methyl]pyridine *N,P,P′*-trioxide) have been structurally characterized by x-ray crystallography as heteroleptic complexes with nitrate as co-ligands.[9,10,11] Preliminary solvent extraction studies of a NOPOPO complex of Th(IV), a model ion for Pu(IV), has shown that these complexes can be extracted from nitric acid with $CHCl_3$. Although this preliminary result shows promise for a new generation of ligands for solvent extraction of radionuclides, more work is needed to improve selectivity for plutonium over other, more abundant metal ions.

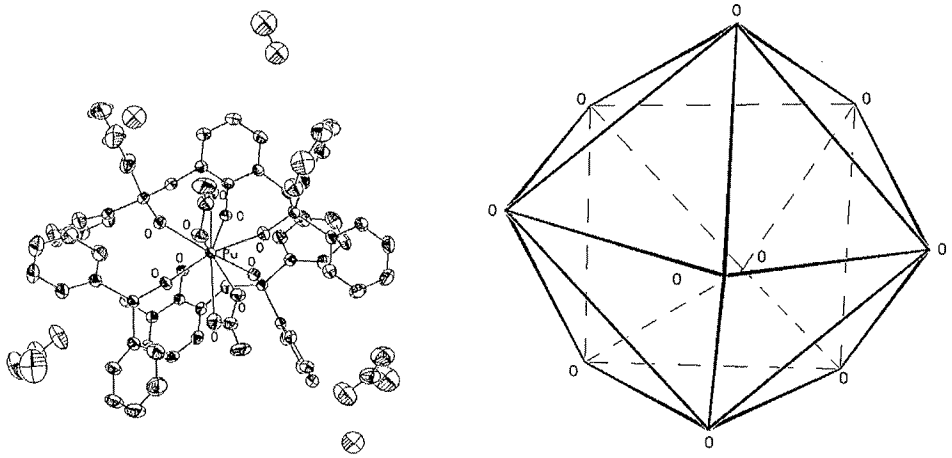


Figure 2: (Left) Thermal ellipsoid plot of $[Pu(NOPOPO)_2(NO_3)_2^{2+}][(NO_3)_2^{2-}] \bullet 1.5\ H_2O \bullet 0.5$ MeOH. (Right) Coordination sphere for $[Pu(NOPOPO)_2(NO_3)_2^{2+}][(NO_3)_2^{2-}] \bullet 1.5\ H_2O \bullet 0.5$ MeOH with phenyl rings and outer-sphere nitrates omitted for clarity.[8]

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