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Rational Design of Metal Ion Sequestering Agents

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Research Objective

This project addresses fundamental issues and requirements in developing hazardous metal ion separation technologies needed in the treatment and disposal of radioactive and chemical toxic waste. It encompasses the synthesis of new agents, followed by their characterization and evaluation, with the aim to optimize their metal ion sequestering properties for use in applied technologies. This research is focused on the following key areas: (i) basic design and synthesis of new metal ion specific sequestering ligands; (ii) structural and thermodynamic investigations of these ligands and their complexes formed with the targeted metal ions; and (iii) development of sequestering agents and their incorporation into systems designed to be prototypes of inexpensive and highly effective materials for hazardous metal ion decontamination. Basic studies of the sequestration of relevant toxic metals are required in order to develop processes that will treat effluents sufficiently well to allow direct release into the environment and minimize the production of secondary wastes.

Research Progress and Implications

This report summarizes work after 6 months of a 3-year project. Several previously synthesized ligands containing between one and four Me-3,2-hydroxypyridinone (HOPO) groups (Fig.1) were thermodynamically characterized using Ce(IV) as a model for Pu(IV) coordination.

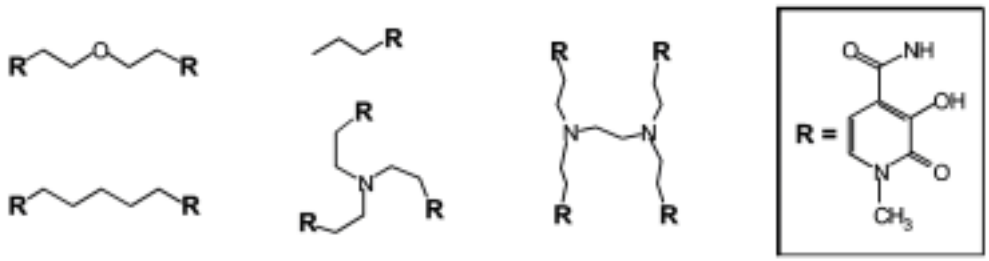

Figure 1. Structure of Me-3,2-HOPO amide ligands of various denticity.

The identical charges and nearly equal radii of Ce(IV) and Pu(IV) make the former ion an excellent model for the latter. Close parallels in the coordination and redox chemistry of these ions have been established previously. Ce(IV) offers a special advantage in modeling Pu(IV) complexation because of its electrochemistry which allows one to determine even very large formation constants for Ce(IV) complexes from those of the corresponding Ce(III) complexes and the redox potentials of the Ce(IV)/ Ce(III) pairs. Redox potentials were measured by both static methods (potentiometry) and kinetic methods (cyclic voltammetry and Osteryoung square wave voltammetry).

The stability constants for Ce(III) complexes were determined by either potentiometric or spectrophotometric titration. They are, to a good approximation, a linear function of the number of HOPO groups bound to the metal (the linear fit of log b versus the number of HOPO groups has a slope of 4.80 and an intercept of 1.33). Because of the much stronger coordination of Ce(IV) than Ce(III), only the overall stability constants for coordinatively saturated complexes of Ce(IV) (with 4 HOPO groups per metal ion) could be determined based on electrochemical methods. In all cases (with bi-, tetra-, hexa- and octadentate ligands), the formal potential for Ce(IV)/Ce(III) in such saturated complexes was approximately 1.6 V lower than the formal potential for the aqueous Ce^{4+}/Ce^{3+} pair (+1.7 V vs. NHE), meaning that the Ce(IV) complexes have stability constants approximately 27

orders of magnitude larger than those of the Ce(III) complexes. Since a typical value for a stability constant of a Ce(III) complex with 4 HOPO groups is 10^{20}, a typical one for complexes of Ce(IV) is 10^{47}. Calculations for Ce(IV) and the octadentate ligand (total metal concentration 10^{-6} M and total ligand concentration 10^{-5} M) lead to pM=46.0 at pH 7; 24.3 at pH 2 and 12.5 at pH 0. Given that similar numbers are expected for Pu(IV), these results imply that HOPO ligands are able to bind the metal strongly even at very low pH, and are therefore perfectly suited as extractants from acidic waste. As we have shown in a separate study, solid-supported ion exchange materials based on HOPO groups can extract Pu(IV) in up to 5 M HNO_3 with loading capacities of 70-90%.

Several complexes of Ce(IV) with the same ligands were synthesized from either organic solvents or water, and the structures of three of these complexes (with bidentate and tetradentate ligands) were determined by single crystal X-ray diffraction studies. In all these cases, a total of 8 oxygen atoms (2 from each HOPO group) were coordinated to the metal. Least-squares shape analysis of these complexes demonstrated that their coordination geometry may vary significantly (from nearly a trigonal dodecahedron to nearly a square antiprism) with subtle changes in the ligand backbone or when water was used instead of an organic solvent. The observed conformational flexibility implies that there are no rigorous steric requirements towards the ligand, and simple (bidentate) HOPO fragments attached to a flexible polymeric chain may be as affective as the octadentate ligand. This implication is corroborated by the similar formal potentials of all Ce(IV)/Ce(III) pairs (see preceding paragraph) and by tests of polystyrene-supported bidentate HOPO ligands with Pu(IV) conducted at LLNL.

Planned Activities

Part of our next efforts during this year will be directed towards the thermodynamic characterization of the extraction agents and polymer-based materials with HOPO ligands which have shown great promise as Pu(IV) sequestering agents (fast kinetics, stability in acidic and alkaline conditions, and high affinity for Pu(IV) in the presence of EDTA or Fe(III) in large excess). Another route of investigation will be the thermodynamic characterization of uranyl complexes of HOPO and catecholamide ligands, since the uranyl ion has very different coordination chemistry from that of Pu(IV). In the second year of this project, we plan to synthesize new liquid-liquid and polymer-supported extractants with improved properties and simplified preparation, based on our better understanding of their chemistry as a result of our studies.

Other Access To Information

Web page: **http://www.homestead.com/knr/HomePage.html**

Xu, J., Raymond, K.N., Durbin, P.W., Kullgren, B. *J. Med. Chem.*,1995, *38*, 2606.
Sofen, S.R., Cooper, S.R., Raymond, K.N., *Inorg. Chem.*,1979,*18*., 1611.
Kappel, M.J. *Ph.D. Thesis*, University of California, Berkeley, 1983.
Kappel, M.J.; Nitsche, H.; Raymond, K.N. *Inorg. Chem.*, 1984, *24*, 605.