

Project ID: **60370**

Project Title: **Rational Design of Metal Ion Sequestering Agents**

**Lead Principal Investigator:**

Dr. Kenneth N. Raymond  
Profesor  
Department of Chemistry  
Lawrence Berkeley National Laboratory  
One Cyclotron Road  
Berkeley, California 94720  
Telephone: 510-486-6145  
e-mail: [RAYMOND@GARNET.Berkeley.EDU](mailto:RAYMOND@GARNET.Berkeley.EDU)

**Co Principal Investigators:**

Jide Xu  
Staff Researcher  
Department of Chemistry  
University of California  
C/O Raymond Group  
Berkeley CA 94720  
USA  
Telephone: 510-642-2516  
e-mail: [jide@uclink2.berkeley.edu](mailto:jide@uclink2.berkeley.edu)

Christine Gramer  
Graduate Student  
same as above  
Telephone: same as above  
e-mail: [beene@uclink4.berkeley.edu](mailto:beene@uclink4.berkeley.edu)

## Research Objectives

This project addresses the fundamental issues and requirements for developing hazardous metal ion separation technologies applicable to the treatment and disposal of radioactive waste. Our research encompasses the following areas: the design and synthesis of metal ion specific sequestering ligands, structural and thermodynamic investigations of these ligand and the complexes formed with targeted metal ions, and the development and incorporation of these ligands into applied separation technologies as highly effective materials for hazardous metal ion decontamination.

## Research Progress and Implications

This report summarizes our advances over the last year investigating new catechol-based ligands for Pu(IV). The metal ions Fe(III), Ce(IV), and Th(IV) are convenient to use as Pu(IV) surrogates because they are all hard Lewis acids with similar charge-to-size ratios. Herein is described the synthesis, thermodynamic studies, and extractant properties of our current chelators.

The ligands currently under investigation, illustrated in Figure 1, are the 2,3-dihydroxyterephthalamides **1** (TAMs) and the 3,4-dihydroxysulfonamides **2** (SFAMs). The acidity of the catechol protons of PTAM **3** is correlated with a strong affinity for Fe(III).<sup>1</sup> The pM value<sup>2</sup> of 22.8 is higher than for any other bidentate ligand and the overall stability constant<sup>3</sup> of 43.1 is the second highest for any bidentate ligand with Fe(III). In addition, the two amides provide sites for functionalization to suit specific applications.

We have chosen to investigate sulfonamide derivatives as a new class of actinide chelators to take advantage of the excellent chelating properties for highly charged metals. The one bidentate ligand with a higher overall formation constants with Fe(III) is 4,5-dihydroxy-1,3-benzenedisulfonate **4**. The stability constant is 46.3 however the pM value of 20.7 is lower than the TAMs. We can also control the solubility properties through proper functionalization of the sulfonamides.

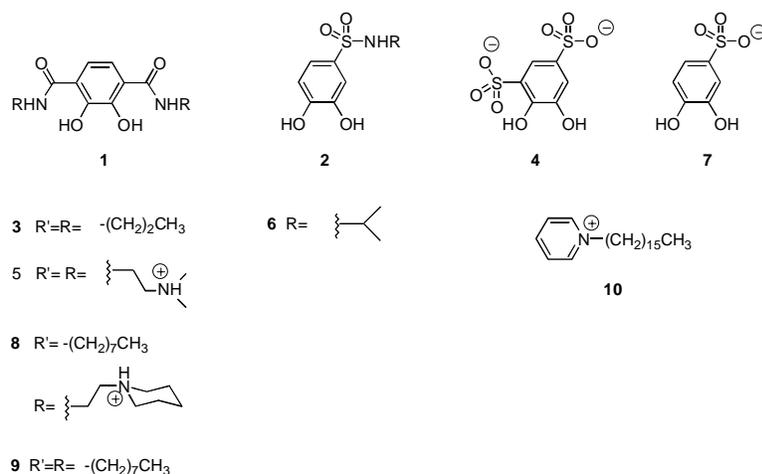


Figure 1. The structures of the catechol-based ligands discussed in this report.

**Ligand synthesis.** We have improved the synthesis of TAMs by developing a general procedure that avoids the protection and deprotection of the catechol oxygens. This has streamlined the synthesis by reducing the synthetic steps from six to two. This procedure has also been extended to the synthesis of unsymmetrically substituted amides. Perhaps more importantly, the use of hazardous and expensive reagents used to install and remove the methyl protecting groups is avoided.

For the sulfonamide catecholates, a 3-step synthesis was developed that installs a single sulfonamide in the 4-position of the catechol ring. A large number of bidentate ligands of this type have been synthesized, as well as tetra and hexa-dentate ligands. Progress has been made towards the synthesis of three other isomers: the 3-sulfonamide catecholate, the 3,5-disulfonamide catecholate (the sulfonamide of **4**), and the 3,6-sulfonamide catecholate (analogous to TAM).

**Solution Thermodynamic Measurements.** The protonation constants and Th(IV) and Fe(III) stability constants were determined for DMETAM **5** and 3,4-dihydroxy-benzene-*i*-propyl sulfonamide **6**.

These numbers are summarized in the table below and the constants for **3**, **4** and **7** are included for comparison.

	PTAM <b>3</b> <sup>1</sup>	DMETAM <b>5</b>	i-PrSFAM <b>6</b>	<b>4</b> <sup>4</sup>	<b>7</b> <sup>5</sup>
pKa1	6.0	5.4	7.6	8.3	8.4
pKa2	11.0	10.95	11.9	12.0	12.5
$\beta_{130} \text{FeL}_3$ <sup>3</sup>	43.1	45.68	43.3	46.3	40.1
pM <sup>2</sup>	22.8	25.83	19.5	20.7	13.7
$\beta_{140} \text{ThL}_4$ <sup>3</sup>	----	47.52	52.6	----	----
pM <sup>2</sup>	----	19.9	19.0	----	----

Table 1. Summary of the protonation constants and Fe(III) and Th(IV) stability constants determined for the ligands **5** and **6** and comparison with known values for ligands **3,4**, and **7**.

**5** was investigated because it is highly water soluble and more acidic than **3**. The increased acidity translates into higher pM values for the Fe(III) and Th(IV) complexes than any other ligand. It is remarkable that the addition of one sulfonamide group to the catechol ring has a greater electron withdrawing effect on the catecholate protons than two sulfonate groups; however, this is not mirrored in the Fe(III) formation constants. Since **6** has higher formation constants with Fe(III) than the **7**, we expect that bis-sulfonamides will have Fe(III) formation constants that are higher than the Fe(III) complex of **4**.

**Extraction studies.** We are currently examining some of these ligands as liquid-liquid extractants. Unfortunately TAMs and SFAMs form anionic metal complexes that are recalcitrant to organic extraction. By incorporating a positively charge substituent into one of the ligand side arms, the overall charge on the ligand will be -1, resulting in neutral metal complexes. Variations of both amide substituents are currently being evaluated for metal ion extraction.

It was necessary to evaluate the extraction using a competing ligand (NTA) for several reasons. We expect the ligands to function best at pHs above 5, so a water soluble ligand was required to prevent Fe(OH)<sub>3</sub> precipitation. Secondly, because the stability constants of the TAMs with Fe(III) are high and we expect the distribution coefficients to also be high, we want to maintain conditions where the metal is not 100% extracted. This allows for a more accurate determination of distribution coefficients and extraction constants. The extraction experiment is conducted with a buffered aqueous phase and a range of ligand concentrations. The amount of Fe(III) in the organic phase is monitored by UV-Vis spectroscopy.

The ligand **8** was found to be an excellent extractant at pH 5 using CHCl<sub>3</sub> as the extracting solvent. The distribution coefficients range from 10<sup>10</sup> to 10<sup>12</sup> for ligand stoichiometry ranging from 2 to 5 mole equivalents. As expected, a plot of Log D vs. Log [L] gave a straight line with a slope of approximately 3, the stoichiometry of the extracted species. The 3:1 L:Fe stoichiometry was also confirmed by the UV-Vis spectra and mass spectrometry of the organic phase. From this plot, the extraction constant was determined to be 10<sup>22</sup>.

We also discovered that the symmetrical highly lipophilic ligand **9** would extract Fe(III) into ethyl acetate if a suitably lipophilic counter cation, cetyl pyridinium **10**, was used. Again, the distribution coefficients range from 10<sup>10</sup> to 10<sup>11</sup> for 2 to 5 molar equivalents of ligand. However, due to the large number of components that can constitute the extracted complex, we have not conclusively determined the species distribution in this system. This system is quite promising as an industrial extraction process because the ligands are inexpensive and efficiently synthesized and the cations are also inexpensive and commercially available. Qualitative experiments have shown that this extraction procedure is permissive to a variety of TAMs and SFAMs.

### Planned Activities

In the area of solution thermodynamics, the Ce(IV) and ultimately Pu(IV) stability constants will be determined. The complexes will be structurally characterized. For the extraction studies, we will try to functionalize the TAMs to improve the solubility in industrially useful extraction solvents such as kerosene. The ion pair extraction system will be further characterized and our panel of previously synthesized ligands will be examined. Th(IV) extraction experiments are currently underway and Pu(IV) extraction experiments will begin this summer.

### Information Access

- 1) Garrett, Miller, and Raymond. *Inorg. Chem.*, 1988, 28, 128-133.
- 2)  $pM = -\log [M^{n+}]$  at pH 7.4 and  $[M^{n+}] = 0.1\text{mM}$  and  $[L] = 1.0\text{mM}$
- 3)  $\beta_n = [ML_n] / [M^{n+}][L^{2-}]^n$
- 4) Shridah and Ohzeki. *Analyst*, 1986, 111, 197.
- 5) Murakami, Nakamura. *Bull. Chem. Soc. Jpn.*, 1963, 36, 1408