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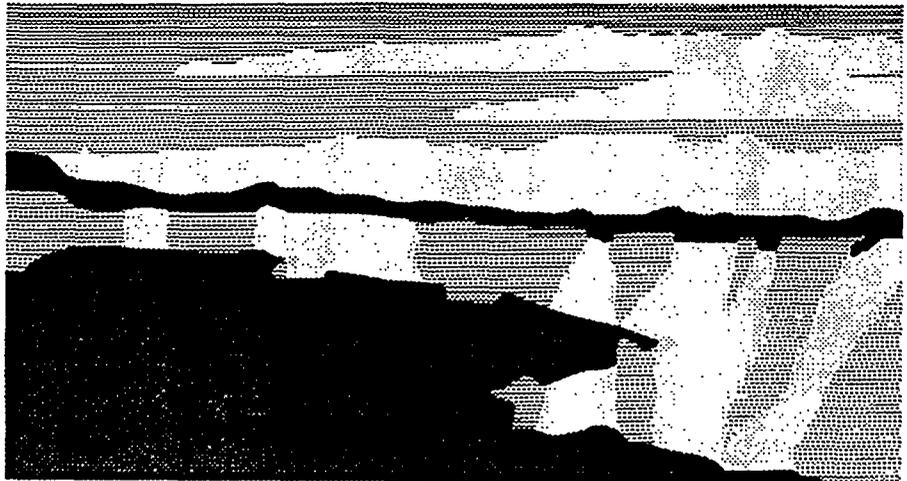
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## Separations Chemistry of Toxic Metals

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### Abstract

This is the final report of a three-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). Sequestering and removing toxic metal ions from their surroundings is an increasingly active area of research and is gaining importance in light of current environmental contamination problems both within the DOE complex and externally. One method of separating metal ions is to complex them to a molecule (a ligand or chelator) which exhibits specific binding affinity for a toxic metal, even in the presence of other more benign metals. This approach makes use of the sometimes subtle differences between toxic and non-toxic metals resulting from variations in size, charge and shape. For example, toxic metals such as chromium, arsenic, and technetium exist in the environment as oxyanions, negatively charged species with a characteristic tetrahedral shape. Other toxic metals such as actinides and heavy metals are positively charged spheres with specific affinities for particular donor atoms such as oxygen (for actinides) and nitrogen (for heavy metals). In most cases the toxic metals are found in the presence of much larger quantities of less toxic metals such as sodium, calcium and iron. The selectivity of the chelators is critical to the goal of removing the toxic metals from their less toxic counterparts. Our approach was to build a ligand framework that complements the unique characteristics of the toxic metal (size, charge and shape) while minimizing interactions with non-toxic metals. We have designed ligands exhibiting specificity for the target metals; we have synthesized, characterized and tested these ligands; and we have shown that they exhibit the proposed selectivity and cooperative binding effects.

### 1. Background and Research Objectives

The development of receptors for ions and molecules is at a stage where one can effectively design, using molecular modeling, receptors for single cations, anions or neutral

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molecules; there are numerous examples of such receptors in the literature. Thus, the field of molecular recognition is ripe for the development of specific receptors that perform very well-defined functions. We are actively involved in this process and have made significant contributions to this field. The work described in this project effectively augments the field of coordination chemistry and thus allows for new approaches in separations chemistry. We sought to design and synthesize ligand systems with two binding sites that exhibit cooperative and/or antagonistic binding.

Biological systems often display cooperative binding effects. In particular, the binding of one substrate to a receptor with more than one binding site enhances the binding of a second substrate. Hemoglobin is a common example where upon binding one oxygen molecule, the second binds more strongly. Antagonistic effects can also be observed whereby the addition of a second substrate reduces the binding affinity of the substrate of interest. We sought to develop these concepts using synthetic systems possessing two binding sites. In effect, we sought to design chelation switches whereby the addition of an ion into one of the binding sites would either "turn on" or "turn off" the ability of the second site to bind its substrate.

We felt that we could add a new dimension of control to the field of separations chemistry by developing a fundamental understanding of these concepts in synthetic systems. We have targeted toxic metals in this project as a result of the current atmosphere of environmental concern among Department of Energy (DOE) laboratories and industry. Whereas the term "toxic metals" encompasses many possibilities, we have chosen to focus this work on metal oxyanions (chromate, arsenate, and pertechnetate), actinides (plutonium and americium), and heavy metals (cadmium, lead, and mercury). Our interest in toxic oxyanions arises from their importance at sites with heavy metal contamination and as wastes from electroplating and nuclear processing. Transition metals and main group elements are often found as tetrahedral oxyanions ( $\text{CrO}_4^{2-}$ ,  $\text{TcO}_4^-$ ,  $\text{AsO}_4^{3-}$ ,  $\text{SeO}_4^-$ ) in the environment. These species are extremely mobile in ground waters and thus create a major concern. Viewed as a class, these anions present a surprisingly difficult problem for selective recovery. While it is known that these compounds bind to standard ion exchange columns, the understanding of this process is simplistic at best. The binding of anionic or cationic molecules such as  $\text{NH}_4^+$ , dicarboxylates (oxalate, malonate) and halides to synthetic receptor sites has been demonstrated. We sought to extend this chemistry through the synthesis of selective receptors for metal oxyanions.

A major goal of this research was to develop a new class of chelators for toxic metals that have the capacity to bind two species and in which the binding of one substrate affects the binding of the second. In the process we sought to gain a fundamental understanding of the key parameters that govern selective toxic metal ion binding as it applies to separations

chemistry. We sought to synthesize and evaluate a class of chelators that add a new dimension to coordination chemistry, namely cooperative and/or antagonistic binding. The chemistry involves the development and synthesis of ditopical receptors that contain two binding sites in close proximity to each other. In systems with cation and anion sites, the simultaneous binding of both a cation and an anion can enhance the overall binding constants relative to either one binding alone. Conversely, we sought to design receptors in which the binding of one substrate is detrimental to the binding of the second. A potential application for this idea involves the possibility of "reversing" the "irreversible binding" of metal ions. As part of an ongoing program in chelate design we also planned to design and evaluate chelators/receptors that would selectively bind toxic metals including actinides, heavy metals and metal oxyanions. Perhaps more important than the choice of the target metal is our unique approach of designing chelators which exhibit cooperativity and/or antagonism to gain an additional element of control.

## **2. Importance to LANL's Science and Technology Base and National R&D Needs**

Over the past decade, Los Alamos has established an internationally recognized program in ligand design for actinide and lanthanide coordination chemistry and separations. This project utilizes established synthetic laboratories with state-of-the-art facilities for the synthesis, characterization and evaluation of ligands, ligand-metal complexes, solvent extractants and polymer bound metal recovery systems. It also utilizes analytical and spectroscopic facilities as well as facilities for the X-ray and neutron diffraction structural characterization of actinide complexes. Laboratory capabilities in molecular orbital, mechanics, and dynamics calculations (CACHe) allow for the assessment of the importance of configuration changes and steric interactions for new organic ligand systems as well as their relevant metal complexes. The application of this expertise and the accompanying technologies to problems in toxic metal recovery and separations is critical. For example, we expect that the water soluble polymers that have been made will have uses in the removal of pertechnetate from Hanford tank wastes. This project supports LANL core competencies in earth and environmental systems as well as nuclear and advance materials.

## **3. Scientific Approach and Results to Date**

A major portion of the chemistry in this project is based on our recent studies of the octaaza cryptand. This cryptand is unique in that it binds fluoride at low pH and heavy metals

at near neutral pH and above. Its fluoride binding behavior is an example of cooperative binding. The binding constants for fluoride increase as the amount of acid is increased and the protonation state of the cryptand increases. Conversely, when fluoride ion is present the cryptand has a higher affinity for protons than it does in the absence of fluoride. The opposite phenomenon is observed when the same cryptand binds heavy metals such as mercury. Since metals and protons are both positively charged, they compete for the nitrogen lone pairs. Thus, the cryptand binds metals better at high pH because there are fewer protons in solution to compete with the binding sites. This ligand system has demonstrated a unique dual capability of selective binding of both cations and anions.

The systems we used to study the cooperativity effects are derivatized forms of this cryptand. Our choice of the cryptand was based on the following considerations: 1) we have developed an efficient synthetic method for this material and currently have gram quantities available, 2) we have studied the binding properties with many different types of metal ions and have a clear understanding of the types of metals and anions that are appropriate for this cavity size, and 3) the six secondary amines provide sites for attachment to other binding groups and yet still leave one lone pair on each amine for binding cations or anions within the cryptand. We have derivatized the cryptand with coordinating functional groups to create additional binding sites capable of chelating other species. We are utilizing this series of derivatives to evaluate systematically the fundamental factors that determine how various metal ions and anions interact with the chelators independently and in the presence of one another. The key results of the work are summarized below.

- The metal binding constant for cadmium by octaazacryptand **L**, where  $\text{L} = \text{N}(\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2)_3\text{N}$ , was determined by potentiometry,  $\log \text{bML} = 18.3(1)$ .
- Calculation of  $\text{pM}$  values ( $\text{pM} = -\log[\text{M}]$ ) show that **L** has the highest reported binding affinity for cadmium relative to other [2.2.2] polyoxa-polyaza cryptates.
- Two cadmium cryptate complexes,  $[\text{CdL}](\text{BF}_4)_2$  (**1a**) and  $[\text{CdL}](\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (**1b**), were synthesized by metallation of the free cryptand.
- The molecular structures of compounds **1a** and **1b** were determined by X-ray diffraction. Crystallographic data for **1a**: trigonal,  $P1c$ ,  $Z = 2$ ,  $a = 9.581(2) \text{ \AA}$ ,  $c = 17.003(4) \text{ \AA}$ ,  $V = 1351.2(5) \text{ \AA}^3$ . Crystallographic data for **1b**: monoclinic,  $C2/c$ ,  $Z = 4$ ,  $a = 10.500(2) \text{ \AA}$ ,  $b = 14.782(3) \text{ \AA}$ ,  $c = 19.395(4) \text{ \AA}$ ,  $b = 99.30(2)^\circ$ ,  $V = 2971(1) \text{ \AA}^3$ .
- The cadmium ions in both complexes are eight coordinate and display similar coordination geometries but different ligand conformations, designated as parallel and oblique. The cadmium coordination sphere is best described as a bicapped octahedron.

- Through two-dimensional NMR experiments we have found that the Cd is in a symmetric environment and the conformation of the ligand in solution is consistent with the parallel conformation observed in one of the solid state structures.
- The  $^{113}\text{Cd}$  NMR shift of this eight-coordinate amine complex is 75 ppm relative to 0.1 M aqueous  $\text{Cd}(\text{ClO}_4)_2$ , which correlates with shifts observed for other [2.2.2] cadmium polyoxa-polyaza cryptates.
- We have synthesized and structurally characterized 1,2-diguanidinoethane sulfate (Eng), *bis*(2-guanininoethyl)amine sulfate (Dieng), *tris*(2-guanidinoethyl)amine sulfate (Treg), and *m*-xylylene diguanidium sulfate.
- We have established that molecules containing flexible five-atom bridges bind more effectively than those having rigid or shorter bridges.
- We have shown that the Dieng structure shows cooperative binding with the water molecule.
- We have potentiometric titration data which indicates that there is interaction between  $\text{CrO}_4^{2-}$  and Dieng at  $\text{pH} > 8.5$ .
- We have found that  $^1\text{H}$ ,  $^{15}\text{N}$  and  $^{13}\text{C}$  NMR studies to probe anion binding interactions have been unsuccessful to date due to limited solubility and high proton exchange rates.
- We have determined that the two anion receptors, TREN TRIS(PHEN) and TRIS(PHEN) lacked the solubility characteristics and flexibility to optimize binding interactions.
- We have synthesized 2,9-*bis*(aminomethyl)-1,10-phenanthroline and begun probing its binding interaction with lead.
- We have synthesized two new potential receptors, phenanthroline-containing hexaazamacrocyclic and hexaazacryptand, which have fluorescent chromophores built in to allow for the observation of binding through changes in fluorescence.
- We have modified and streamlined the synthesis of an octaazacryptand by shortening the isolation procedure and we have improved the purification and drying methods.
- We have investigated the use of several different solvents in the preparation of the octaazacryptand and found similar yields using more convenient solvents such as ethanol.
- We have investigated the use of a complexed transition metal to protect the active amine positions of the octaazacryptand, providing a means of monofunctionalization by subsequent activation of one amine position through deprotonation with a strong base. Lead complexes were prepared, but were not sufficiently soluble in the solvents needed for the deprotonation with the strong base.
- To provide octaazacryptand complexes with sufficient solubility in solvents appropriate for the chemistry mentioned above, several complexes with various lanthanide metals have been prepared. Octaazacryptand complexes have been prepared with europium,

neodymium, lanthanum, gadolinium, and ytterbium, and their formation confirmed with nuclear magnetic resonance spectrometry. Crystals that are of X-ray crystallographic quality have been grown for the europium complex, and its structure determination is pending. These complexes show promising solubility characteristics.

- We have developed the first synthesis of an octaazacryptand fully substituted with six acetate groups to provide a chelator with dual chelating ability; a cavity on the inside as well as pendant chelating groups that are outside the cavity. Synthesis was both facile and high yield.
- The octaazacryptand has been attached to a lightly cross-linked chloromethylated polystyrene. Cross-linking was minimized by using a large excess of the octaazacryptand, which was fully recovered during workup.

### Publications

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- [3] Thompson, Julia A.; Barr, Mary E.; Ford, Doris K.; Silks, Louis A.; McCormick, B. Jack; and Smith, Paul H. , "Solution and Solid State Characterization of a Cadmium Octaazacryptand Complex," *Inorg. Chem.* , accepted (1995).
- [4] Sabel, D. M.; Thompson, J. A.; Butcher, R. J.; and Smith, P. H. , "2-Carboxyl-9-Diol-1,10- Phenanthroline Complexes of Co and Cu," *Acta Cryst. Sect. C.* , accepted (1995).

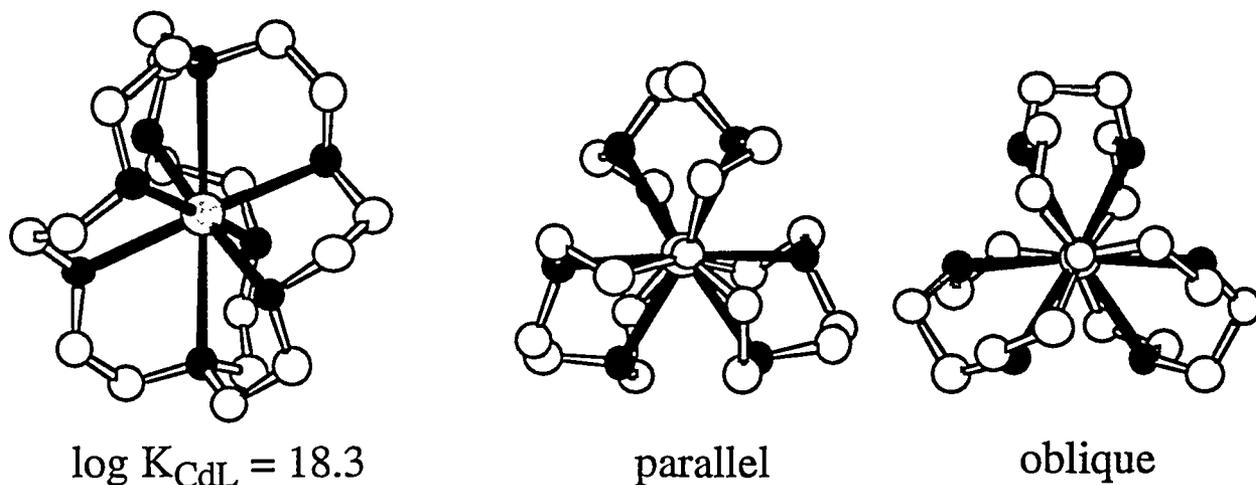
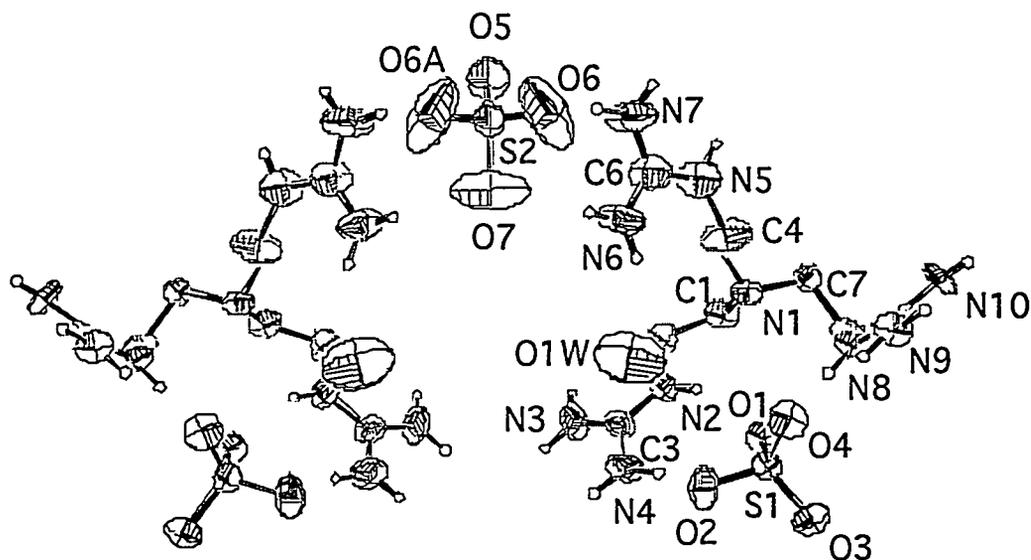


Fig. 1. The octaazacryptand L, where  $L = \text{N}(\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2)_3\text{N}$ , exhibits a high affinity for cadmium,  $\log b_{\text{ML}} = 18.3(1)$ . Calculation of  $\text{pM}$  values ( $\text{pM} = -\log[\text{M}]$ ) show that L has the highest reported binding affinity for cadmium relative to other [2.2.2] cadmium polyoxa-polyaza cryptates. In the solid-state the cryptand ligand is capable of adopting two conformations, parallel or oblique, with negligible influence upon the Cd coordination sphere. NMR experiments indicate the parallel conformation is favored in solution.



N1-C1	1.448 Å	N2-O1	2.843 Å
N1-C4	1.518 Å	N4-O2	2.942 Å
N1-C7	1.429 Å	N6-O7	3.140 Å
C-N(guan. ave)	1.330 Å	N8-O1	2.843 Å
		N9-O4	2.916 Å

**Fig. 2.** We have synthesized and structurally characterized 1,2-diguanidinoethane sulfate (Eng), *bis*(2-guanidinoethyl)amine sulfate (Dieng), *tris*(2-guanidinoethyl)amine sulfate (Treg) (shown above), and *m*-xylylene diguanidinium sulfate, which represent a series designed to systematically vary the number of atoms in the chain connecting the two guanidinium units. We are using sulfate in the initial studies due to its similarity in size and shape to chromate ion and to its lower reactivity and toxicity. We have shown that a five-atom bridge between guanidinium units is preferable to a two-atom bridge because it allows both guanidinium units to bind a single sulfate ion. In the 1,2-diguanidinoethane structure, no pre-organization occurs and the two arms are associated with two different sulfate ions.

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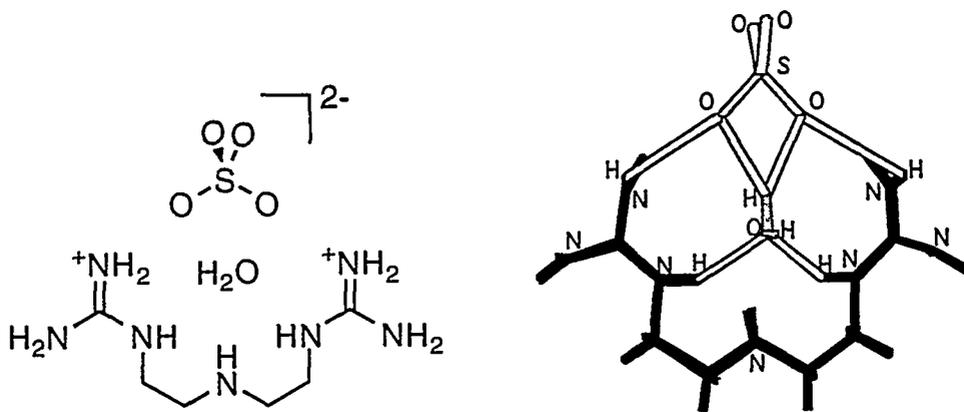


Fig. 3. Chemical and structural diagrams illustrating the capacity of *bis(2-guanininoethyl)amine sulfate (Dieng)*, to act both as a chelator for sulfate anion and as a cooperative binding system for sulfate and water. We have discovered a system that demonstrates cooperative binding. In this case, water is bound inside the cavity, apparently assisting in the preorganization of the guanidinium units to chelate the sulfate. Therefore, it appears that cooperative binding is necessary in this complex if chelation of oxyanions is to occur. The crystal structure of this supramolecular complex is illustrated above.