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Project Title: **Supramolecular Chemistry of Selective Anion Recognition for Anions of Environmental Relevance**

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PROGRESS REPORT NUMBER 3

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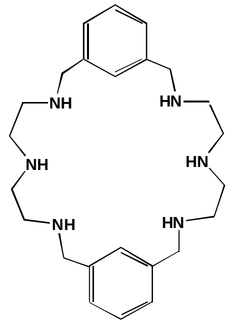
RESEARCH OBJECTIVE: This project had as its original focus the design and synthesis of polyammonium macrocyclic receptors for oxoanions of environmental importance and specifically those found in high level waste tanks. This third year of the project, we have added the goal of synthesizing lipophilic amide-based receptors in order to increase the potential for obtaining workable receptors for both separations and sensing applications. Three areas of emphasis are being explored. Major efforts are being made in the design and synthesis of receptors that exhibit highly selective binding for specified anions. A basic research component inherent in this effort is to devise new and improved synthetic techniques that would allow for obtaining economically feasible receptors. A second effort includes structure determination and thermodynamic studies in order to ascertain structural criteria for anion binding as well as to determine the strength of binding. A third area of thrust is in theory and involves molecular dynamics simulations in order to assess the solution characteristics of the interactions between anions and their receptors. Theoretical studies are being performed in collaboration with Professor Krzysztof Kuczera. Additionally, two applications-oriented efforts are being explored. The fabrication of systems for liquid-liquid separations is being explored in a subcontract with Dr. Bruce Moyer at Oak Ridge

National Laboratory. At the University of Kansas, a method known as ITIES (Interface between Two Immiscible Electrolyte Solutions) is being explored as a means to achieve sensors for the *in situ* quantitative determination of a variety of anions in groundwater. This is a collaborative effort with Professor George Wilson.

RESEARCH PROGRESS AND IMPLICATIONS: This report summarizes work after 2 years and 7 months of a three year project. To date we have focussed on the design and synthesis of selective receptors for oxo anions with considerable effort on nitrate.

Synthesis. In year one of the project polyaza macrocycles and macrobicycles were identified which bind the desired anions and are easy to synthesize via two step Schiff base/reduction processes with high yields. During year one most of our studies focused on monocyclic systems, e.g., **1**. In year two (as a result of findings from molecular dynamics simulations) we began to examine bicyclic macrocycles, e.g., **2**. In year three, in an effort to synthesize receptors which do not have the pH dependence that **1** and **2** have and which have a greater solubility in organic media, we synthesized a series of lipophilic tripodal amides, e.g., **3**.



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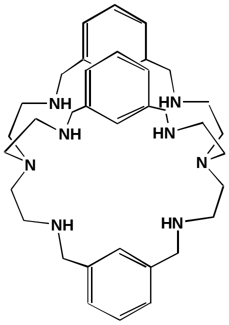

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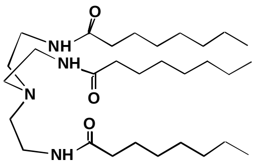

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Structural studies. A number of crystal structures have now been obtained for anion complexes including nitrate, sulfate, phosphate, chloride, and fluoride. While the monocycles rarely bind the anions inside the ring, we have several structures of bicyclic complexes with anions inside the cavity. These include a "dinitrate" complex and a fluoride complex in which both fluoride and water are in the cavity, both with receptor **2**. With respect to the dinitrate structure, this exciting result indicates that these bicycles hold considerable promise as receptors for trigonal anions. To our knowledge this is the first example of a receptor incorporating two discrete anions within a single cavity. Another unique crystal structure of **3** with nitrate shows the formation of bilayers with channels holding the nitrate ions. Very few crystal structures have been reported with lipophilic species such as ours.

Molecular dynamics (MD) studies. Simulations on several complexes using the program CHARMM indicate that hydration effects tend to govern the structure of the receptor in solution so that it becomes relatively planar even if the solid state structure indicates a folded conformation. MD studies have also indicated that water plays an important role in solution, in forming relay networks to the macrocyclic receptor from surrounding nitrates.

Potentiometric studies. Protonation and binding constants were determined for monocycles and bicycles using potassium *p*-toluenesulfonate as electrolyte, based on the assumption that the *p*-toluenesulfonate anion is sufficiently large to exhibit negligible binding affinity and thus does not compete with the anions under investigation. The results of the potentiometric studies indicate that for monocycles, association constants are lower that the bicycles (K_{as} *ca*. 10-100) with the exception of sulfate (dinegative charge enhances binding). This finding is undoubtedly due to the interfering or competing influence of hydration on anion binding, as noted in the molecular dynamics studies during the first year of the grant. However, affinities of the bicyclic receptors for nitrate are all considerably larger with K_{as} ranging from $10^3 - 10^5$. Binding studies have also been performed for the lipophilic receptors such as **3** and indicate as anticipated that affinities are somewhat lower than for the polyammonium bicycles. Affinities for the amides are about the same order of magnitude as the monocycles.

Separations studies. (Subcontract with Bruce Moyer at Oak Ridge National Laboratory) Studies at Oak Ridge began last summer. Using the lipophilic receptors (**3**) Moyer found that extraction of $CsNO_3$ was enhanced when a dual receptor system (the lipophilic amide in conjunction with a crown ether) was used. These results are very exciting and perhaps represent the first example of the use of a dual receptor in separations technology.

Planned Activities. This is the last year of the project. We are finishing titrations of the polyammonium and lipophilic amide receptors. The most promising aspects of earlier findings are being pursued further (and will provide the preliminary data for new proposals). These aspects include the bicycles capable of incorporating multiple anions, the new lipophilic receptors, and the dual receptor systems for cation-anion pairs in both separations and sensors.

Information Access. The structure of the nitrate complex of **2** may be viewed at the following web site: http://129.237.102.17/~kuczera/kristin/animate.html.

Publications:

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Invited Lectures:

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XXIV International Symposium on Macrocyclic Chemistry, Bellaterra (Barcelona) July 18-23, 1999, Plenary Lecture: Supramolecular Chemistry of Anions and Macrocycles

Books and Chapters:

Supramolecular Chemistry of Anions, A. Bianchi, K. Bowman-James, E. García-Espana, Eds. Wiley-VCH: New York, 1997, 461 pp.

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