PROGRESS REPORT

Project Title: Supramolecular Chemistry of Selective Anion Recognition for Anions of Environmental Relevance
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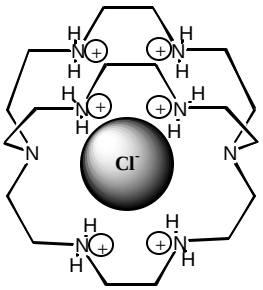
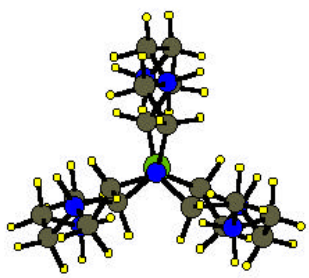
RESEARCH OBJECTIVE: This project involves the design and synthesis of receptors for oxoanions of environmental importance and specifically those found in high level waste tanks. Polyammonium macrocycles as receptors and nitrate as anion were the focus of the first phase of this project. A second phase involved the synthesis of lipophilic amide-based receptors in order to increase the potential for obtaining workable receptors for both separations and sensing applications on site. A three tier approach was employed: **I.** Design, synthesis, and physical and structural characterization of receptors; **II.** Examination of the technique known as ITIES, Interface Between Two Immiscible Electrolyte Solutions, as an analytical probe for anion analysis; and **III.** Investigation of dual ion pair extraction using lipophilic amide receptors for anion binding. More recent efforts in the renewal of this project are focusing on sulfate and new designs for receptors. These efforts will also have impact on low activity waste, for example in the vitrification process.

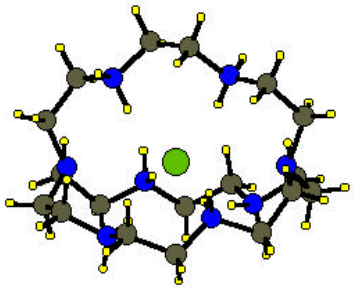
Results since previous report (submitted with renewal application spring 2000).

This report summarizes work after three months of start of the renewal of the initial EMSP project funded in 1996. The project has been ongoing since that time.

Halide binding. In addition to fluoride NMR techniques used to probe solution structure of the interaction of fluoride with receptor systems,[1] we discovered new binding properties of a previously established receptor for fluoride known as the octaazacryptand, **1**.[2] The extremely small size of this receptor and binding studies performed using potentiometric pH-metric techniques originally indicated that only fluoride would be capable of fitting in the tiny cavity. However, at low pH (<2.5) we found a greatly enhanced binding affinity for chloride. Crystallographic data for crystals obtained under acidic conditions indicated encapsulated chloride (shown below). Such a finding may be important for certain sites, and particularly INEEL, where conditions are very acidic, and there is currently concern about halides such as chloride and fluoride.[3] As can be seen from the NMR titration of the three independent proton signals, while fluoride clearly binds at higher pH (observed chemical shift from tosylate salt of receptor), only at pH 2.5 and below does chloride binding begin (plot shown below) .







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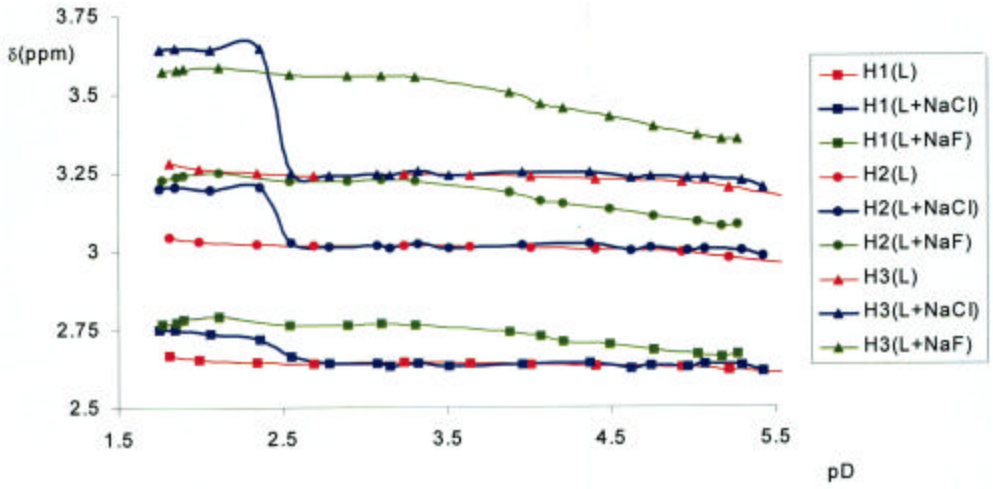


[1] Clifford, T.; Mason, S.; Llinares, J. M.; Bowman-James, K. *J. Am. Chem. Soc.* **2000**, *122*, 1814-1815.
[2] Hossain, M. A.; Llinares, J. M.; Miller, C.; Bowman-James, K. *Chem. Commun.* **2001**, 973-974.
[3] TFA Workshop, March 12-15, Salt Lake City, Utah

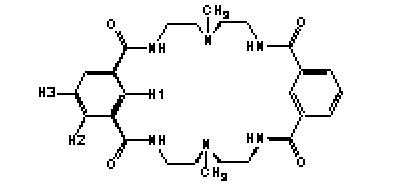
New receptor systems.

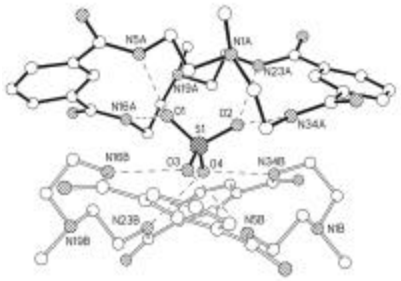
We are exploring a new class of receptors, containing amides more suited for applications involving separations. The first class of these receptors has now been synthesized and binding studies have commenced. The macrocyclic amide **2** shows selective binding for both phosphate and sulfate (**Table 1**).[4] The crystal structure indicates a highly unusual sandwich complex, shown below. This is a result that could be immediately used by DOE/EM and plans are underway with Bruce Moyer to explore preliminary separations. If successful, we hope to carry out field tests.

Table 1. Binding Constant Data of L^1

Anions	Δδ(N-H), ppm	Log K, M^{-1}
Phosphate	2.16	4.66(4)
Sulfate	2.14	4.50(4)
Nitrate	0.57	2.15(2)
Perchlorate	0.20	<1
Chloride	1.32	2.70(3)
Iodide	0.57	2.13(2)

2



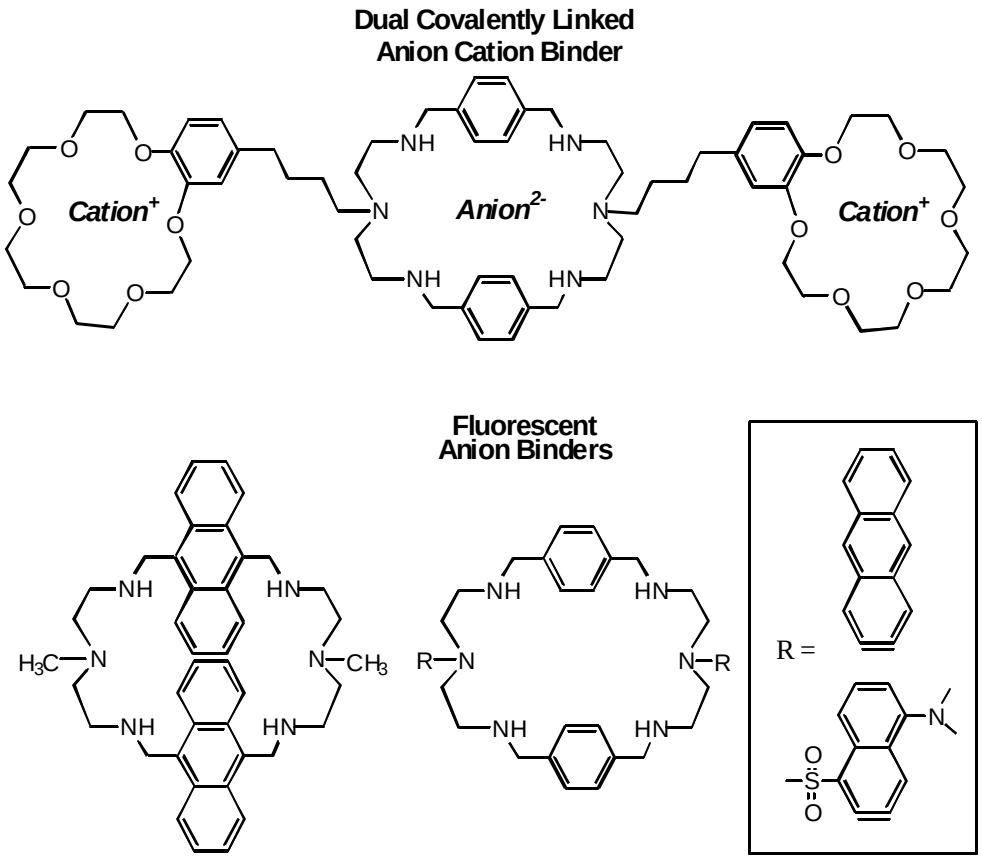


We have also synthesized a series of new macrocycles based on **2** shown above. The first of these, **3,** is the extension of our studies with Bruce Moyer at Oak Ridge on dual anion cation receptors, and consist of crown ethers covalently linked to the macrocycle. Preliminary binding studies for this receptor are currently underway.

Planned Activities

The new systems are currently being characterized using a variety of methods including NMR, X-ray crystallographic, and where appropriate potentiometric pH-metric techniques. Using these methods selectivity preferences are being explored, and modifications will be made in accordance with the preliminary findings to maximize the selectivities. Key compounds will be sent to Bruce Moyer at Oak Ridge for investigation. The PI (KBJ) will be on sabbatical leave in the Fall semester, and plans to spend considerable effort on this project, as well as time at Oak Ridge in order to further advance the goals of the program. Two basic areas will be explored, the dual anion cation focus as well as a newer area of fluorescent receptors, which will possibly allow for sensor development.

[4] Hossain, M. A.; Llinares, J. M.; Powell, D.; Bowman-James, K. *Inorg. Chem.* **2001**, *40*, 0000.



Information Access.

Publication Type: Journal articles.

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