ANNUAL REPORT

Supramolecular Chemistry of Selective Anion Recognition for Anions of Environmental Relevance

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Annual Report for Environmental Management Science Program Project 74019, corresponding to Oak Ridge National Laboratory FWP No. ERKP600. This is a joint program led by the University of Kansas, under Grant No. DEFG0796ER-62307. The attached report is a joint report submitted by the Principal Investigator, Prof. Bowman James. The report will be posted on the EMSP web site, URL http://emsp.em.doe.gov/ .

This research was sponsored by the Environmental Management Science Program of the Offices of Science and Environmental Management, U. S. Department of Energy, under a) contract number DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC and b) Grant number DEFG0796ER-62307 with the University of Kansas.

PROGRESS REPORT

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

Award Number: DEFG0796ER-62307

Awardee Account Number: EMSP 74019/Acct. 440801-707

Publication Date: June 10, 2004

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RESEARCH OBJECTIVE: The last three years of this project have focused on the basic chemical aspects of anion receptor design of functional pH independent systems, with the ultimate goal of targeting the selective binding of sulfate, as well as design of separations strategies for selective and efficient removal of targeted anions. Key findings during these years include: (1) the first synthetic sulfate-selective anion-binding agents; (2) simple, structure-based methods for modifying the intrinsic anion selectivity of a given class of anion receptors; and (3) the first system capable of extracting sulfate anion from acidic, nitrate-containing aqueous media. Areas probed during the last funding period include: **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 anion and dual ion pair extraction using lipophilic amide receptors for anion binding.

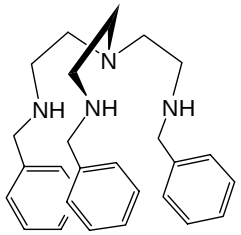
I. Design, synthesis, and physical and structural characterization of receptors.

As of June 1, 2004, this report summarizes work for the last year from June 1, 2003 to May 31, 2004.

Amide/Amine-based Acyclic Receptors. An investigation into the amide/amine and amine tripodal acyclic receptors was finished. Findings indicated that neither binds anions well, but the crystal structures for two of the amine receptors were published and are shown below.

Table 1. Binding data of $[H_3\mathbf{L}][OTs]_3$ with anions in $CDCl_3$.

Anions	log *K* (M^{-1})
$H_2PO_4^-$	3.25
HSO_4^-	3.20
NO_3^-	1.55
Cl^-	1.80
Br^-	1.70



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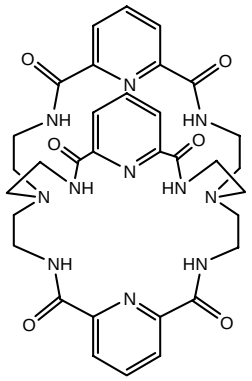
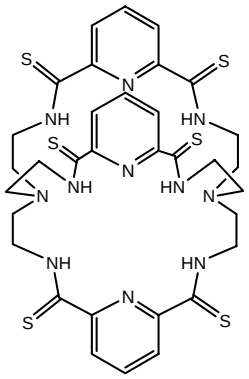
Amide/Thioamide/Sulfonamide-based Receptors. The entire complement of cryptand receptors **L1 – L4**, has now been synthesized. Binding constants for sulfate in DMSO appear to be relatively low with the exception of the sulfonamide (**Table 2**)



L1



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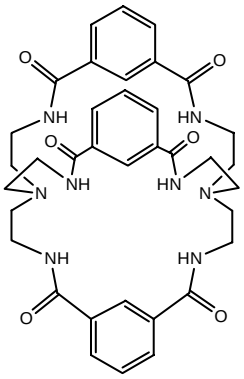
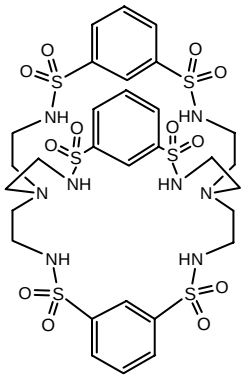


L3



L4

Table 2. Binding of **L1** – **L4** (K_a, M^{-1}) with anions in DMSO.

Ligand	F^-	Cl^-	Br^-	I^-	HSO_4^-	$H_2PO_4^-$	NO_3^-	ClO_4^-
L1	8.1×10^5	3020	40	20	68	2042	85	98
L2	3.2×10^4 [a]	35	<10	<10	49	2527	<10	<10
L3	3.3×10^4	820	<10	<10	*c*	*c*	<10	<10
L4	*c*	350	304	92	770	*c*	150	<10

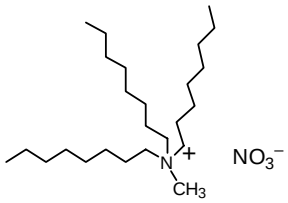
[a] In DMSO-d_6. [b] In CD_3CN. [c] Peak broadening prevented measurement.

II. ITIES Studies

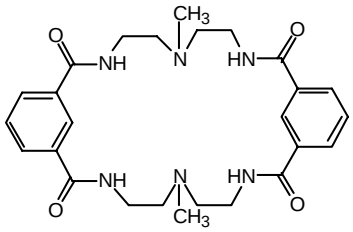
These were essentially complete as of last year and were reported then.

III. Extraction Studies

Efforts this year went toward understanding the synergistic anion exchange in the presence of a quaternary ammonium nitrate salt **Q**NO_3 with a tetramido macrocycle (MMEAM) Experiments were performed in $CHCl_3$.



QNO_3



MMEAM

Preliminary equilibrium analysis confirmed synergistic anion exchange for MMEAM (**Figure 1**).

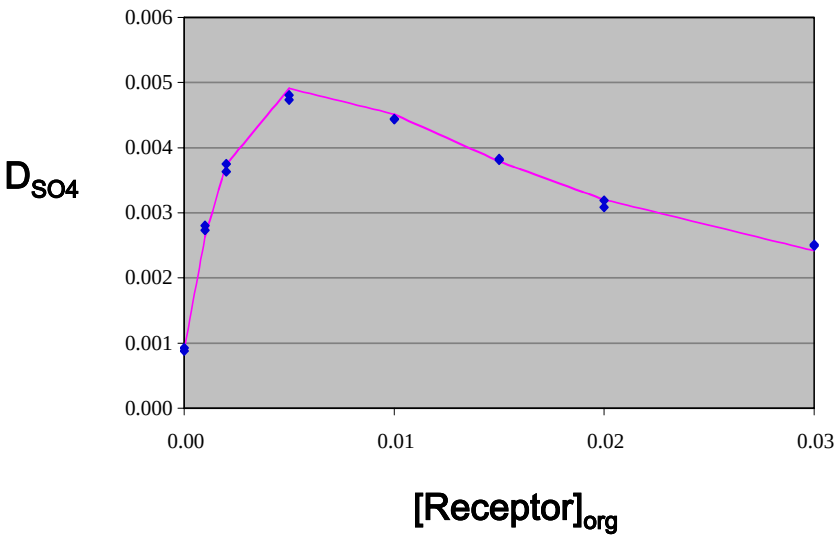


Figure 1. Distribution coefficient as a function of concentration of MMEAM (M) with 10 mM **QNO_3** in $CHCl_3$. Aqueous layer = 5 mM $NaNO_3$ and 0.1 mM Na_2SO_4.

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Synthetic Receptors for the Binding of Anions. S.-O. Kang, K. C. Nam, and KI. Bowman-James

New Synthesis of N-Functionalized Macrocycles, J. Kut, M. A. Hossain, J. M. Llinares, and K. Bowman-James

Detecting Anionic Cascade Complexes Inside a Cryptand Cavity. J. M. Llinares, K. Bowman-James, M. A. Hossain, S. Mason, P. Morehouse, and D. Powell

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