Project 90301
Supramolecular Chemistry of Selective Anion Recognition for Anions of Environmental Relevance

Kristen Bowman-James
University of Kansas

RESULTS TO DATE:

PROGRESS REPORT RESEARCH OBJECTIVE: This project have focusses 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 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: the design, synthesis, and physical and structural characterization of receptors and investigation of anion and dual ion pair extraction using lipophilic amide receptors for anion binding. A new collaboration has been added to the project in addition to the one with Dr. Bruce Moyer at Oak Ridge National Laboratory, with Professor Jonathan Sessler at the University of Texas at Austin.

RESULTS: This project has now reached a stage where there is significant data concerning structures, selectivities, and magnitudes of anion binding to a wide variety of anion receptors. The factors examined include hydrogen bonding groups (amines, amides, thioamides, sulfonamides), charge (positively charged vs neutral receptors), dimensionality (acyclic, monocyclic, and bicyclic cryptands), and topology. In the past two years KBJ has visited Oak Ridge to plan for the future efforts in our collaboration with Bruce Moyer. Now that we have added a new collaborator, we are planning to meet every six months to plan and to communicate progress.

Acyclic Amines and Amides. An investigation into the amide/amine and amine tripodal acyclic receptors was finished. Findings indicated that neither binds anions well, but binding was significantly higher for the oxoacids dihydrogen phosphate and monohydrogen sulfate. Crystal structures for two of the amine receptors were published recently along with the binding results of the acyclic tripodal amines. Another paper is currently in progress on the corollary amide receptors. Amide/Thioamide-based Monocyclic Receptors. The proposed cryptand receptors with amide and thioamide functionalities has now been synthesized for monocyclic (two dimensional) systems. The results are quite surprising. For the monocyclic systems, which also contain two tertiary amines, significant selectivity was observed for the oxoacids above other oxo anions and halides. Affinities for bisulfate in DMSO are log K ~ 3.0 for the amide and slightly higher for the thioamide. The receptors also bind dihydrogen phosphate strongly. We suspect that the affinity is linked to the secondary amine which acts synergistically to attract the protonated anion. The structure of the tetraamido complex with sulfate shows a very strong multiple hydrogen bonding network of eight hydrogen bonds holding the sulfate in a sandwich-like structure. This chelation is undoubtedly also responsible in part for the high observed affinity. We also observed the monocycles with pyridine spacers show higher affinity that those with simple m-xylyl or thiophene spacers. We attribute this to a type of preorganization effect, where the pyridine amines help to orient the NH hydrogens inward to the cavity for a better placement to hydrogen bond with the anions. In extraction studies performed at Oak Ridge in Bruce Moyer?s group, insight to selective sulfate extraction is being gained and we are attempting to make ligands similar to those we observe to have high affinity for sulfate, but with appendages that will make them very insoluble in water and soluble in n-octanol and other hydrocarbon solvents that would be preferable for functional extraction purposes.

Amine/Amide/Thioamide/Sulfonamide-based Bicyclic Receptors. All of these receptors have now been synthesized with both pyridine and m-xylyl spacers in some cases. With the exception of the amine

cryptands, disappointingly, these systems are more selective for the halides rather than oxo anions showing an extremely high affinity for fluoride (log K > 5.0 for fluoride). For the amide, thioamide and sulfonamide receptors, the finding is opposite to what is observed in the amine receptors, where very high binding with sulfate is observed in water. Crystal structures of several inclusion complexes of sulfate have been obtained, including one in an amine cryptand and another in an amide cryptand. These structures, along with the sandwich structure seen for the monocycle provide very significant insight to binding propensities of sulfate. The amine cryptand binds sulfate internally via five hydrogen bonds. This receptor is totally protonated (+8 charge) and has a m-xylyl spacer. Thus it is not subject to preorganization as could be provided by a pyridine spacer, and there are six hydrogen bonding sites that are not utilized by binding with the sulfate, i.e., inefficient coordination. On the other hand the amide cryptand is preorganized because of pyridine spacers. It is dipositively charged and is thus perfectly suited for binding sulfate in terms of charge complementarity. Insight to Corollaries between the Coordination Chemistries of Transition Metals and Anions. Over the period of funding of this project, we have achieved a significant catalog of crystal structure data, which allows us to understand the chemistry of anion binding with synthetic receptors. It is now obvious that anion complexes also bind in a fashion that achieves a certain coordination number with a common geometrical shape. We have observed coordination numbers from one through nine, each being able to be described in a common geometry. In fact, for sulfate we now see three geometries, square prism for the sandwich complex, trigonal bipyramid for the amine cryptand, and dicapped trigonal prism for the amide cryptand. To our knowledge researchers in the area have not previously noted this interesting phenomenon, i.e., as Werner stated, geometries that are derived from ?symmetrical groupings of atoms about a centre.? (Alfred Werner Nobel Address) A paper describing the sulfate work has just been accepted in Chemical Communications.

DELIVERABLES: Information Access. Publication Type: Journal articles. S. Mason, T. Clifford, L. Seib, K. Kuczera, and K. Bowman-James, Unusual Encapsulation of Two Nitrates in a Single Bicyclic Cage, J. Am. Chem. Soc. 1998, 120, 8899-8900. C&E News concentrate. September 7, 1998, page 30, "Two nitrates in a cage." J. Wiorkiewicz-Kuczera, K. Kuczera, C. Bazzicalupi, A. Bencini, B. Valtancoli, A. Bianchi, and K. Bowman-James, Solid State to Solution: Crystal Structure and Molecular Dynamics Simulations of a Polyammonium Nitrate Host, New J. Chem. 1999, 23, 1007-1013. O. A. Gerasimchuk, S. Mason, J. M. Llinares, M. Song, N. W. Alcock, and K. Bowman-James, Phosphate Binding in a Hexaaza Polyammonium Macrocycle, Inorg. Chem., 2000, in press. T. Clifford, S. Mason, J. M. Llinares, and K. Bowman-James, Snap-shots of Fluoride Binding in an Azacryptand, J. Am. Chem. Soc., 2000, 122, 1814-1815 A. Danby, L. Seib, N. W. Alcock, and K. Bowman-James, Novel Structural Determination of a Bilayer Network Formed by a Tripodal Lipophilic Amide in the Presence of Anions,? Chem. Commun., 2000, 973-974. K. Kavallieratos, A. Danby, G. J. Van Berkel, M. A. Kelly, R. A. Sachleben, B. A. Moyer, K. Bowman-James, Tris(2-Aminoethyl)amine (tren) Triamide Derivatives Enhance CsNO3 Extraction in 1,2-Dichloroethane via a Dual-Host Strategy, Anal. Chem. 2000, 72, 5258-5264. Q. Qian, G. S. Wilson, K. Bowman-James, H. H. Girault, MicroITIES Detection of NO3- by Facilitated K+ Transfer, Anal. Chem. 2001, 73, 497-503. M. A. Hossain, J. M. Llinares, D. Powell, K. Bowman-James, Multiple Hydrogen Bond Stabilization of a Sandwich Complex of Sulfate between Two Macrocyclic Tetraamides, Inorg. Chem. 2001, 40, 2936-2937. J. A. Aguilar, T. Clifford, A. Danby, J. M. Llinares, S. Mason, E. Garcia-Espana, K Bowman-James, Fluoride Ion Receptors: A Comparison of a Polyammonium Monocycle versus its Bicyclic Corollary, Supramolec. Chem. 2001, 13, 405-417 T. Clifford, A. Danby, J. M. Llinares, S. Mason, N. W. Alcock, D. Powell, J. A. Aguilar, E. Garcia-Espana, K Bowman-James, Anion Binding with Two Polyammonium Macrocycles of Different Dimensionality, Inorg. Chem. 2001, 40, 4710-4720. Md. A. Hossain, J. M. Llinares, S. Mason, P. Morehouse, D. Powell, and K. Bowman-James, Parallels in Cation and Anion Coordination: A New Class of Cascade Complexes, Angew. Chem., Int. Ed. Engl. 2002, 41, 2335-2338. M. A. Hossain, S. O. Kang, D. Powell, and K. Bowman-James, Anion Receptors: A New Class of Mixed Amide/Quaternized Amine Macrocycles and the Chelate Effect, Inorg. Chem. 2003, 42, 1397-1399. M. A. Hossain, J. M. Llinares, N. W. Alcock, D. Powell, and K. Bowman-James, Structural and Anion Binding Effects of the Tiny Octaaza Cryptand, J. Supramolec. Chem. 2003, 2, 143-149. M. A. Hossain, J. M. Llinares, D. Powell, and K. Bowman-James, Elite New Anion Ligands: Polythioamide Macrocycles, Inorg. Chem. 2003, 42, 5043-5045. S. O. Kang, D. Powell, and K. Bowman-James, New Polyamide Cryptand for Anion Binding, J. Am. Chem. Soc. 2003, 125, 10152-10153. P. Morehouse, M.A.

Hossain, J. M. Llinares, D. Powell, K. Bowman-James, A Ditopic Azacryptate Proton Cage, Inorg. Chem. 2003, 42, 8131-8133.

M. A. Hossain, J. A. Liljegren, D. Powell, and K. Bowman-James, Anion Binding with a Tripodal Amine, Inorg. Chem. 2004, 43, 3751-3755.

S. O. Kang, M. A. Hossain, D. Powell, and K. Bowman-James, Encapsulated Sulphates: Insight to Binding Propensities, Chem. Commun. 2004, in press.

Publication Type: Papers K. Bowman-James, Supramolecular Chemistry of Anions, American Chemical Society, Boston. August, 1998. S. Mason, 216th National Meeting of the American Chemical Society, Boston, MA, August, 1998. K. Kavallieratos, R. A. Sachleben, J. C. Bryan, B. A. Moyer, A. M. Danby, and K. Bowman-James, New Anion receptors and their Role in Solvent Extraction. 217th National Meeting of the American Chemical Society, Anaheim, CA March, 1999. K. Bowman-James, Plenary Lecture: Supramolecular Chemistry of Anions and Macrocycles XXIV International Symposium on Macrocyclic Chemistry, Bellaterra (Barcelona) July 18-23, 1999. K. Bowman James, G. Wilson, B. Moyer, The Supramolecular Chemistry of Anion Recognition for Anions of Environmental Relevance. Department of Energy Environmental Management Sciences Workshop. Atlanta, Georgia, April 25-27, 2000. K. Bowman-James, Symposium Lecture: Explorations in Anion Coordination Chemistry, XXV International Symposium on Macrocyclic Chemistry, Saint Andrews, Scotland, July 2000. K. Bowman-James, Supramolecular Chemistry for Selective Anion Recognition for Anions of Environmental Relevance, DOE Tanks Focus Area Workshop. Salt Lake City, Utah, March 12-14, 2001. K. Bowman-James, Explorations in Anion Coordination Chemistry, National Science Foundation, April 27, 2001. American Chemical Society, Southeast Regional Meeting, Charleston, SC, Nov. 13-15, 2002. Symposium on Supramolecular Chemistry. Anion Coordination Chemistry with Macrocyclic Ligands

Inorganic Gordon Conference, July 15-19, 2001: Explorations in Anion Coordination Chemistry. American Chemical Society, Chicago, August 26-30, 2001. Symposium on Fundamentals and Applications of Anion Separations: Explorations in Anion Binding Concepts. Pittcon 2002, New Orleans, March 17-22, 2002. Symposium on Next Generation Environmental Sensors: Supramolecular Chemistry of Selective Anion Recognition for Anions of Environmental Relevance. XXVII Symposium on Macrocyclic Chemistry, Park City, Utah, June 23-27, 2002: Corollaries between Transition Metal and Anion Coordination Chemistry. K. Bowman-James, J. M. Llinares, M. A. Hossain, S.-O. Kang

Midwest ACS Meeting Award Address. K. Bowman-James, Coordination Chemistry of Anions, November, 2003. American Chemical Society Meeting, Anaheim, CA, March 28, 2004. K. Bowman-James, Alfred Werner Revisited: The Coordination Chemistry of Anions. American Chemical Society Meeting, Philadelphia, PA, August 23, 2004. K. Bowman-James, Synthetic Macrocycles: The Ultimate Versatile Ligands for Anions and Cations

Publication Type: Books and Chapters: Kavallieratos, K.; Bryan, J. C.; Sachleben, R. A.; Van Berkel, G. J.; Espetia, O. D.; Kelly, M. A.; Danby, A.; Bowman-James, K.; Moyer, B. A. ?Dual Host Combinations: Using Tripodal Amides to Enhance Cesium Nitrate Extraction by Crown Ethers, in Fundamentals and Applications of Anion Separations;? B. A. Moyer and R. Singh, Eds.; ACS Symposium Series, Kluwer Academic/Plenum: New York, 2004, in press.