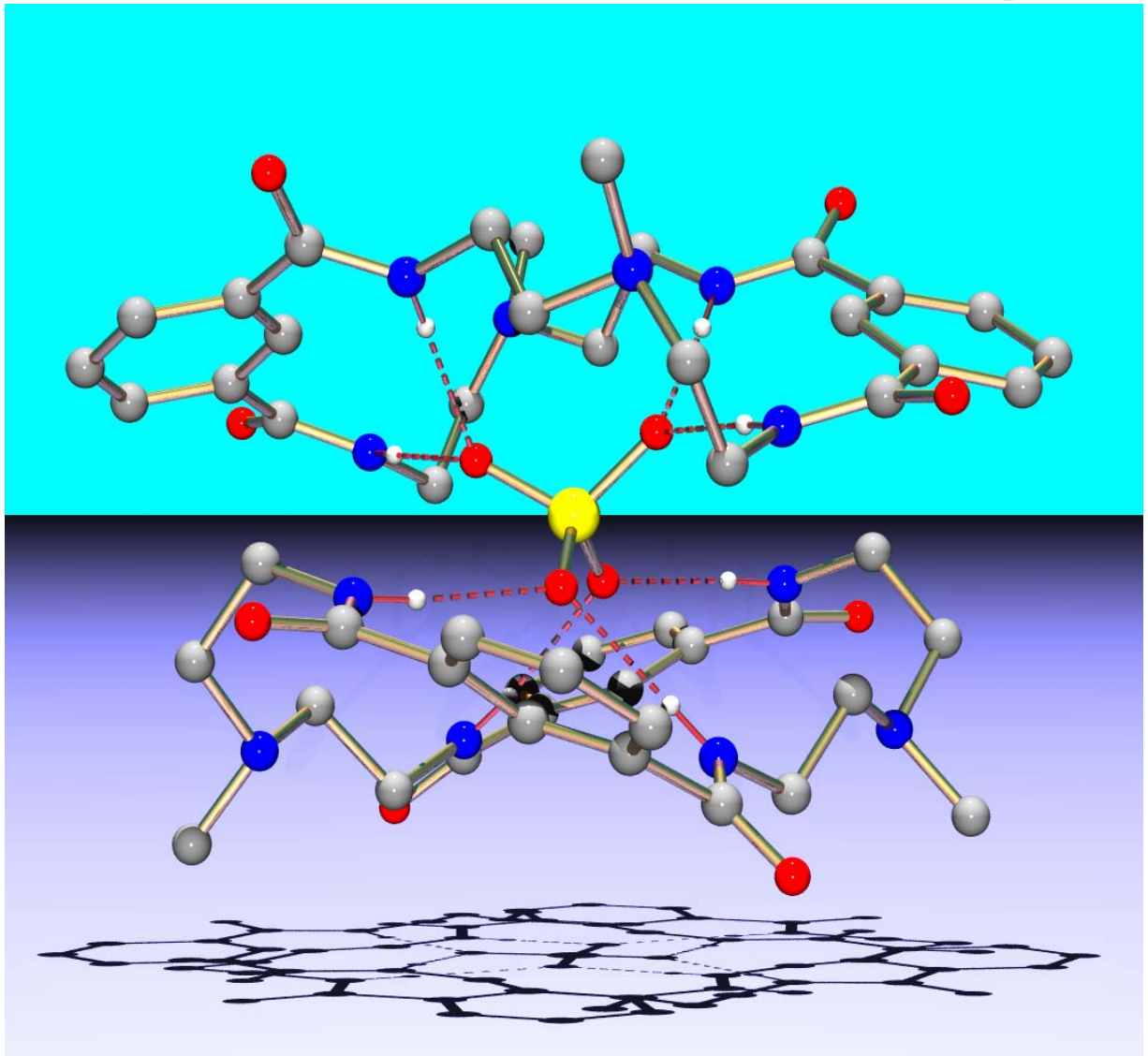
Supramolecular Chemistry of Selective Anion Recognition



Supramolecular Chemistry of Selective Anion Recognition for Oxoanions of Environmental Relevance

DE-FG07-96ER-62307

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DE-FG02-04ER63745

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Goals

- To determinine the basic chemical aspects of anion receptor design of functional pH independent systems
- To target the selective binding of sulfate, and
- To design separations strategies for selective and efficient extraction of targeted anions from waste

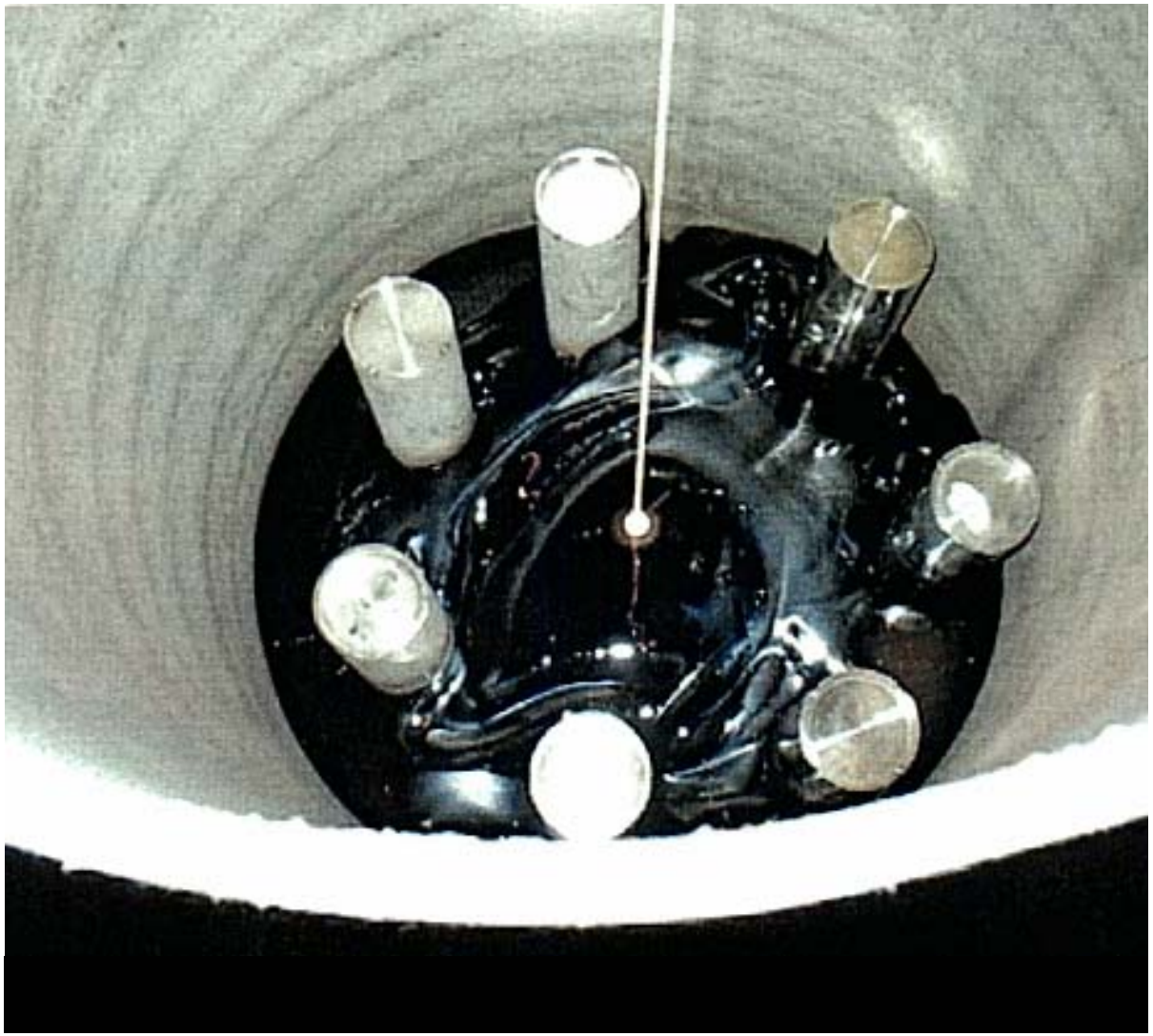
Key Findings

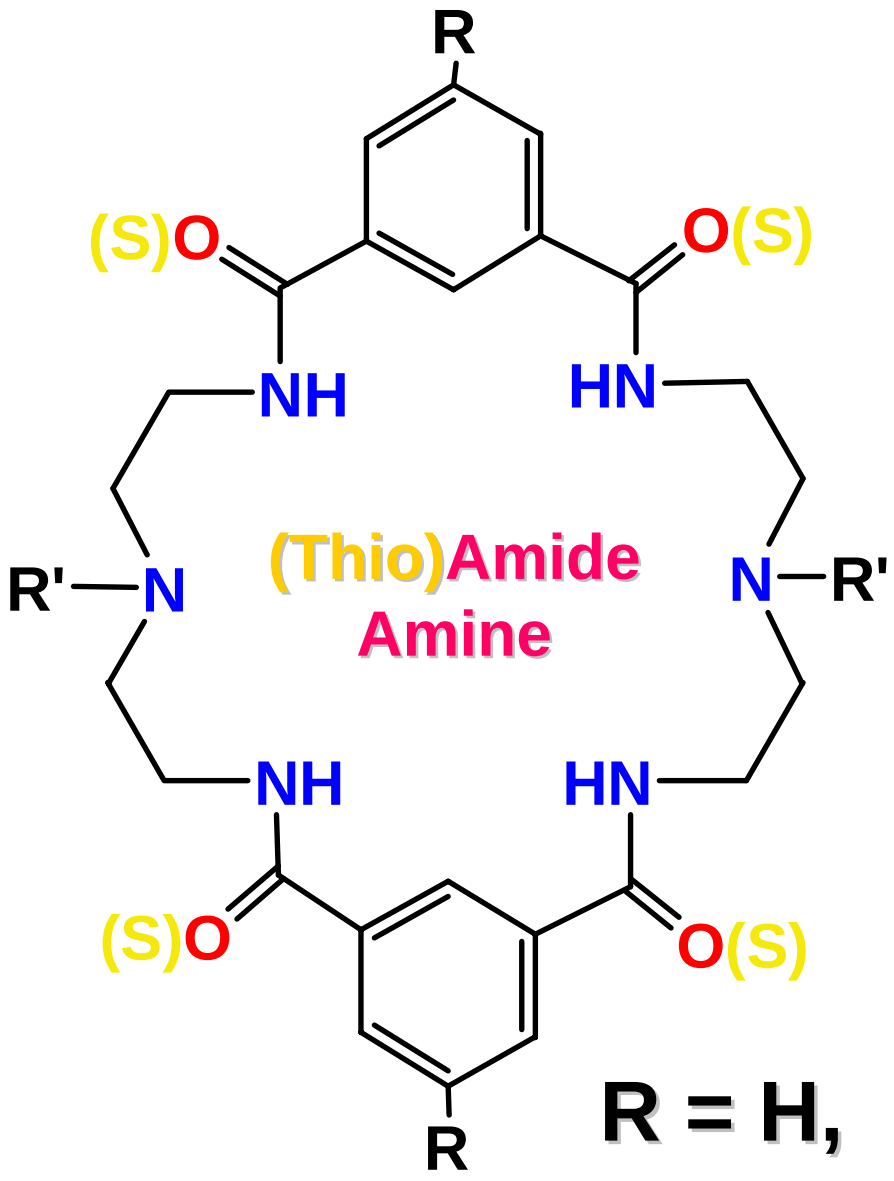
- The first synthetic sulfate-selective anion-binding agents;
- Simple, structure-based methods for modifying the intrinsic anion selectivity of a given class of anion receptors; and
- Use of dual cation/anion receptors for syntergized extraction

Hanford Site Needs

RL-WT101 Sulfate Mitigation – targeting methods for detection and removal of sulfate in LAW. Potential savings: $YY M.

Sulfate present in LAW results in the need for 20% more glass to be produced for vitrification purposes.

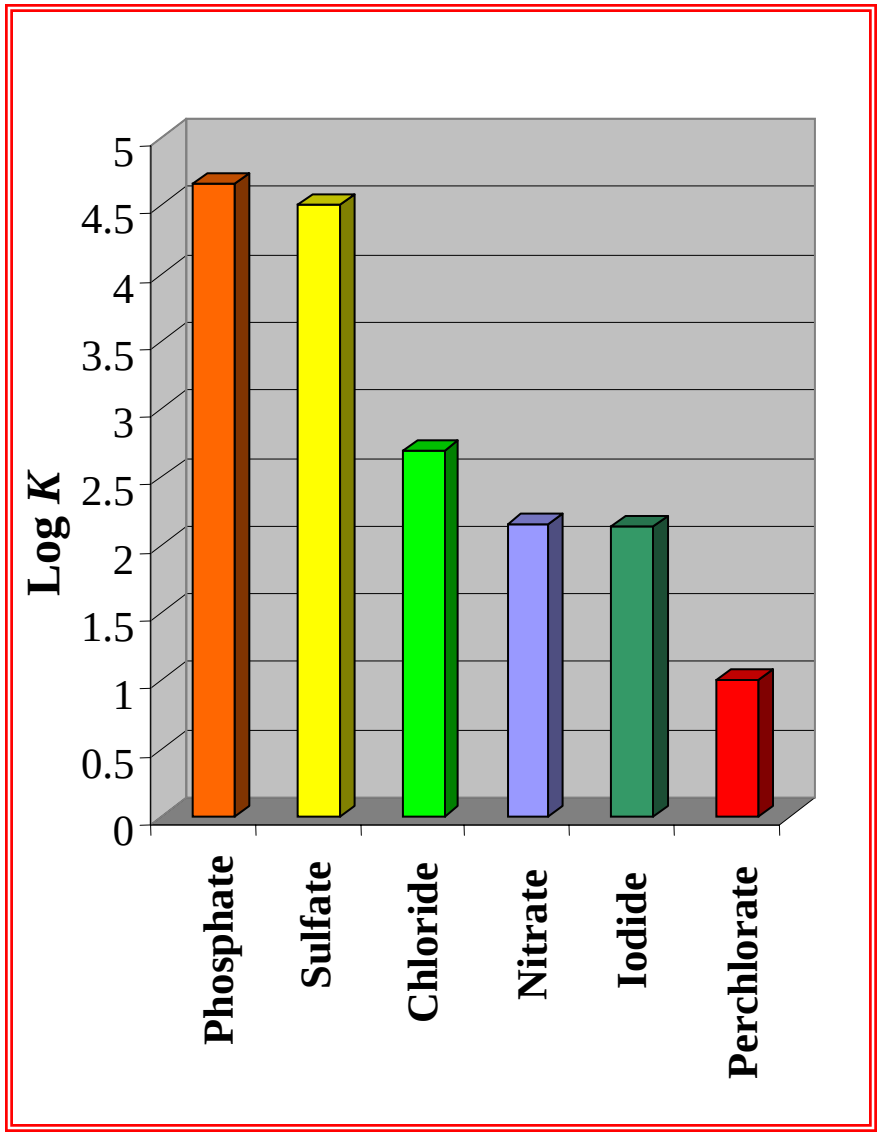




R = H, *t*-Bu

R' = CH_3, dansyl

Inorg. Chem., **2001**, *40,* 2936**.**



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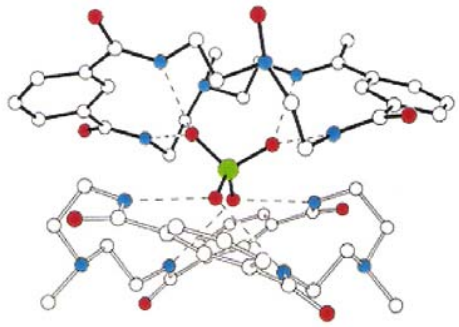
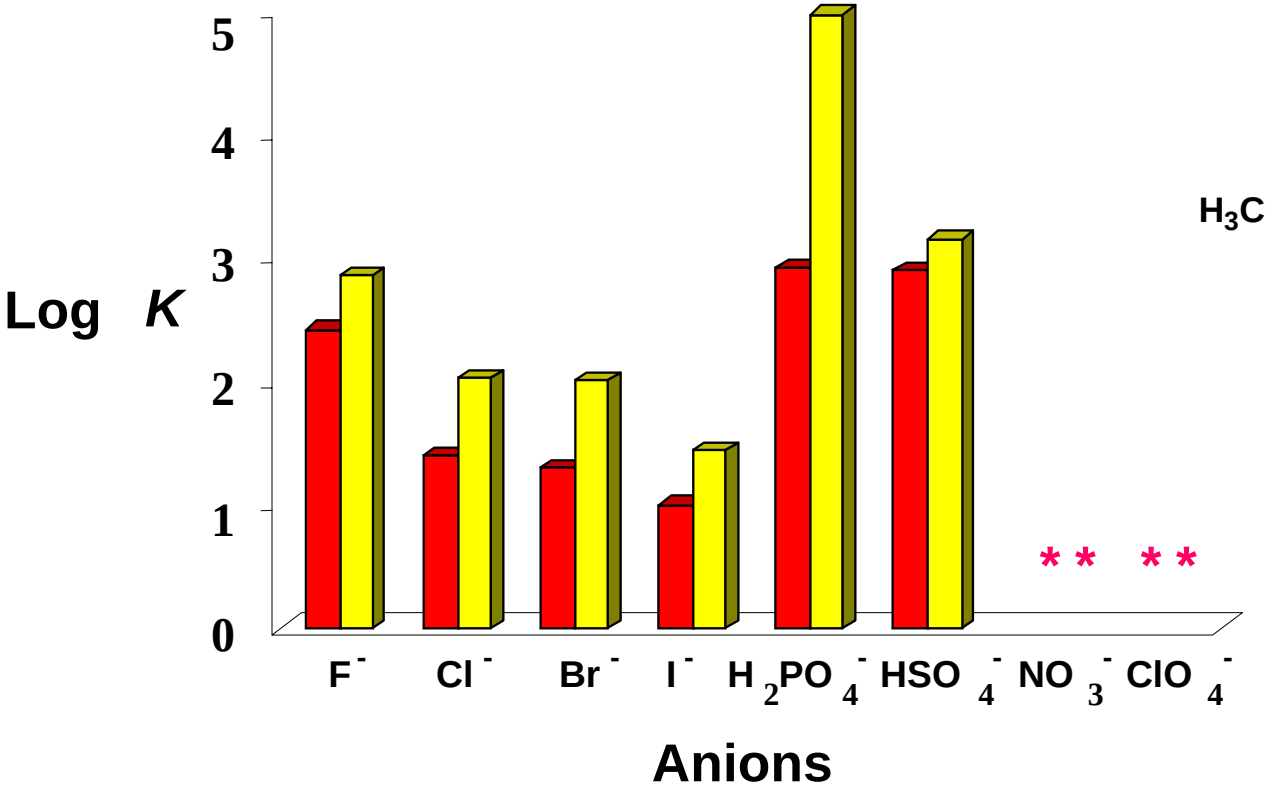
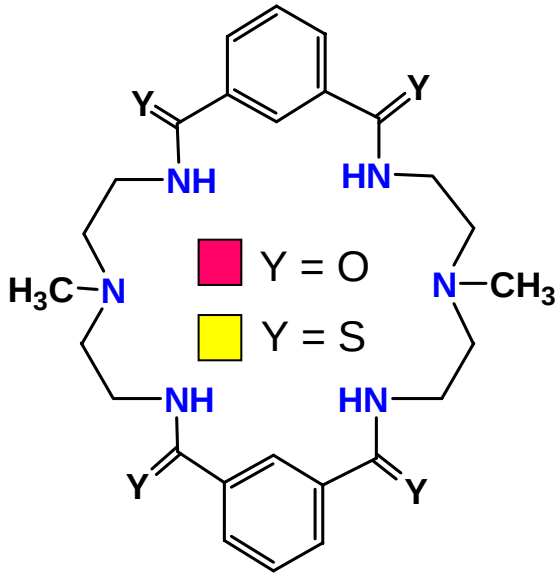
Sulfate ion sandwich

A new anion receptor designed by chemists at the University of Kansas could be used in sensors or in environmental remediation. Postdocs Md. Alamgir Hossain and José M. Llinares, working with chemistry professor Kristin Bowman-James and crystallographer Douglas Powell, synthesized and characterized a tetraamide macrocycle with high affinity for sulfate and phosphate [*Inorg. Chem.*, **40,** 2936 (2001)]. A crystallographic study indicates that the macrocycle forms a sandwich complex with sulfate (shown)--analogous to transition-metal sandwich complexes--in which one sulfate ion is held between two macrocycles by hydrogen bonds to eight amide hydrogens. "Lots of times you get layered complexes, but it is unusual to get a free-standing complex as a sandwich with an oxo anion in the center," Bowman-James says. The top macrocycle forms hydrogen bonds with the two sulfate oxygen atoms that are pointing upward, and the lower macrocycle is rotated 90° to form hydrogen bonds with the other two oxygen atoms.



Binding Studies

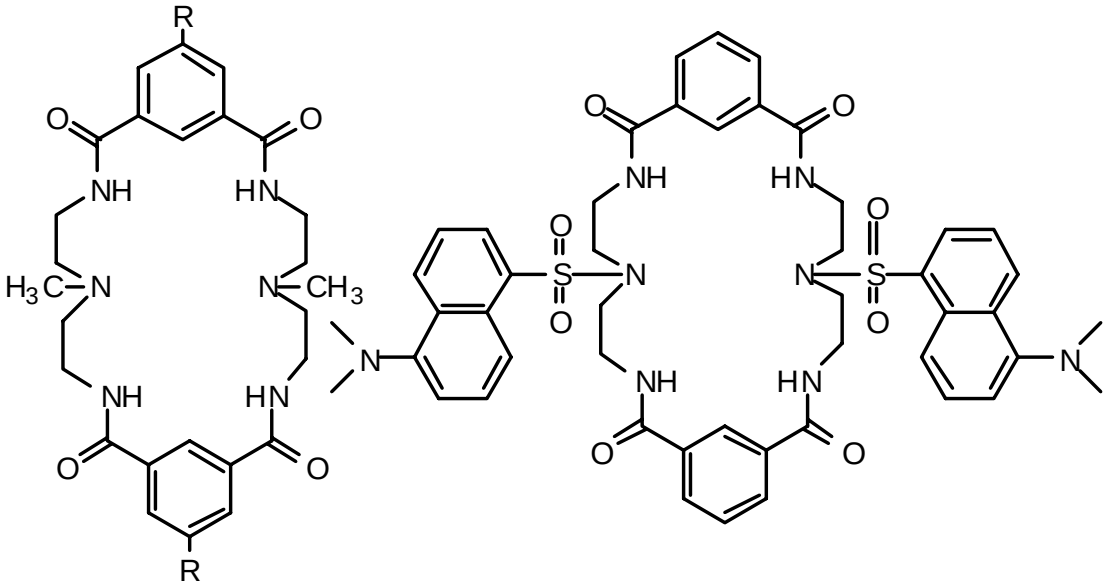




NMR in DMSO-d_6

Anion Hosts

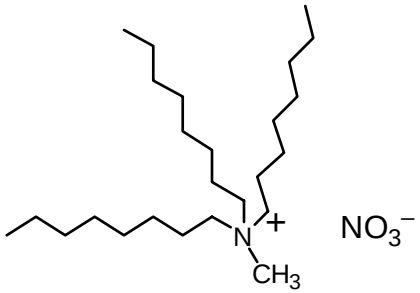
Mac Tetraamides (Bowman-James):



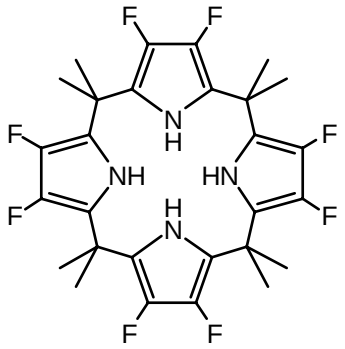
MMEAM/t-BuMEAM

DsMEAM

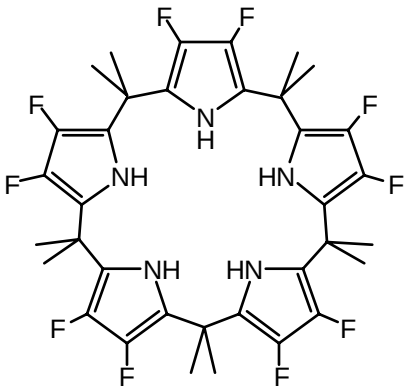
Lipophilic Quat. Ammonium Salt:



Calixpyrroles (Sessler):

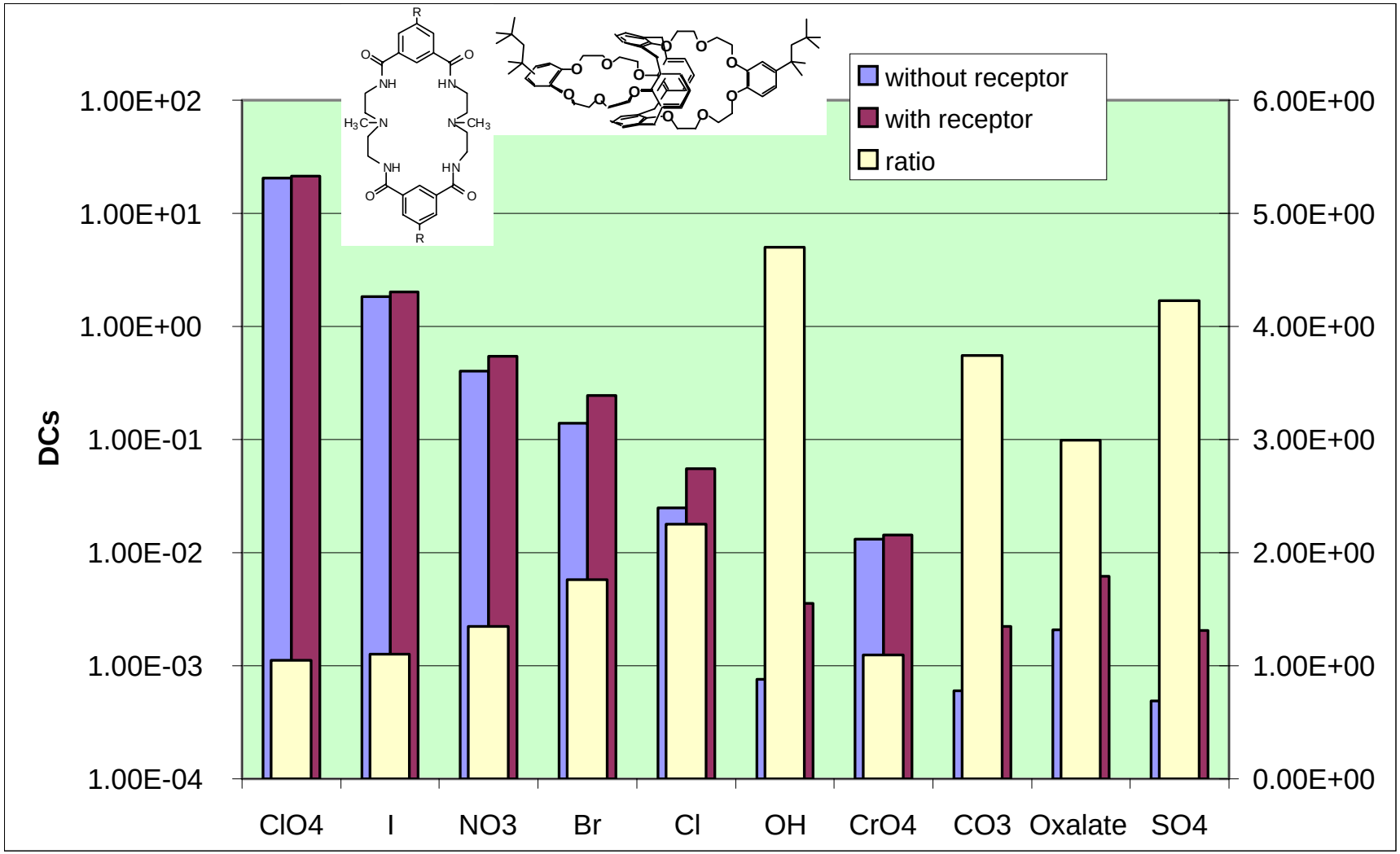


F8C4P



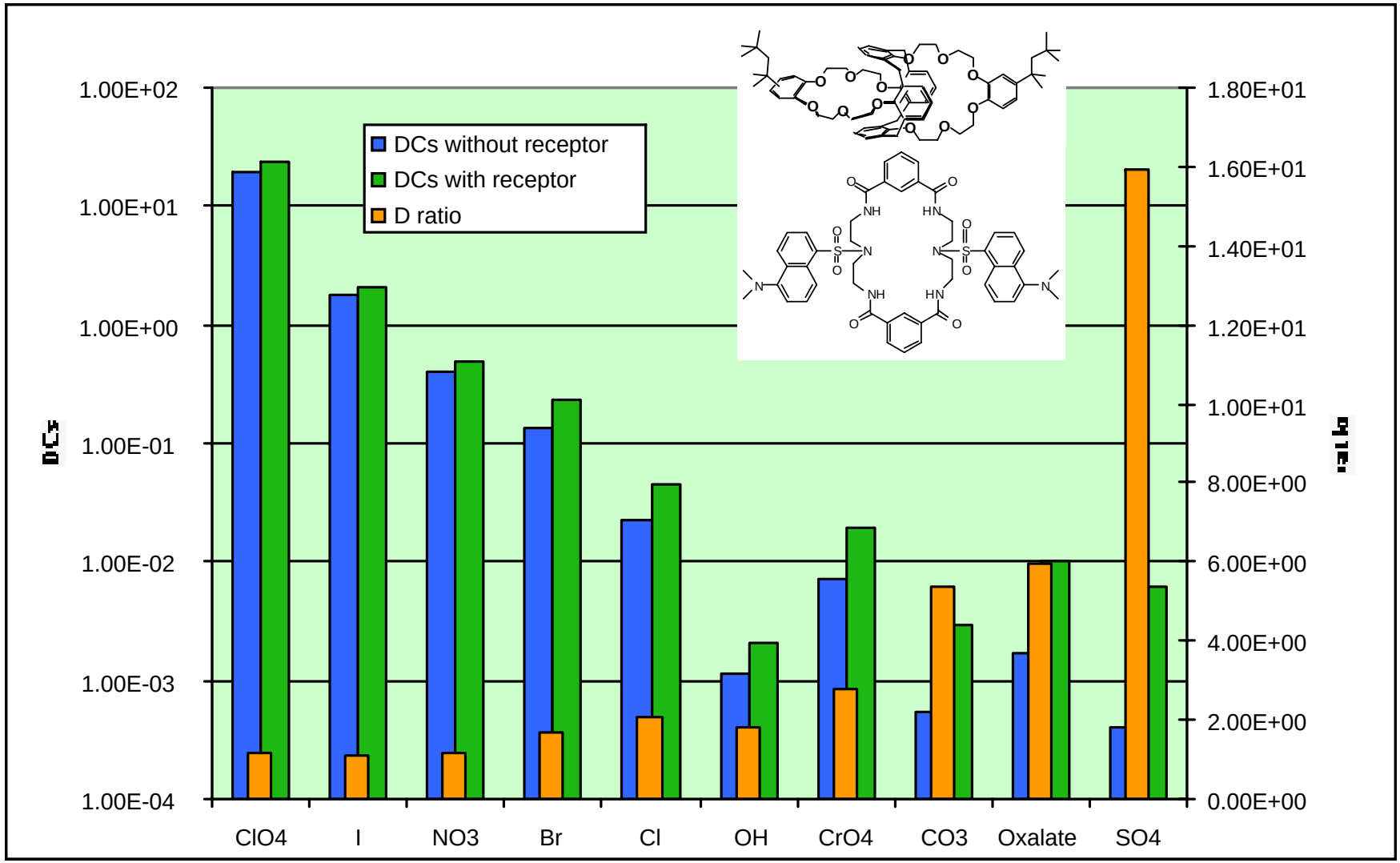
F10C5P

Synergized Extraction with BOBCalixC6



[BOBCalixC6] = 10 mM, [MMEAM] = 10 mM in NB; aq Cs salt concentration variable; O/A = 1, 25 °C

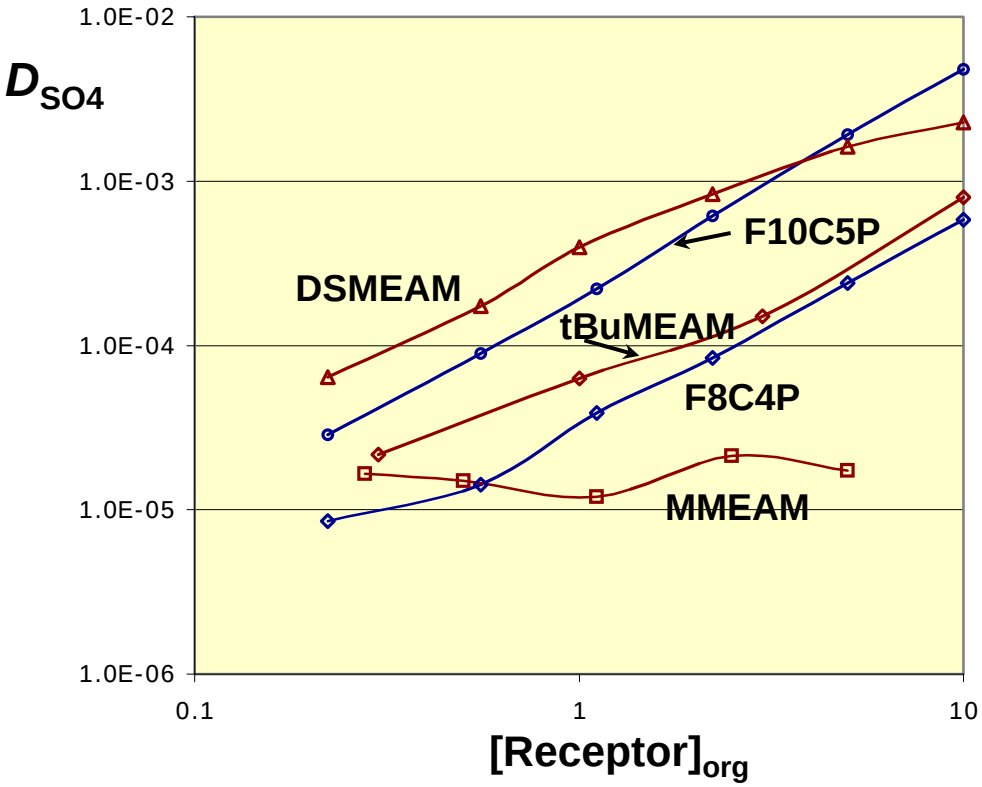
Synergized Extraction (cont.)



[BOBCalixC6] = 10 mM, [DSMEAM] = 3 mM in NB; aq Cs salt concentration variable; O/A = 1, 25 °C

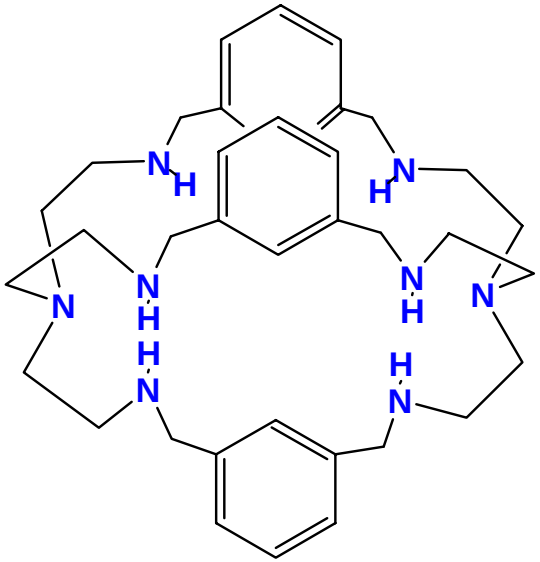
Synergized Anion Exchange

- $Q^+NO_3^-$ alone is weak
- Strong synergistic effect
- F10C5P > F8C4P
- Substituents affect amides – possibly a solubility issue

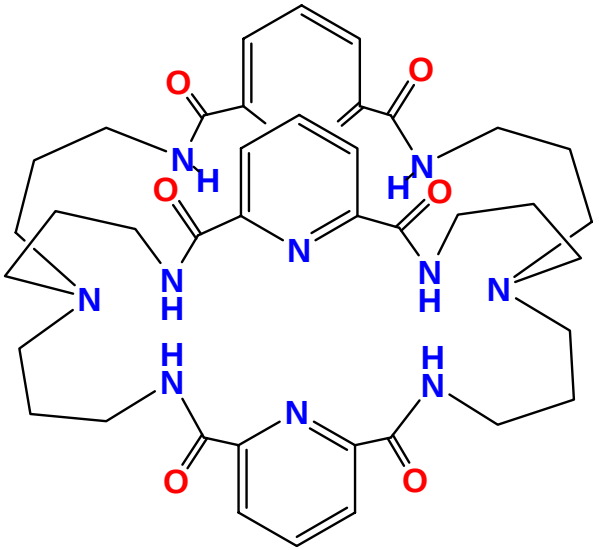


Org: 0.25–10 mM Receptor, 10 mM $Q^+NO_3^-$ in $CHCl_3$
Aq: 10 mM $NaNO_3$, 0.1 mM Na_2SO_4, 1 mM NO_3
O/A = 1, 25 °C

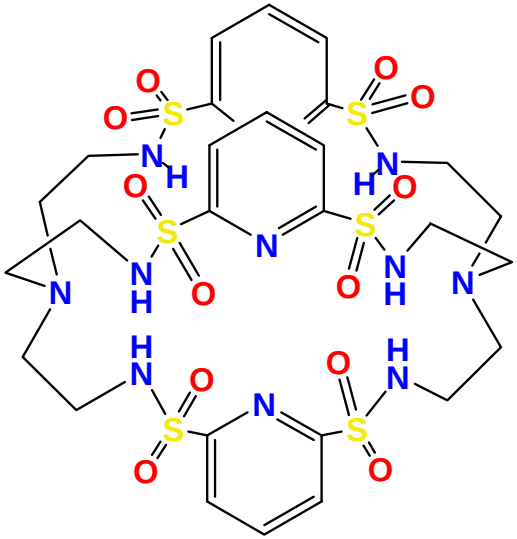
Cryptands



Amine

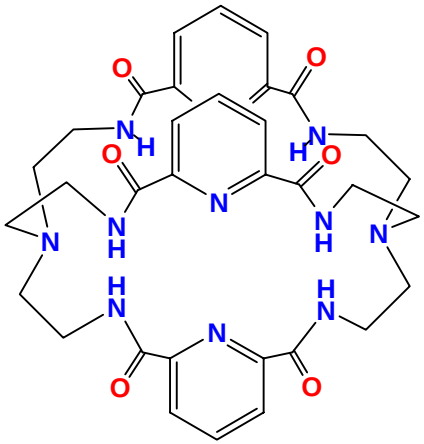


Amide/Thioamide

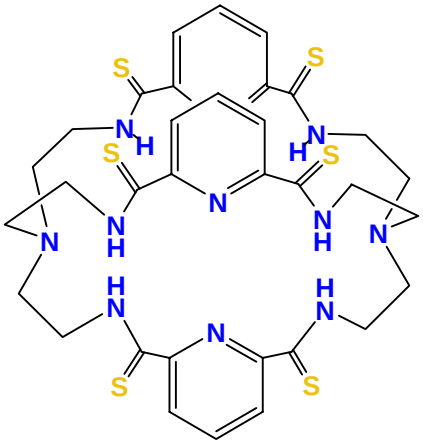


Sulfonamide

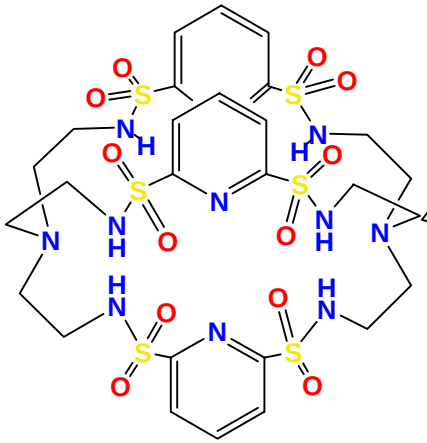
Sulfate Binding



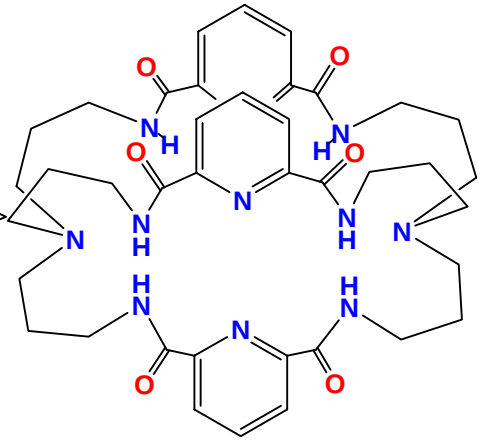
L1



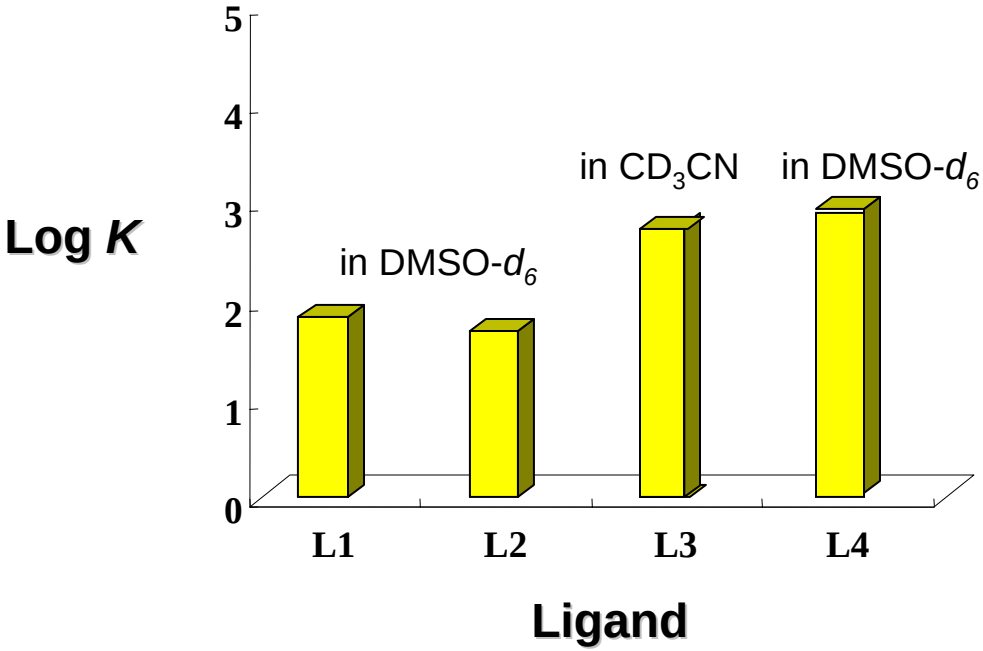
L2



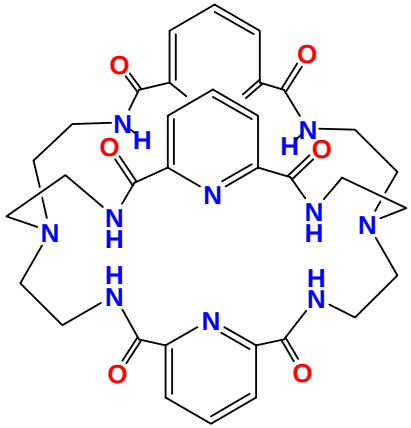
L3

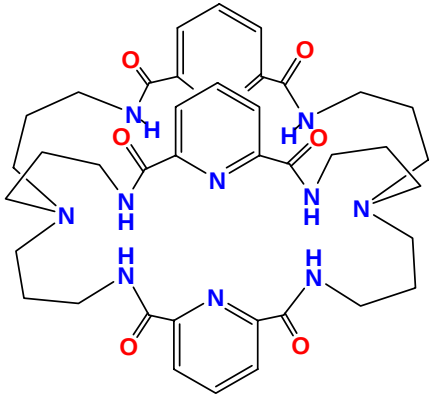


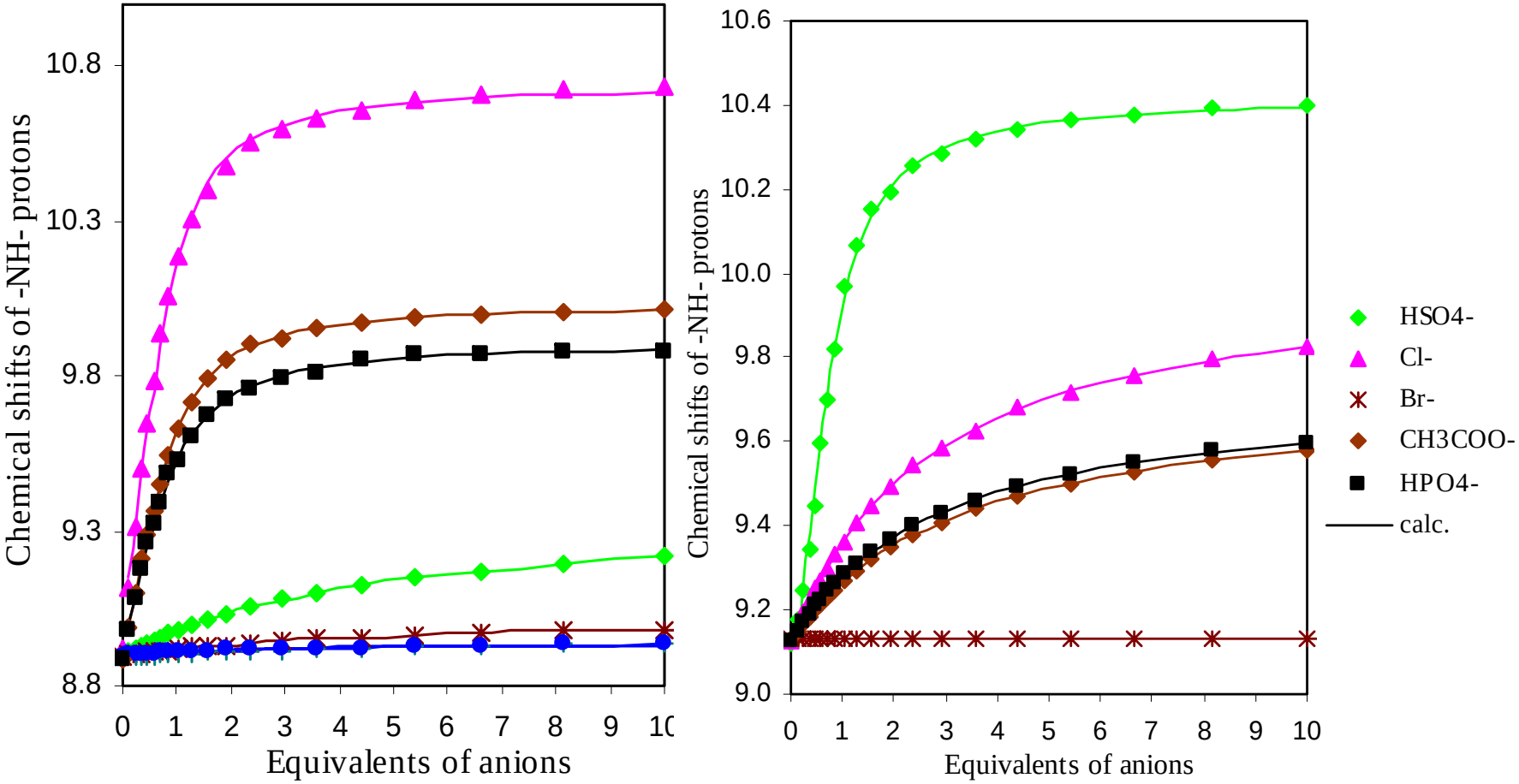
L4



Binding Studies







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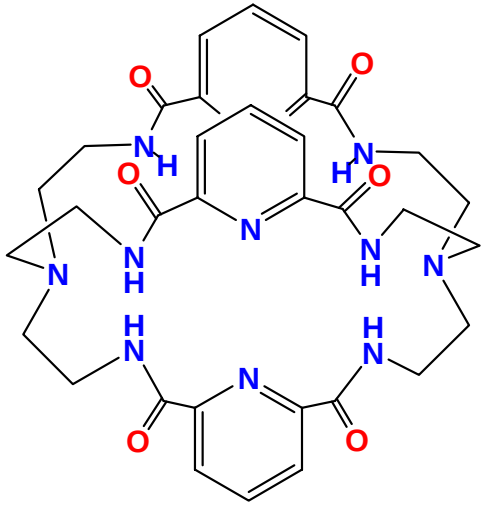
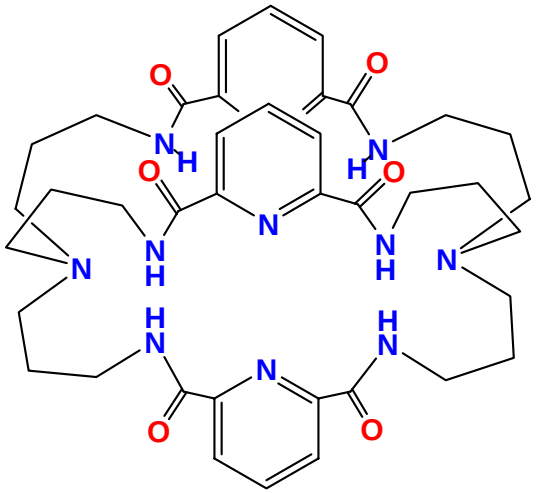


L1

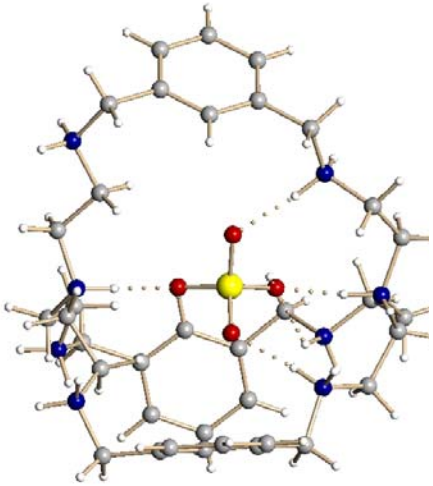


L4

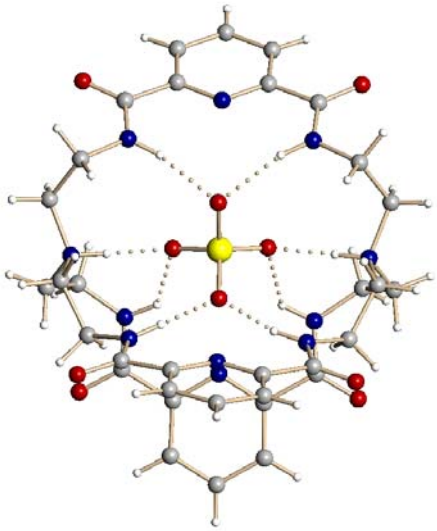
K/M^{-1} (DMSO-d_6)

Ligand	Cl^-	Br^-	I^-	HSO_4^-	$H_2PO_4^-$	NO_3^-	ClO_4^-	CH_3COO^-
L1	3020	40	20	68	2042	85	98	2408
L4	180	7	0	**2720**	166	0	0	130

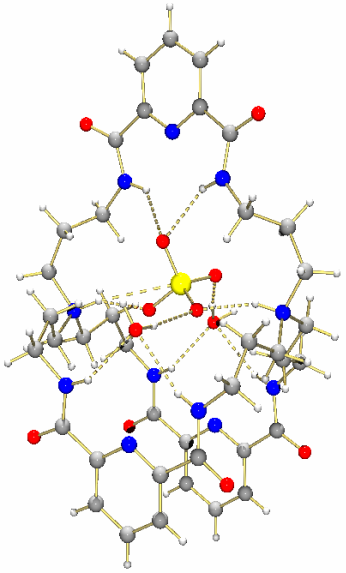
Structures



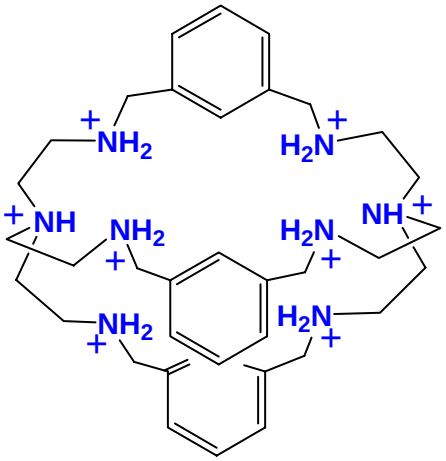
Five-coordinate

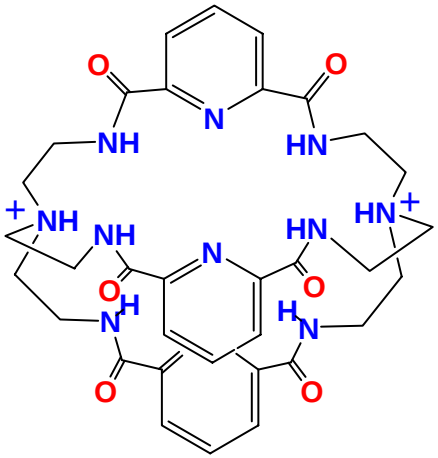


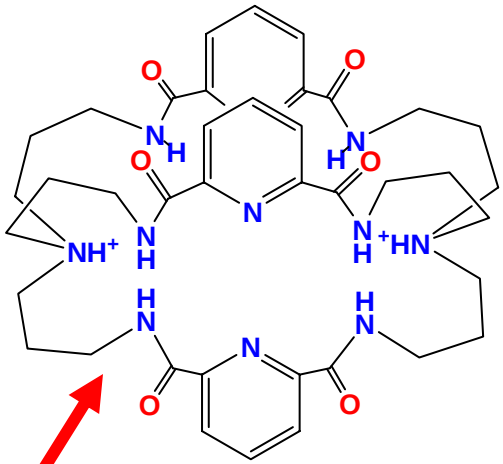
Eight-coordinate



Seven-coordinate



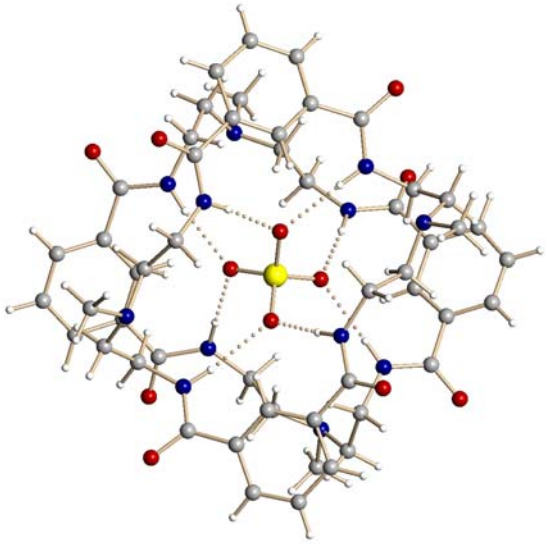


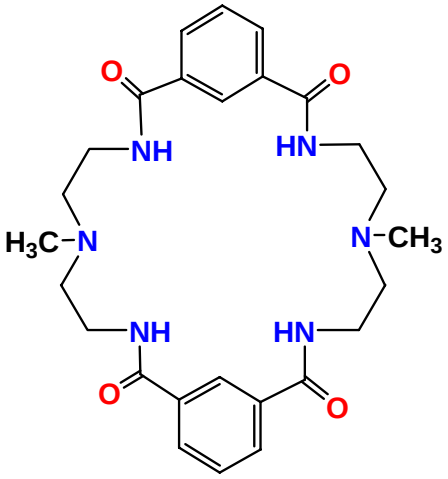


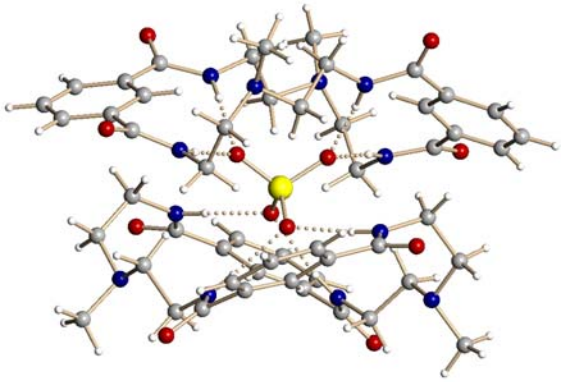
Chem. Commun. **2005**, 328.

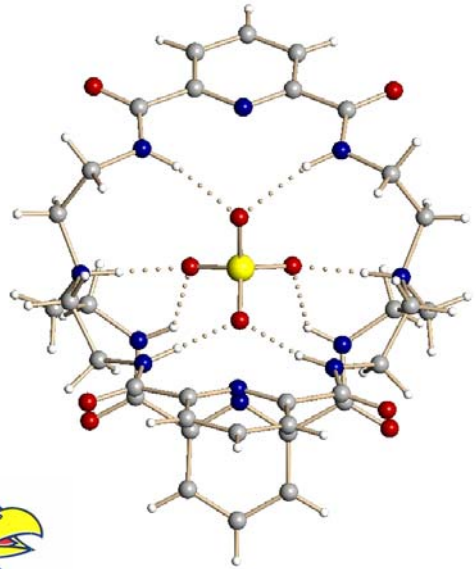
NEW

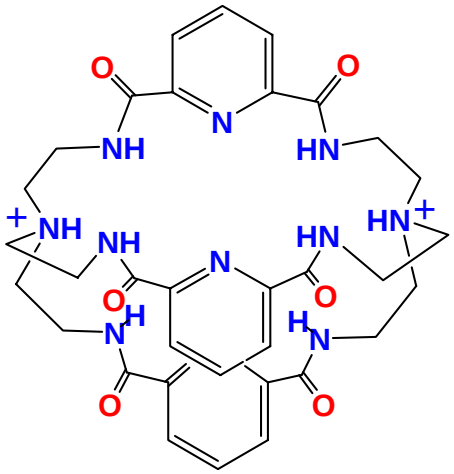
Eight-coordinate

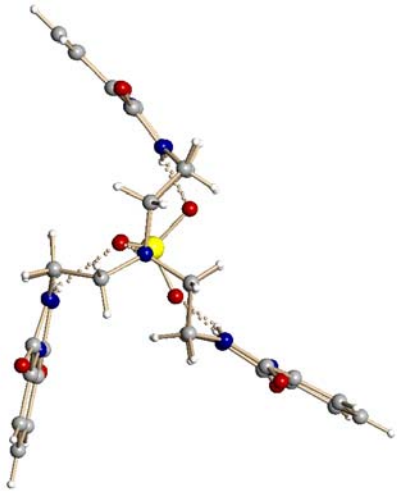












Inorg. Chem. **2001**, *40,* 2936**.**
Chem. Commun. **2005**, 328.

Future Goals

- To modify the monocyclic systems to obtain greater solubilities in organic and especially hydrocarbon solvents.
- To examine the bicyclic cryptand systems for selective extraction of sulfate.
- To modify the bicyclic cryptand systems by substituents such as *t*-butyl groups on the aromatic spacers to make them more soluble in organic solvents.
- To synthesize hybrids between the calixpyrroles and the amido-based systems.

Researchers

Graduate Students

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