Cage-functionalized, Nitrogen-containing Crown Ethers and Podands; Potential New Host Systems for Extraction of NaOH from Wastes

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Abstract. The objective of this study is to synthesize suitable host systems that can be used to separate sodium hydroxide and other predominant sodium salts from high-level alkaline nuclear tank waste stored at various U. S. Department of Energy sites. To this end, a series of cage-functionalized monoaza, diaza, and triaza macrocyclic crown ethers have been prepared along with two novel, cage-functionalized, nitrogen-containing dendrimers. Properties of these unusual host systems as selective NaOH complexants and extractants will be assessed.

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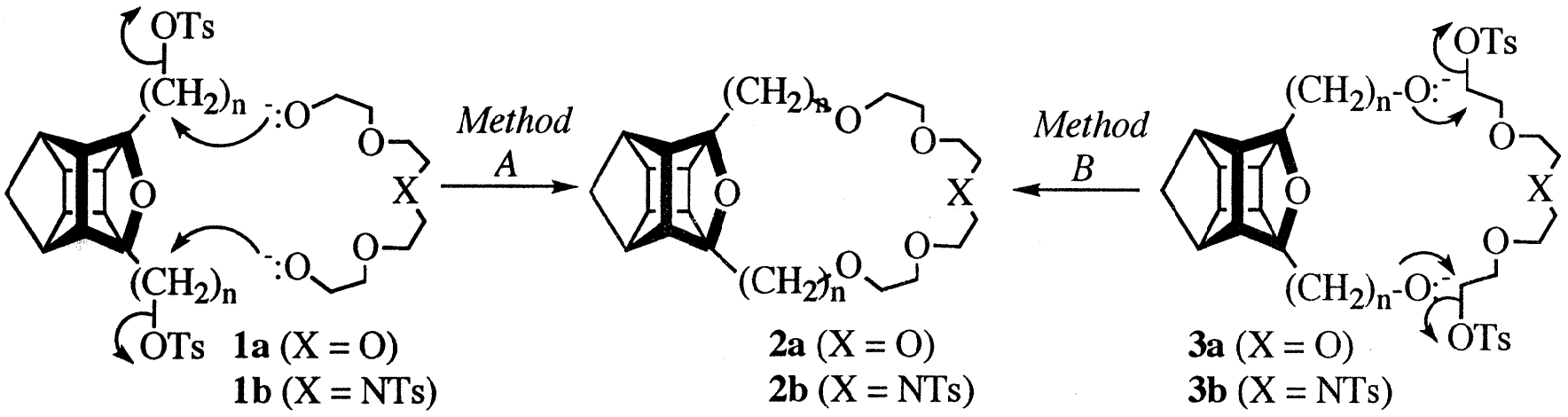
Breakout Session 4: *Tanks Focus Area -*
Waste and Radionuclide Chemistry and Separations

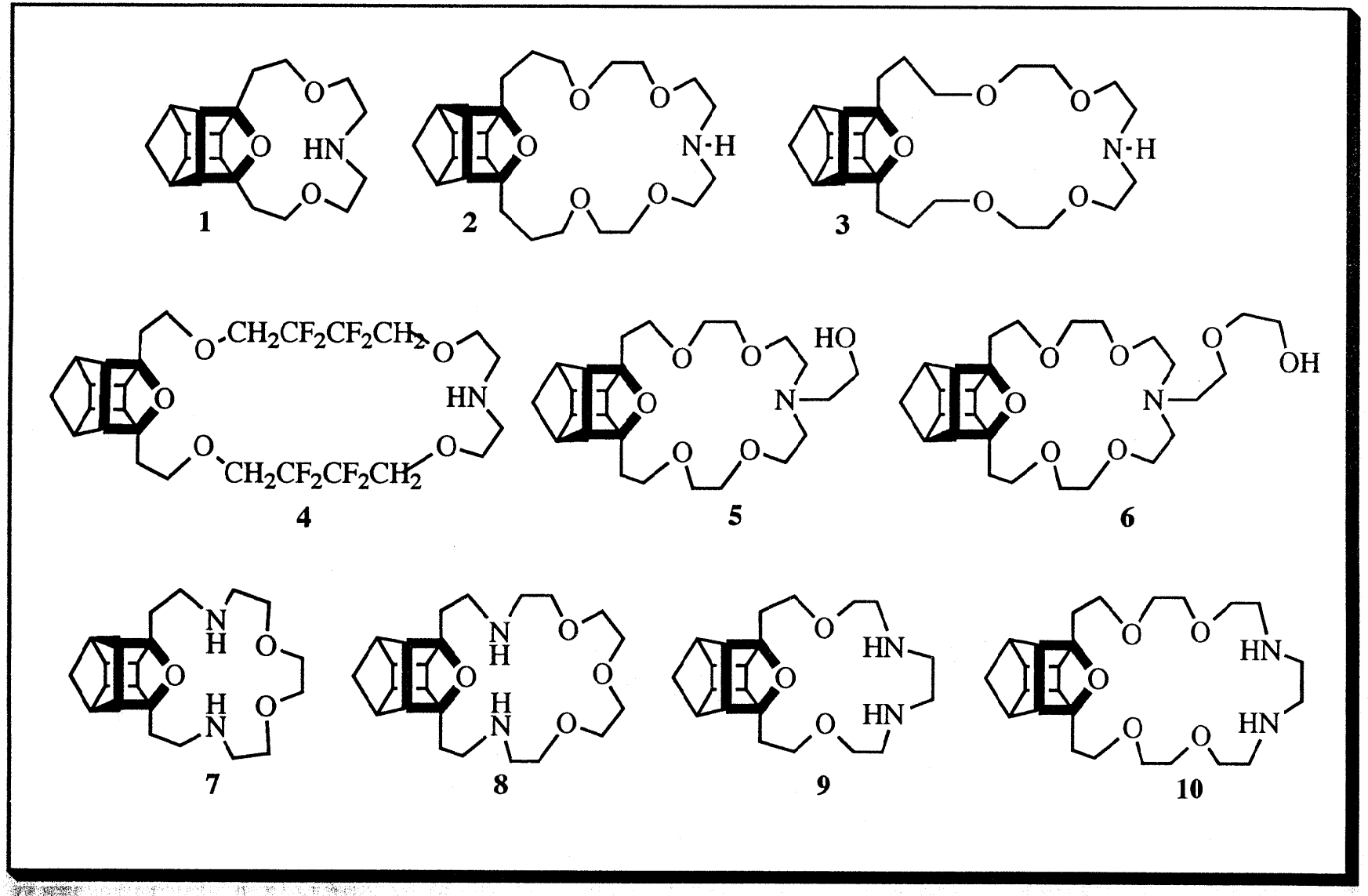
DOE Problem Under Investigation: Disposal of high-level waste from storage tanks requires sludge-washing with NaOH. If NaOH could be separated from tank waste and recycled, the addition of fresh NaOH during the washing process could be avoided, thereby reducing the final waste volume and associated disposal costs.

Research Objective and Methodology: New liquid-liquid extraction approaches to the selective separation of NaOH from alkaline high-level wastes stored in underground tanks at the Hanford and Savannah River sites are being pursued. Secondary priority is given to separating K^+ and abundant anions, e.g., nitrate, nitrite, aluminate, and carbonate. A comprehensive approach toward understanding the extractive chemistry of these salts is underway that involves systems of varying complexity, i.e., from the use of simple solvents to new bifunctional host molecules for ion-pair recognition. The overall goal of this research is to provide a scientific foundation upon which the feasibility of new liquid-liquid extraction chemistry applicable to bulk reduction of the volume of tank waste can be evaluated. To this end, a series of cage-functionalized monoaza (**1-6**), diaza (**7-10**), and triaza macrocyclic crown ethers (**11** and **12**) have been prepared along with two novel, cage-functionalized, nitrogen-containing dendrimers (**13** and **14**) .

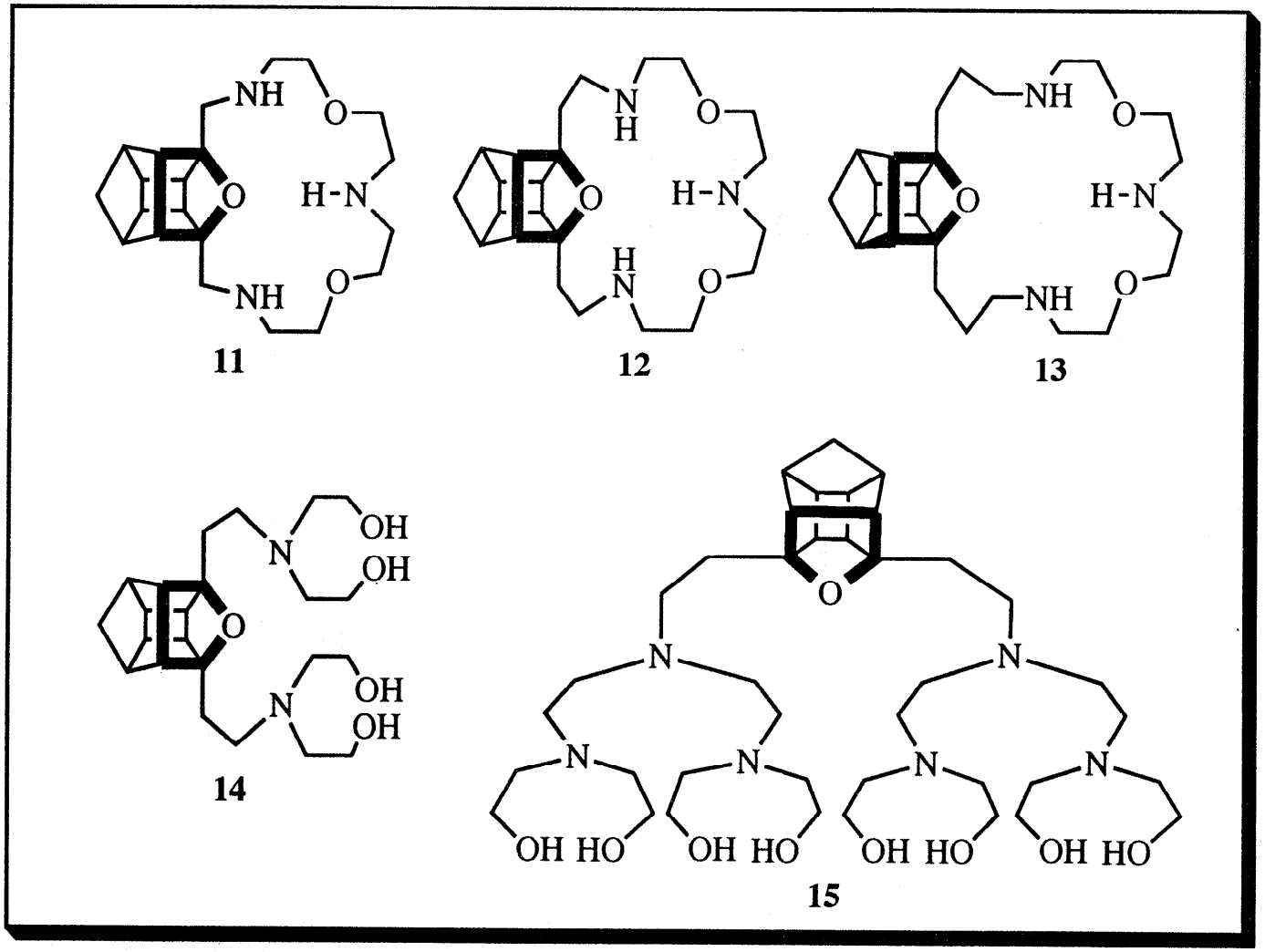
Synthetic methods used to prepare cage-annulated crown and azacrown ethers



New cage-annulated monoaza- (**1**-**6**) and diaza-crown ethers (**7**-**10**) synthesized in this study



New cage-annulated triazacrown ethers (**11-13**) and nitrogen-containing dendrimers (**14** and **15**) synthesized in this study



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Summary of Research Progress

1. Dr. Bruce A. Moyer and coworkers at Oak Ridge National Laboratory (ORNL) have demonstrated their ability to ex-tract NaOH selectively in several systems that involve simple aqueous phases and complex waste simulants.

2. Quantitative recovery of NaOH by stripping with water has been demonstrated by the ORNL team; during their investigation, these investigators also demonstrted that certain solvents could be cycled several times without loss of performance. Selectivity for HO^- over NO_3^- transfer exceeds 20 : 1. Caustic recycle applications include recycle of NaOH at several DOE sites as well as in certain industrial processes.

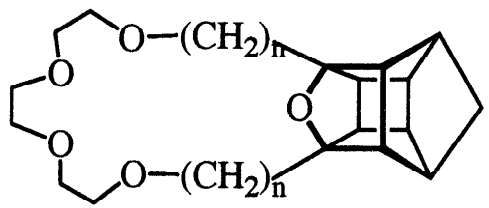
3. Synthesis of novel cage-functionalized crown ethers and podands is being carried out at the University of North Texas (UNT). These cation receptors offer the potential to enhance NaOH separation efficiency and selectivity, and indeed this has been shown to be the case among several nitrogen-containing macrocycles that have been prepared at UNT and tested at ORNL. These successful initial investigations provide valuable information that guides our continuing efforts to design more effective host systems

Evaluation of Binding Selectivities of Cage Annulated Crown Ethers via Electrospray Ionization/Quadrupole Ion Trap Mass Spectrometry

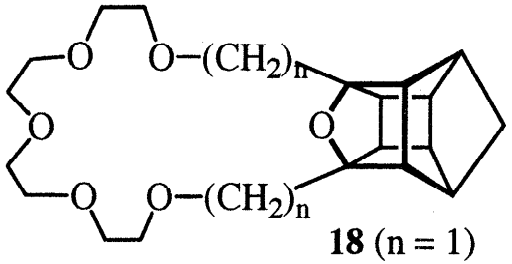
Electrospray ionization (ESI) has proved to be a useful tool for investigating host-guest and other non-covalent interactions.

In the present study, binding selectivities of five cage annulated crown ethers (i.e., 1-5, below) were evaluated by using ESI/quadrupole ion trap mass spectrometry.

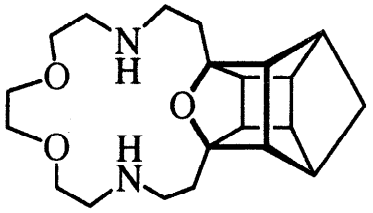
The results thereby obtained have been compared qualitatively with the corresponding values obtained for corresponding non-cage annulated crown ethers ("model compounds").



16 (n = 1)
17 (n = 3)

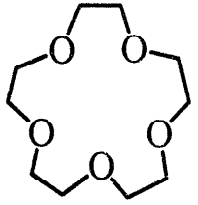


18 (n = 1)
19 (n = 3)

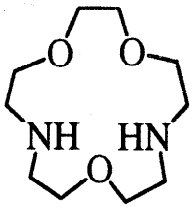


7

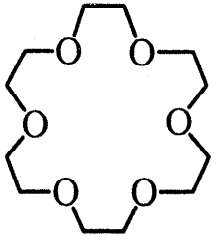
Model Compounds:



15-crown-5



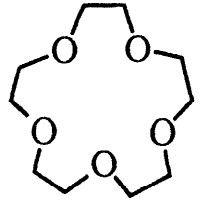
1,7-diaza-15-crown-5



18-crown-6

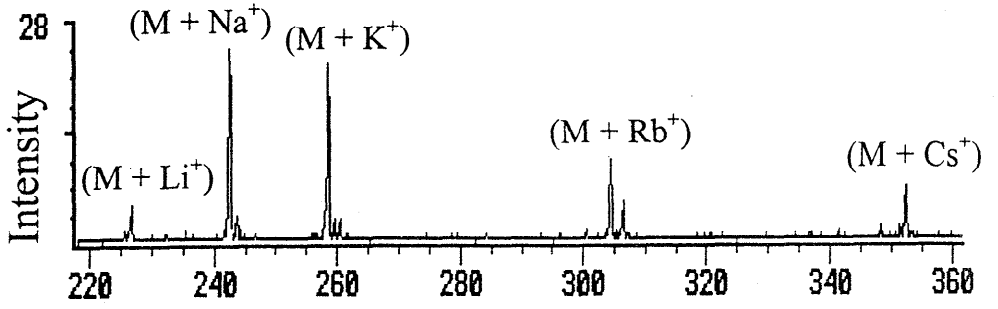
Syntheses: Dr.Hyun-Soon Chong, Mr. Zhibing Chen, Mr. Zilin Huang, *University of North Texas*

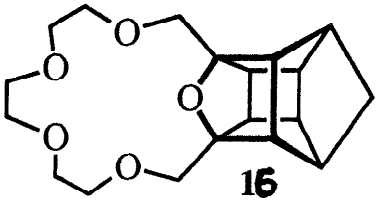
Electrospray ionization (ESI) mass spectra of (A) 15-crown 5- and (B) compound 1 with LiCl, NaCl, KCl, RbCl, and CsCl (1:1:1:1:1:1) in MeOH. Each ligand and alkali metal chloride is 1.5×10^{-4} M initially.



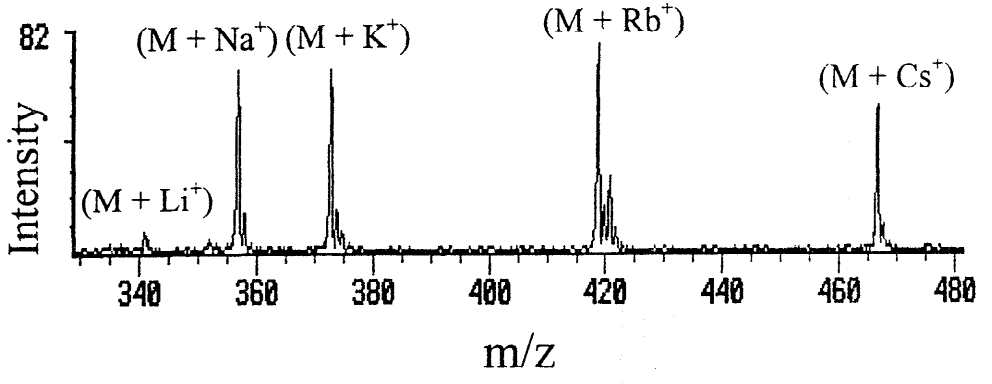
15-crown-5

A





B

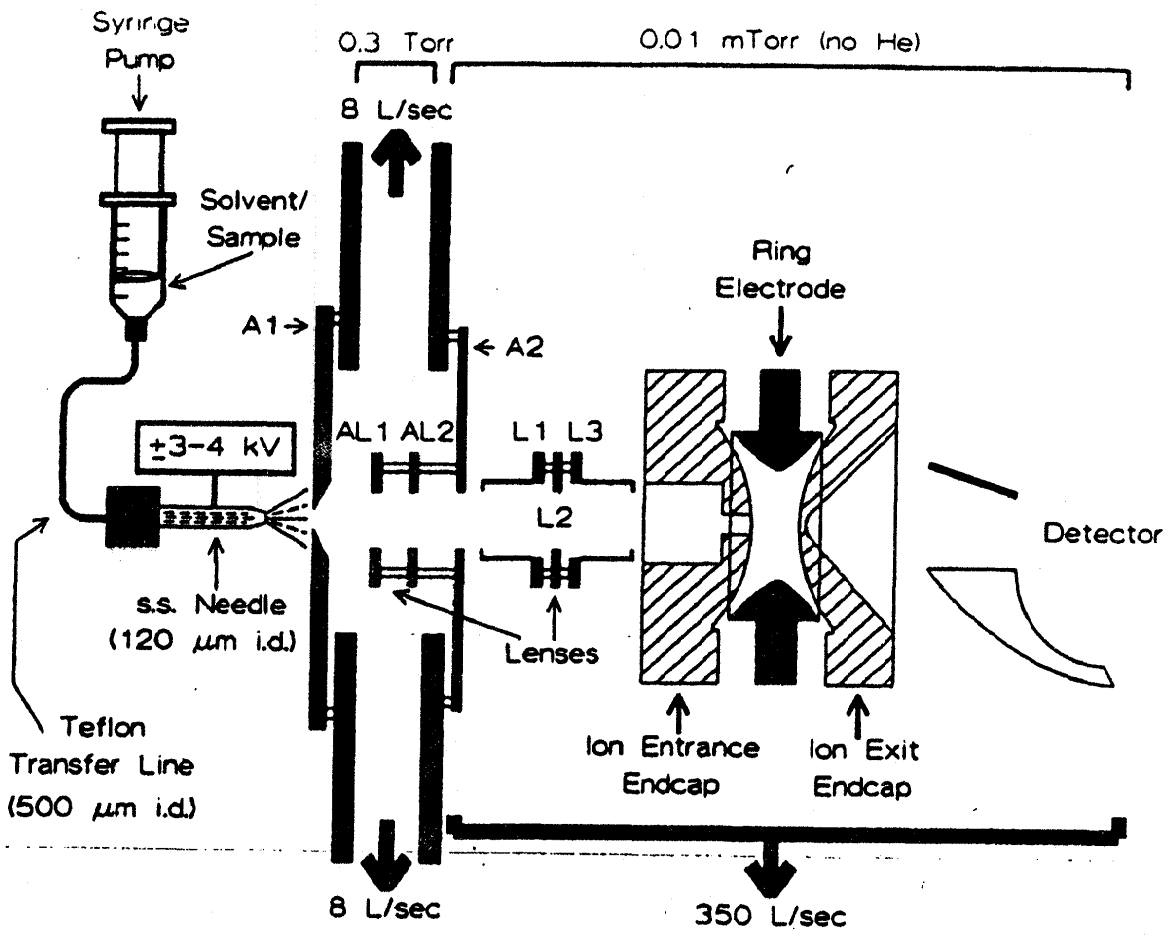


Conclusions:

1. Compound **1** displays enhanced selectivity toward binding of the larger alkali metal cations, i.e., Rb^+ and Cs^+ *vis-à-vis* that of 15-crown-5.

2. Incorporation of the cage moiety appears to make **1** somewhat more rigid and more open than the flexible 15-crown-5- ring, thereby rendering **1** more amenable to binding with larger cationic guests.

ESI-QID mass spectral studies were performed by Professor Jennifer S. Brodbelt ahd Ms. Michelle L. Reyzer, *Department of Chemistry, University of Texas at Austin, Austin, Texas 78712-1167.*



Cross-sectional view of the instrumental configuration for electrospray ionization into a quadrupole ion trap. Diagram reprinted from "Electrospray Ionization Combined with Ion Trap Mass Spectrometry" by Van Berkel, G. J., Glish, G. L., and McLuckey, S. A., *Anal. Chem.*, **1990**, *62*, 1284-1295.

Binding Selectivity Data[a]

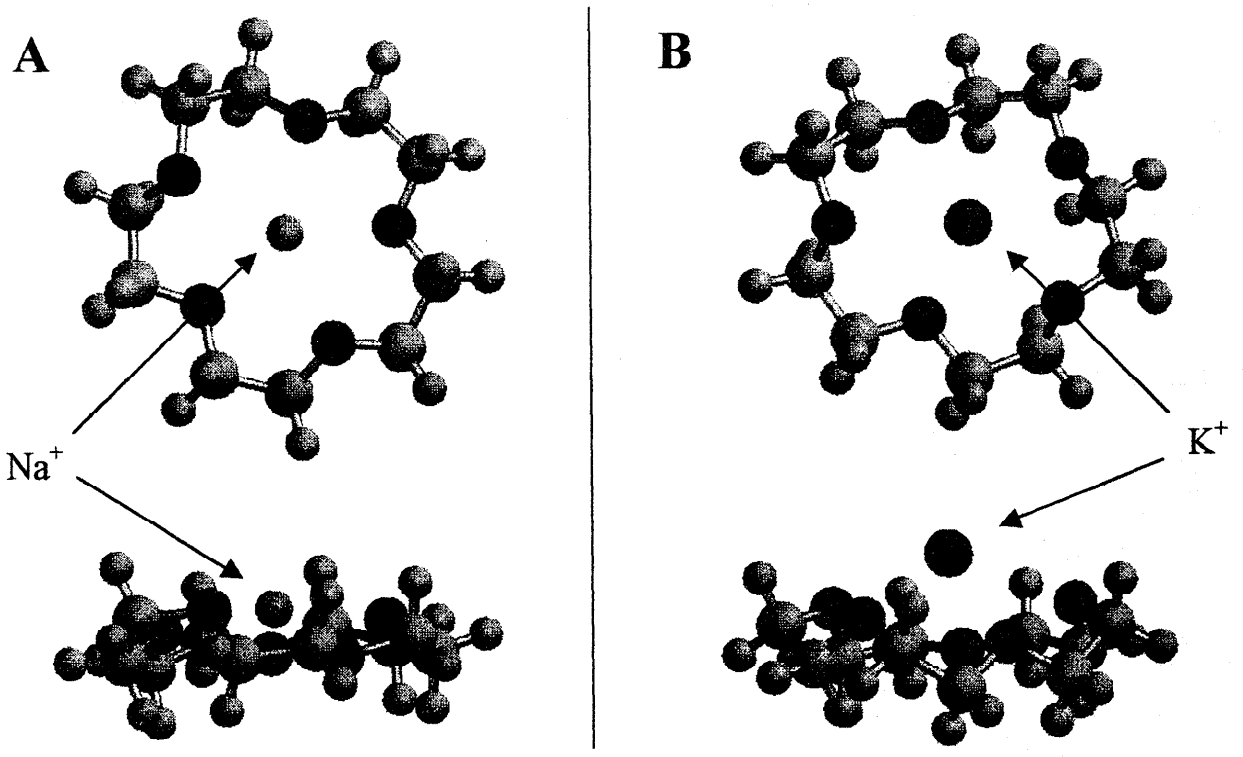
Ion	15-Crown-5		16	17	Diaza-15-crown-5	7	18-Crown-6		18	19
	Theory[b]	Experiment	Experiment	Experiment	Experiment	Experiment	Theory[c]	Experiment	Experiment	Experiment
$[M + Li]^+$	0%	6%	3%	2%	22%	14%	N/A	1%	0%	4%
$[M + Na]^+$	34%	36%	28%	11%	**52%**	**58%**	3%	6%	6%	11%
$[M + K]^+$	40%	34%	26%	**52%**	12%	10%	**61%**	**60%**	**68%**	24%
$[M + Rb]^+$	14%	16%	**29%**	28%	8%	12%	32%	24%	22%	30%
$[M + Cs]^+$	12%	8%	**13%**	6%	6%	6%	4%	8%	3%	**31%**

[a]Experimental values expressed as percent of [M + alkali metal$^+$] present in a 1:1:1:1:1:1 solution, calculated as the peak intensity of [M + alkali metal$^+$] divided by the sum of the peak intensities of each complex present (average of two trials). The total percentages include the contribution from the isotopic peaks. All values ±5% for data sets collected on different days. Initial concentrations of all species employed in this study were 1.5×10^{-4} M.

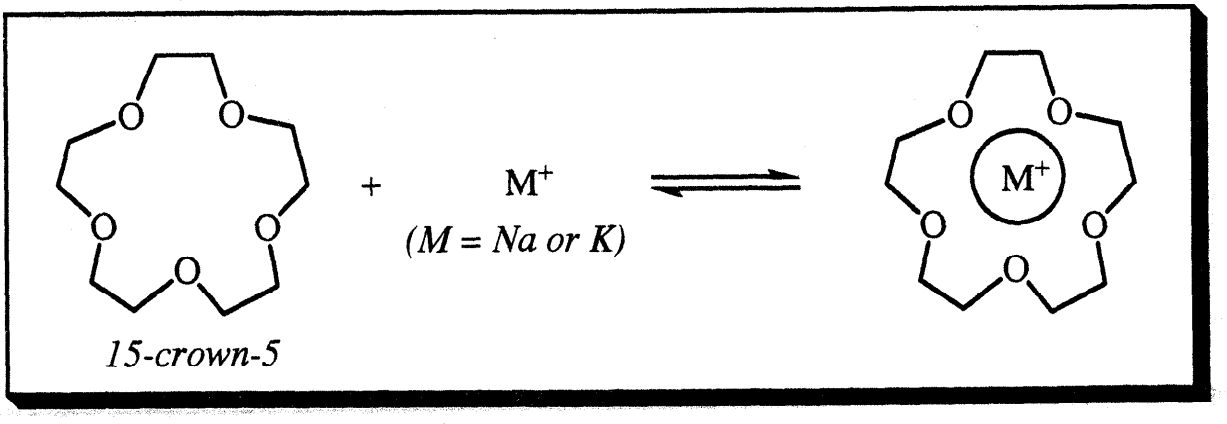
[b]Theoretical values were obtained by using MINEQL+ solution equilibria software, version 4.01, available from Environmental Research Software, Hallowell, ME) and the following log K values that have been reported in prior literature: Li^+ = 1.21, Na^+ = 3.31, K^+ = 3.38, Rb^+ = 2.88, Cs^+ = 2.8.

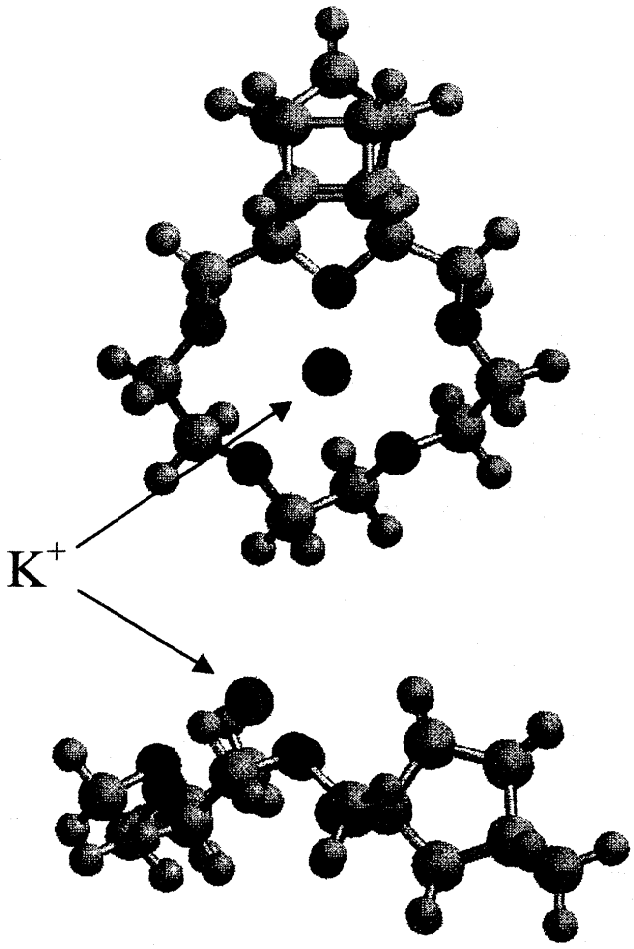
[c]Theoretical values were obtained by using MINEQL+ solution equilibria software, version 4.01, available from Environmental Research Software, Hallowell, ME) and the following log K values that have been reported in prior literature: Li^+ (no data available), Na^+ = 4.46, K^+ = 6.20, Rb^+ = 5.73, Cs^+ = 4.49.

ESI-QID mass spectral studies were performed by Professor Jennifer S. Brodbelt and Ms. Michelle L. Reyzer, *Department of Chemistry, University of Texas at Austin, Austin, TX 78712*

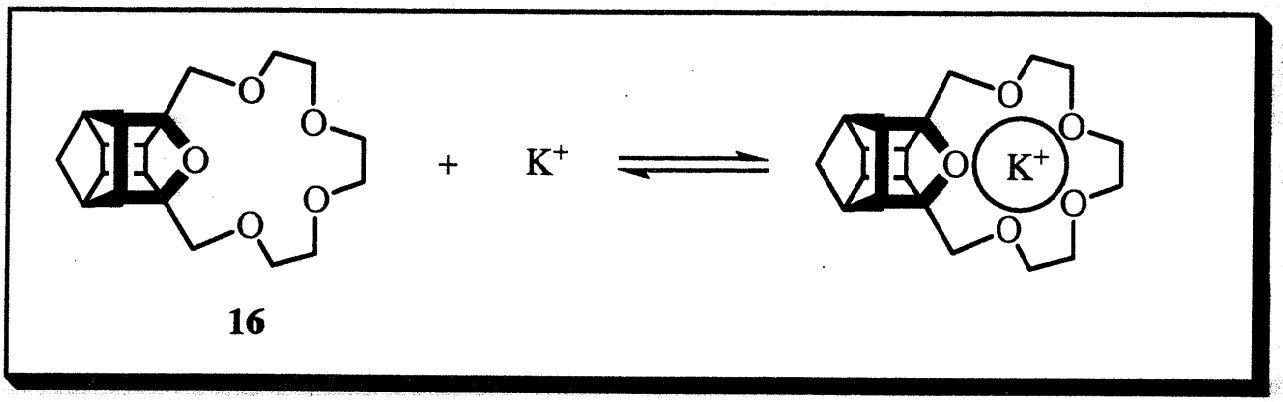


Low energy conformers of 15-crown-5 binding **(A)** Na^+ and **(B)** K^+. Atom key: small grey = hydrogen, medium grey = carbon, red = oxygen, yellow = Na^+, green = K^+.





Low energy conformer of the 15-crown-5 caged analog binding K^+. Atom key: small grey = hydrogen, medium grey = carbon, red = oxygen, green = K^+.



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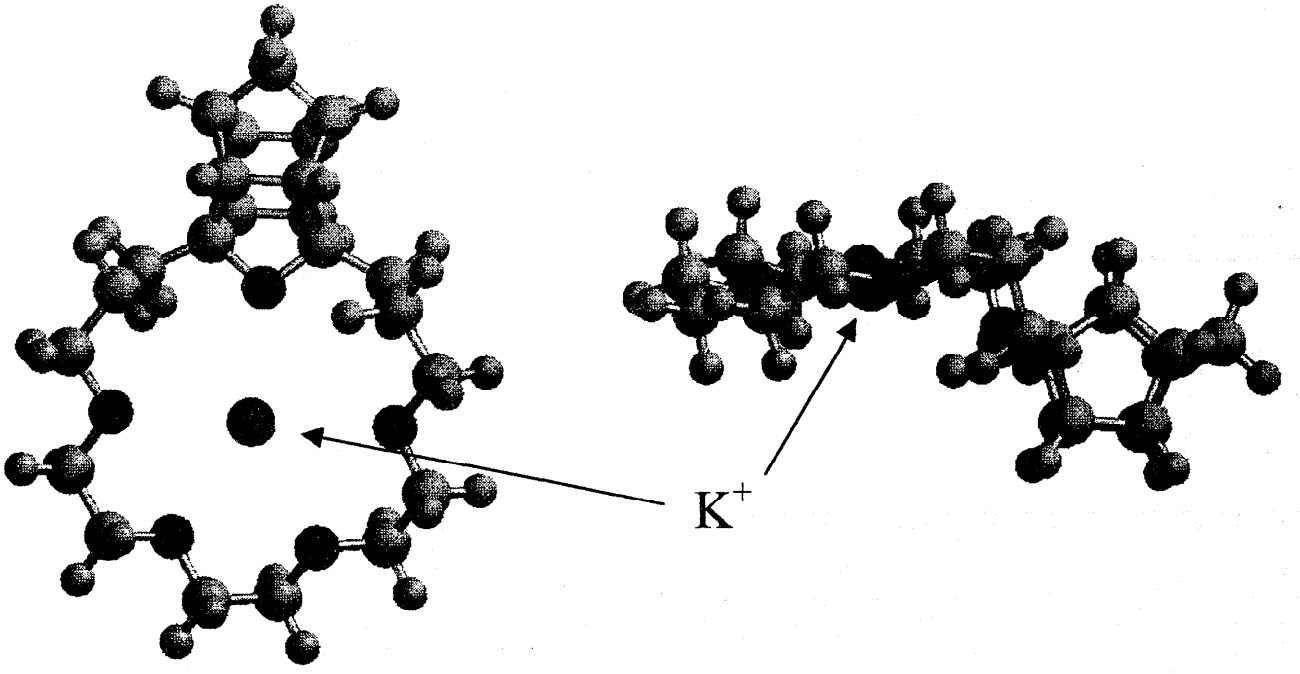
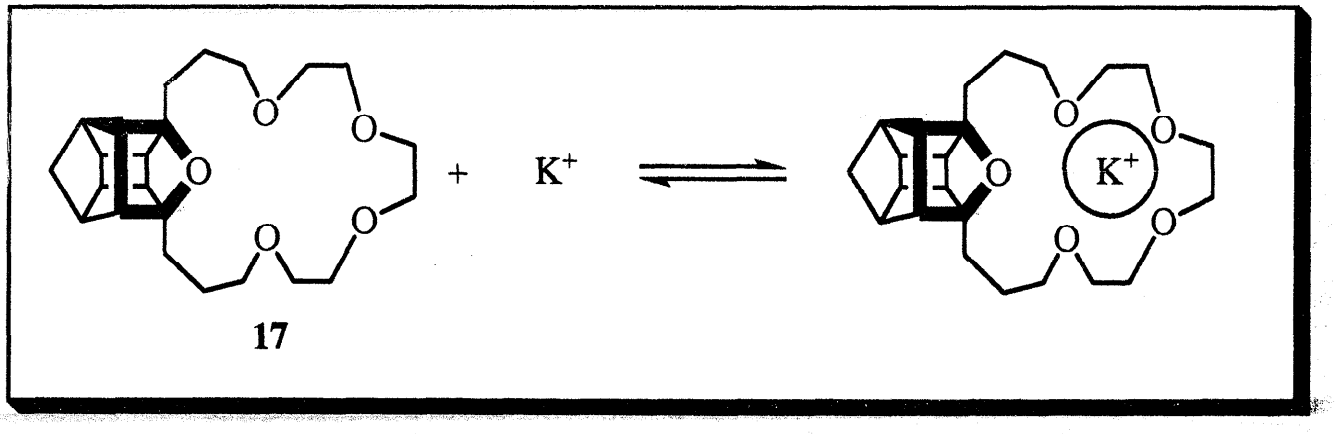


Low energy conformer of the large caged analog of 15-crown-5 binding K^+. Atom key: small grey = hydrogen, medium grey = carbon, red = oxygen, green = K^+.



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