Crown Ethers: The Search for Selective Ion Ligating Agents

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Introduction

Pedersen's publication in 1967[1] reporting the synthesis and metal ion complexation properties of a large number of macrocyclic polyethers stimulated great interest by the scientific community in the interesting and unusual ligating properties of these compounds. Within two decades, this expanding interest and the resulting increased knowledge base resulted in the awarding of the 1987 Nobel Prize in Chemistry to three prominent researchers in macrocyclic chemistry, C. J. Pedersen,[2] D. J. Cram,[3] and J.-M. Lehn.[4] The unusual ability of crown ethers to recognize cations in a selective fashion was summarized in a 1974 review.[5] The early work demonstrated a correlation between cavity radius and cation radius using alkali and alkaline earth metal ions, as is illustrated in Figure 1.[6] This correlation was an appealing one, but later studies, particularly by Hancock and coworkers,[7] employing a wide variety of cations and ligands, demonstrated that the concept has limited applicability.

Our research program has combined organic synthesis and various cation complexation properties of crown ethers and their derivatives in an effort to design and prepare macrocycles that will selectively bind specific cations. We have varied the ligands by changing the dimensions and rigidity of the macrocycle and have substituted sulfur and nitrogen atoms for part or all of the crown ether oxygen atoms. The crown ethers with only neutral oxygen donor atoms are excellent for binding alkali, alkaline earth, and a few posttransition metal ions. Sulfur atoms in the form of sulfide groups have great affinity toward soft acid metal ions such as Hg^{2+}, Pd^{2+},

and some borderline acids such as Cu^{2+}. Recently, we have prepared novel lariat crown ethers in which the lariat arms are chelating agents. These ligands have a high degree of cation selectivity.[8,9] Much of our work together with the innovative results of others in the area of selective ion–macrocycle interaction has been reviewed.[10–12] In this Account, we present some examples from our laboratory of the synthesis and cation complexation properties of crown ethers followed by the use of macrocycles in the selective separation of ions using liquid membrane and solid-phase extraction (SPE) techniques. Finally, some commercial applications of SPE procedures are described.

Synthesis and Cation Complexation Properties of Crown Ethers

Our initial studies involved the synthesis of thiacrown ethers where one or more of the crown ether ring oxygen atoms were replaced by sulfur atoms. Ligands **2** and **3** (Figure 2) were prepared by treating pentakis(ethylene glycol) dichloride or tris(ethylene glycol) dichloride with 1,2-ethanedithiol or 3,6-dioxa-1,8-octanedithiol and base, respectively.[13-15] Replacement of the oxygen atoms in the crown ether by sulfur atoms completely changes affinities of the ligands for metal ions. Ligands **2** and **3** did not interact with the alkali metal ions,[16] but the log K (H_2O) values for their interactions with Ag^+ at 25 °C increased markedly from 1.50 for 18-crown-6 (18C6) to 3.02 and 4.34 for **2** and **3**, respectively. Similar increases in log K (H_2O) values were observed[16] for the interactions of 18C6 and dithia-15-crown-5 with Hg^{2+}. No size selectivity for cations was observed for the thiacrown ether ligands. Indeed, X-ray crystal structures of the uncomplexed thiacrown ethers showed that the sulfur atoms almost always are directed out of the macroring cavity.[17] Cation selectivity by the thiacrown ethers resulted from the large

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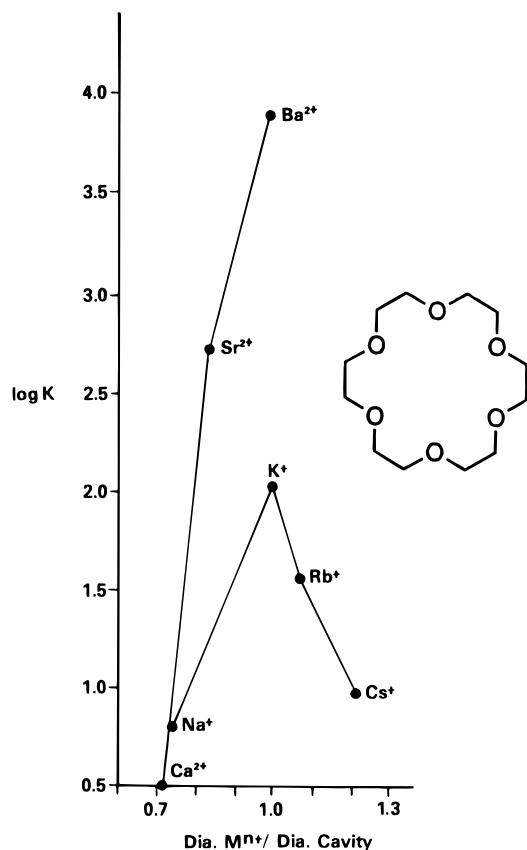
FIGURE 1. Selectivity of 18C6: log K (H$_2$O) values at 25 °C for 18C6 interaction with M^{n+} vs ratio of cation diameter to 18C6 cavity diameter.[6]

affinity of the soft sulfur donor atoms for the soft metal cations.

Proton-ionizable pyridono- (**4**–**7**), 4-hydroxypyridino- (**8**–**10**), and triazolocrown (**11**–**16**) ethers (Figure 2) were prepared to study the possiblity of selectively separating metal ions by proton-driven cation transport across a liquid membrane (see Cation Separations Using Liquid Membranes). Scheme 1 shows the syntheses of **5**[18,19] and **12**.[20] The 3,5-bis(chloromethyl)-1-(tetrahydro-2-pyranyl)-1H-1,2,4-triazole needed to prepare **12** was prepared as shown in Scheme 2.[20] ***Caution***: *the bis(chloromethyl)-substituted triazoles are terrible blistering agents.* Proton-ionizable **8**–**10**[21] and **14**–**16**[22] were prepared by treating THP-protected dimethyl chelidamate or benzyl-protected dimethyl 2,5-triazoledicarboxylate, respectively, with the appropriate oligo(ethylene glycol) using molecular sieves to remove the methanol byproduct. The THP protecting group was removed in acid solution, and the benzyl group was removed by reduction.

The structures and physical properties of pyridonocrown ethers **4**–**6** are different from those of 4-hydroxypyridino diester crowns **8**–**10** as are the properties of the two sets of triazolocrown ethers (**11**–**13** versus **14**–**16**). Ligands **8**–**10** and **14**–**16** are much stronger acids than their non-ester analogues. The pK_a (H$_2$O) value for **9** is 8.49[21] as compared to 10.98[18] for **5**. The difference is not so great with the triazolocrown ethers where the pK_a (H$_2$O) value for **15** is 8.4[22] and that for **12** is 9.55.[20] The more acidic diester crown ethers react with alkylamines to form alkylammonium salts wherein the amine removes a proton and the pyridone or triazole unit becomes an anion. For example, the crystal structure of the solid product formed when **9** was treated with benzylamine contained one molecule of **9** hydrogen bonded to the complex of benzylammonium ion with the corresponding pyridono diester crown as shown in Figure 3.[21] Benzylamine removed the proton from one molecule of **9** to become the benzylammonium ion complexed to the resulting pyridone anion. Crystal structure determinations show that uncomplexed **5** has the 4-pyridone structure,[19] uncomplexed **9** has the 4-hydroxypyridine structure,[21] uncomplexed **12** has the proton on triazole position 1 (outside the macroring cavity),[20] and uncomplexed **15** has the proton on triazole position 4 (inside the macroring cavity)[22] as illustrated in Figure 2.

Incorporating a pyridone binding subunit into a thiacrown ether to form **7** causes the unusual selectivity order of Ag$^+$ over Hg^{2+}.[23] In general, the dithiacrown ethers (such as **2** and **3,** Figure 2) interact much more strongly with Hg^{2+} than with Ag$^+$. The log K (H$_2$O) value for the interaction of **3** with Hg^{2+} is 19.5, while that for Ag$^+$ is 5.27.[23] Ligand **7** with one sulfur atom and the pyridone subunit interacts with Hg^{2+} with a log K (H$_2$O) value of only 3.99, while the log K value for the **7**–Ag$^+$ interaction is 5.36.[23] A ^{13}C NMR spectral study of the complexes of **7** with Ag$^+$ and Hg^{2+} shows that Hg^{2+} does not interact with the pyridone portion of the molecule, while Ag$^+$ does.[23] Thus, there is a dramatic decrease in log K for the Hg^{2+}–**7** interaction over that for the Hg^{2+}–**3** interaction. The log K values for Ag$^+$ interaction with the two ligands are similar. This reversal of the normal selectivity of Hg^{2+} over Ag$^+$ can be attributed to a combination of the special affinity of the pyridone nitrogen for Ag$^+$ and the inclusion of Ag$^+$ into the preorganized macrocycle cavity.[23]

The pyridono- and triazolocrown ether ligands have their proton-ionizable groups as part of the macroring. Proton-ionizable groups can also be attached to the nitrogen atoms of the azacrown ethers to form the N-pivot lariat ethers.[24] Lariat ethers containing many types of ligating groups on the lariat arms have been shown to be effective cation binders and, indeed, effective cation-transport agents through bulk liquid membrane systems because of their three-dimensional coordination with metal ions.[24–27]

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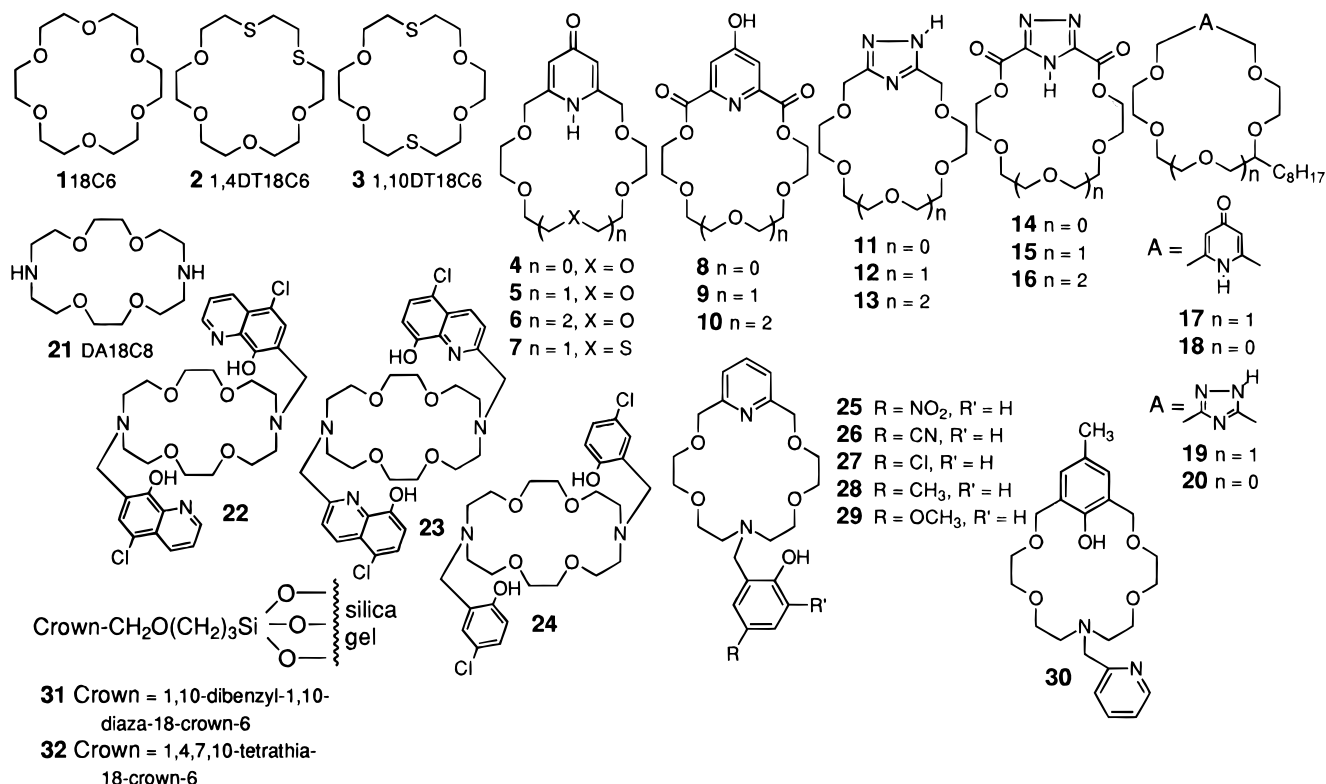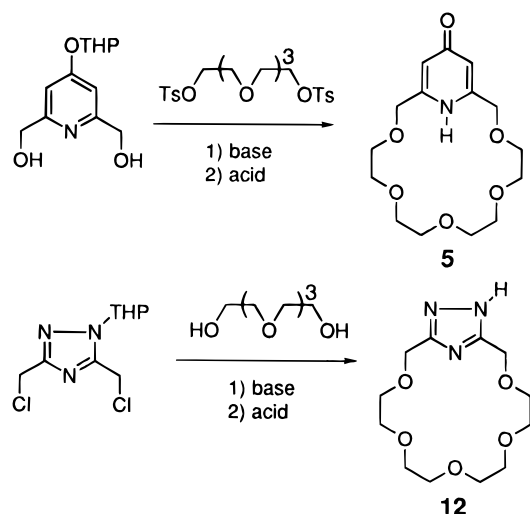
FIGURE 2. Crown ether macrocycles discussed in this Account.

Scheme 1. Preparation of Pyridono- and Triazolo-18-crown-6 Ligands

Phenol-containing lariat azacrown ethers extract cations from an aqueous solution into an organic phase and, in some cases, are chromogenic reagents for various metal ions.[28,29] The phenol substituents are usually attached by treating the azacrown with a halomethyl-substituted phenol. Lukyanenko and co-workers found that a modified Mannich aminomethylation reaction of a methoxymethyl-substituted azacrown and phenol is a superior way to attach a 2-hydroxybenzyl group to the azacrown.[30,31] We recently attached substituted phenols and phenolic

Scheme 2. Preparation of 3,5-Bis(chloromethyl)-1-(tetrahydro-2-pyranyl)-1*H*-1,2,4-triazole
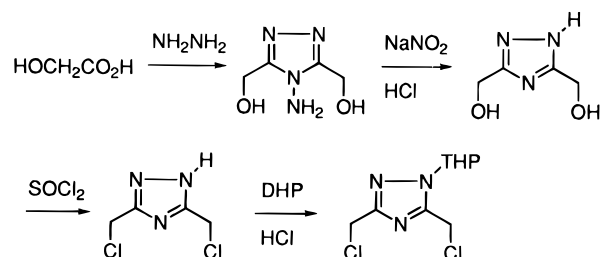
chelating agents to the azacrown and pyridinoazacrown ethers. Scheme 3A shows attachment of two (5-chloro-8-hydroxyquinoline) (CHQ) groups onto diaza-18-crown-6 (DA18C6) (**21**) by treating 1,10-bis(methoxymethyl)-1,10-diaza-18-crown-6 with CHQ in refluxing benzene.[9] The two CHQ groups of **22** are attached through the CHQ position 7. A different bis-CHQ-substituted DA18C6 was prepared from 2-(bromomethyl)-CHQ as shown in Scheme 3B.[8,9] The two CHQ groups of **23** are attached through the CHQ position 2. The site of attachment has profound consequences for the cation complexation properties of these ligands.

The log K values in Table 1 show that **24** with two phenol arms has improved affinity for some cations over DA18C6. However, **22** and **23**, containing two CHQ groups, exhibit remarkable interactive abilities for certain metal ions.[9] Ligand **22**, with the CHQ attached through its position 7, is selective for Mg^{2+} over the other alkali

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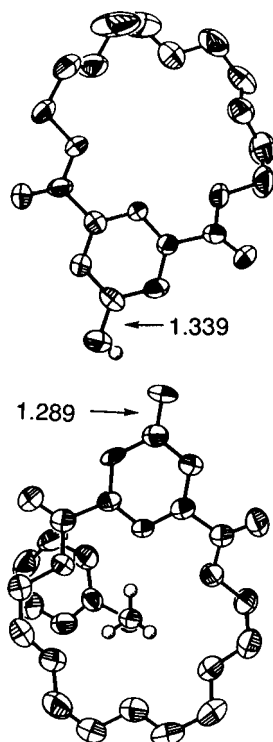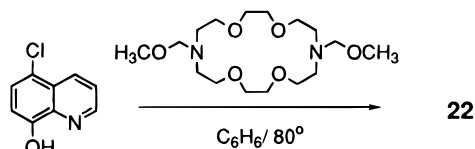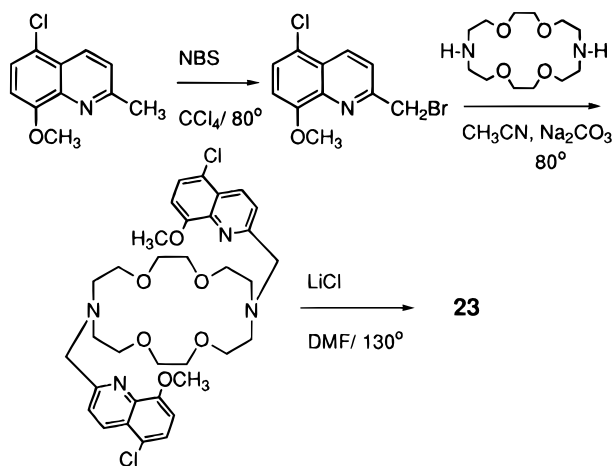
FIGURE 3. Computer drawing of the asymmetric unit of the benzylamine complex of 9. All hydrogens except HOA4 are omitted for clarity.[21]

Scheme 3. Preparation of 5-Chloro-8-hydroxyquinoline-Substituted Diaza-18-crown-6 Ligands

A. Attachment through CHQ position 7

B. Attachment through CHQ position 2

and alkaline earth metal ions. The remaining ligands either do not form complexes with Mg^{2+} or, in the case of DA18C6, forms a much weaker complex. The UV spectrum for the Mg^{2+}−**22** complex has a new peak at 265 nm that could be used to measure minute amounts of Mg^{2+} in solution in the presence of the alkali and alkaline earth cations which do not have this absorption.[9] Ligand **22** also shows remarkable selectivity for Cu^{2+} and Ni^{2+} over neighboring transition metal ions.

Table 1. Log K (CH_3OH) Values Valid at 25 °C for the Interactions of DA18C6,[a] 24,[b] 22,[b] and 23[b] with Various Cations

cation	DA18C6	**24**	**22**	**23**
Na^+	1.5	2.85	2.89	3.74
K^+	1.83	2.76	3.39	6.61
Cs^+		*c*	*c*	2.70
Mg^{2+}	3.4	*c*	6.82	*d*
Ca^{2+}	3.87	4.48	5.31	4.71
Sr^{2+}	5.99	<2	4.43	4.67
Ba^{2+}	6.12	3.52	3.60	12.2
Co^{2+}	3.56	2.27	5.14	4.8
Ni^{2+}	4.17		11.4	>5.5
Cu^{2+}	8.48	4.14	10.1	4.7
Zn^{2+}		4.21	5.12	ppt

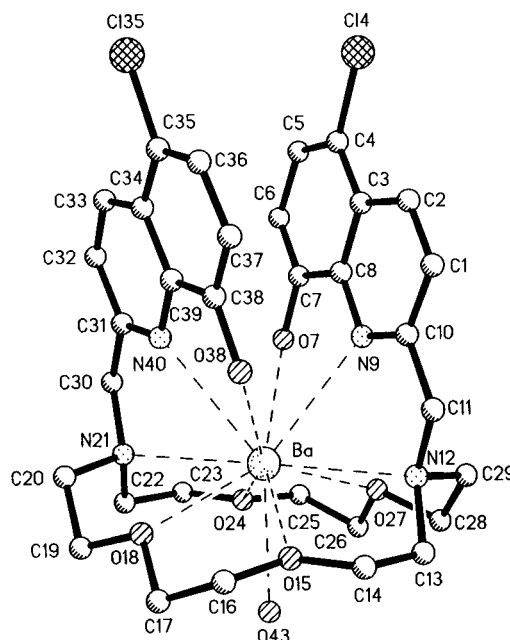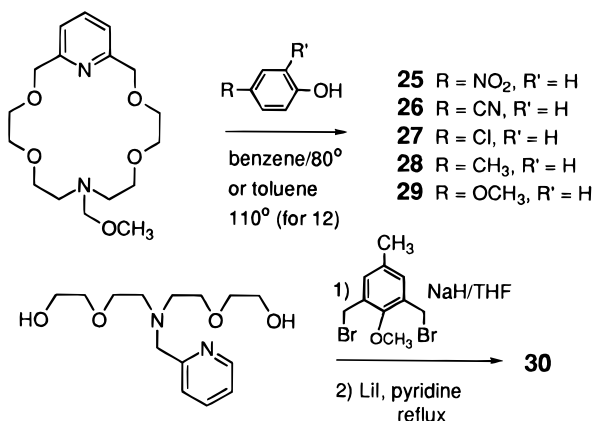[a] Reference 11. [b] Reference 9. [c] No measurable heat.

FIGURE 4. Crystal structure of the **23**−Ba^{2+} complex. The hydrogen atoms, the two Br^- anions and the solvent molecules not involved in the coordination are omitted for clarity.[8]

Ligand **23,** with the CHQ attached through its position 2, exhibits remarkable selectivity for K^+ over the other alkali metal ions and for Ba^{2+} over all other metal ions studied (Table 1).[9] Indeed, the log K (CH_3OH) value for the interaction of **23** with Ba^{2+} (12.2) is very similar to that for the interaction of cryptand [2.2.2] with Ba^{2+} (12.9).[32] The chemical shifts of the CHQ protons in the ^{1}H NMR spectrum of the Ba^{2+}−**23** complex move significantly upfield in relation to the free macrocycle. These shifts are indicative of an overlap of the two CHQ substituents.[8] The crystal structure of the Ba^{2+}−**23** complex (Figure 4) shows that Ba^{2+} is in the center of a pseudo-cryptand with the DA18C6 forming two arms and the two overlapping CHQ rings forming the third arm. This pseudo-cryptand can form if the metal ion has the proper dimensions to fit in the cavity. Similar upfield shifts for the CHQ protons were observed in the ^{1}H NMR spectrum of the K^+−**23** complex. The log K (CH_3OH) value for the K^+−**23** interaction is significantly greater than those for the other alkali metal ions, suggesting that the K^+−**23** complex, also, is

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Scheme 4. Preparation of Phenol-Substituted Pyridinoaza-18-crown-6 Ligands 25–29 and Pyridine-Substituted Phenol-Containing Ligand 30

25 R = NO$_2$, R' = H
26 R = CN, R' = H
27 R = Cl, R' = H
28 R = CH$_3$, R' = H
29 R = OCH$_3$, R' = H

benzene/80°
or toluene
110° (for 12)

1) NaH/THF

30

2) LiI, pyridine
reflux

FIGURE 5. Pyridono-18-crown-6-mediated K$^+$ transport flux in a bulk liquid membrane system as a function of initial source phase pH and initial receiving phase pH using 5 and 17 as carriers.[40]

in the form of a pseudo-cryptand. Thus, changes in the position of attachment of the azacrown ether to the CHQ group in these lariat ether ligands make significant differences in their interactions with metal ions.

The Mannich aminomethylation reaction has also been used to prepare a series of phenol- and CHQ-substituted pyridinoazacrown ethers. As shown in Scheme 4, *N*-methoxymethyl-substituted pyridinoaza-18-crown-6 was treated with various phenols and CHQ to form a variety of proton-ionizable pyridinoaza-18-crown-6 ligands.[33] Addition of the phenolic groups to pyridinoaza-18-crown-6 has a profound effect on its complexing ability with metal ions. The parent pyridinoazacrown ether does not interact with Na$^+$ in methanol, while **25–29** form strong complexes with Na$^+$ with log K (CH$_3$OH) values of 3.06, 3.10, 3.29, 3.49, and 3.59, respectively.[34] The log K (CH$_3$OH) values for these interactions are consistent with the increasing electron donating ability of the substituents on the phenol ring. These ligands also exhibit high selectivities in methanol for Ag$^+$ (log K values of >9) over Na$^+$ (log K values of 3.06–3.59), K$^+$ (log K values of 3.17–3.62), and Tl$^+$ (log K values of 4.20–4.40).[34] Ligand **28** forms stronger complexes with Na$^+$, K$^+$, and Ag$^+$ in methanol than does **30,** which has the phenol as part of the macrocyclic ring and pyridine as the substituent. The log K (CH$_3$OH) values for the interaction of **28** with Na$^+$, K$^+$, and Ag$^+$ are 3.49, 3.53, and >9, respectively, while those for **30** are 2.75, 3.00, and 6.33, respectively.[34] Ag$^+$ prefers linear coordination and shows a high affinity for nitrogen atoms. The disposition of the two nitrogen atoms in **28** is ideal for complexation of Ag$^+$, so **28** forms a stronger complex with Ag$^+$ than does **30**. Thus, different arrangements of the ligating groups in the host have profound effects on guest ion selectivities.

Cation Separations Using Liquid Membranes

The selective separation of cations from one another is of interest in a variety of chemical fields. Ion selectivity can be designed into liquid membrane systems through

the use of ion selective carrier molecules such as **17** (Figure 5). We have studied macrocycle-mediated selective cation transport in bulk, emulsion, thin sheet supported, hollow fiber, and two-module hollow fiber liquid membranes.[35–37] Transport was successfully modeled in a well-characterized thin sheet supported membrane system for single and multiple cation systems.[38]

Several examples illustrate the use of liquid membranes to study selective metal ion separations. In the bulk liquid membrane, the source and receiving aqueous phases are separated by a dense CH$_2$Cl$_2$ phase.[39] The use of proton-ionizable macrocycles in these systems avoids the need for an anion to accompany the cation–macrocycle complex in the transport process. In this case, transport is driven by opposite M$^+$ and H$^+$ concentration gradients between the source (M$^+$) and receiving (H$^+$) phases. In Figure 5, flux values (J_M) are plotted vs the source phase pH for the transport of K$^+$ through a bulk H$_2$O–CH$_2$Cl$_2$–H$_2$O liquid membrane using **5** and **17** as carriers.[40] The pK_a (H$_2$O) values for **5** (10.98)[18] and **17**, the *n*-octyl-substituted form of **5**, should be nearly the same. At low source pH values, these ligands are predominantly in the protonated form and do not interact with K$^+$. Thus, no K$^+$ is transported below pH = 11. At high pH values, the proton is removed and the anionic ligand complexes with K$^+$. The **5**–K neutral complex is soluble in water, so the ligand rapidly goes into the aqueous source phase and is lost to the membrane. Because of the *n*-octyl substituent, the **17**–K neutral complex is not soluble in water and remains in the CH$_2$Cl$_2$ membrane. At pH 12, an appreciable amount of **17**–K is present and this amount

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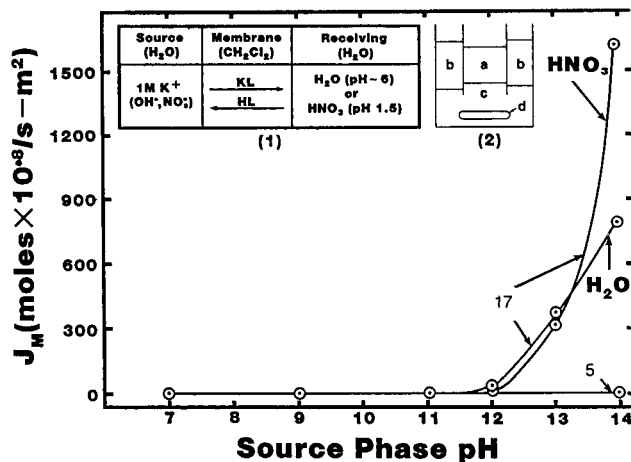
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would increase as the pH of the source phase increases. The transport of K^+ is driven by both H^+ and K^+ concentration gradients which act in opposite directions as indicated in the inset in Figure 5. The relatively high fluxes due to **17** at high pH values are possible only because it is not necessary to transport the highly hydrated OH^-.[41] Additional confirmation of this transport mechanism is found by adjusting the receiving phase pH to 1.5 with HNO_3. The increased K^+ transport by **17**, but not by **5** under these conditions, confirms that K^+ transport is coupled to H^+ transport in the opposite direction, that the macrocycle must reside predominantly in the organic phase for transport to occur, and that an important driving force in the process is water formation at the source phase$-CH_2Cl_2$ interface.[40]
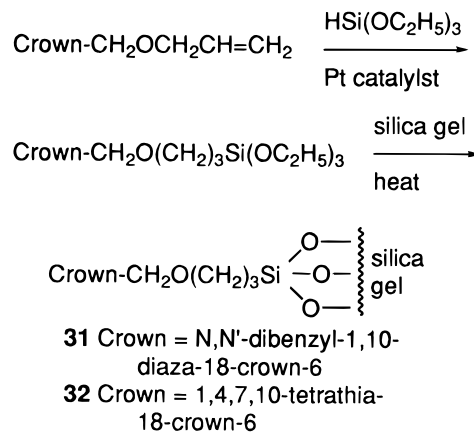
Competitive transport experiments were performed in bulk liquid membrane systems in which the source phase contained K^+ and one or two other cations in equimolar mixtures using **17** as the carrier.[40a] In all cases, K^+ was transported selectively over the remaining cation(s). In the two-cation mixtures, selectivity for K^+ at source phase pH = 14 and receiving phase pH = 7 is 4.6-fold over Na^+, 2.7-fold over Rb^+, and 6.3-fold over Cs^+. Where mixtures of K^+, Rb^+, and Cs^+ were present, selectivity for K^+ was 2.9-fold over Rb^+ and 8.8-fold over Cs^+. Thus, a proton-ionizable macrocycle that has selectivity for one cation over others can be used in a liquid membrane system to physically separate that cation.

The proton-ionizable pyridono- and triazolocrowns have great affinity for Pb^{2+} and Ag^+. Octyl-substituted pyridonocrown **18** selectively transported Ag^+ from an equimolar Ag^+/Pb^{2+} mixture in a bulk liquid membrane system, while **17** selectively transported Pb^{2+} in the same system.[42] In both cases, transport was best into a neutral receiving phase and the neutral host transported both the cation and anion (NO_3^-) of the salt as shown by an increase in NO_3^- concentration in the receiving phase. Proton-ionizable triazolocrowns **19** and **20** exhibited remarkable selectivity in transporting Ag^+ from an equimolar Ag^+/Pb^{2+} mixture. Transport was greatly enhanced when an acidic receiving phase was present indicating that transport was proton driven. In single ion transport experiments, the flux for the transport of Pb^{2+} into a neutral receiving phase was higher than that of Ag^+. In this case, Pb^{2+} was transported as $PbNO_3^+$. However, Ag^+ was selectively transported in the binary system.[42] The affinity of Ag^+ for the triazole moiety, the good fit of Ag^+ into the 18-crown-6 sized cavity, and the presence of only one proton-ionizable group in the ligand combined in this case to produce highly selective transport of Ag^+ over Pb^{2+} into the acid receiving phase.[42]

Separations Using Solid-Phase Extractions (SPE)

Bulk and other liquid membrane systems have a major disadvantage in that the carrier ligand is slowly removed from the organic into the aqueous phase(s).[35] Attaching

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Scheme 5. Preparation of Silica Gel-Bound Crown Ether Ligands

$$Crown-CH_2OCH_2CH=CH_2 \xrightarrow[\text{Pt catalylst}]{HSi(OC_2H_5)_3}$$

$$Crown-CH_2O(CH_2)_3Si(OC_2H_5)_3 \xrightarrow[\text{heat}]{\text{silica gel}}$$

$Crown-CH_2O(CH_2)_3Si$ —O— silica gel

31 Crown = N,N'-dibenzyl-1,10-diaza-18-crown-6
32 Crown = 1,4,7,10-tetrathia-18-crown-6

the ligating crown ethers to a solid support removes this disadvantage and has made possible the design of systems capable of selective and quantitative separation of cations from aqueous solutions. These SPE systems can be operated indefinitely without loss of the expensive ligating group. Such systems have been prepared by heating a mixture of silica gel and crown ether-containing ethoxysilanes as shown in Scheme 5.[43−46] The ligands are attached to the solid silica gel through stable C−Si and SiOSi bonds. Thus, they are permanently bound and cannot be removed unless the silica gel is destroyed, as in concentrated aqueous base.[43] Equilibrium constants for the association of metal cations with the silica gel-bound crown ethers are comparable to log K (H_2O) values for the association of the same cations with the unbound ligands.[47]

The SPE procedure has been used to selectively remove and concentrate specific cations from mixtures of metal ions. For example, 1 L of water containing ppb levels of Hg^{2+} and Pb^{2+} as well as ppm levels of Ca^{2+}, Mg^{2+}, Na^+, and K^+ as the NO_3^- salts was passed through a column of 2−4 g of gel **31**.[47] Log K (H_2O) values are 15.38 and 8.39 for the interaction of N,N'-dimethyldiaza-18-crown-6 (N,N'-dimethyl-**21**) with Hg^{2+} and Pb^{2+}, respectively, and are very low for interaction with the other metal ions.[11] As expected, gel **31** completely retained the Hg^{2+} and Pb^{2+} and allowed the other ions to pass through. A small volume (mL) of 1 M aqueous HCl was used as the eluent. The macrocyclic amines were protonated, releasing the bound metal ions in a concentrated form.[47] EDTA or other agents which form stronger complexes than the macrocycle with the metal ions can also be used. Gel **32** was used in a similar manner to remove and concentrate Au(III) from a mixture of Au(III) and Fe(III) ions[45] and to separate Au(III), Pd(II), and Ag(I) from each other and from Pt(IV), Rh(III), Fe(III), and Ni(II).[48]

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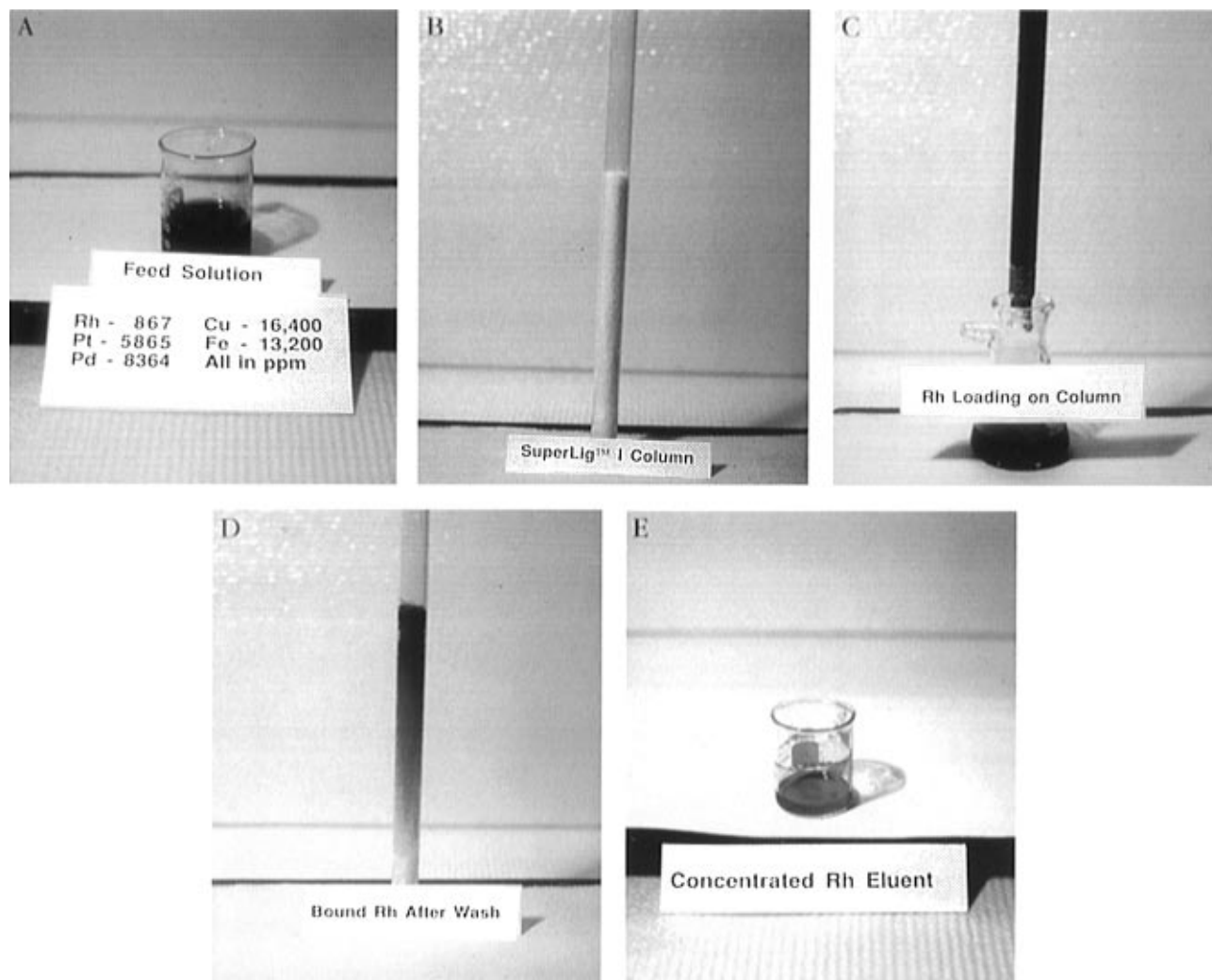
FIGURE 6. Removal and recovery of Rh(III) from a mixture of 857 ppm of Rh(III), 5865 ppm Pt(IV), 8364 ppm PD(II), 16 400 ppm Cu(II), and 13 200 ppm Fe(III) in acid solution.

The process of using solid supported macrocyclic ligands to remove, separate, and concentrate metal ions-sfrom aqueous mixtures of metal ions has been commercialized by IBC Advanced Technologies, Inc. (IBC) of American Fork, UT. IBC is a spin-off company from our research program at BYU. The proprietary ligand–solid support systems used by IBC are designed for specific separations and are termed SuperLig when used for large-scale industrial separations and AnaLig when used for analytical purposes. IBC has used the SPE procedure to remove impurities from Superfund sites, refinery streams, plating baths, and other solutions;[49,50] recover and purify precious and other metals;[35,49,50] separate selectively components of nuclear waste streams;[50] recover and purify metals from environmental wastes;[50] and separate ions

for analytical analysis.[51] The procedure in each case involves the use of appropriate SuperLig or AnaLig materials capable of highly selective interaction with the target species. Several examples are now given.

In Figure 6, the removal of Rh(III) from a mixture of Rh(III) (867 ppm), Pt(IV) (5865 ppm), Pd(II) (8364 ppm), Cu(II) (16,400 ppm), and Fe(III) (13,200 ppm) in acid solution is illustrated. In A, a black aqueous mixture is seen. This could be a mixture isolated from the oxidation of the catalyst from an automobile catalytic converter. B shows the solid support containing the proprietary SuperLig material. C shows the column loaded with the Rh(III) and still containing residual feed solution which imparts the dark color to the column. No detectable Rh(III) is observed in the receiving phase. The column is washed with acid to remove the residual solution revealing the red Rh(III) loaded on the column (D). Rh(III) is washed off the column using solutions of thiourea or bromide ion both of which form stronger complexes than the ligand with Rh(III) (E). The recovered Rh(III) is over 99.9% pure using this process. The remaining Pt(IV) and

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Table 2. Bismuth Removal Efficiency from a Copper Refinery Tankhouse[50]

	concn in mg/L (ppm)	
stream	Bi	Cu
feed[a]	275	29 611
Barren feed after going through SuperLig	b	29 117
0.1 M sulfuric acid wash	b	14 802
elution	19 960	b

[a] Solutions are in a sulfuric acid matrix. [b] Below analytical detection limits.

Table 3. Rapid Removal of Low Level Sr^{2+} from Hanford HNO_3 Mimic Matrix[a] Using 0.2 g of SuperLig in an Empore Disk[50]

sample description	Sr^{2+} concn (ppm or mg L^{-1})
original solution	100
10 L of feed after column treatment[b]	<1
0–2 mL of 0.03 M Na_4EDTA eluent[b]	500 000
2–4 mL of 0.03 M Na_4EDTA eluent[b]	200

[a] 1 M NaOH, 5 M $NaNO_3$, 0.1 M KNO_3, plus several other salts mimicking Hanford Supernatant. Column was acclimated with 1 M HNO_3 prior to use. [b] Flow rate of 40 mL/min was used.

Pd(II) can be separated from the other metal ions and from each other by known techniques.

Increased requirements for higher product purity have resulted in the need to lower trace levels of metal ions in metal refinery streams. For example, if excessive bismuth is present in copper refinery electrolyte solutions, the quality of the cathode copper is reduced, resulting in excessive breakage of copper wire. Conventional techniques have not been effective in controlling the bismuth levels. However, SuperLig systems are able to accomplish this control effectively with on-line equipment. It is seen in Table 2 that bismuth can be removed effectively in this system.[50] The bismuth can also be recovered for resale as a pure byproduct.

SPE systems are effective in the removal of Cs^+ and Sr^{2+} from radioactive waste solutions. IBC and 3M jointly have developed Empore membranes containing embedded SuperLig materials which are highly selective for Sr^{2+}. These membranes show high stability toward radioactivity. Typical results for removing Sr^{2+} using an Empore disk are shown in Table 3.[52] SuperLig has high selectivity for Sr^{2+} even in the presence of much higher sodium concentrations. 3M and IBC are jointly marketing a strontium rad disk for the rapid analysis of radioactive Sr^{2+} in any aqueous sample. This procedure received an R&D-100 award in 1996 for the development of a product of high technological significance.[53]

IBC has made good progress in devising SPE systems for the separation of anions from aqueous solutions. Anion separations are of great industrial interest. Systems are available for the following separations:[50] Cl^- from aqueous solution; F^- from excess SO_4^{2-} and Cl^-; TcO_4^- from excess NO_3^- and OH^-; $Ge(OH)_6^{2-}$ from excess SO_4^{2-}; and MoO_4^{2-} and WO_4^{2-} from SO_4^{2-}, NO_3^-, and Cl^-.

Conclusions

Crown ethers and their derivatives show unique and interesting selectivities toward metal ions. Ligand DT18C6 (**3**) has high selectivity for Hg^{2+} over Ag^+. However, changing one sulfur atom in (**3**) for a pyridone nitrogen (to form **7**) reverses the selectivity to Ag^+ over Hg^{2+}. Bis-(5-chloro-8-hydroxyquinoline) (CHQ)-substituted DA18C6 with the CHQ group attached through its position 7 (**22**) has a high affinity for Mg^{2+}, Cu^{2+}, and Ni^{2+}. Ligand **23**, with the CHQ attached through its position 2, has high affinities for K^+ and Ba^{2+} and does not complex with Mg^{2+}. In bulk liquid membrane systems using octyl-substituted crown ether compounds as carriers, K^+ can be separated from all other alkali metal ions using octyl-substituted pyridono-18-crown-6 (**17**). Attaching the selective ligating agents to solid supports allows the removal, separation, and recovery of specific metal ions. This SPE process has been commercialized and applied to the selective separation of a variety of ions, often from difficult matrices such as highly acidic solutions, highly basic solutions, and/or high concentrations of competing ions. This technology has a bright future for the separation of unwanted trace ions or for the purification of valuable metals or solvents. It embodies many of the principles of molecular recognition set forth so well by Lehn.[54] Information is stored in the host that allows it to recognize a target guest to the exclusion of other chemically similar and/or competing matrix species. The successful use of this concept to design and construct practical systems demonstrates the power of supramolecular chemistry in meeting current industrial and environmental separations needs.

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