Silica gel-bound aza-crowns for the selective removal and concentration of metal ions

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Abstract - Silica gel-bound macrocycles have been prepared by first hydrosilylating a macrocycle-containing alkene with triethoxysilane followed by coating and heating the resulting macrocycle-containing triethoxysilane on 60-200 mesh silica gel. The macrocycle is attached to silica gel by stable hydrocarbon-ether groups. The aza-crown-containing alkenes were prepared in good overall yields by convenient three- and four-step reactions using N-[2-(2-chloroethoxy)ethyl]acetamide as a synthon. The silica gel-bound macrocycles were found to be stable at aqueous pH values below 11. In numerous determinations, the log K values for the interaction of the bound-macrocycle with various cations were found to be similar to those for the analogous unbound macrocycle with the same cations in aqueous solution. This result indicates that the bound- and unbound-macrocycles are solvated and form complexes in the same manner. Several separations of heavy metal ions from aqueous mixtures of ions are described.

INTRODUCTION

Selective separation and concentration of chemical species is of great importance for many biological and industrial applications (ref 1,2). Macrocyclic ligands are pre-organized to allow the fitting of host to guest in a complementary fashion. The macrocycles have been used to selectively separate metal ions from mixtures of metal ions in bulk liquid membrane and/or solvent extraction systems (ref. 3-7). Those metal ions which form the most stable complexes with the macrocycle are generally transported or extracted selectively.   The selective macrocycle-mediated transport of potassium (ref. 7), lithium (ref. 8) and silver (ref. 9) ions by macrocycles containing proton-ionizable pyridone and triazole subcyclic groups have been reported. A number of separation studies of heavy metal cations by neutral macrocyclic ligands have also been reported (see ref. 10 and 11 for two examples). In each case, the desired cation(s) was(were) selectively transported from a mixture of that cation with at least one other cation.

The macrocyclic ligands are expensive to prepare and even a very slow loss of these materials from the organic layer of a liquid membrane or solvent extraction system cannot be tolerated. The problem of ligand loss has been solved by covalently attaching the crown ligands to silica gel. Thus, 15-crown-5 (1), 18-crown-6 (2), 21-crown-7 (3), and the two dialkyldiaza-18-crown-6 ligands (5,6) have been attached to silica gel through a stable hydrocarbon-ether linkage (see Scheme 1) (ref. 12-15). Log K values for the interaction of these silica gel-bound macrocycles towards various metal ions were found to be nearly the same (± 10%) as those for the analogous unbound macrocycles with the same cations in water. This paper describes the synthesis of silica gel-bound aza-crowns, the metal ion complexation properties of some of them, and their use in the selective separation, removal and concentration of certain metal ions from multiple ion mixtures in aqueous solutions.

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SYNTHESIS OF SILICA GEL-BOUND CROWNS AND AZA-CROWNS

Silica gel-bound crowns (Scheme 1)

The procedure for the attachment of crown ligands to silica gel is shown in Scheme 1. The allyloxymethyl-substituted macrocycle was reacted with an excess triethoxysilane (diethoxymethylsilane has also been used) using a platinum catalyst to form the crown-containing triethoxysilane. The latter material was coated and heated on silica gel (60-200 mesh) to effect the covalent attachment. The macrocycle to gel ratio varies from about 1:10 to about 3:10 (w/w). This hydrocarbon-ether bonding of silica gel to the carbon framework of the macrocycle is permanent and the system can be used indefinitely to perform separations and recoveries of metal ions without measurable loss of the crown. Furthermore, the bound macrocycles have the same affinity as unbound macrocycles for metal ions in aqueous solution as will be shown below. Others have attached various macrocycles to silica gel through amide type linkages (ref. 16,17) or through a macroring nitrogen atom (ref. 18).

The starting allyloxymethyl-substituted crowns and pyridino-crown needed for the synthesis of silica gel materials 1-4 were prepared as reported (ref. 19,20). The synthesis of the allyloxymethyl-substituted diaza- and triaza-crowns needed to prepare gel materials 5-10 will be reviewed in the next sections. Also, the procedure to prepare allyloxymethyl-substituted tetra-aza crowns containing 24-, 27- and 30-ring members is included below. These latter large-ring compounds have not yet been attached to silica gel.
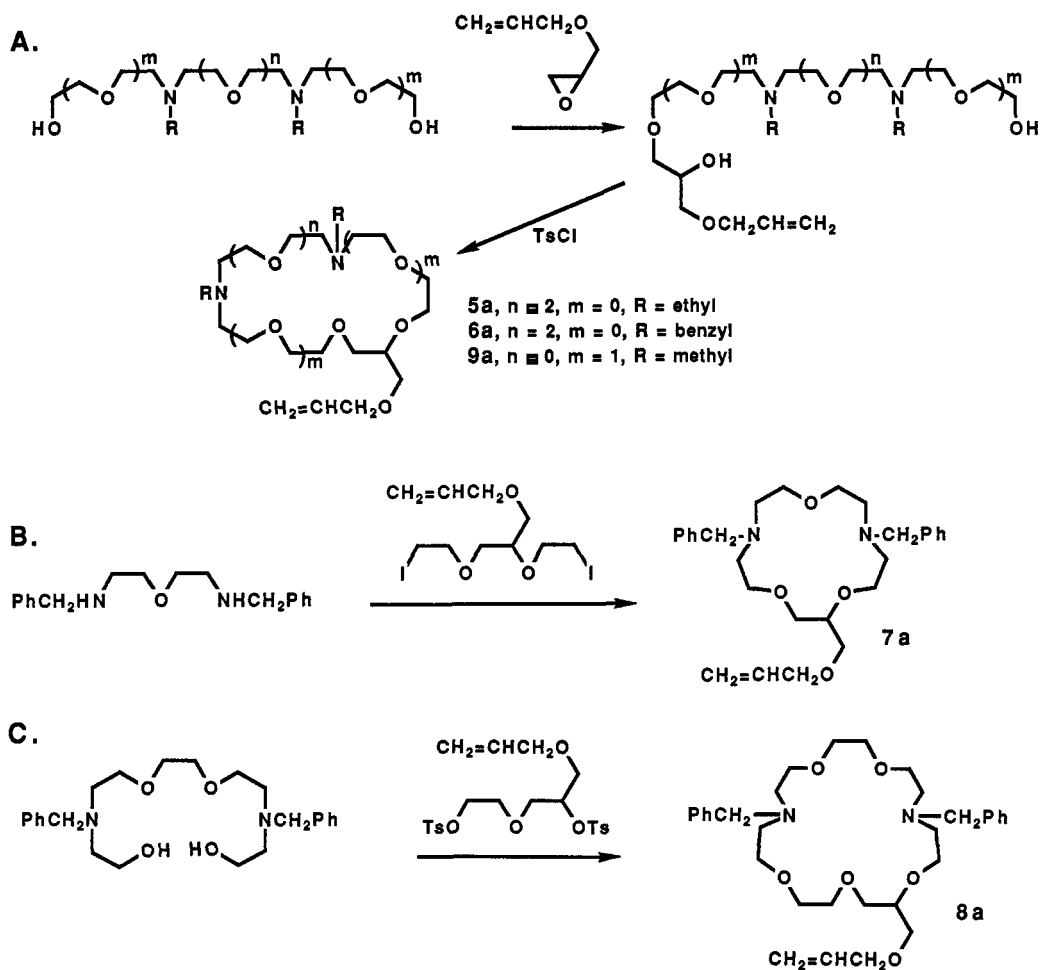
Scheme 1
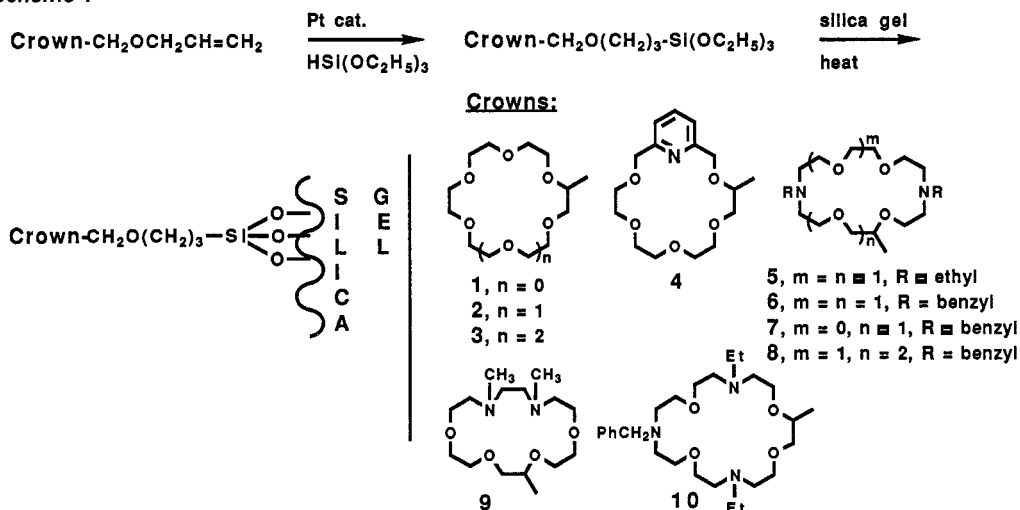
Preparation of Silica Gel-Bound Crown Compounds

Diaza-crown (Scheme 2)

The diaza-crowns have been much studied because they are key intermediates in the synthesis of cryptands and other N-substituted ligands (ref. 21,22). The diaza-crowns can also be attached to synthetic polymers (ref. 23). The diaza-crowns are excellent complexing agents particularly for the 'soft' transition metals (ref. 3). It is important to note that N-alkyl-substituted aza-crowns have about the same affinity for metal ions as do the non-N-substituted aza-crowns (ref. 3). Aza-crowns with alkyl groups substituted on all of the nitrogen atoms can be attached to silica gel for the selective removal of cations. Thus, there is no need for N-blocking groups (tosyl, benzyl, etc.) on any of the aza-crown starting materials which greatly complicate the synthesis of these aza-crowns. The synthetic methods described below (Schemes 2-4) are convenient three- or four-step procedures to prepare per N-alkyl-substituted aza-crowns which can be attached to silica gel by the Scheme 1 procedure.

The most popular procedure used to prepare the diaza-crowns is to react an oligoethylene oxide diamine with an oligoethylene oxide glycolyl dichloride with the subsequent reduction of the macrocyclic diamide (ref. 22,24). This procedure requires many steps for the preparation of allyloxymethyl substituted crowns and in the preparation of 6a (Scheme 2), gave only a 12% overall yield (ref. 13). A more useful method for the preparation of diaza-crown-containing alkenes is shown in Scheme 2A. The starting diazapentaethylene glycol needed to prepare diaza-18-crown-6 (m - 0, n - 2) was prepared in one step from N-benzyl- or N-ethylethanolamine and triethylene glycol dichloride (ref. 25). Commercially available allyl glycidyl ether was used in the second step. The ring closure step with tosyl chloride was developed by Okahara and his co-workers for the synthesis of a variety of crown compounds (ref. 26). The overall yield for the preparation of crown 6a using the procedure shown in Scheme 2A was 34% (ref. 13). Comparable yields were obtained for crowns 7a-9a shown in Schemes 2A-2C (ref. 27).
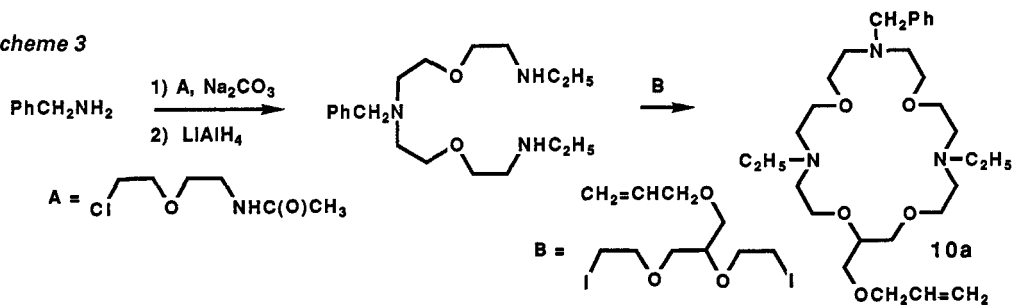
Scheme 2

A.

5a, n = 2, m = 0, R = ethyl
6a, n = 2, m = 0, R = benzyl
9a, n = 0, m = 1, R = methyl

B.

C.

Synthesis of Allyloxymethyl-Substituted Diaza-Crown Compounds

Polyaza-crowns (Schemes 3 and 4)

Although there are few log $\underline{K}$ data for the interaction of the polyaza-crowns with metal ions, it is apparent that increasing the number of nitrogen atoms in the macroring increases the affinity of the ligand for certain metal ions. For example, the log $\underline{K}$ values for the interaction of Zn^{2+} with diaza-18-crown-6, tetraaza-18-crown-6 and hexaaza-18-crown-6 (cyclam 6) are 4.31, 10.90 and 17.8, respectively (ref. 3). Thus, preparation of silica gel-bound polyaza-crowns should facilitate the effective removal of heavy metal cations.

Scheme 3 shows a novel method for the preparation of triaza-crown compounds in only three or four steps (ref. 28). N-[2-(2-Chloroethoxy)ethyl]acetamide (compound A) is the key reactant for this novel synthetic scheme. Compound A was prepared by treating the corresponding N-[2-(2-hydroxyethoxy)ethyl]acetamide with thionyl chloride. It is important to note that the

Scheme 3

Synthesis of Allyloxymethyl-Substituted Triaza-Crown Compounds

Scheme 4

11, n = 0, R = methyl
12, n = 1, R = benzyl
13, n = 2, R = benzyl

Synthesis of Allyloxymethyl-Substituted Tetraaza-Crown Compounds
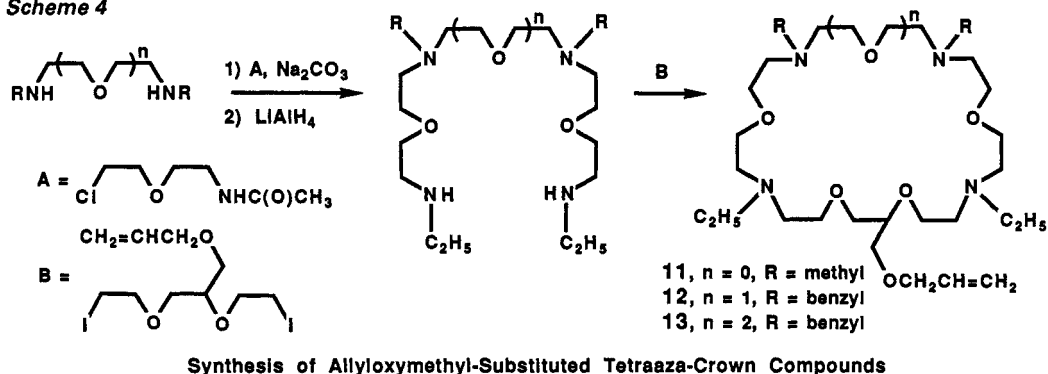
benzamide and sulfonamide derivatives similar to A spontaneously cyclized to form the corresponding morpholinyl compounds (ref. 29). Compound A was reacted with benzylamine followed by reduction to form a triamine containing secondary amine functions at each end. This latter synthon was reacted with allyloxymethyl-substituted triethylene glycol diiodide (ref. 13) to obtain 10a. The overall yield for the preparation of 10a was 30% (ref. 28).

Scheme 4 shows a similar method to prepare tetraaza-crown compounds (ref. 28). Two equivalents of compound A were reacted with an oligoethylene oxide diamine followed by reduction to form the oligoethylene oxide tetraamine intermediate. This tetraamine synthon was reacted with a diodide to form the tetraaza-crowns 11-13 in moderate yields (about 20%) (ref. 28). These macrocycles have not yet been attached to silica gel.

COMPLEXATION AND SEPARATION RESULTS

Metal-ion complexation

Log $\underline{K}$ values for the interaction of the silica gel-bound macrocycles have been determined. Small amounts of the silica gel material were equilibriated with known concentrations of the cations studied. After equilibration was reached, the amount of bound cation was determined by stripping the column with a complexing agent or, in the case of the aza-crowns, with an acid solution and analyzing the concentrate for the desired metal ions. The log $\underline{K}$ values were then determined as reported (ref. 12). Table I lists the log $\underline{K}$ values for the interaction of various M^{n+} with five of the silica gel-bound materials and with the analogous unbound macrocycles. The agreement between the two sets of log $\underline{K}$ values is excellent.

The similarity of the log $\underline{K}$ values for the two sets of interactions suggests that the silica gel-bound crowns are effectively solvated by the aqueous solutions. Thus, they form complexes in the same manner as do the free crowns in water. On the other hand, the bonding of macrocycles to hydrocarbon polymers, such as polystyrene, causes a considerable modification in metal ion binding properties in both organic solvents and aqueous solutions. In particular, aqueous solutions cannot be treated effectively because the hydrocarbon polymers are not wetted by water (ref. 16,30). The similarity of the sets of log $\underline{K}$ values determined in the present study to those involving the unbound macrocycle, also suggests that prediction of metal separations using silica gel bonded to other macrocyclic ligands should be possible using log $\underline{K}$ values for the interaction of unbound macrocycles with the desired metal ions. Thus, one has a powerful tool to predict separations using available compilations of log $\underline{K}$ values (ref. 3).

Cation separation, removal and concentration

Aqueous mixtures of cations were passed through a known amount of the silica gel-bound macrocycle material to determine relative selectivities (ref. 14). The columns were found to quantitatively remove specific cations or groups of cations. Silica gel-crown material 2, for example, was selective for Ba^{2+}, Sr^{2+} and Ca^{2+} over Mg^{2+} by an infinite amount (ref. 14). Among the cations Ba^{2+}, Sr^{2+} and Ca^{2+}, Ba^{2+} was selective over Sr^{2+} by a ratio of 10 and over Ca^{2+} by a ratio of 339 and Sr^{2+} was selective over Ca^{2+} by a ratio of 54. It is important to note that the selectivity ratios demonstrated here are nearly the same as the predicted

Table I. Comparison of Log $\underline{K}$ Values for the Interaction of M^{n+} With Silica Gel-Bound and the Analogous Free (in Parentheses) Crown Compounds (1-4 and 6)[a].

Log $\underline{K}$

Cation	1	2	3	4	6
H^+(1)				5.1^b (5.22^d)	8.9^c (9.08^e)
H^+(2)					7.5^c (7.94^f)
K^+		2.10^c (2.03)			
Sr^{2+}	0.57^c (2.63^f)	2.83^c (2.72)			2.4^c (2.57^e)
Ba^{2+}		3.56^c (3.87)	2.93^b (5.44^f)		
Cd^{2+}		0.39^c (3.0^f)			5.0^c (5.25^e)
Pb^{2+}		3.96^c (4.27)			
Tl^+	1.38^b (1.23)	2.01^c (2.2)			
Cu^{2+}				1.8^b (4.63^f)	
Ni^{2+}		$<0.2^c$ (2.9^f)			
Ag^+	0.90^b (0.94)	1.61^c (1.50)		2.7^b (5.5^f)	8.2^c (7.8^e)

[a]Data for unbound crowns take from ref. 3. [b]Data from ref. 20. [c]Data from ref. 15. [d]Data for pyridine. [e]Data for diaza-18-crown-6 in ref. 3. [f]Values valid in methanol. These values have been shown to be 2-3 log $\underline{K}$ units higher than in water (ref. 3).

selectivities based on the ratios of the unbound macrocycle $\underline{K}$ values. These predicted selectivities are 93-930 for Ba^{2+}/Ca^{2+}, 7-66 for Sr^{2+}/Ca^{2+}, 14 for Ba/Sr^{2+} and infinite for Ba^{2+}, Sr^{2+}, or Ca^{2+}/Mg^{2+} (ref. 3). The ranges given for the first two cases are due to some lack of agreement in the measurement of some of the log $\underline{K}$ values for the interaction of unbound macrocycles with those cations.

The separation of certain heavy metal ions from aqueous mixtures of heavy metal ions and the common metal salts has been observed. For example, ethyldiaza-18-crown-6, 5, has been used to efficiently and selectively remove 1 ppm Cu^{2+} (1.6×10^{-5} M) from aqueous solutions also containing 10^{-3} M levels of Ca^{2+} and Mg^{2+}. This separation is similar to that required to remove toxic levels of Cu^{2+} from potable water. Despite the much greater concentrations of Ca^{2+} and Mg^{2+}, the amount of Cu^{2+} which binds to the ligand is 400 times greater than that of Ca^{2+} and infinitely greater than that of Mg^{2+} (Mg^{2+} binding to the macrocycle was undetectable). Furthermore, when the Cu^{2+} was eluted from the solid material using 1 M HNO_3 or HCl, the Cu^{2+} was recovered at a concentration of 1050 ppm or a concentration factor of 1050. These results are possible because of the high selectivity of macrocycle 5, either bound or unbound, for Cu^{2+} over cations such as the alkaline earth and alkali metal ions and the pH chemistry of the ligand. Hence, the binding of the ligand allows for these desirable properties to be used in a reusable system of engineering feasibility.

Acknowledgements

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