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Evaluation of Binding Selectivities of Bis-crowned Clefts by Electrospray Ionization/Quadrupole Ion Trap Mass Spectrometry

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Electrospray ionization (ESI) was used in conjunction with quadrupole ion trap mass spectrometry to measure metal binding selectivities of bis-crowned clefts in methanol solution. Each of the three cleft compounds contained two 15-crown-5 rings separated by different quinoline spacers. Binding selectivities were compared qualitatively with previous extraction results obtained for three bis-crown clefts complexing with the alkali metals sodium, potassium and rubidium in aqueous solution. The bis-crowned cleft molecules were found to form 1:1 and 2:1 metal—cleft complexes, and, in a few cases where larger alkali metals were involved, two cleft molecules were able to form 2:2 metal–cleft complexes cooperatively. The binding selectivity is greatly affected by the size of the alkali metal and by the flexibility of the quinoline bridge, factors that influence the degree of electrostatic repulsion between the two crown ether rings. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: binding selectivity; cleft; electrospray ionization; quadrupole ion trap mass spectrometry; complexation

INTRODUCTION

Host–guest interactions play a key role in the understanding of many biological processes such as enzyme and antibody reactions. In addition, the selectivity aspects of host–guest complexation are responsible for the elegant types of molecular recognition identified in binding at active sites and the sequestration or transport of metal ions.[1] Furthermore, industrial applications of these types of processes include (i) preparation of polymeric membranes of ion-selective electrodes that are used to detect alkali metals[2] and (ii) the preparation of chiral catalysts for use in the construction of natural products.[3] Much research effort over the past decade has been devoted to the design and synthesis of increasingly elaborate and novel hosts for numerous purposes. Synthetic hosts may serve as model biological receptors. They can be used to study ion transport, or they can be developed for analytical applications such as ion sensors and chromatographic agents.

One of the more interesting classes of synthetic hosts includes the bis-crowned clefts. Bis-crowned clefts were developed as enzyme mimics and for possible environmental applications, for example, extraction of metals from water, owing to their ability to bind and to transport various metals from one medium to another.[4]

Previous methods for probing aspects of molecular recognition and selectivity of molecular cleft compounds involved conventional techniques such as extraction methods. For example, an organic cleft dissolved in an organic phase can be used to extract metal ions from an aqueous phase. The depletion of metal ions from the aqueous phase would be monitored to determine the amount of metal extracted by the host compound.[5] These methods suffer from several shortcomings. First, when sample availability is limited, it is necessary to work with small volumes, thereby increasing the systematic error inherent in the technique. Thus, for very precious and limited samples, the extraction method does not afford superior detection limits. Second, the extraction method is an equilibrium process that is governed by solubilities, and this method does not allow for thorough mixing of the immiscible host and guest phases, which may result in low extraction efficiencies. Finally, this technique produces excess organic waste. Other methods used to measure binding selectivities, such as potentiometric methods, have other limitations. For example, potentiometric methods are typically restricted to aqueous solutions and are not applicable to all types of guest ions.

Recently, electrospray ionization (ESI) has proved to be a useful tool for the investigation of host–guest and other non-covalent interactions.[6] The use of ESI mass spectrometry to evaluate aspects of molecular recognition has been validated for use with polyether-containing compounds, such as crown ethers and cryptands, including the estimation of binding selectivities.[7,8]

In a previous study, alkali metal and ammonium ion binding selectivities were measured for a series of crown ethers. Excellent correlation between the ESI spectral data and calculated binding selectivities was obtained

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for solutions containing a single host with two similar guest ions, such as alkali metal ions.[8]

In the present study, binding selectivities of three clefts were evaluated by using ESI/quadrupole ion trap mass spectrometry. The results thereby obtained were compared qualitatively with the corresponding values obtained via conventional solution extraction methods which use chloroform and water. Although all of the present ESI experiments were performed in methanol for solubility purposes, water and many low surface tension solvents, such as chloroform and acetonitrile, are routinely used in ESI measurements. Therefore, it is possible to perform a conventional extraction experiment and analyze the chloroform layer using ESI-MS, but these types of experiments were not emphasized in this study.

Each cleft molecule consists of two 15-crown-5 rings that are connected by a quinoline-containing bridge. The host cleft molecule is able to bind cations such as alkali or alkaline earth metal ions in two ways, i.e. by formation of 1:1 and/or 1:2 cleft–metal complexes. As shown here, complexes containing a single metal or two different metal ions can be observed.

EXPERIMENTAL

All ESI-MS experiments were performed with a Finnigan quadrupole ion trap mass spectrometer operated in the mass-selective instability mode with modified electronics to allow axial modulation.[9] The electrospray interface is based on a design developed by Oak Ridge National Laboratory.[10] The Harvard syringe pump system was set at 1.5–3 μl min^{-1}. Cleft compounds were sprayed in 100% methanol solution at a needle voltage of 2.8–3.0 kV. The vacuum chamber was operated at a pressure of 1 mTorr (1 Torr = 133.3 Pa) with helium. Each spectrum taken was an average of at least 25 scans.

The cleft compounds were prepared in anhydrous methanol and mixed individually with sodium chloride, potassium chloride or rubidium chloride, resulting in a 1:2 concentration ratio of cleft to metal. Spectra of the individual cleft–metal (1:2) solutions were taken. The individual solutions were then mixed to form a 1:1:1 solution of a single cleft–metal 1–metal 2, and the resulting spectrum was taken. All metal-containing compounds were purchased from Aldrich Chemical (Milwaukee, WI, USA) and used without further purification.

Compounds **D-108**, **D-109** and 2,3-(4′-amino-5′-formylbenzo)-1,4,7,10,13-pentaoxacyclopentadecane (**2**) were prepared by using previously published procedures.[12] High-resolution mass spectral data was obtained at the Midwest Center for Mass Spectrometry, Department of Chemistry, University of Nebraska, Lincoln, NE, USA.

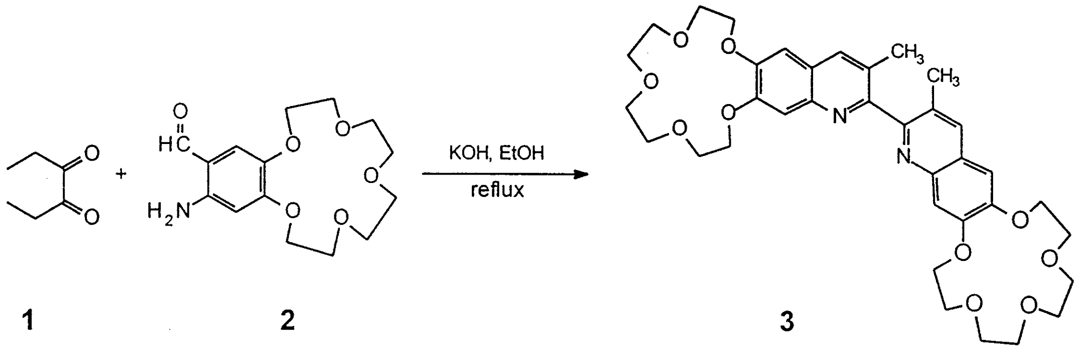
Friedländer condensation of hexane-3,4-dione with 2

To a solution of hexane-3,4-dione (**1**, 57 mg, 0.50 mmol) and **2**[12] (311 mg, 1.0 mmol) in absolute EtOH (20 ml) was added a solution of KOH (25 mg, 0.45 mmol) in absolute EtOH (1 ml) and the resulting mixture was refluxed for 44 h. The reaction mixture was allowed to cool gradually to ambient temperature and then concentrated *in vacuo*. Water (40 ml) was added to the residue and the resulting aqueous suspension was extracted with $CHCl_3$ (3 × 50 ml). The combined organic extracts were dried (Na_2SO_4) and filtered and the filtrate was concentrated *in vacuo*. The residue was purified via fractional recrystallization from $CHCl_3$–EtOAc. Pure **3** (**D-107**, 125 mg, 38%) was obtained as a colorless microcrystalline solid: m.p. 264–265 °C (uncorrected); IR (KBr), 2878 (s), 1621 (m), 1503 (s), 1261 (s), 1158 (s), 966 cm^{-1} (m); ^{1}H NMR ($CDCl_3$), δ 2.22 (br s, 6H), 3.64–4.05 (m, 24H), 4.10–4.30 9 (m, 8H), 6.98 (s, 2H), 7.36 (s, 2H), 7.84 (s, 2H); ^{13}C NMR ($CDCl_3$), δ 18.5 (q), 68.1 (t), 68.7 (t), 69.1 (t), 69.3 (t), 70.2 (t), 70.3 (t), 71.25 (t), 71.32 (t), 106.0 (d), 109.1 (d), 129.8 (s), 127.5 (s), 135.2 (d), 143.5 (s), 149.9 (s), 151.8 (s), 157.2 (s). Analysis: calculated for $C_{36}H_{44}N_2O_{10}$, M_r^+ 664.2996; found (high-resolution mass spectrometry), M_r^+ 664.2983.

RESULTS AND DISCUSSION

Overview of structural effects and metal complexation of clefts

Each of the three clefts contains two 15-crown-5 rings with cavity sizes of 1.7–2.2 Å[11] that are separated by quinoline spacers (Fig. 1) and are capable of binding metals in several ways, depending on the spacer group and the type of metal ion involved. The clefts are known to form 1:1 cleft–metal sandwich complexes and/or 1:2 cleft–metal complexes.[12,13] The alkali metal ions have



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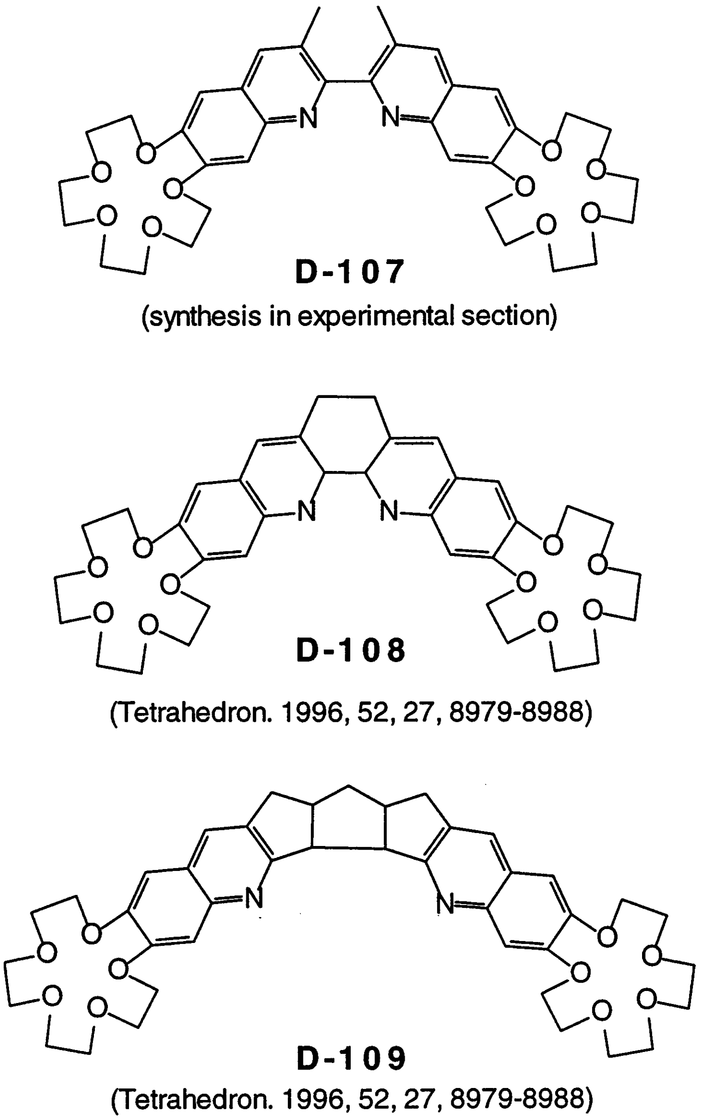


D-107

(synthesis in experimental section)

D-108

(Tetrahedron. 1996, 52, 27, 8979-8988)

D-109

(Tetrahedron. 1996, 52, 27, 8979-8988)

Figure 1. Cleft structures.

ionic diameters of 1.86 Å for sodium, 2.27 Å for potassium and 2.48 Å for rubidium.[14] Based on these sizes, it is clear that only the sodium ion can be entirely encapsulated by the 15-crown-5 cavity. D-107 possesses the most flexible spacer, thus allowing the greatest folding and mutual interaction between the two crown ether rings. D-108 and D-109 contain more rigid spacers that disfavor any type of cooperative interaction between the crown ether rings.[12] Moreover, the spacer of D-109 is considerably larger than that of the other two clefts.

In addition to these structural differences among the clefts, the sizes of the metal ions may also play a role in the complexation reactions. As the size of the metal increases, it becomes more likely to perch outside the cavity of the crown ether,[15] thus preventing complexation of a second large metal ion in the other ring due to deleterious coulombic and steric effects. This brief overview of size effects and structural factors provides a fundamental insight into some interesting aspects of the complexation behavior of the three clefts.

ESI strategy and Na^+/K^+ complexation

The binding selectivities of the three clefts were evaluated by a series of experiments that involve electrospray ionization of mixtures of metal salts and clefts at well defined concentrations. First, solutions that contain a single cleft with a single metal salt at a cleft to metal concentration ratio of 1 : 2 were sprayed. Next, solutions that contain a single cleft with two metal salts at a cleft : metal 1 : metal 2 concentration ratio of 1 : 1 : 1 were sprayed.

A typical sequence is shown in Fig. 2 for the complexation of D-107 with sodium and potassium ions. Binding selectivities are determined by direct integration of the peak areas of the complexes in the mixture [Fig. 2(C)]. No corrections for differences in ESI efficiencies for the different types of complexes were made, because a previous study confirmed that corrections are unnecessary when the host molecule remains constant and the metal guest ion varies. Under these conditions,

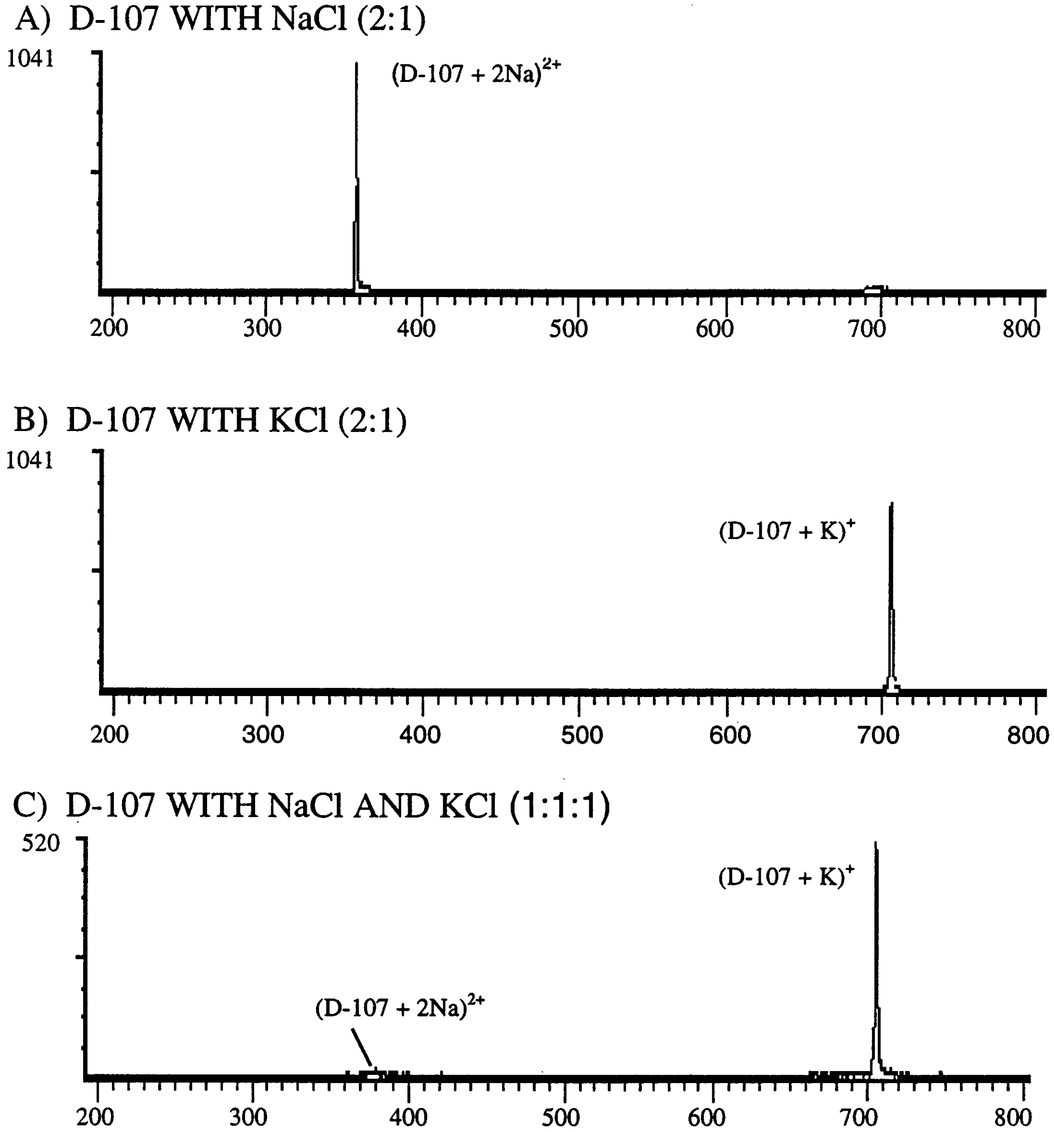


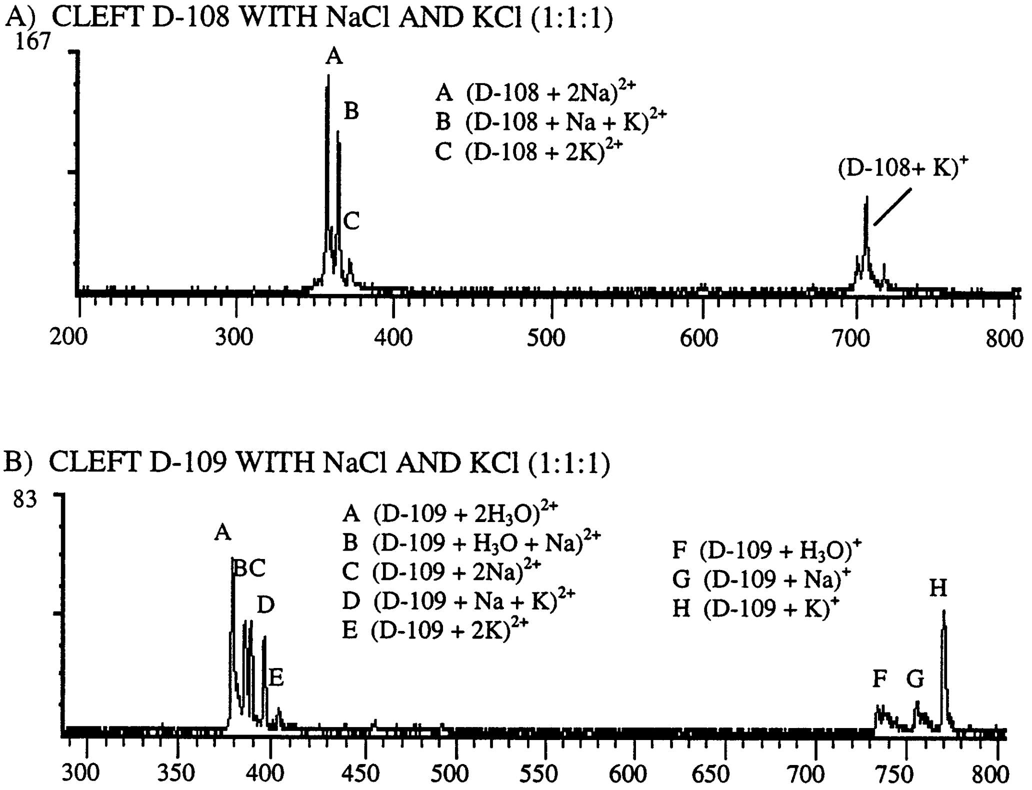
Figure 2. Complexation of cleft D-107 with Na^+ and K^+ ions. (A) D-107 with NaCl (2:1); (B) D-107 with KCl (2:1); (C) D-107 with NaCl and KCl (1:1:1).

the desolvation energies of the host–guest complexes and ESI response factors remain roughly constant.[8] As shown in Fig. 2(A) and (B), D-107 shows a distinct preference for binding two sodium ions or one potassium ion, respectively. However, overall, D-107 displays a preference for binding a single potassium ion compared with one or two sodium ions [Fig. 2(C)].

It is interesting that D-107 shows a distinct preference for binding two sodium ions over a single sodium ion. This observation suggests that each sodium ion is sufficiently well solvated and encapsulated by one of the crown ethers to permit little if any electrostatic repulsions to exist between two metal ions when one is bound to each polyether ring of the cleft.

For D-107, two potassium ions could bind in such a way that each would sit partially outside the cavity of each 15-crown-5 ring. However, electrostatic repulsions between the two metal ions effectively prevent formation of these 1:2 cleft–metal complexes.

The results for the complexation of the other two clefts with potassium and sodium are summarized in Fig. 3. In contrast to the results described for D-107, both D-108 and D-109 display a preference for the formation of the 1:2 cleft–metal complexes *vs.* the 1:1 complexes. In these cases, the complexes may incorporate two sodium ions, one sodium and one potassium ion, or even one sodium ion and one hydronium ion. However, complexes that incorporate two potassium ions are of extremely low intensity. Hydronium ion complexation is not uncommon with crown ether compounds in methanol solutions, as seen in Fig. 3(B) and 4(C).[16] The formation of the hydronium ion complexes may be influenced by a number of experimental factors, so these complexes were not studied in detail owing to the inability to control the amount of water found naturally in the laboratory air. Both D-108 and D-109 contain more rigid quinoline spacers that prevent significant interaction between the two crown ether rings, thus allowing the metal or hydronium ions to remain isolated and well solvated when bound to each ring. The larger size of potassium probably accounts for the low intensities of the 1:2 cleft–potassium complexes


A) CLEFT D-108 WITH NaCl AND KCl (1:1:1)

B) CLEFT D-109 WITH NaCl AND KCl (1:1:1)

Figure 3. Complexation of clefts D-108 and D-109 with Na^+ and K^+ ions. (A) Cleft D-108 with NaCl and KCl (1 :1 :1); (B) Cleft D-109 with NaCl and KCl (1 :1 :1).

because of the greater degree of electrostatic repulsion between the two potassium ions that occurs when they are bound to the polyether rings. The larger potassium ions are not fully encapsulated by the crown ether rings, causing the charges to be less shielded, which leads to electrostatic repulsion, an interaction that destabilizes those 1 : 2 complexes.

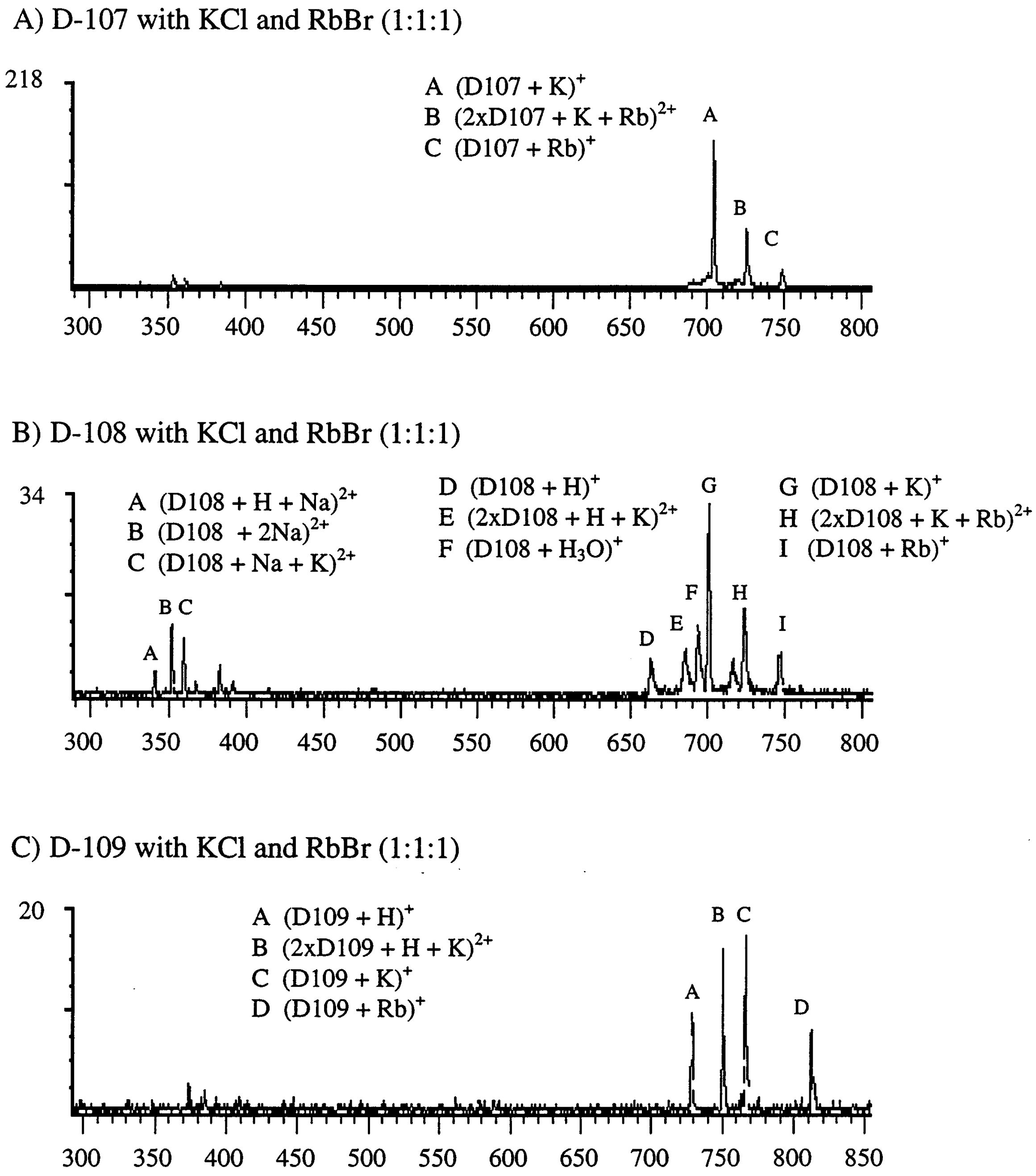
Comparison with previous solution studies

Previous solution-phase ($CHCl_3$–H_2O) binding studies of clefts D-108 and D-109, but not D-107, have been reported.[12] An extraction method was used to evaluate the stability constants of D-108 and D-109 for complexation of alkali metals in which alkali metal picrates or perchlorates were present in aqueous solutions, while the cleft compounds were dissolved in chloroform. Cleft D-109 showed a greater selectivity for Na^+ over K^+, but the formation of 1 : 2 cleft–metal complexes was not discerned. Based on the ESI results shown in Fig. 3, D-109 shows a preference for binding a single K^+ ion over a single Na^+ ion, but there is also evidence for favorable formation of complexes containing two sodium ions. The alkali metal picrate extraction method proved unsuccessful for monitoring complexation of cleft D-108 owing to the formation of precipitates at the solution interface. With the use of alkali metal perchlorates, the extraction method showed the selectivity of D-108 as $Na^+ > K^+$. The ESI results in Fig. 3 indicate that D-108 has a preference for K^+ in the 1 : 1 complexes, but the 1 : 2 cleft–metal complexes favor Na^+. Previous studies of D-107 by the extraction method have not been reported.

The ESI results may differ from the extraction results for several reasons. First, the ESI results were obtained for a methanolic solution, not a two-phase mixture, and the solvation energies of the alkali metals are substantially lower in methanol than in water. The more polar environment of water is known to alter binding selectivities of host ligands owing to the increased solvation of the metal ions by the polar medium. Second, the extraction method involves intermixing of the clefts and metals in two very different solvents, thereby creating a range of perturbed solvation shells. Third, the presence and importance of 1 : 2 cleft–metal complexes could not be monitored via the extraction method. In general, the ESI method provides an alternative way to estimate selectivities of the clefts and also permits the examination of the unusual 1 : 2 complexes.

Selective complexation of other models

It is of interest to compare the ESI results obtained previously for the complexation of 15-crown-5, an analog of the polyether rings found in the clefts, with the present results obtained for alkali metal complexation by these clefts. In a recent study, it was confirmed that 15-crown-5 slightly favors complexation of K^+ over Na^+ in methanol.[8] For example, at a 15-crown-5 : Na^+ : K^+ concentration ratio of 8 : 1 : 1 for in methanol, 15-crown-5 prefers to bind K^+ over Na^+ by a factor of 1.1 ± 0.2.[8] This selectivity qualitatively parallels the trend observed for the 1 : 1 cleft–metal complexes, in which complexation of a single K^+ ion is favored over complexation of a single Na^+ ion, as seen in Figs


A) D-107 with KCl and RbBr (1:1:1)

B) D-108 with KCl and RbBr (1:1:1)

C) D-109 with KCl and RbBr (1:1:1)

Figure 4. Complexation of clefts and K^+ and Rb^+ ions (A) D-107 with KCl and RbBr (1 :1 :1); (B) D-108 with KCl and RbBr (1 :1 :1); (C) D-109 with KCl and RbBr (1 :1 :1).

2(C) and 3. The selectivity issue is complicated by the formation of 1:2 cleft–metal complexes which clearly cannot be formed by the 15-crown-5 models.

In order to model further the selective complexation of the cleft compounds, the binding selectivity of benzo-15-crown-5 was examined by the ESI-MS method. The benzo substituent reduces the basicity of the adjacent oxygen atoms relative to the other oxygen atoms, thus causing a reduction in the Na^+ *vs.* K^+ selectivity.[17] The presence of the benzo substituent models the effect of the quinoline spacers on the 15-crown-5 rings in the cleft compounds. Utilizing the same method that was used for the study of 15-crown-5 with alkali metals described above,[8] benzo-15-crown-5 was determined to have unit selectivity for Na^+ and K^+ in methanol at a benzo-15-crown-5 : Na^+ : K^+ concentration ratio of 8:1:1. This confirms that the aromatic rings slightly affect the binding selectivities of the crown ether rings relative to 15-crown-5, i.e. reducing the preferences for K^+ relative to Na^+.

K^+/Rb^+ complexation

Comparisons of potassium *vs.* rubidium complexation were also undertaken by using the ESI method in order to allow further comparison with the prior extraction results reported for the clefts. The results are summarized by the spectra in Fig. 4. All three clefts show a preference for K^+ over Rb^+, and formation of 1:2

cleft–metal complexes does not occur. The latter result is predicted because the large sizes of the K^+ and Rb^+ ions permit only partial encapsulation by the crown ether rings, causing the charges to be less shielded. This factor leads to electrostatic repulsion between the metals in the 1 : 2 complexes and correspondingly reduces their stabilities. The results of prior extraction studies of D-108 and D-109 showed that the clefts favor complexation of K^+ over Rb^+, in agreement with the present ESI results and despite the different solvent conditions used in the two studies.

Several unusual products appear in the ESI spectra in Fig. 4 for D-107 and D-108. These products correspond to 2 : 2 cleft–metal complexes and presumably represent structures in which two metal ions are sandwiched between two clefts. Here one polyether ring from each cleft shares one metal ion. These assignments were confirmed by collisionally activated dissociation (CAD) experiments in which the 2 : 2 complexes were isolated and activated. An example is shown in Fig. 5 for $2 \times$ D-107 $+ K^+ + Rb^+$. The complex dissociates into two 1 : 1 complexes, D-107 $+ K^+$ and D-107 $+ Rb^+$, thus demonstrating that each D-107 ligand retains one metal ion during disassembly of the 2 : 2 complex. The formation of the 2 : 2 complexes is favored only when the alkali metal ions are sufficiently large to project outside the cavity of the 15-crown-5 moieties, thereby permitting binding of each metal ion to occur to two different crown ether rings.

CONCLUSIONS

Electrospray ionization offers a rapid method to evaluate selectivities of the clefts and requires relatively small samples. The size of the alkali metals has a significant effect on the binding selectivities of the clefts and the stoichiometries of the complexes in methanol solution. The results of ESI experiments indicate that the clefts favor binding a single potassium ion over a single sodium ion, but cleft D-108 prefers to bind two sodium ions or one potassium ion and one sodium ion over a single potassium ion. The formation of 1 : 2 cleft–metal complexes is greatly enhanced for the clefts that possess a more rigid quinoline spacer, presumably because the metal ions can be encapsulated separately in each 15-crown-5 ring and thereby prevent coulombic repulsions. The clefts also favor complexation to potassium ion over the larger rubidium ion, as expected on the basis of the known selectivity of 15-crown-5. Formation of cleft $+ K^+ + Rb^+$ complexes does not occur, because the metal ions are sufficiently large to project from the cavities of the crown ether rings and thereby to create

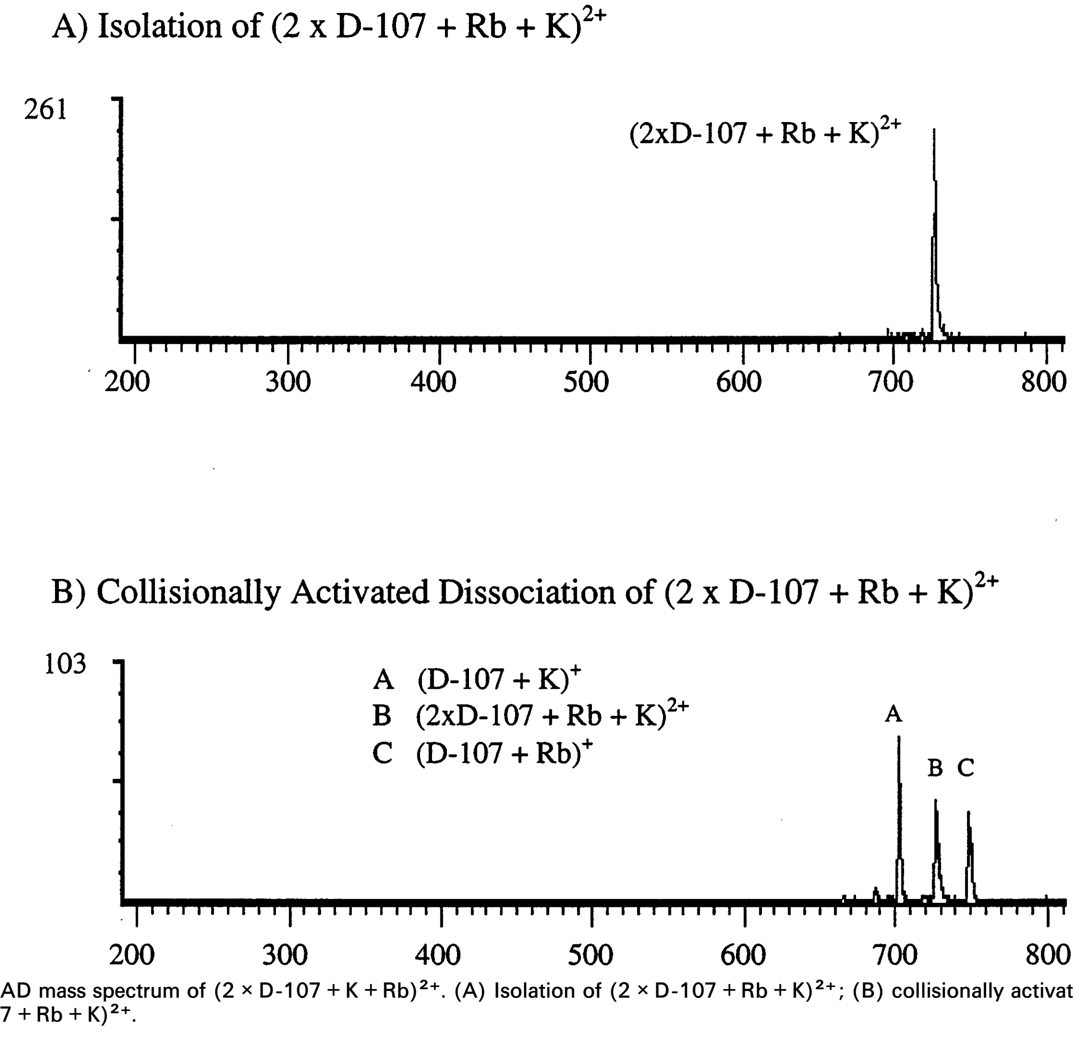


Figure 5. CAD mass spectrum of $(2 \times \text{D-107} + K + Rb)^{2+}$. (A) Isolation of $(2 \times \text{D-107} + Rb + K)^{2+}$; (B) collisionally activated dissociation of $(2 \times \text{D-107} + Rb + K)^{2+}$.

electrostatic repulsions between the rings. However, unusual 2 × cleft + K^+ + Rb^+ dimer complexes form for D-107 and D-108. These latter products are particularly interesting, because they represent structures in which two clefts share two metal ions. This type of 2:2 complexation occurs because the metal ions are large enough to project out the cavities of each of the crown ether rings. Hence the use of the electrospray method has permitted the first examination of 1:2 and 2:2 cleft–metal complexes to be made. The use of ESI to analyze one phase of a two-phase host–guest extraction mixture is under further investigation.

Acknowledgements

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