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COMMUNICATION

Multiple cation binding by bola-amphiphilic crown ethers: assessment by fast atom bombardment mass spectrometry

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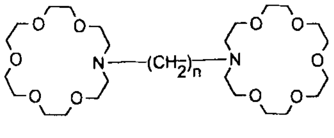
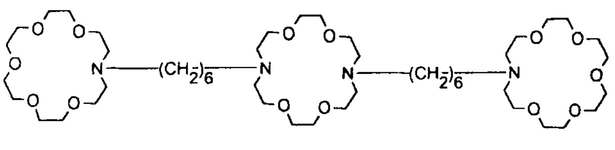
Bola-amphiphiles having two aza-18-crown-6 ether rings attached by a covalent spacer (O—O) and an analogous tris(macrocycle) (O—O—O) have been prepared and their cation complexation behavior has been assessed by fast atom bombardment and collisionally activated dissociation tandem mass spectrometry; the key finding is that two cations may simultaneously be complexed by a two- or three-crown system and that this complexation may also involve an anion.



1, n = 10; **2**, n = 16; **3**, n = 22



Bola-amphiphiles[1] are compounds having two polar 'head' groups separated by a lipophilic spacer that is conceptually equivalent to a hydrophobic tail in the more common amphiphiles. They may be represented as O—O whereas the latter are usually schematized as O—. The name bola-amphiphile was suggested by Fuhrhop[1] who has prepared several representatives of this interesting class of compounds. Membranes of this general type are known in nature[2] and are especially interesting because they appear capable of remaining intact under conditions that are extreme both in terms of temperature and pH. We have recently reported the preparation of bola-amphiphiles based upon the crown ether head-group and demonstrated their ability to form stable, ultrathin monolayer membranes.[3] Mass spectrometry is proving increasingly important in cation binding studies.[4] We now report the application of fast atom bombardment mass spectrometry (FAB/MS) to assess cation binding in these multi-ring compounds that are extremely difficult to analyze by other techniques.

The bola-amphiphiles or bolytes studied in this effort were prepared by treatment of an azacrown with a diacid dichloride followed by reduction as previously reported.[3] The hitherto unknown tris(macrocyclic) system $\langle 18N\rangle$—$(CH_2)_6$—$\langle N18N\rangle$—$(CH_2)_6$—$\langle N18\rangle$[5] (**5**) is fully characterized[6] but has not previously been reported.

The FAB mass spectra[7] of bolytes **1**, **2**, and **3** were dominated by the $[M + H]^+$ and $[M + 2H]^{2+}$ species. For example the FAB spectrum of **1** (mw 664) contained $[M + H]^+$ at m/z 665 and $[M + 2H]^{2+}$ at m/z 333. As usual, the doubly-charged ions were distinguished from their singly-charged counterparts by the difference in resolution. When cations were present in the FAB matrix, ions were observed at masses consistent with complexation of one or more cations depending upon structure.

FAB spectra of **2** were determined in the presence of varying amounts of K^+SCN^- (see Table 1). When the ratio K^+:**2** was less than 1.0, the spectrum showed four ions of interest. The singly charged ions, $[M + H]^+$ (m/z 749) and $[M + K]^+$ (m/z 787), were less intense than the doubly charged ions and the peak attributed to $[\mathbf{2} + H]^+$ was more intense than the potassium-bound counterpart. Doubly charged ions having masses corresponding to $[M + 2H]^{2+}$ (m/z 375) and $[M + H + K]^{2+}$ (m/z 394) dominated the spectrum with the former being preponderant. When

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*Address correspondence concerning FAB/MS to B.C.L. and concerning structures to G.W.G.

Table 1 FAB/MS Data for 2 in the presence of K^+A^-

	m/z 749 [M + H]$^+$	m/z 787 [M + K]$^+$	m/z 375 [M + 2H]^2 +	,/z 394 [M + H + K]^2 +	,/z 413 [M + 2K] 2	m/z 884 [M + K + KA] +
No Cation	53%	-	100%	-	-	-
K:2 = 05	41%	18%	100%	46%	8%	-
K:2 = 2	38%	60%	65%	100%	63%	4%
K:2 > 50	-	96%	-	9%	100%	20%

The percentages given in the table are relative abundances.

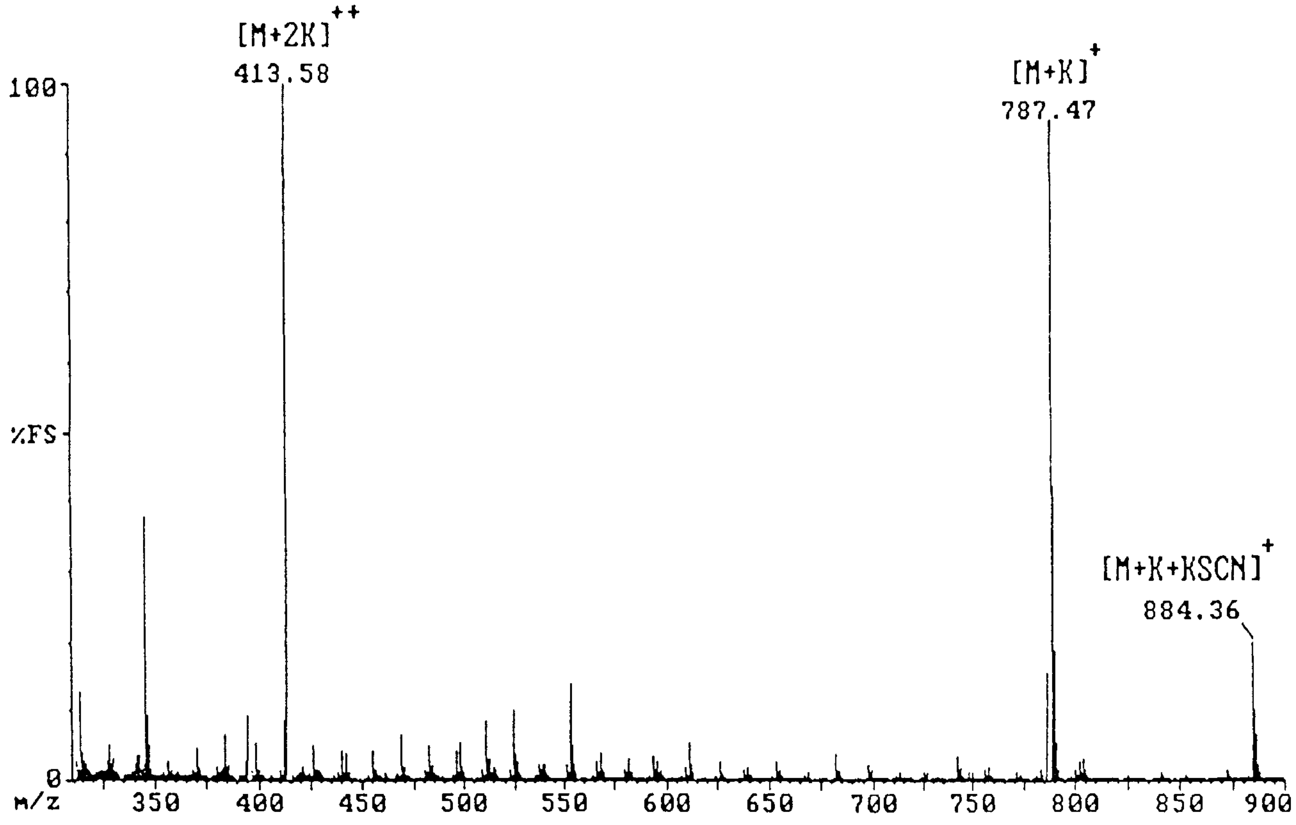

Figure 1 FAB Spectrum of 2 plus K^+ (K^+:2>50).

the ratio of K^+:**2** was 2 (i.e. one K^+ for each ring) five major ions were observed. The singly charged ions were noted as above but their intensities were reversed probably because K^+ is so much more abundant and therefore presumably more accessible than in the previous experiment. The doubly-charged ions again dominated the spectrum but included a new ion, $[M + 2K]^{2+}$ (m/z 413) in which **2** apparently binds one K^+ in each macroring. When a greater than stoichiometric amount of K^+ (SCN^-, ratio of K^+:**2** > 50) was added, only three ions were observed in the FAB spectrum. The ions previously ascribed to protonated species were no longer in evidence. Three ions were observed: $[M + K]^+$ (m/z 787), $[M + 2K]^{2+}$ (m/z 413), and an ion having m/z 884. The latter mass corresponds to a species having the stoichiometry **2**·K^+·KSCN. Incorporation of the anion in this complex was remarkable and surprising. Other potassium salts (K^+A^-, $A^- = Cl^-$, NO_3^-, ClO_4^-) produced similar [M + K + KA] species having the respective anions incorporated. It is, of course, possible that this cationization takes place in the selvedge region; in the absence of evidence to the contrary, we believe that these data reflect the expected solution, rather than gas phase, chemistry.

The amide precursor to **2**, i.e. ⟨18N⟩—CO—$(CH_2)_{14}$—CO—⟨N18⟩, **4**, showed entirely different behavior. Under conditions in which K^+ was present in large excess, the dominant ion was $[M + K]^+$ (m/z 815). Moreover, $[M + 2K]^{2+}$ (m/z 427) had only about 20% relative abundance and $[M + K + KSCN]^+$ was completely absent. The binding ability of each macroring in amide **4** was attenuated by the rigid amide link which has a resonance form placing a formal positive charge within the macroring. The amide carbonyl, on the other hand, is potentially a powerful donor. We presume that both macrorings in **4**, and perhaps the carbonyls as well, contribute to binding a single cation in the sandwich arrangement.

Collisionally activated dissociation (CAD) tandem mass spectrometry[8] was applied in the **bol**·K·KCl (**bol** = **1** or **2**) case and to several other systems not discussed here. In all cases studied, over a wide range of collision energies and collision cell pressures, the only product ion observed was $[M + K]^+$ suggesting that K^+A^- rather than A^- alone was stripped off in every case. For example, the CAD spectrum of **1**·K·KCl contained only two ions. The first we attribute to the precursor $[\mathbf{1}\cdot K\cdot KCl]^+$ (m/z 777). The second (m/z 703) corresponds to the product ion $[\mathbf{1}\cdot K]^+$. No other ion was observed. Energetically, this result implies to us that loss of neutral KCl is favored over loss of Cl^- alone. Loss of KCl could afford a sandwich complex of a single K^+ whereas loss of Cl^- might afford a complex in which K^+ cations are retained in each crown ring at opposite ends of a connecting chain. Other structural arrangements are obviously possible but none can yet be deduced with certainty.

This phenonemon was explored further by extension of the bolytes to the previously unreported class of crowns: tris(macrocycle) **5**. In the presence of excess K^+, four ions of interest were observed. These included the expected $[M + K]^+$ and $[M + 2K]^{2+}$, $[M + K + KSCN]^+$ and the surprising $[M + K + 2KSCN]^+$. No triply-charged species having three potassium ions as part of its structure could be identified. Note that the macrorings (and thus cation complexes) in this case are separated by only 6 carbons rather than at least 10 in **1**–**4** and the central ring contains only four rather than five oxygen atoms. It thus appears essential in this case for a part of the three K^+ charges to be neutralized by associated anions.

This series of remarkable observations is currently being extended by studies involving other cations, other anions, and other novel multimacroring structures and will be reported in due course.

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5 The symbol ⟨18N⟩ is a shorthand representation of aza-18-crown-6; ⟨N18N⟩ represents 4,13-diaza-18-crown-6.

6 Compound **5** was isolated as a colourless oil (67%) from the reaction of *N,N′-bis*(6-chlorohexyl)-4,13-diaza-18-crown-6 with aza-18-crown-6. Full details are presented in the supplementary material.

7 FAB mass spectra (VG Trio 2) were obtained on samples desorbed from *m*-nitrobenzyl alcohol matrix using a 6.5 kV xenon atom beam. For the complexation studies, an appropriate concentration of cation in methanol, the selected bolyte, and the matrix were mixed on the FAB probe. The CAD spectra were acquired on a VG Trio 3 mass spectrometer using source conditions as described above. The collision gas (Ar) pressure was varied from 0.5 to 2.0 mbar and the collision energy was varied from 5 to 50 eV (lab frame).

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