Selective cation binding of crown ether acetals in electrospray ionization mass spectrometry

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Diphenyl-substituted 11- to 20-membered ring crown ether acetals 1a–d exhibit selective cation complexation with alkali metal ions and NH_4^+ in electrospray ionization mass spectrometry (ESI-MS). In addition, cation-bound crown ether dimers (sandwiches) and trimers have also been observed, especially for the smaller crown ethers. However, their binding ability is completely lost upon acetal hydrolysis. It has been found that these crown ether acetals tend to preferentially bind smaller ions as compared with the corresponding simple crown ethers possessing the same number of ring oxygen atoms. These results are discussed on the basis of ring-contracted deformation, hydrophobic effects of the diphenyl group and the reduced solvation energies of the complexes.

Introduction

Crown ethers bind a large array of metallic and organic ions.[1] Recently, much effort has been expended in order to clarify such host–guest complexation of crown ethers by mass spectrometry using various types of soft-ionization techniques (ESI,[2] FAB,[3] CI,[4] PD,[5] *etc.*). Electrospray ionization mass spectrometry (ESI-MS) in particular was found to be a powerful analytical method for the characterization and identification of these non-covalently bound polar species,[6] and increasingly ESI-MS studies are now being conducted for an assessment of these complexations.[7]

In previous papers, we have shown that a novel and expeditious redox reaction of diazoalkanes with quinones in the presence of oligoethylene glycols provides so-called 'crown ether acetals' in fair to good yield.[8] This new type of macrocyclic polyether **1** has a ring-contracted structure with one methylene unit as compared with the usual crown ethers possessing the same number of oxygen atoms. These compounds underwent hydrolysis and have been argued to possess selective cation binding ability as reflected by the rate-retarding effects of added alkali metal cations upon hydrolysis.[9] However, only a few papers report on the cation binding of crown ether acetals by generally established methods.[10] This is probably because of a lack of general and useful syntheses for such acid-sensitive macrocyclic compounds.[11]

In this paper, we will describe an ESI-MS study of the alkali metal and NH_4^+ ion complexation of 11- to 20-membered ring crown ether acetals **1a**–**d** [abbreviated hereafter as 11-crown-4 **1a**, 14-crown-5 **1b**, 17-crown-6 **1c** and 20-crown-7 **1d**, according to generally accepted convention] to assess their cation binding behaviour as compared with that of simple crown ethers such as **2**.

Results and discussion

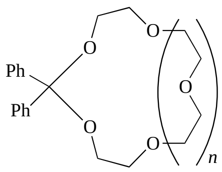
Cation complexation of crown ether acetals

The first set of ESI-MS experiments was carried out on a sample solution (H_2O–CH_3CN = 1 : 4 by volume) containing a crown (0.1 mM) and a mixture of five alkali metal perchlorates (each 0.1 mM). In these measurements, major mass peaks attributable to the 1 : 1 ion–crown complexes were observed along with those of the 1 : 2 (and the 1 : 3, but only for crown **1a**) complexes as represented by the case of crown **1a** (Fig. 1). Interestingly, the addition of one drop of dilute hydrochloric acid resulted in the disappearance of these mass peaks due to ring-opening by acetal hydrolysis,[12] providing direct evidence for the cation binding of **1**. In contrast, similar treatment of the benzo-18-crown-6 **2** complexes caused no appreciable change in their mass spectra.

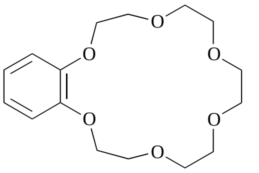
Table 1 Peak intensity data for ESI-MS analysis for complexation of crown ethers **1a**–**d** and **2** with alkali metal ions[a]

		Relative intensity I_m (%)				
Complex[b]	*n*	Li	Na	K	Rb	Cs
$[(\mathbf{1a})_n\cdot M]^+$	1	100	72	42	31	26
	2	9	37	20	13	9
	3	6	6	7	8	7
$[(\mathbf{1b})_n\cdot M]^+$	1	64	100	65	52	39
	2	0	6	11	10	7
$[(\mathbf{1c})_n\cdot M]^+$	1	6	60	100	59	36
	2	0	0	2	6	4
$[(\mathbf{1d})_n\cdot M]^+$	1	6	45	100	83	47
	2	0	0	0	3	2
$[(\mathbf{2})_n\cdot M]^+$	1	5	11	100	50	17
	2	0	0	0	0	3

[a] Solvent: H_2O–CH_3CN = 1 : 4 (v/v); crown (0.1 mM) and metal ion (each 0.1 mM). [b] Counter anion was omitted. M = Li, Na, K, Rb or Cs as indicated.



1a *n* = 0
1b *n* = 1
1c *n* = 2
1d *n* = 3



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The 1 : 1 ion–crown complexes

To survey the selective cation binding, the relative intensities (I_m) of ESI mass spectra of the 1 : 1 ion–crown complexes were obtained for each crown by dividing the respective peak height by that of the most intense base peak. Isotope corrections were applicable to the experimental data for Li^+, K^+ and Rb^+ complexes. The data set is summarized in Table 1. Here, any

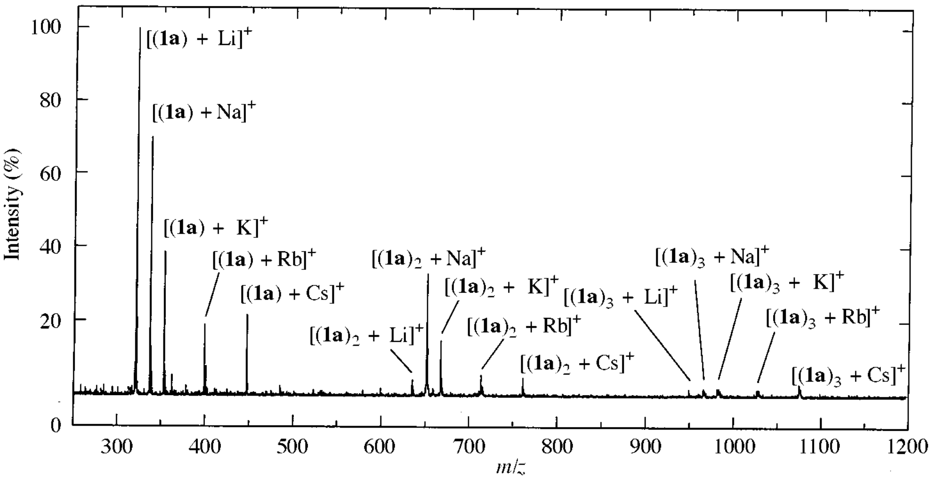


Fig. 1 ESI mass spectrum of crown ether acetal **1a** binding M$^+$ (=Li$^+$, Na$^+$, K$^+$, Rb$^+$ and Cs$^+$). [**1a**] = 0.1 mM, [M$^+$] = 0.1 mM (each), solvent; H_2O–CH_3CN = 1:4 (v/v).

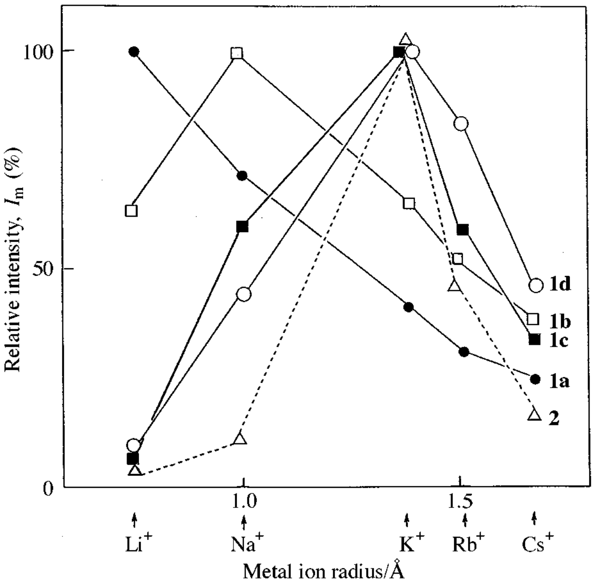


Fig. 2 Plots of relative intensity (I_m) of ESI mass spectra *vs.* metal ion radius for 1:1 crown–ion complexes; **1a**: 11-crown-4, **1b**: 14-crown-5, **1c**: 17-crown-6, **1d**: 21-crown-7, **2**: benzo-18-crown-6

Table 2 Peak intensity data for ESI-MS analyses for complexation of a mixture of crowns with K$^+$ and $NH_4^{+\,a}$

	Relative intensiy I_m (%)				
1:1 Complex^b	K	NH_4	2:1 Complex^b	K	NH_4
[**1a**·M]$^+$	4	4	[**1b**·**2**·M]$^+$	2	6
[**1b**·M]$^+$	7	5	[**1c**·**2**·M]$^+$	4	20
[**1c**·M]$^+$	34	15	[**1d**·**2**·M]$^+$	<1	6
[**1d**·M]$^+$	68	75	([(**1c**)$_2$·M]$^+$ +[**1b**·**1d**·M]$^+$)	5	8
[**2**·M]$^+$	100	100			
			[**1c**·**1d**·M]$^+$	<1	6
			[(**1d**)$_2$·M]$^+$	<1	4
			[(**2**)$_2$·M]$^+$	0	3

^{a} Solvent: H_2O–CH_3CN = 1:4 (v/v); crowns (each 0.1 mM) and K$^+$ (0.5 mM) and NH_4^+ (0.5 mM). ^{b} Counter anion was omitted. M = K or NH_4 as indicated.

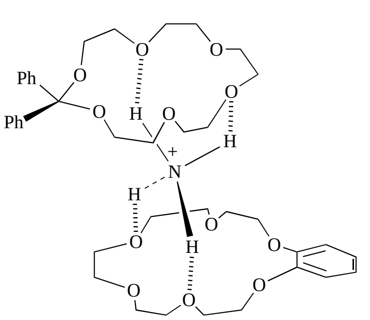
straightforward quantification of the EIS-MS data gained in the gas phase presents some difficulty because it is uncertain whether the I_m values reflect exactly the solution phenomena under study.[13] A possible misinterpretation of the EIS-MS data was demonstrated for the alkali metal ion binding of oxaamide ionophores[14] and for the cyclodextrin inclusion of amino acids and small peptides.[15] In contrast, several workers discovered some correlation of solution and gas phase complexation of 18-crown-6[16] and cryptand [2.2.2][16a] with alkali metal cations in a comparison of cation-binding selectivities by EIS-MS and by well-established methods.[1c]

The metal ion responsible for the base peak was Li$^+$ for 11-crown-4 **1a**, Na$^+$ for 14-crown-5 **1b** and K$^+$ for both 17-crown-6 **1c** and 20-crown-7 **1d**, respectively. As expected from the literature references,[17] K$^+$ was the preferred guest for benzo-18-crown-6 **2**.

The selective cation binding caused by the preferential ion–dipole interaction can be more explicitly visualized in the plots of I_m *vs.* metal ion radius (Fig. 2). The smallest 11-crown-4 **1a** showed a monotonous decrease with increasing ion radius from Li$^+$ to Cs$^+$. The binding property can be explained by its smaller cavity size compared to the simple 12-crown-4 (cavity radius 0.60–0.75 Å).[18] Thus, the ring size of **1a** is too small to envelop the alkali metal cations; *i.e.* Li$^+$ (ionic radius 0.76 Å), Na$^+$ (1.02 Å), K$^+$ (1.38 Å), Rb$^+$ (1.52 Å) and Cs$^+$ (1.67 Å).[19] In conformity with the poor binding ability, crown **1a** exhibited rather weak mass spectra attributed not to the size-fitted 'ion-in-the-hole' complex[20] but the 'nesting' or the less-favourable 'perching' one.[21] For 14-crown-5 **1b** with one oxyethylene unit elongation, the base peak was achieved at Na$^+$, though almost the same slope for the decreasing line as for **1a** was maintained for the larger-sized K$^+$ to Cs$^+$ cations. The maximum intensity at Na$^+$ can also be explained by the nesting interaction, because the 14-membered **1b**, which is smaller than 15-crown-5 (0.86–0.92 Å),[18] is insufficient to accommodate the larger sized Na$^+$ (1.02 Å).

With respect to 17-crown-6 **1c** and 20-crown-7 **1d**, the intensity profiles are closely similar to that of 18-membered **2**, in spite of the ring-contraction by one methylene unit or the ring-enlargement by one oxymethylene unit as compared with **2**. This is probably because these crowns have increased flexibility in the macrocyclic rings and a suitable number of donor oxygen atoms for the preferential uptake of K$^+$. More careful perusal of the binding profiles shows that the 17-membered **1c** provides a higher I_m value for smaller Na$^+$ and a lower value for larger Rb$^+$ and Cs$^+$ than does the 20-membered **1d**. This phenomenon is also consistent with the generally accepted size-fitting concept that crowns with a given cavity size are more selective for cations with radii better matching that of the cavity.[22]

Next, we examined the relative complexation of a mixture of **1a**–**d** and **2** towards the selected K$^+$ (Table 2). The binding affinities decreased significantly in the order **2** > **1d** > **1c** > **1b** > **1a**. This is also the case for the tetrahedral NH_4^+. The poor affinity of **1d** and **1c** may be mainly attributed to the presence of the bulky *gem*-diphenyl group which will hinder the approach of



$[\mathbf{1c}\cdot\mathbf{2}\cdot\mathrm{NH_4}]^+$

Fig. 3 Hypothetical structure of $[\mathbf{1c}\cdot\mathbf{2}\cdot\mathrm{NH_4}]^+$ *via* hydrogen bonding

ions and loosen the electrostatic attraction by the increased hydrophobicity. Indeed, a dramatic substituent effect like this was experienced in the acid-catalysed hydrolysis of variously-substituted crown ether acetals. In this case, the present crown ether acetals suffered a less effective rate retardation by added alkali metal ions as compared with the monophenyl-substituted homologues.[9b] Furthermore, the conformational deformation induced by the ring contraction would considerably contribute to the reduction in cation-binding ability, as observed for the case of unsubstituted 14- and 17-membered homologues.[10]

The higher stoichiometric complexation

As seen in Table 1, 1:2 ion–crown complexes are observed mainly for the smallest 11-crown-4 **1a** which even exhibited the formation of 1:3 complexes (6–8% relative intensities) in addition to 1:2 complexes (8–37%) for all alkali metal ions. The values of I_m for the 1:2 complexes tended to diminish with increasing ring size of **1** when compared with the same cation. This phenomenon reflects the increased looseness of the dimer spherical cavity and thus its ability to wrap a given ion in going from **1a** to **1d**.[23] In line with this, it was also found that the most intense dimer $[(\mathbf{1})_2\cdot\mathrm{M}]^+$ peak for each crown moves to the next larger cation than that responsible for the 1:1 base peak. Accordingly, 1:2 complex peaks were found with all of the alkali metal ions for **1a**, $\mathrm{Na^+}$–$\mathrm{Cs^+}$ for **1b**, $\mathrm{K^+}$–$\mathrm{Cs^+}$ for **1c**, $\mathrm{Rb^+}$–$\mathrm{Cs^+}$ for **1d** and only $\mathrm{Cs^+}$ for **2** under the present experimental conditions.

Although the detailed gas phase structure of the dimer $[(\mathbf{1})_2\cdot\mathrm{M}]^+$ and the trimer $[(\mathbf{1a})_3\cdot\mathrm{M}]^+$ complexes has not yet been clarified, the geometry of such molecular clusters would satisfy the steric and electrostatic requirements for the most favourable complexation. The production of such a metal-bound crown trimer has been observed in very low abundance (I_m 0.2%) by tandem quadrupole mass spectrometry for 12-crown-4 and $\mathrm{Cs^+}$.[24] Since diphenyl-substituted crowns are more hydrophobic than other common crowns, the reduced solvation energies of the complexes are expected to be responsible for the noticeable appearance of these labile 1:2 and 1:3 complexes. The solvation energy is a key parameter in the ion yield in ESI-MS and the mass spectral response of the ion is also linked to this energy.[16a]

The heterogeneous 1:2 ion–crown complexation

Besides the homogeneous dimers, where both crowns are the same, heterogeneous ones consisting of two different crowns were also detected between the crowns **1b**–**d** and **2** (Table 2). It is noted that the I_m values for the dimeric complexes are larger for $\mathrm{NH_4^+}$ than for $\mathrm{K^+}$, suggesting the more stable complexing of $\mathrm{NH_4^+}$ by multi-hydrogen bonding, as formulated in Fig. 3. The absence of homogeneous dimers for smaller **1a** and **1b**, and also the lack of heterogeneous dimers $[\mathbf{1a}\cdot\mathbf{2}\cdot\mathrm{M}]^+$ under these experimental conditions are attributable to their negligible population, judging from the low binding ability of these crowns toward $\mathrm{K^+}$ and $\mathrm{NH_4^+}$ (I_m = 4–7% for the 1:1 complexes).

Table 3 Alkali metal ion selectivity for crown ether acetals **1a**–**d** and crown ethers

Crown ether acetal[a]		Crown ether[b]	
11-crown-4	$\mathrm{Li^+}$	12-crown-4	$\mathrm{Li^+} \approx \mathrm{Na^+}$
14-crown-5	$\mathrm{Na^+}$	15-crown-5	$\mathrm{K^+}$
17-crown-6	$\mathrm{K^+}$	18-crown-6	$\mathrm{K^+}$
20-crown-7	$\mathrm{K^+}$	21-crown-7	$\mathrm{Cs^+}$

[a] Estimated from the present ESI-MS study. [b] Taken from ref. 1(c).

A comparison with other crown ethers

Little has been reported on the selective cation binding ability of ring-contracted crown ether acetals. Kawakami *et al.* synthesized a series of unsubstituted 11- to 20-membered ring acetals and examined the extractability of alkali metal picrates in dichloromethane–water binary phase.[10a] The extraction efficiency for potassium picrate decreased with decreasing ring size, though the binding ability was considerably lower as compared with the corresponding common crowns bearing the same number of oxygen atoms. With the same compounds, Inoue *et al.* have also shown that the 17-membered ring is the selective extractor for $\mathrm{K^+}$ over any other alkali metal ions, but the 14-crown-5 possesses no clear-cut selectivity.[10b] In contrast, an ESI-MS analysis for our diphenyl-substituted homologues exhibited the more discriminating cation-binding phenomenon described above (Table 1 and Fig. 2). Thus, it is implied that ESI-MS is more sensitive and can be successfully employed to assess the cation binding properties of macrocyclic ligands such as crown ethers.

In Table 3 are listed cations selectively bound by the present 11- to 20-membered crown ether acetals **1a**–**d**, together with the cations that reportedly bind with common 12-crown-4 to 21-crown-7.[1c,e] Our crown ether acetals have a tendency to complex with rather smaller cations than do the corresponding crown ethers. Apparently, these results can be envisaged from the prevalent theory that the size and the conformation of macrocyclic rings, as well as the steric effects of ring-substituents, are important for the stabilities of complexes.[1b,c]

Conclusions

In the present ESI-MS study, we have found that diphenyl-substituted 11- to 20-membered crown ether acetals **1a**–**d** exhibit cation selectivity for 1:1 and 1:2 (and 1:3 for **1a**) bound complexes with alkali metal ions and the ammonium ion. Due to the ring-contraction by one methylene unit and the presence of a *gem*-diphenyl group, these crown ethers showed a reduction in the binding affinity as well as a tendency to preferentially bind the smaller ions as compared to the corresponding simple crowns possessing the same number of oxygen atoms. The enhanced hydrophobicity caused by the diphenyl group may also be suited to the ESI-MS detection of labile multi-bound complexes, because the decrease in the solvation energy of ion-complexes is favourable towards the ES ionization/desolvation process.

Experimental

The crowns **1a**–**d** were prepared according to the method previously described.[8] The crown ether **2** (Nakarai Chemical Co. Ltd.) was of commercial origin and used without further purification. All alkali metal and ammonium perchlorates were extra pure and were used without further purification. Spectrally pure acetonitrile (Dojin Co. Ltd.) was used in sample solutions by mixing with deionized water. The ESI mass spectra were obtained on a sector-type mass spectrometer (JEOL-D300) equipped with a laboratory-made electrospray interface.[25] A sample solution was sprayed at a flow rate of 2 µl $\mathrm{min^{-1}}$ at the tip of a needle biased by a voltage 3.5 kV higher than that of a counter electrode. A 70 °C N_2 gas stream was used for the desolvation of charged droplets. The sample solution was 20% H_2O in CH_3CN (v/v). For the present study, solutions of crowns **1** and **2** containing metal and NH_4^+ ions were prepared (ambient temperature, *ca.* 25 °C) by mixing a given volume of the acetonitrile solutions of crowns **1** and **2** and aqueous solutions of metal and ammonium perchlorates to afford the desired final concentration and solvent composition.

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