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Study of complexation between cyclofructans and alkali metal cations by electrospray ionization mass spectrometry and density functional theory calculations

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Cyclofructans, cyclic fructofuranose oligomers, form complexes with a variety of metal cations in solution. ESI-MS was used to investigate both solution and gas phase selectivities of cyclofructans for alkali metal cations. In the gas phase, cyclofructans bind to alkali metal cations in the order of $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. The gas phase selectivity, obtained by competitive dissociation of ternary complexes between one cyclofructan and two different metal cations, was confirmed with density functional theory calculations. The calculated binding strength is from −99 to −383 kJ mol^{-1} for cyclofructan 6 and the alkali metal cations. The cyclofructan's 3-position oxygens are the most likely interaction points for the alkali metals. For the solution phase study, sodium and potassium complexes of cyclofructans were the most abundant species in the ESI-MS spectra. Compared with previous solution phase studies of cyclofructans, ESI-MS produced higher abundance of complexes with Li^+ and lower abundance of complexes with larger metal cations. The relative intensities of different cyclofructan–metal cation complexes observed in the ESI-MS spectra was a reflection of both the solution phase and gas phase stability of different complex ions.

1. Introduction

Cyclofructans are β-(2 → 1)-linked cyclic fructofuranose oligomers that have unique crown ether cores (see Fig. 1) [1,2]. Native and derivatized cyclofructans have been found to complex with a variety of metal cations [3–9], and have been used as ion trapping agents in various applications [10,11]. The X-ray structure of permethylated cyclofructan 6 (CF6) and barium isothiocyante [7], along with NMR studies [5,7], revealed that the crown ether moiety in permethylated CF6 did not participate directly in metal complexation as did other synthetic crown ether analogues. However, the selectivities of permethylated cyclofructans for alkali metals are found to be identical to their counterpart crown ethers: i.e., permethylated CF6 binds to alkali metals in the decreasing order of $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$ [5,7]. Surprisingly, there are only limited host–guest studies for native cyclofructans [4,8,9].

ESI-MS has been widely used for host–guest studies of many crown ethers and their related analogues in solution and in the gas phase [12–16]. The Brodbelt group has extensively studied the selectivity of crown ether type hosts for different metal cations with known stability constants in solution using ESI-MS [13]. Generally, the selectivity of a host for different guests, predicted from ion intensity in the mass spectrum, correlated well with that in solution. On the other hand, the Liu group reported that corrections for ionization efficiency of different complex ions were necessary when studying the alkali metal complexes of a series of lariat ethers [17,18]. ESI-MS also has been used to study complexation between oligosaccharides and alkali metal cations. Reale et al. studied the metal complexation of β-cyclodextrin (β-CD), an isomer of cyclofructan 7 (CF7) [19]. With competitive binding ESI-MS experiments, they found that sodium, among the alkali metals, had the highest affinity for β-CD in solution [19]. Both 1:1 and 1:2 β-CD-metal cation complexes were observed in the ESI-MS spectra. Shizuma et al. studied the complexation between permethylated cyclofructans with alkali metal cations using ESI-MS along with other approaches [5]. According to their results, relative peak intensities in ESI mass spectra were not always a true reflection of the distribution of species in the solution. Surprisingly, there is no reported ESI-MS study of complexation by native cyclofructans.

In this paper, we study the complexation of native cyclofructans with alkali metal cations using ESI-MS, and compare the solution phase selectivity deduced from ESI-MS spectra with previous results from a thin layer chromatography study [8]. In addition, the gas phase selectivity of cyclofructans for alkali metal cations is studied using both the competitive dissociation method and density functional theory calculations.

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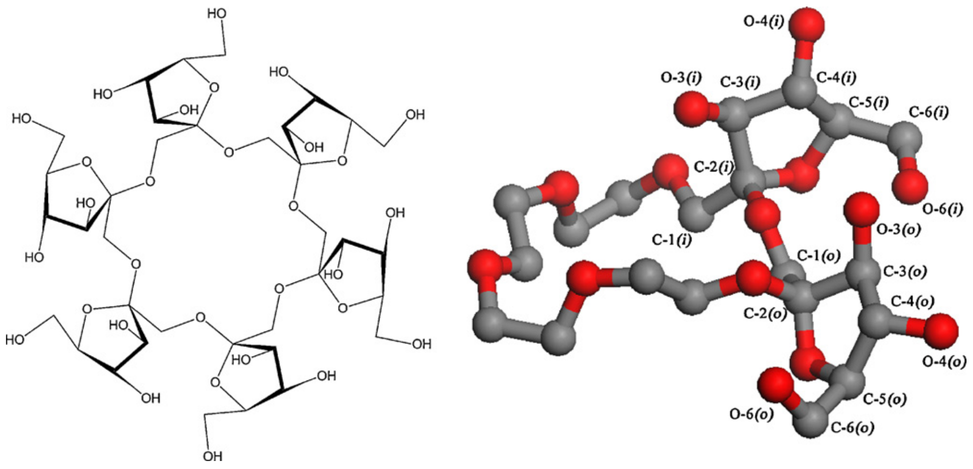

Fig. 1. (A) Molecular structure of CF6. (B) 3D structure of CF6 with only 18-crown-6 skeleton and two neighboring fructofuranose units: one is "inward-inclinded" and the other is "outward-inclinded". All hydrogen atoms have been removed for visual clarity. Color coding: carbon, gray; oxygen, red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

2. Materials and methods

2.1. Material

All chloride salts of alkali metal cations were purchased from Sigma–Aldrich (Milwaukee, WI, USA). LC–MS grade methanol and water were purchased from VWR (Bridgeport, NJ, USA). Cyclofructans were generous gifts from Mitsubishi Kagaku Co. (Tokyo, Japan): CF6 was used as-received whereas CF7 was purified before use according to a previously published method [20].

2.2. Methods

All mass spectrometry experiments were performed with a Thermo Finnigan LXQ mass spectrometer equipped with a syringe pump, an ESI source and a linear ion trap mass analyzer. The syringe pump flow rate was set at 5.0 μl/min. Compound mixtures were sprayed in 50% aqueous methanol solution at a source voltage of 3.5 kV. The vacuum chamber was operated at a pressure of 1 mTorr with helium. Each spectrum was sampled for 1 min (~300 scans). Triplicate spectra were averaged for each experimental data point. The collisional induced dissociation study was carried out with 30 ms activation time, a 0.25 *Q* value, and the normalized collisional energy between 5% and 30% for different species. Density functional theory calculations were computed using Gaussian 03 program [21].

3. Results and discussion

Fig. 1(A) shows the molecular structure of CF6. The 18-crown-6 ring serves as the skeleton core of CF6, with six fructofuranose units attached on its rim. The fructofuranose units are alternatively pointing towards and away from the molecular center, which are described as "inward-inclined" and "outward-inclined" by Immel et al., respectively [22]. These two types of fructofuranose units are depicted in Fig. 1(B). The numberings of C and O atoms on the fructofuranose units are also labeled in Fig. 1(B).

The complexes between cyclofructans and metal cations are sufficiently stable to be observed directly by ESI-MS. Fig. 2 shows the mass spectrum of 1×10^{-4} M CF6 and equimolar NaCl in 50% aqueous methanol solution. The *m*/*z* 995 and *m*/*z* 509 peaks correspond to the 1:1 and 1:2 complexes between CF6 and Na^+. Minor peaks at

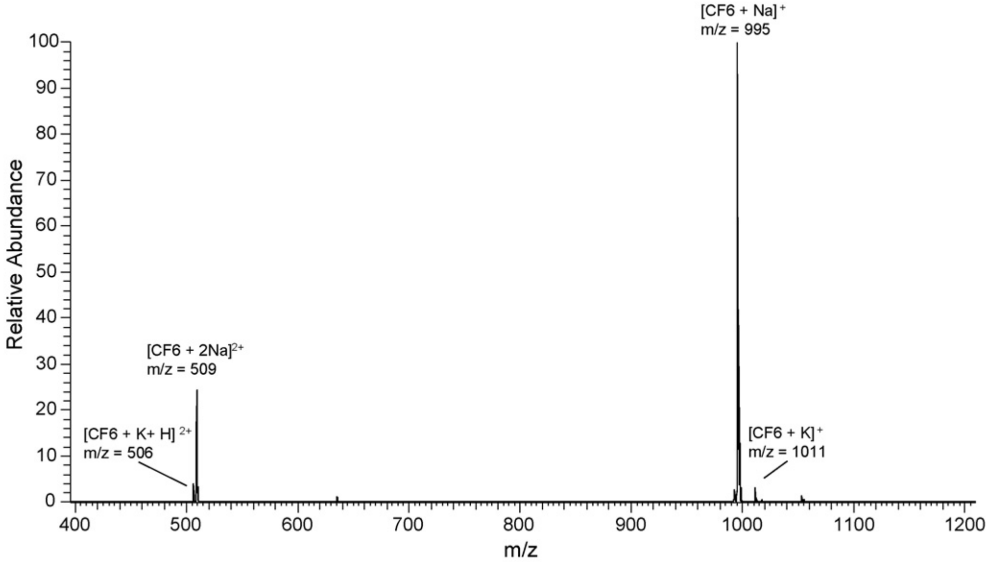

Fig. 2. Sample mass spectrum obtained by electrospraying 50% aqueous methanol solution of 1:1 (1.0×10^{-4} M each) CF6 and NaCl.

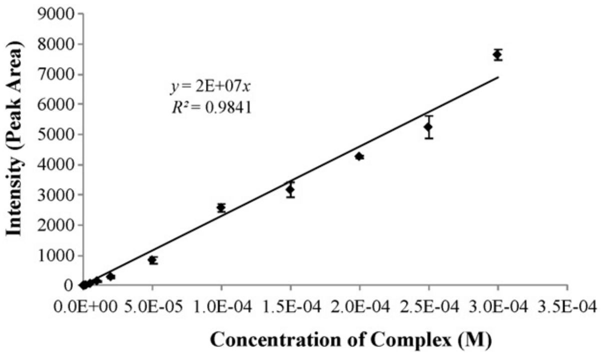

Fig. 3. The linear fit of ESI-MS peak intensity vs. concentration of 1:1 CF6 and NaCl in 50% aqueous methanol solution. Error bars represent one standard deviation from the mean.

m/z 1011 $(\text{CF6}+\text{K})^+$ and m/z 506 $(\text{CF6}+\text{K}+\text{H})^{2+}$ were also observable due to trace amounts of potassium present in the MS system. In order to establish the solution concentration for our study, the dependence of the signal intensity (characterized by the peak area of all isotope peaks) on the solution concentration was examined over the range from 1×10^{-8} to 3×10^{-4} M. As shown in Fig. 3, a linear response was observed for the studied range of concentrations ($R^2 = 0.9841$ for the fitted linear line passing the origin point). The linear range is comparable to the reported range for crown ethers [23]. As a result, a working concentration of 1×10^{-4} M was chosen for our study.

3.1. Complexation ratio

Crown ethers form stable complexes with metal cations. Both 2:1 and 1:1 crown ether–metal complexes have been observed by mass spectrometry [24]. However, crown ethers do not typically complex with multiple metal cations, with an exception of a few bis-crowned hosts [25]. In our study, a substantial abundance of 1:2 cyclofructan–metal cation complexes was observed for small alkali metals even at a solution host-to-guest concentration ratio of 1:1 (Fig. 2). Cyclofructans have a crown ether macrocycle as the core/skeleton. The formation of 1:2 cyclofructan–metal cation complexes implies that at least one other structural feature of cyclofructan is responsible for its complexation with metal cations, if the crown ether moiety is even responsible at all.

Table 1 lists the relative intensities observed for 1:1 and 1:2 cyclofructan–metal cation complexes. The 1:2 complexes were observed for Li^+ and Na^+ with CF6, and for Li^+, Na^+, and K^+ with CF7. Clearly, the extent of 1:2 complex formation depends on the sizes of the hosts and guests. The columbic repulsion between two cations in the ternary complex is reduced for the larger size host. In addition, the greater polarizability for the larger size host also enhances the stability of its ternary complexes. As a result, only CF7 is able to complex with two larger metal cations (i.e., K^+). For the same alkali metal cation, the relative intensities of 1:2 complexes, compared to 1:1 complexes, is always higher for CF7 versus CF6.

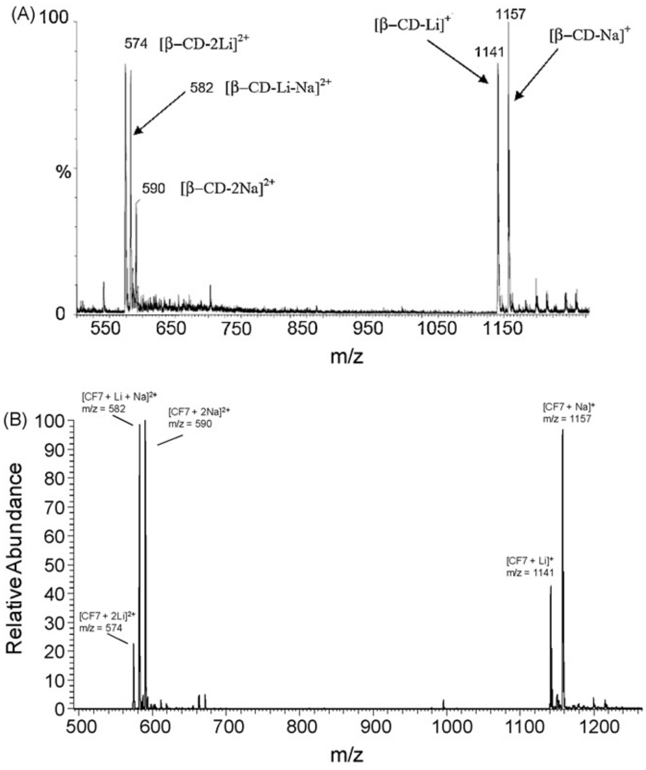

Fig. 4. Comparison of ESI-MS spectra between the β-CD and CF7 when complexing with Li^+ and Na^+. (A) 1:2 complexes is more favorable for Li^+ than for Na^+; (B) CF7 gives the opposite trend, i.e., 1:2 complexes is more favorable for Na^+ than for Li^+. (A) is reprinted from Ref. [19] with permission.

For both CF6 and CF7 hosts, Na^+ has the highest tendency among the alkali metals to form 1:2 rather than 1:1 host–guest complexes. β-cyclodextrins, which are isomers of CF7, also have the capability to complex with 2 Li^+ or 2 Na^+ [19]. Unlike CF7, $(\beta\text{-CD}+2\text{Li})^{2+}$ has a higher relative intensity (to its 1:1 complexes) than that of $(\beta\text{-CD}+2\text{Na})^{2+}$ (Fig. 4) and β-CD does not form 1:2 complexes with K^+ [19].

3.2. Solution phase selectivity

Fig. 5 shows the mass spectrum of an equimolar solution of cyclofructan and every alkali metal chloride salts in 50% aqueous methanol solvent. The relative intensities of these cyclofructan–alkali metal cation peaks (based on the peak area of all isotopic peaks) are listed in Table 2.

Uchiyama et al. studied the relative complexation strength between alkali metal cations and cyclofructans by a thin layer

Table 1
The ratios between 1:2 and 1:1 cyclofructan–metal cation complexes electrosprayed form 1:1 solutions of cyclofructan and metal chloride salts. The peak intensities are scaled relative to the 1:1 cyclofructan–metal complexes within each set. “NA” represents less than 1% of 1:2 complexes observed. Standard deviation for three measurements are given.

	CF6	CF7
Li	(7 ± 1):100	(46 ± 6):100
Na	(18 ± 1):100	(58 ± 5):100
K	NA	(8 ± 1):100
Rb	NA	NA
Cs	NA	NA

Table 2
Relative abundance of cyclofructan–alkali metal cation complexes obtained from ESI-MS experiment for the equimolar (10^{-4} M) solution of cyclofructan, alkali metal and ammonium chloride salts (refer to Fig. 5 for mass spectra). Standard deviation for three measurements are given.

	CF6	CF7
Li	41 ± 1	38 ± 1
Na	100	100
K	88 ± 1	61 ± 1
Rb	44 ± 1	24 ± 1
Cs	8 ± 1	4 ± 1
NH_4	2 ± 1	1 ± 1

chromatographic (TLC) method [8]. There seemed to be a size dependence aspect to the complexation strength: CF6 was found to bind the strongest to Rb^+, while the CF7 binds the strongest to Cs^+, among all of the alkali metal cations. Interestingly, Reijenga et al. reported the opposite relative binding strength for CF6–Rb^+ and CF6–K^+ complexes, based on their apparent mobility in a capillary electrophoresis study [4]. These are the only two systematic complexation studies between native cyclofructans and alkali metal cations which can be found in literature. In our study, by directly comparing the complex ion intensities in the ESI mass spectra, the apparent cationic selectivity for CF6 was $Na^+ > K^+ > Rb^+ > Li^+ > Cs^+$, and the selectivity for CF7 was $Na^+ > K^+ > Li^+ > Rb^+ > Cs^+$ (as shown in Table 2). The Na^+ and K^+ complexes of cyclofructans were the two most abundant species detected for both CF6 and CF7 hosts. The Li^+ was found to have negligible binding towards cyclofructans according to the TLC study by Uchiyama et al. [8]. However, a substantial abundance of cyclofructan–Li^+ complexes (~40% of the most abundant species) were detected in our ESI-MS study for both CF6 and CF7. On the other hand, the Rb^+ and Cs^+ complexes were among the least abundant species in the ESI-MS spectra, whereas Rb^+ and Cs^+ were reported to bind strongly to cyclofructans in the previous TLC study.

Shizuma et al. studied the alkali metal cation preference of permethylated cyclofructans using similar ESI-MS methods [5]. Permethylated CF6 was found to bind to alkali metal cations in the decreasing order of $K^+ > Rb^+ > Cs^+ > Na^+$ (Li^+ was not studied), which correlated well with that observed in the solution phase via a NMR study. On the other hand, there was an underestimation of the CF7-Cs^+ complex abundance by the ESI-MS technique, compared to the NMR study. The cesium cation was found to form the second strongest complex (right after Rb^+) with permethlyated CF7, yet the $(CF7 + Cs)^+$ ion peak was observed as the least abundant signal in the mass spectrum.

The ability of the ESI mass spectra to accurately portray the equilibrium of ionized species in solution is still an issue of heated debate [13,26]. Different species usually have different ionization efficiencies. A common way to correct the ionization efficiency difference is to incorporate a response factor, which is deducted from a known solution-concentration and the mass spectral ion intensity of certain species [13]. Unfortunately, we cannot correct for the ionization efficiencies of cyclofructan–alkali metal complexres due to the current lack of available complexation constants for these systems. In addition to ionization efficiency differences among complex ions, the relative stabilities of the ions in the mass

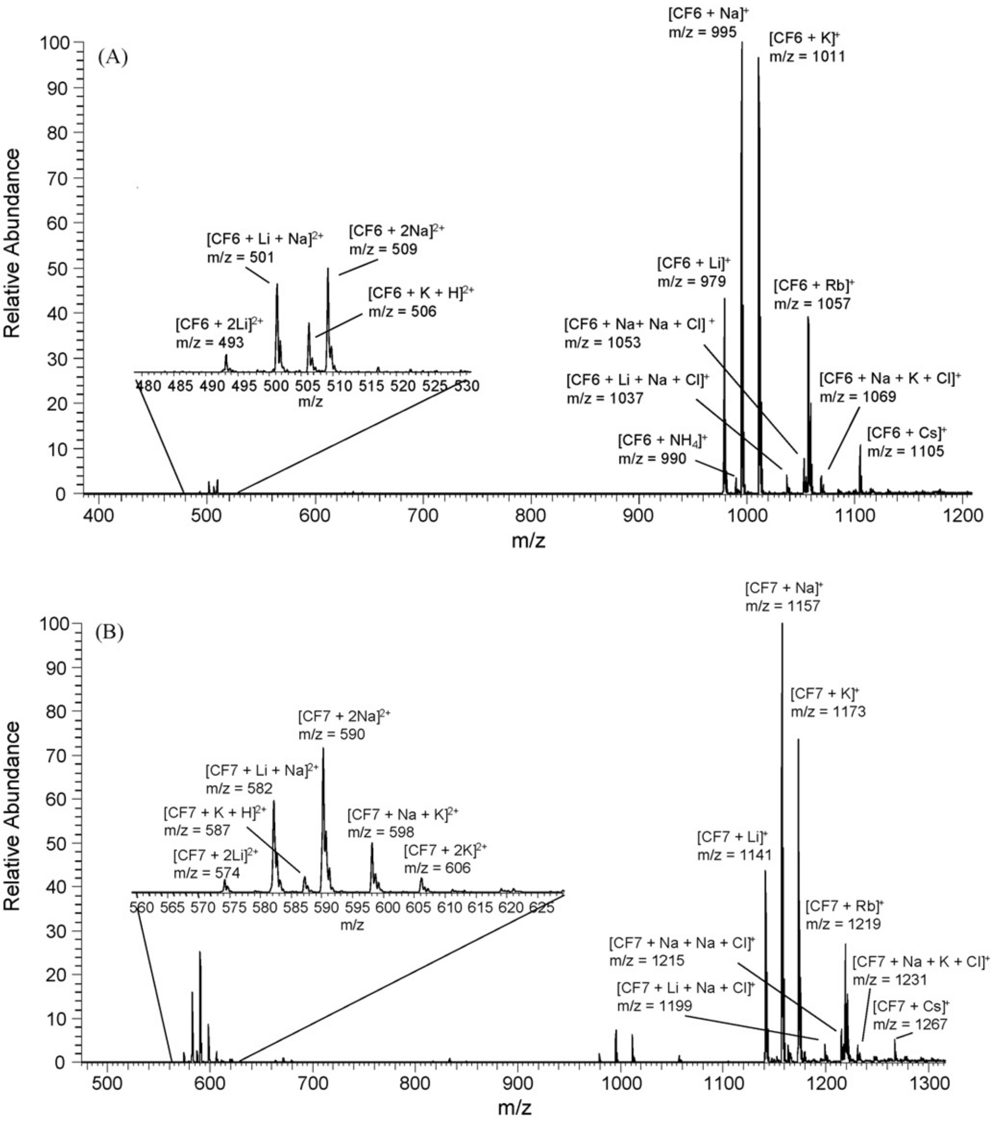

Fig. 5. Competitive binding of (A) CF6 and (B) CF7 with all alkali metal cation and ammonium chlorides.

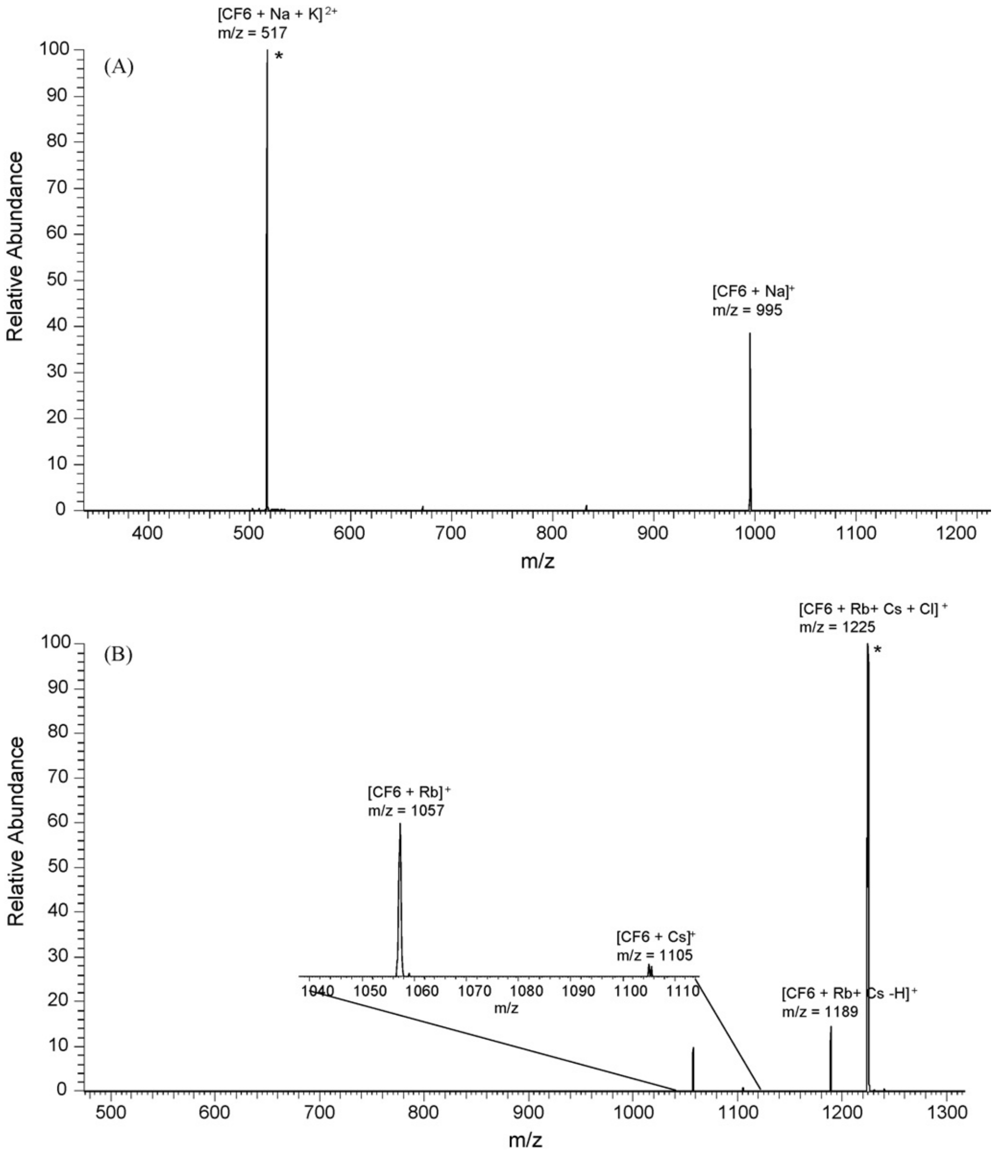

Fig. 6. Collision induced dissociation mass spectra of complexes formed by ESI-MS: (A) $(CF6 + Na + K)^{2+}$ and (B) $(CF6 + Rb + Cs + Cl)^+$.

spectrometer may also dictate the relative peak intensities. The gas phase stability of cyclofructan–alkali metal complexes was thus studied in an attempt to help explain the differences observed between our ESI-MS studies and the previous TLC study.

3.3. *Gas phase selectivity*

The gas phase selectivities of cyclofructans for the alkali metal cations were studied by competitive dissociation of ternary complexes, in a manner similar to the kinetic method [16,27]. As shown in Fig. 6(A), the parent ion $(CF6 + Na + K)^{2+}$, subjected to collision induced dissociation, produced almost exclusively a $(CF6 + Na)^+$ fragment by loss of a potassium cation. Consequently, the Na^+ was determined to have a higher affinity than K^+ for cyclofructan in the gas phase. Because both dissociation channels ($(CF6 + Na)^+$ and $(CF6 + K)^+$) were not observed, calculations of product ratios, typically recorded using the kinetic method, could not be evaluated. The data did, however, show conclusive binding preferences. Large alkali metal cations, such as rubidium and cesium, form negligible doubly charged complexes with cyclofructans. Instead, the complex of cyclofructan with Rb^+, Cs^+ and one Cl^- was isolated for the CID study (as shown in Fig. 6(B)). Three fragment ions were observed: $(CF6 + Rb + Cs - H)^+$, $(CF6 + Cs)^+$, and $(CF6 + Rb)^+$, corresponding to the parent ion losing one HCl, one RbCl, and one CsCl, respectively. The significantly higher abundance of the $(CF6 + Rb)^+$ signal compared to the $(CF6 + Cs)^+$ signal was interpreted as the result of the preferential binding of CF6 towards Rb^+ in the gas phase. By mixing cyclofructan with all possible combinations of two alkali metal complexes, the selectivity of both CF6 and CF7 for alkali metal ions is determined to be $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. Similar studies have been conducted for synthetic crown ethers: 18-crown-6 and 21-crown-7 bind the most strongly to Na^+ and K^+ cations, respectively [16]. Only small crown ethers (e.g., 15-crown-5) have a similar gas phase preference for alkali metal cations to the cyclofructans [16].

The same gas phase selectivity of $Na^+ > K^+ > Rb^+ > Cs^+$ (Li^+ not studied) was reported for 18-crown-6 using threshold CID methods by Armentrout et al. [28,29]. The size and charge density of guest cations were proposed to dictate the complexation strength. “Smaller alkali cations have greater charge density and can get closer to the crown to create a stronger electrostatic field to bind the electron-donating ligands [28].” The different alkali metal selectivi-

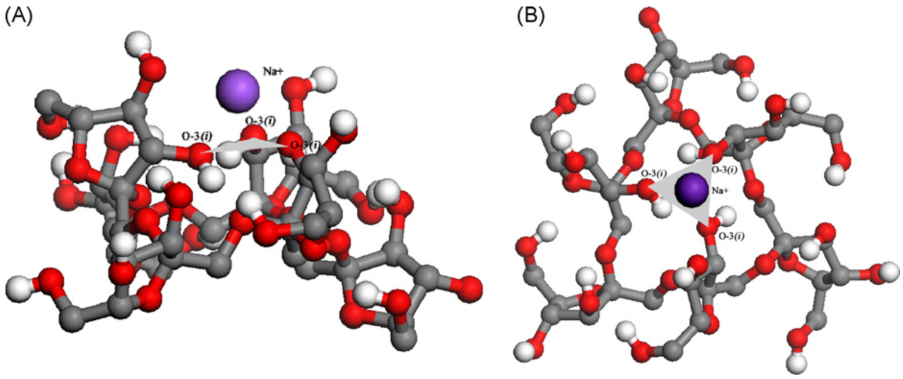

Fig. 7. Ball and stick model of optimized CF6–Na$^+$ complex: (A) side view; (B) top view. Color coding: sodium, blue; carbon, gray; oxygen, red; hydrogen, white. The plane defined by three O-3(i) atoms is shaded light gray. The size of sodium is enlarged in order to differentiate from C, H, and O atoms. Hydrogen atoms attached to the carbons have been removed for visual clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

ties of 18-crown-6 obtained using kinetic method can be attributed to the intrinsic limitation of kinetic methods, i.e., "separation of entropic from enthalpic effects on ion abundance is not rigorously possible" when using kinetic methods [27].[1] Crown ethers undergo large conformational changes on complexation with metal cations, and the kinetic method does not account for entropy effects of such conformational change. In our case, however, less conformational change is expected for the more rigid cyclofructans upon complexation. As a result, it is reasonable to suggest that our competitive dissociation method suffers less from entropic effects arising from complexation-induced folding.

The gas phase complexation between CF6 and alkali metals also was studied by B3LYP density functional theory calculations using the cc-pVDZ basis for C, H, and O [30–32], and the SDD (Stuttgart/Dresden) ECP basis set [33] for metal cations. The input coordinates of CF6 were obtained from the X-ray structure [2]. The side and top view of the central 18-crown-6 plane in CF6 are illustrated in Fig. 7. Metal cations, in principle, can approach CF6 from either side of the CF6 central plane. However, previous computational results showed that the two sides are dramatically different in their electrostatic potential profiles. One side is aligned with 1- and 6-methylene moieties of fructofuranose units, and is "pronouncedly electropositive", whereas the other side is occupied with hydroxyl groups in the 3- and 4-positions of the fructofuranose units (top side in Fig. 7(A)), and is "distinctly electronegative" [22]. Previous NMR studies of metal complexation of native and derivatized cyclofructans also revealed that the 3-OH and 4-OH groups are responsible for cyclofructan–metal cation interactions [9]. In addition, the X-ray structure analysis of permethylated CF6 complexed with Ba^{2+} showed that the cation (Ba^{2+}) is positioned on the molecular rotational axis on the electronegative side (top side in Fig. 7(A)) of the molecule [7]. Consequently, we placed metal cations on the electronegative side of CF6, right above the plane defined by three O-3(i) atoms (which will be referred to as the O-3(i) plane in following discussions), as shown in Fig. 7. There was no obvious structure relaxation of CF6 after energy minimization of the complex. The calculated binding energies are between −99 and −383 kJ mol^{-1} (Table 3, column 4) for the studied complexes. Our results compare well with experimental data obtained by threshold CID studies for the binding energies between crown ethers and alkali metal cations (see Table 3) [34]. According to our calculations, CF6 binds to alkali metal cations in the decreasing order of Li$^+$ > Na$^+$ > K$^+$ > Rb$^+$ > Cs$^+$, which is in good agreement with the results obtained by the MS study.

By comparing the optimized complex structures, it can be inferred that the gas phase selectivity of CF6 is dictated by the size of the metal cations. Table 3 lists the elevation of metal cations above the O-3(i) plane (shaded plane in Fig. 7): the distance increases with increasing size of the metal cation. The small Li$^+$ ion is able to nestle inside the plane, whereas larger cations can only perch above the plane. Note that the size of a cation is predominately determined by its (electrostatic) charge density. As can be seen from Table 4, only the distance between Li$^+$ and O-3(i) is smaller than the sum of the ionic radii and therefore may have some covalent character. The relative position of the metal cations to the O-3(i) plane bears important consequences. First, the distances between metal cations and the three O-3(i) atoms increase as the metal cations perch higher above the plane. Secondly, according to the "best fit" model developed for crown ether and metal complexes [35], the nestling provides stronger binding than perching. Finally, the crown ether ring in CF6 is located on the side opposite to the metal cations. The Li$^+$, nestling inside the O-3(i) plane, is closer to the crown ether ring in CF6 than a larger metal cation perching above the plane. As a result, the electrostatic interaction between oxygen atoms on the crown ether ring in CF6 is stronger with Li$^+$

Table 3
Binding energy (kJ mol^{-1}) between alkali metal cations and crown ethers and CF6. Values for crown ethers are obtained from threshold CID experiments [31], and values for CF6 are obtained from DFT calculations.

	18-crown-6	15-crown-5	12-crown-4	CF6
Li$^+$	NA	NA	−372	−383
Na$^+$	−296	−294	−252	−234
K$^+$	−235	−205	−189	−152
Rb$^+$	−191	−114	−93	−121
Cs$^+$	−168	−100	−85	−99

Table 4
Optimized structural parameters for complexes between CF6 and alkali metal cations.

	d, plane[a]	M-O1[b]	M-O2[b]	M-O3[b]	$r_{M^+} + r_{O^{2-}}$ [c]
Li$^+$	0.56	1.92	1.87	1.88	2.16
Na$^+$	1.76	2.36	2.28	2.44	2.42
K$^+$	2.26	2.74	2.71	2.86	2.78
Rb$^+$	2.51	3.03	2.95	2.93	2.92
Cs$^+$	2.81	3.53	3.12	3.13	3.07

[a] Between neighboring distance (in the unit of Å) between metal cations to the plane consisting of three 3-position oxygen atoms.

[b] Bond length (in the unit of Å) between metal cations (M) and three 3-position oxygen atoms (O1, O2, and O3).

[c] Sum ionic radius (in the unit of Å) of metal cation and oxygen anion (numbers obtained from Ref. [33]).

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[1] Reviewer's comments.

than with larger metal cations. All these three factors contribute to a gas phase selectivity for CF6 of $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$.

4. Conclusions

Complexes of one cyclofructan and two guest cations were observed for small alkali metals using ESI-MS. The larger size CF7 is more likely to form 1:2 complexes with alkali metal cations than CF6. By direct inference from the ESI-MS spectra, both CF6 and CF7 favor the mid-size alkali metal cations (e.g., Na^+ and K^+) in solution. Our ESI-MS results differ from the previous TLC results by overestimating the Li^+ complexes and underestimating the Rb^+ and Cs^+ complexes, which could be explained by relative gas phase stabilities of complex ions.

The gas phase selectivity of both CF6 and CF7 is determined to be $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ by the competitive dissociation method. The density functional theory calculations of CF6–alkali metal cation complexes reveal that the gas phase selectivity of CF6 is determined by the size of metal cations: smaller size metal cations approach closer to the interaction plane, and are able to form stronger electrostatic-dipole interactions with CF6.

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