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Theoretical study of cation/ether complexes: 15-crown-5 and its alkali metal complexes

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Abstract

A combination of classical force field molecular dynamics and electronic structure calculations were used to identify the low-lying, gas phase conformations of isolated 15-crown-5 and complexes it forms with a single alkali cation (Li^+, Na^+, K^+, Rb^+, and Cs^+). The computed binding enthalpies are compared with recent gas phase, collision-induced dissociation measurements. While agreement is reasonably good for sodium and potassium, it worsens for the larger cations, where theory and experiment differ by as much as 20 kcal/mol. Tests of the sensitivity of the predicted binding enthalpies to the size of the basis sets were conducted with large, diffuse-function-augmented, correlation consistent basis sets. Despite the increase in size and flexibility of the basis sets, they resulted in relatively little change in the computed binding energies. A possible explanation of these differences, first proposed for M^+/12c4, is discussed. It assumes that the experiment measures dissociation from higher-lying metal/ether complexes, rather than the global minimum which serves as the reference point for the theoretical values. However, a limited search for a much higher energy Rb^+/15c5 structure proved unsuccessful. A cluster-based metal exchange reaction, which crudely models the binding preference in aqueous solution, reproduces the low selectivity of 15-crown-5 relative to that of 18-crown-6 in solution. (Int J Mass Spectrom 201 (2000) 41–58) © 2000 Elsevier Science B.V.

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1. Introduction

Crown ethers are an important class of organic compounds that are widely used in chemical separation processes. They are known to bind specific metal cations in the presence of complex mixtures of chemically similar ions. As part of an on-going effort to develop and calibrate theoretical methods capable of accurately modeling crowns and metal/crown complexes, we have previously studied 12-crown-4 (12c4) [1,2], 18-crown-6 (18c6) [3–5], and s18-crown-6 (s18c6) [6]. These theoretical studies benefited from the availability of gas phase experimental data on 12-crown-4 [7] and smaller acyclic ethers that represent crown subunits [8–12]. Agreement between theory and collision-induced dissociation (CID) experimental cation binding enthalpies (ΔH: M^+/ether $\rightarrow$ M^+ + ether, M = Li–Cs) has been generally good, although differences of as much as 14 kcal/mol were noted for 12c4 complexes with some of the heavier cations [2].

The small size and rigid nature of 12c4 made the identification of its lowest energy, gas-phase confor-

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mation a relatively easy task. Nor did the M^+/12c4 complexes pose more of a problem, since even the smallest of the alkali cations was too large to fit completely within the 12c4 macrocycle. All of the M^+/12c4 complexes were characterized by a structure in which the ether functional units bent out of plane, so as to point the electron-donating oxygens toward the cation. 18c6 differed from 12c4 in that its 18-membered ring was large enough to possess several low energy conformations and it could completely enclose cations up to the size of K^+. However, a large body of gas phase theoretical and crystal phase experimental work had shown that isolated 18c6 preferred a C_i symmetry structure because of favorable 1,5 $H \cdots O$ cross ring interactions. The structure of K^+/18c6 was also well-established as possessing D_{3d} symmetry [13–21]. Experimentally, 18c6 is the most widely studied of the oxygen-bearing crowns and is known to select K^+ over other alkali metals in solution [22,23].

In contrast to the large body of information available on 18c6, relatively few theoretical studies have focused on the smaller 15-crown-5 (15c5). Paulsen et al. [24,25] recently reported a molecular mechanics (MM) conformational analysis of 15c5 using the MM3 force field [26]. Of the more than 3600 unique conformers identified, about 35 were found to lie within 3 kcal/mol of the global minimum on the basis of their gas phase strain energies. A much smaller number of conformers was identified in an earlier molecular dynamics (MD) study by Howard et al. [27] using the AMBER force. The two force field studies differed greatly in their ordering of common structures.

Gas phase, CID binding enthalpies were very recently reported for 15c5 by More et al. [12]. Since previous comparisons between theory and experiment had sometimes revealed larger than expected differences for complexes involving multiple ligand–metal bonds (i.e. multidentate systems), it was of interest to see how well theory and experiment agreed for crown. In the present work we report the results of a conformational analysis of uncomplexed 15c5 in the gas using a combination of classical force field MD and ab initio electronic structure calculations. Metal–ligand binding enthalpies will be computed for the alkali metal cations (Li^+–Cs^+) and comparisons will be made to the corresponding M^+/12c4 and M^+/18c6 complexes.

2. Methods

2.1. Isolated 15c5

A number of sophisticated algorithms have been proposed for identifying conformational isomers in large molecules [28–30]. Within the constraints imposed by finite computer resources, a decision must be made as to how to allocate resources between the search for new conformations versus the sophistication of the theory used to evaluate energy differences. In practice, conformational studies usually emphasize extensive sampling of as large a fraction of the accessible conformational space as possible [31–35] as opposed to using high-level methods to evaluate the energy of each structure. Relative conformational orderings are often based on empirical force field or semiempirical molecular orbital energies [36]. Occasionally a small subset of the most stable conformers are selected for low-level quantum mechanical calculations [37,38]. In the present work we focus our attention on 15c5 conformations within several kcal/mol of the lowest energy structure and ignore the higher energy isomers. Consequently, we performed a somewhat restricted conformational search, choosing instead to emphasize the use of moderately high-level ab initio calculations in defining each conformation's energy. The likelihood of overlooking an important low-lying structure was reduced for this particular crown by the availability of the exhaustive molecular mechanics search of Paulsen et al. [24] which served as an independent source of conformations.

Initial 15c5 geometries were generated with high temperature MD simulations, using the consistent valence force field (CVFF) [39]. Partial charges (H: $0.03e^-$, C: $0.15e^-$, O: $-0.42e^-$) for CVFF were obtained from the CHELPG [40] algorithm in GAUSSIAN 94 [41] using a common crystal conformation [42]. All MD simulations and subsequent MM minimizations were performed with the code ARGUS [43]. Simulations were equilibrated to 2000 K in five steps of 0.2 ps each, followed by runs of 1000 ps with a 0.5 fs timestep. Nonbonded cutoffs were set at 110.0 Å. Configurations were saved every picosecond, for a total of 1000 configurations. These 1000 conformations were then subjected to geometry optimization at 0 K using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) [44] method. The lowest energy structure resulting from this procedure was used as a starting point for additional simulations at 1000 and 500 K, whose purpose was to uncover additional low-lying conformations.

Of the 1000 15c5 conformations minimized at the MM/CVFF(2000 K) level of theory, approximately half of them were found to be unique. The energy span encompassed by the unique conformations was ~16 kcal/mol. The two lower temperature simulations generated 425 (1000 K) and 213 (500 K) unique structures. After combining the results of the three simulations and eliminating redundant structures, the 34 lowest energy forms (spanning an energy range of ~3 kcal/mol) were reoptimized using restricted Hartree–Fock (RHF) wavefunctions with the 3-21G basis set [45]. The switch from MM to low-level RHF/3-21G calculations resulted in a doubling of the spread in energies and a significant amount of reordering of the conformations. This is reflected in the maximum change in relative energy for any single structure of 4.3 kcal/mol. The mean for all 34 conformations was 1.6 kcal/mol.

The 18 lowest energy RHF/3-21G structures were then used as starting geometries for larger basis set optimizations. For this purpose we chose the 6-31+G* basis set on oxygen and the 6-31G* basis on hydrogen and carbon [46–48]. This hybrid combination of basis sets will be referred to simply as the 6-31+G* set. The same combination of basis sets was used in our previous work on 12c4 and 18c6. All RHF geometry optimizations were performed with GAUSSIAN 94, using the "tight" convergence criterion, which corresponds to a maximum force on all atoms of 1.5×10^{-5} E_h/bohr. MP2 geometry optimizations were performed with a combination of GAUSSIAN 94 and NWCHEM 3.3 [49]. Vibrational normal mode analyses were performed at the RHF/6-31+G* level to ensure that each optimized structure was a true minimum on the potential energy surface.

The importance of correlation recovery was explored in a series of second order Møller–Plesset perturbation theory (MP2) calculations with the 6-31+G* basis set and the diffuse-function-augmented, correlation consistent aug-cc-pVDZ and aug-cc-pVTZ basis sets [50,51]. Because of the expense of such calculations, only a limited number of conformations were treated at the MP2/aug-cc-pVxZ level. Throughout this work, we will abbreviate the name of the correlation consistent basis sets to aVDZ and aVTZ.

2.2. M^+/15c6 complexes

Metal basis sets for use in electronic structure calculations on the M^+/15c5 complexes were obtained from three sources. The 6-31+G* all-electron basis sets were chosen for Li and Na. $[3s,3p]$ contractions of Hay and Wadt's GAUSSIAN primitive set [52], with the accompanying effective core potentials (ECPs), were selected for K, Rb, and Cs. The ECP basis sets were augmented with an additional six-term d set taken from the work of Glendening et al. [4]. These metal basis sets were combined by the 6-31+G* basis set on 15c5. The ECPs were of the so-called "small core" variety, i.e. they excluded the $(n - 1)$ shell of valence electrons from the core, e.g. $3s^2 3p^6$ for K [52,53] and included the dominant atomic relativistic corrections. Calculations performed with the aVDZ and aVTZ basis sets on 15c5 used the following metal basis sets: cc-pVxZ (Li) [54], cc-pCVxZ (Na) [54], and pCVxZ (K) [55]. The $1s^2$ inner shell electrons of carbon, oxygen, lithium, and sodium were treated as frozen cores. All-electron, correlated calculations involving potassium included the $3s^2 3p^6$ electrons in the correlation treatment in order maintain compatibility with the ECP calculations.

M^+/15c5 structures were optimized at the RHF and MP2 levels of theory with the 6-31+G* basis set. As with the isolated crown conformers, normal mode analyses were used to ensure that the optimized structures were true minima. Binding energies are reported for the lowest energy form of the metal/ether complex relative to the lowest gas phase 15c5 conformation. 6-31+G* binding energies were corrected for the undesirable effects of basis set superposition error (BSSE) using the counterpoise (CP) method [56] with relaxed fragment geometries. Binding energies obtained from the aVxZ basis sets were not corrected for BSSE because experience with similar systems has shown that the uncorrected energies are closer to the complete basis set (CBS) limit [1]. Room temperature (298 K) enthalpy corrections to the electronic binding energies were based on standard gas phase expressions [57]. Among these are classical rotational, translational and work terms, zero-point energy differences, and vibrational contributions from harmonically approximated modes. RHF harmonic frequencies were scaled by 0.9 in order to obtain more realistic zero point vibrational energies.

3. Results and analysis

3.1. Gas phase 15c5

The 16 lowest energy conformations generated by the MD → RHF/3-21G → RHF/6-31+G* sequence of steps outlined above are shown in Fig. 1, labeled in order of increasing relative energy. The sequences of skeletal dihedral angles, which represents a convenient way of representing crown macrocycles, are listed in Table 1. The symbols +, 0, and − denote gauche angles of less than 120°, trans angles between 120° and 240°, and gauche angles between 240° and 360°, respectively.

Relative conformer energies are given in Table 2. As mentioned earlier, a significant amount of conformer reordering was observed between the MM/CVFF and RHF/3-21G levels of theory. Additional reshuffling resulting from the increase in level of theory to RHF/6-31+G and MP2/6-31+G was smaller in magnitude, but still significant. The sensitivity of the conformational ordering is partially due to the varying importance each level of theory places on H · · · O trans–annular interactions. Small basis set Hartree–Fock theory suffers from a large BSSE bias in favor of H · · · O interactions. The largest observed difference in conformer energies between the 3-21G and 6-31+G* basis sets was 2.5 kcal/mol.

The RHF/6-31+G* apparent global minimum (structure **1**), which exhibits two trans–annular interactions, is displaced at the MP2 level by structure **11** with five such interactions (see Fig. 2). Reoptimizing the geometries at the MP2 level of theory lowers the individual conformer energies by as much as 8 kcal/mol, but the differential effect is an order of magnitude smaller. The MP2/6-31+G* ordering of conformers represents only a minor reshuffling of the RHF order. Increasing the basis set size still further (to aVDZ) was found to only have effects at the MP2 level.

Among the crystal structures found in the Cambridge Structural Database (CSD) [58], which contained 15c5 complexed with a metal cation, structure **16** was the most frequently observed. It was also one of the lowest energy structures identified in the MM3 study of Paulsen et al. [24], lying only 0.02 kcal/mol higher in energy than conformer **4**. However, when geometries are optimized at the MP2/6-31+G* level, structure **16** was found to be 4.9 kcal/mol higher in energy than **11** (the global minimum) and structure **4** was 2.0 kcal/mol above **11**. Since the MM3 and AMBER force field results showed appreciable differences in their predicted conformer orderings and we find significant sensitivity to the level of electronic structure theory applied to the problem, we conclude that the accurate prediction of low-lying conformational energies in floppy molecules is a challenging task. Of the 35 conformations identified by their dihedral angles in the MM3 work, only five could be matched with the 16 lowest-lying structures obtained from the present electronic structure calculations. Within the electronic structure domain, crown ethers similar in size to 15c5 or 18c6 appear to require the use of geometries optimized at a correlated level of theory and polarized basis sets if an accuracy of ±0.5 kcal/mol is to be achieved.

For an even-membered macrocycle, such as 18c6, the dipole moments of the–CH_2OCH_2–ether functional groups are optimally aligned with respect to a

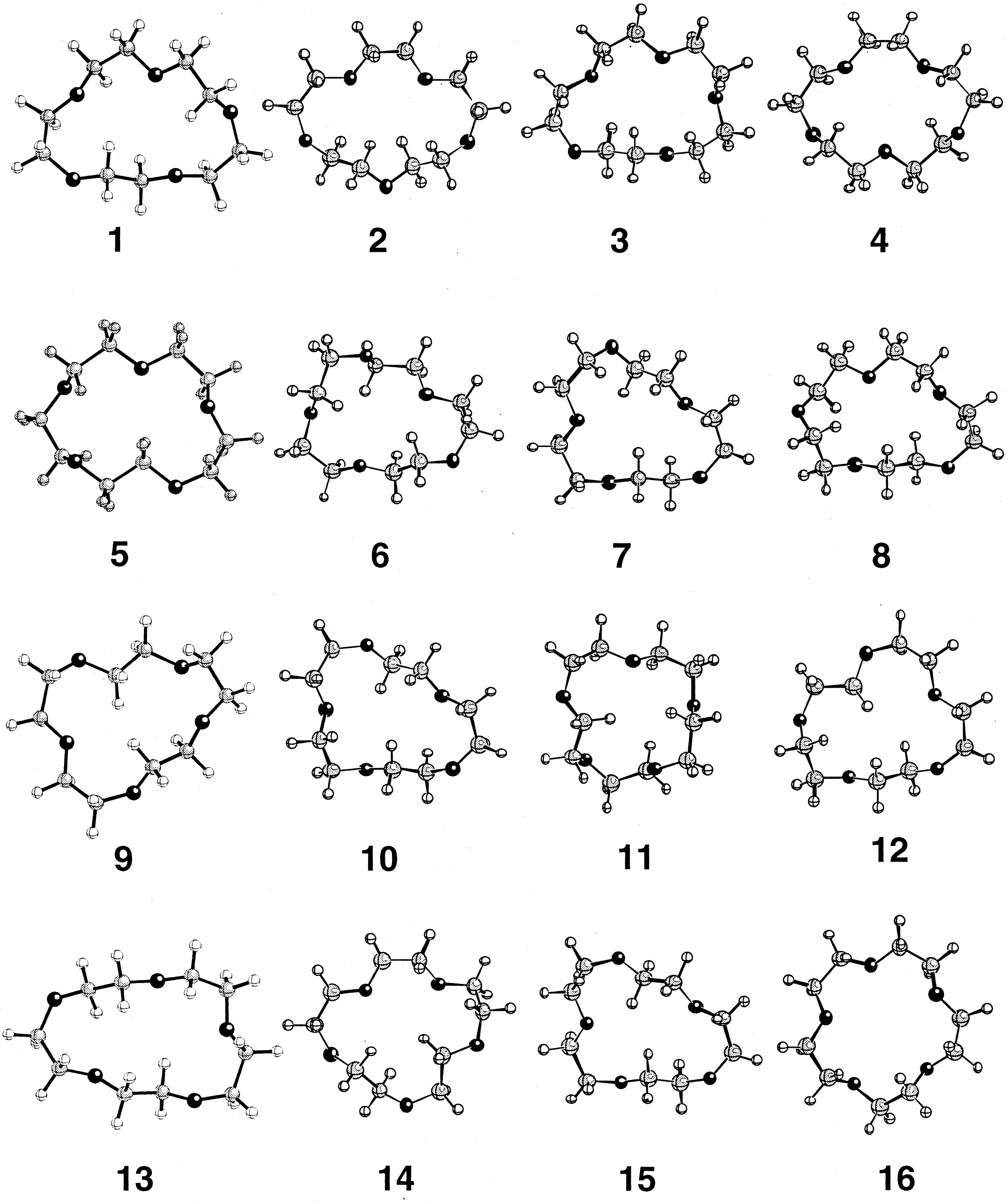

Fig. 1. The 16 lowest energy RHF/6-31+G* structures of 15-crown-5, labeled in order of increasing RHF energy.

Table 1
Sequences of skeletal dihedral angles for gas phase conformers of 15-crown-5[a]

Conformer	Sequences about C–C, C–O, O–C				
1	+00	−+0	000	−+0	+00
2	−00	+−0	0++	00−	+00
3	−+0	+−0	000	++0	+00
4 (C_2)	−00	+−0	−00	−0−	+00
5	−+0	0−0	−+0	+00	+00
6	0−−	+00	+0+	−0−	+00
7	−+0	00+	−00	0−−	+00
8	+00	−+0	00+	+−−	+00
9	−+0	0+0	+−0	00−	+00
10	−+0	000	−+0	00+	+00
11	−+0	++−	+0+	−0−	+00
12	−+0	0−0	−−0	00−	+00
13	0+−	+00	00−	+0+	+00
14	−0−	−+0	0−+	00−	+00
15	00−	++0	+−0	00−	+00
16	−00	+00	−−0	−00	+00

[a] Notation for dihedral angle α is as follows: + denotes ($0 \leq \alpha \leq 120°$), 0 denotes ($120 < \alpha \leq 240°$) and − denotes ($240 < \alpha \leq 360°$). The dipole moments were obtained from RHF/6-31+G* calculations.

Table 2
Number of trans–annular interactions and relative energies of 15-crown-5 conformers

		RHF Opt. Geometry[a]		MP2 Opt. Geometry[a]		
Conformer	# H . . . O[b]	RHF 6-31+G*	MP2 6-31+G*	MP2 6-31+G*	MP2 aVDZ	MM3[c]
1	2	0.00[d]	0.34	0.02	0.03	2.08
2	4	0.45	0.98	1.43		2.90
3	2	0.61	1.33	1.48		
4	2	0.88	1.58	1.98		0.00
5	4	1.04	0.62	1.10		2.25
6	4	1.22	0.82	0.85		
7	4	1.42	1.28	1.61		
8	4	1.43	0.30	0.55	0.48	
9	4	1.46	1.30	1.78		
10	3	1.60	2.04	2.42		
11	5	1.62	0.00[e]	0.00[f]	0.00[g]	
12	3	1.79	2.18	2.86		
13	4	2.04	1.80	1.96		
14	3	2.10	2.36	2.90		
15	4	2.12	2.13	2.50		
16	0	2.20	4.12	4.90	4.51	0.02

[a] Using the 6-31+G* basis set.

[b] Number of # H . . . O cross-ring interactions.

[c] Paulsen and Hay [25].

[d] $E(\text{RHF/6-31+G*}) = -764.577\,09\ E_h$.

[e] $E(\text{MP2/6-31+G*}) = -766.766\,925\ E_h$.

[f] $E(\text{MP2/6-31+G*}) = -766.778\,49\ E_h$.

[g] $E(\text{MP2/aVDZ}) = -767.109\,50\ E_h$.

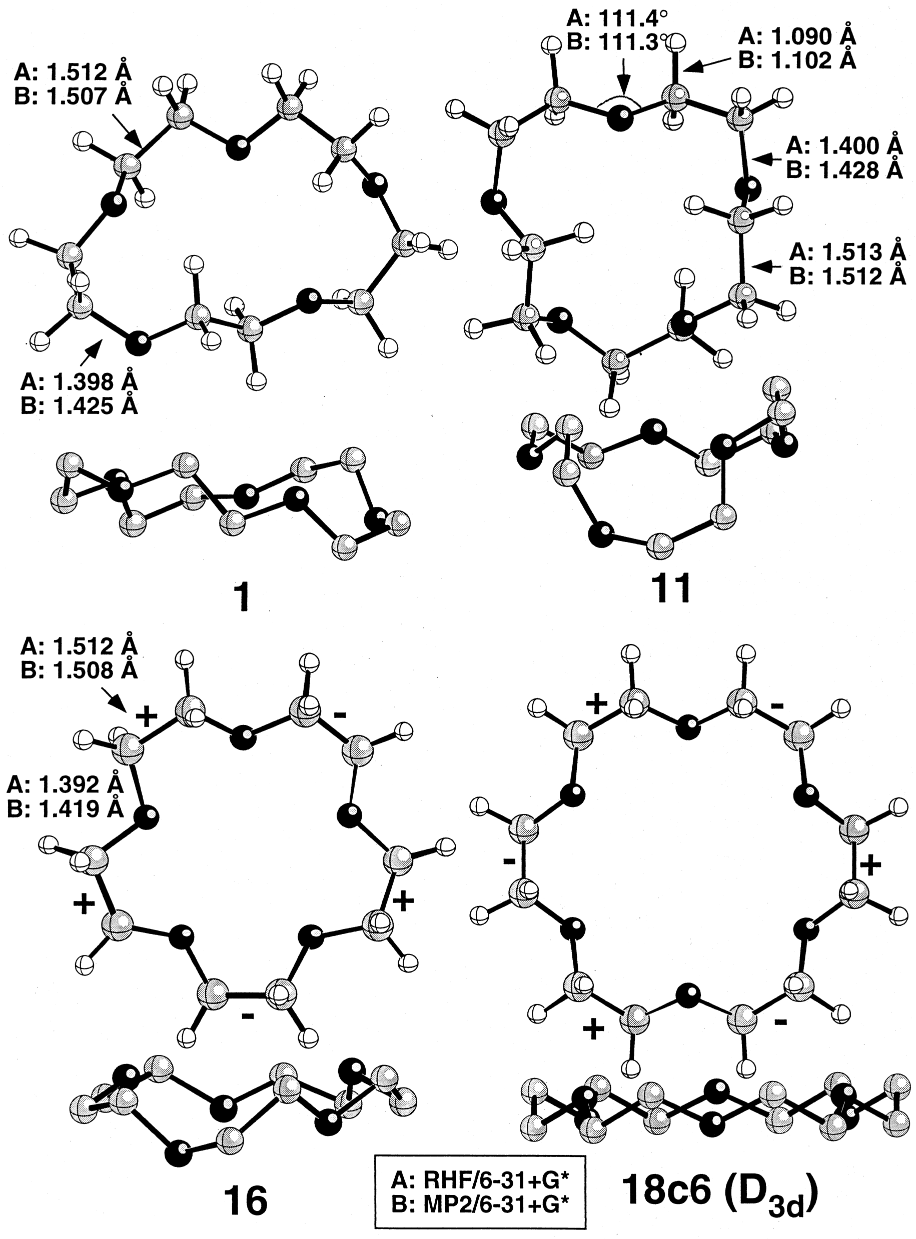

Fig. 2. Expanded views of 15c5 conformers **1**, **11**, **16** and 18c6. Side view is shown below each structure, with hydrogens hidden. The dihedral sequence in 15c5 and 18c6 are indicated as: plus sign = gauche + and minus sign = gauche − dihedral angles about the C–C bond.

centrally located cation when there is an arrangement of *trans*-C–O torsions and *cis*-C–C torsions. However, in order to achieve this arrangement, the ring is forced to assume a perfectly planar configuration that is quite high in energy. In order to avoid this situation, even-membered rings relax *cis*-C–C torsion angles to gauche [59–65,7,66]. In the notation described earlier, the –C–C–O–C– sequence is expected to be +00. For example, 18c6 adopts a D_{3d} symmetry configuration when binding to K^+ by alternating gauche +

and gauche − dihedrals about C–C (see Fig. 2). The global 18c6 minimum has C_i symmetry and is more than 4 kcal/mol lower in energy. Of the 15c5 conformations examined with ab initio methods, structure **16** comes closest to matching the dihedral sequence found in 18c6(D_{3d}). An unavoidable mismatch occurs in the alternation of dihedral angles due to the odd-numbered ring. As was the case with 18c6, the 15c5 global minimum is more than 4 kcal/mol lower in energy, but **16** is the preferred conformation for binding with cations small enough to fit completely within the crown's cavity.

The CSD contains many entries corresponding to 15c5 complexed with a variety of metal cations. Unfortunately, a structure of the isolated crown was not available. Additional starting 15c5 geometries were taken from crystal structure fragments and are listed in Table 3 along with their CSD labels, sequences of dihedral angles, and RHF/6-31+G* relative energies. The high symmetry C_5 conformation is included for the sake of comparison. Conformer LESNEC [42], with the centrally bound cation removed, is equivalent to **16** and conformer FUVUX [67] collapses to **4** after optimization. Conformers CAGTIN (u) and CAGTIN (c) refer to uncomplexed and complexed 15c5 coexisting in the same crystal unit [68]. Following geometry optimization, the energies of the new conformers were all found to be higher than the 16 lowest structures generated by the MD simulations. The conformers increase in energy roughly as the number of mismatches (lack of sign change between adjacent dihedrals about C–C). The C_5 structure has five such mismatches and five compensating dihedral sacrifices, which causes all oxygen atoms to be arranged on the same side of the ring.

3.2. Gas phase M+/15c5

All of the M^+/15c5 crystal structures contained in the CSD database were found to include other constituents in the unit cell, in addition to the negatively charged counterion. Thus, no unambiguous experimental structures were available for comparison with the current ab initio structures. Paulsen and Hay [25] have recently reported a conformational study of M^+/15c5 using the MM3 force field. In the present work we exploit the availability of MM3 conformations from Paulsen and Hay, as well as the results of new MM/CVFF simulations. As with isolated 15c5, expensive 6-31+G* optimization and frequency calculations were performed on only the lowest few MM structures.

A sample of relative conformational energies obtained from RHF/6-31+G* calculations is shown in Table 4, where each structure is labeled **M-*n*** (M indicates the metal and ***n*** is adopted from the labeling convention used in the MM3 paper). The results were found to be in broad overall agreement with the corresponding MM3 results [25]. MM3 and the present electronic structure calculations agree on the global minimum for four out of five metals. Conformer **M-2** has two slightly different variants which were both optimized in RHF calculations to the same structure.

As seen in Fig. 3, the smaller cations (Li^+ and Na^+) form complexes with crown conformations such as LESNEC and FUVFUX, since these conformations maximize favorable charge/dipole interactions without excessive distortions of the macrocycle ring. Li^+/15c5 remains relatively flat, whereas in Li^+/18c6 the crown wraps itself around the metal in order to decrease the Li^+–O distances. The energy difference between the global minimum for isolated 18c6 and the energy of the crown as it exists in the cation/crown complex is referred to as the distortion energy $\Delta E_{\mathrm{distort}}$. For Li^+/18c6, a distortion penalty of 30 kcal/mol is required to wrap the macrocycle around the cation. This penalty is more than compensated for by the electrostatic energy lowering. The smaller 15c5 macrocycle also undergoes a significant distortion in order to bind with Li^+. However, in 15c5 $\Delta E_{\mathrm{distort}}$ is only half as large. As the size of the cation increases, $\Delta E_{\mathrm{distort}}$ monotonically decreases to a limiting value of ~9 kcal/mol, a value similar to the distortion energies found in 18c6. The increased stiffness of 15c5 and the smaller size of its cavity result in a nearly planar Li^+/15c5 complex. Cations larger than Na^+ cannot be completely enclosed within the crown's interior. They prefer to sit atop the crown, with the complex adopting a distorted C_5-like struc-

Table 3
Sample conformers taken from CSD crystals containing 15-crown-5, their sequences of dihedral angles and assigned labels

CSD label	Sequences about C–C, C–O, O–C					Assigned label	Relative energy[a]
DUCNEU[b], FETPEZ[c], FUVFUX(4)[d], GAVPEY[e], TAGGOX[f]	+00	−00	+00	−00	+00	FUVFUX	0.88
KAPDUA[g], KAPFOW[h], KIPDOC[h], KIYKUY[j], KIYLAF[k], LESNEC(16)[l], FANRUH[i], PXCDCB[m]	−00	+00	−−0	−00	+00	LESNEC	2.21
CAGTIN[n] (u)	−0−	−00	−00	+00	+00	CAGTINu	4.75
FABMEA[o], JEPMEW[p], JEPMIA[p]	+00	−−0	−00	+0+	+00	JEPMIA	6.44
VANFUL[q]	−00	++0	−0−	−00	+00	VANFUL	5.73
CUMWAI[r], KOWJOV[s], KOZKUF[t], TAGFEM[u]	−0−	−0−	−00	++0	+00	KOWJOV	7.39
CAGTIN[n] (c)	−00	++−	−00	++0	+00	CAGTINc	5.54
BEKWUJ[v]	−−+	+00	−−0	−−0	+00	BEKWUJ	
FAZLIB[w]	−−0	−−0	−−0	−−+	+00	FAZLIB	9.48
PXCDBA[x]	−−0	−−0	−−+	+0+	+00	PXCDBA	9.87
C_5	++0	++0	++0	++0	++0	C_5	8.82

[a] In kcal/mol. Computed at the RHF/6-31+G* level of theory.
[b] Dejehet et al. [72].
[c] Dejehet et al. [73].
[d] Stark et al. [67].
[e] Dejehet et al. [74].
[f] Larson et al. [75].
[g] Shoham and Cohen [76].
[h] Gutberlet et al. [77].
[i] Rentschler et al. [78].
[j] Wollert et al. [79].
[k] Buchanan et al. [42].
[l] Hough et al. [80].
[m] Arte et al. [81].
[n] Lee et al. [68].
[o] Ward et al. [82].
[p] Ward et al. [83].
[q] Parvez et al. [84].
[r] Rath et al. [85].
[s] Getman et al. [69].
[t] Alcock et al. [86].
[u] Huang et al. [87].
[v] Bunzli et al. [88].
[w] Hough et al. [89].
[x] Feneau-Dupont et al. [90].

ture in which all of the oxygens are oriented toward the cation [69]. Configurations in which the cation is external to the crown macrocycle are more likely to form crown/metal/crown sandwich structures.

MP2/6-31+G* optimizations were performed on the lowest energy RHF structures. Correlation recovery results in a general contraction of the metal–oxygen distances (see Fig. 3) ranging from 0.02 Å for

Table 4
Relative energies at the RHF/6-31+G* and MM3 levels of theory for sample M^+/15-crown-5 conformations

			Relative energies (kcal/mol)	
M	Label[a]	Assignment	RHF/6-31+G*[b]	MM3[c]
Li	**Li-1**	LESNEC	0.00	0.00
	Li-3	FUVFUX	0.02	0.06
	Li-2a	KOW/JEP	1.55	2.50[d]
	Li-4	C_5	13.27	
Na	**Na-1**	LESNEC	0.00	0.69
	Na-2b	KOWJOV	2.52	0.00
	Na-4	C_5	8.14	3.54
K	**K-2b**	KOWJOV	0.00	0.00
	K-1	LESNEC	1.54	3.46
	K-4	C_5	2.31	1.61
Rb	**Rb-2b**	KOWJOV	0.00	0.00
	Rb-4	C_5	1.33	0.64
	Rb-1	LESNEC	2.46	
Cs	**Cs-2b**	KOWJOV	0.00	0.00
	Cs-4	C_5	0.77	0.07
	Cs-1	LESNEC	2.96	

[a] The numeric label following the element symbol is taken from the labeling convention of Paulsen and Hay [25].
[b] This work.
[c] Paulsen and Hay [25].
[d] Ab initio and MM3 conformers differ by one dihedral angle.

the smaller cations to as much as 0.09 Å for the larger metals. The metal–oxygen distances in the M^+/15c5 complexes can be compared to metal–oxygen distances in related compounds that lack the constraints imposed by the ring structure of the 15c5. Dimethyl ether (DME) is an obvious choice, but alkali metals smaller than Cs^+ are unable to directly coordinate five DME ligands. In order to make a rough comparison, we determined an adjustment factor to apply to the metal–oxygen distances in $M^+(DME)_4$ complexes based on the average M^+–O lengthening between $M^+(H_2O)_4$ and $M^+(H_2O)_5$. The resulting estimated strain-free metal–oxygen distances are: Li–O = 1.91 Å, Na–O = 2.24 Å, K–O = 2.71 Å, Rb–O = 2.99 Å, and Cs–O = 3.22 Å, which match the observed RHF distances in Rb^+/15c5 and Cs^+/15c5, but are smaller than the distances found in the Li^+/15c5, Na^+/15c5, and K^+/15c5 complexes by 3–8%, with the largest difference occurring in Li^+/15c5. This analysis is consistent with the earlier comments on the high ring distortion energy for Li^+/15c5.

Total energies for the M^+/15c5 complexes are presented in Table 5. Binding energies, ΔEs, and enthalpies at 298 K, ΔH^{298}, are presented in Table 6 for the reaction

$$M^+ + 15c5 \rightarrow M^+/15c5 \tag{1}$$

ΔEs are based on the lowest energy conformation for each particular level of theory. For example, RHF binding energies were based on conformer **1** of 15c5. The BSSE contribution to ΔE(MP2/6-31+G*) represents a substantial percentage of the total binding energy, ranging from as little as 6.0 kcal/mol to as much as 12.5 kcal/mol. The latter represents 16% of the total binding energy for Na^+/15c5. Based on our experience with the CP correction and calculations with the augmented correlation consistent basis sets, the CP correction was not applied to aVxZ binding energies. Due to a fortuitous but frequently observed cancellation of errors, the raw aVDZ ΔEs are usually closer to the complete basis set limit than the CP-corrected values. The magnitude of the aVDZ CP correction is approximately one third as large as the 6-31+G* basis set value. The similarity of the ΔE(MP2/6-31+G*) values in Table 6 obtained *with*

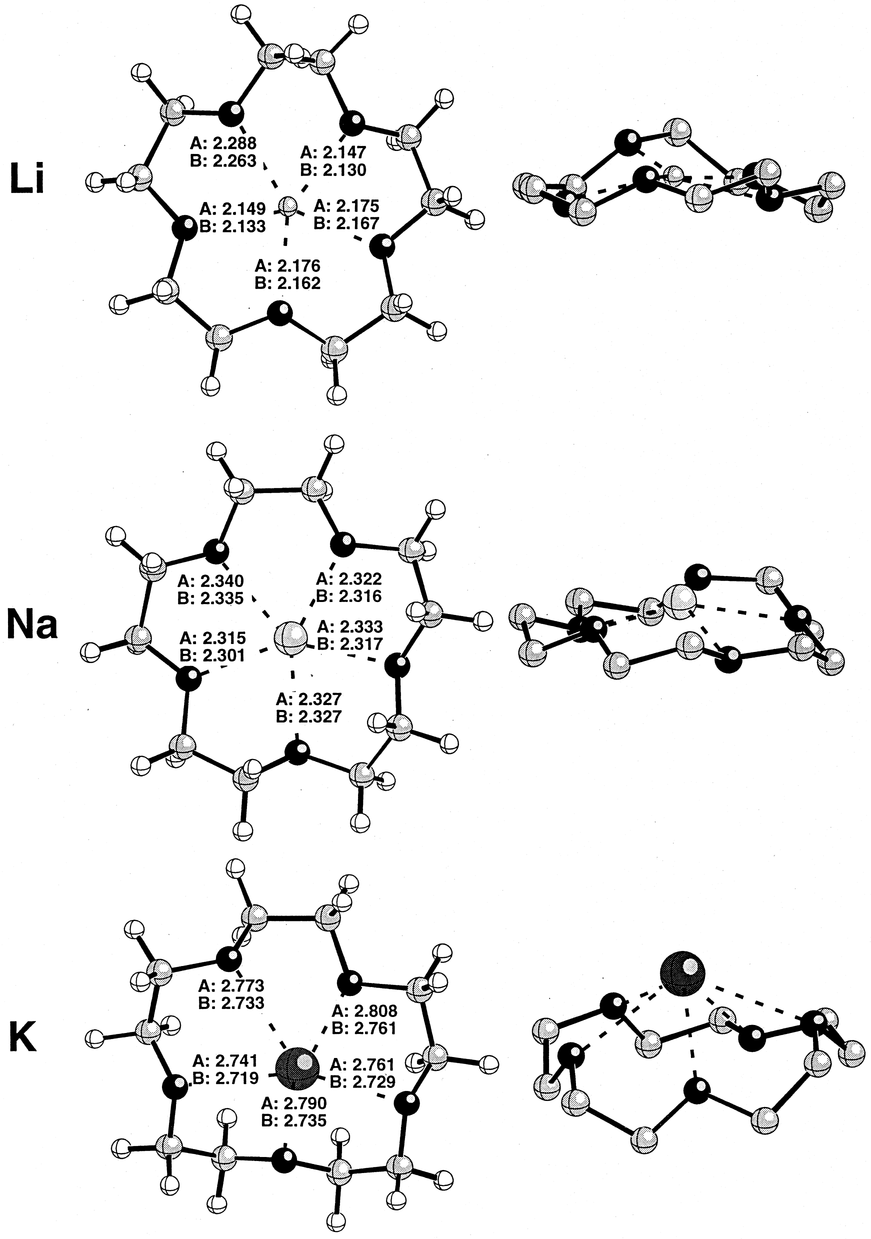

Fig. 3. Lowest energy M^+/15c5 complexes, with metal-oxygen bond lengths shown in Å. A = RHF/6-31+G*, B = MP2/6-31+G*. Side views are shown with hydrogens hidden.

the CP correction and the raw ΔE(MP2/aVDZ) results provides further circumstantial evidence of the appropriateness of the selective application of the correction. At the 6-31+G*(CP) level, the binding energies are not particularly sensitive to further increases in the basis set. Differences between the 6-31+G* and aVDZ results average just 2.4 kcal/mol, with a maximum difference of 5.1 kcal/mol observed for Cs^+/15c5.

Agreement between the current MP2/6-31+G*

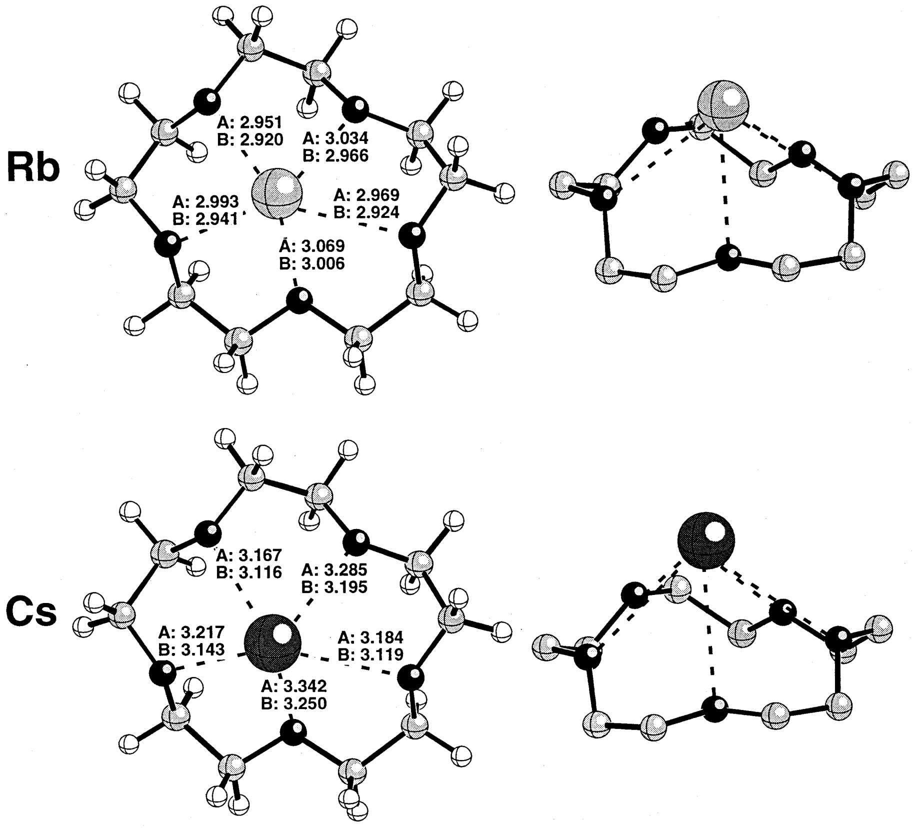

Fig. 3. Lowest energy M^+/15c5 complexes, with metal–oxygen bond lengths shown in angstroms. A = RHF/6-31+G*, B = MP2/6-31+G*. Side views are shown with hydrogens hidden.

theoretical binding enthalpies and recent gas phase collision-induced dissociation measurements by More et al. [12] is mixed. The theoretical values lie just outside the experimental error bars for sodium and potassium (see Table 6 and Fig. 4). However, for the larger rubidium and cesium cations the CID values drastically underestimate the MP2 values. Similar lack of agreement was observed for 12c4, 18c6, and some 1,2-dimethoxyethane (DXE) or DME complexes [7,9–11]. For $Cs^+(DXE)_2$ the situation was unclear, since theory and experiment only differ by 4.5 kcal/mol, whereas in Cs^+/12c4 the difference is 12 kcal/mol.

Although MP2/aVDZ calculations on Rb^+/12c4 and Cs^+/12c4 predicted slightly smaller binding enthalpies, compared to 6-31+G* results, a sizable difference between theory and experiment remained [70]. New MP2/aVDZ results for Na^+/18c6 and K^+/18c6, shown in Fig. 4, indicate similar small shifts in ΔH compared to the 6-31+G*. As discussed below, the evidence to date indicates that the use of even larger basis sets would result in binding enthalpies than are somewhat stronger than those obtained from the aVDZ set. For 15c5 the largest change in ΔH resulting from the use of the aVDZ basis set is a reduction of 5.1 kcal/mol (Cs^+/15c5), compared to the remaining difference with respect to experiment of 12.5 kcal/mol. All MP2/avDZ binding enthalpies were evaluated at the optimal MP2/6-31+G* geometries.

Previous basis set convergence studies of M^+/ether complexes described with the aVxZ sequence of basis

Table 5
M$^+$/15-crown-5 total energies[a]

M$^+$	M$^+$/15c5 conformer	Basis	No. Functions	Geometry	Level	E (E_h)
Li	**Li-1**	6-31+G*	304	RHF/6-31+G*	RHF	−771.984 48
		6-31+G*	304	MP2/6-31+G*	MP2	−774.189 77
		aVDZ	539	MP2/6-31+G*	MP2	−774.502 14
		aVTZ[b]	1000	MP2/6-31+G*	MP2	−775.176 50
Na	**Na-1**	6-31+G*	308	RHF/6-31+G*	RHF	−926.370 75
		6-31+G*	308	MP2/6-31+G*	MP2	−928.582 29
		aVDZ	552	MP2/6-31+G*	MP2	−929.087 49
		aVTZ[b]	1029	MP2/6-31+G*	MP2	−929.842 35
K	**K-2b**	6-31+G*	300	RHF/6-31+G*	RHF	−792.374 49
		6-31+G*	300	MP2/6-31+G*	MP2	−794.657 25
		aVDZ	551	MP2/6-31+G*	MP2	−1 366.370 56
Rb	**Rb-2b**	6-31+G*	300	RHF/6-31+G*	RHF	−788.097 12
		6-31+G*	300	MP2/6-31+G*	MP2	−790.340 08
		aVDZ	551	MP2/6-31+G*	MP2	−790.703 83
Cs	**Cs-2b**	6-31+G*	300	RHF/6-31+G*	RHF	−784.120 19
		6-31+G*	300	MP2/6-31+G*	MP2	−786.368 07
		aVDZ	548	MP2/6-31+G*	MP2	−786.707 95

[a] The $(n - 1)$ shell of electrons are correlated in the MP2 calculations involving Na–Cs. For example, the Na $2s^22p^6$ electrons are correlated. The aVDZ and aVTZ all-electron calculations used core/valence basis sets on the metal.

[b] Diffuse functions were removed from the hydrogens to limit the amount of linear dependency in the basis set.

sets found that the ΔH complete basis set limit was approached from above. In order to test the convergence behavior for M$^+$/15c5 complexes, we performed aVTZ calculations on Li$^+$/15c5 and Na$^+$/15c5 at the optimal MP2/6-31+G* geometry. Diffuse functions were removed from the hydrogens to limit the

Table 6
M$^+$/15-crown-5 electronic binding energies and binding enthalpies (kcal/mol) at 298 K

M$^+$	M$^+$/15c5 conformer	Basis	Level	ΔE	ΔE(CP)[b]	ΔH^{298}	CID expt[a] ΔH^{298}
Li	**Li-1**	6-31+G*	RHF	−107.8	−104.2	−102.8	
		6-31+G*	MP2	−110.3	−102.5	−101.1	
		aVDZ	MP2	−98.2		−96.8	
		aVTZ	MP2	−99.7		−98.3	
Na	**Na-1**	6-31+G*	RHF	−84.3	−80.8	−80.0	−71.2 ± 4.3
		6-31+G*	MP2	−89.7	−77.2	−76.4	
		aVDZ	MP2	−77.1		−76.3	
		aVTZ	MP2	−77.9		−77.1	
K	**K-2b**	6-31+G*	RHF	−57.6	−56.7	−55.9	−49.2 ± 3.3
		6-31+G*	MP2	−65.1	−58.9	−58.1	
		aVDZ	MP2	−57.1		−56.4	
Rb	**Rb-2b**	6-31+G*	RHF	−48.0	−47.1	−46.4	−27.7 ± 1.4
		6-31+G*	MP2	−55.7	−49.4	−48.7	
		aVDZ	MP2	−48.8		−48.1	
Cs	**Cs-2b**	6-31+G*	RHF	−40.2	−39.3	−38.7	−24.1 ± 1.4
		6-31+G*	MP2	−48.6	−42.6	−41.7	
		aVDZ	MP2	−37.5		−36.6	

[a] More et al. [12].

[b] Counterpoise-corrected.

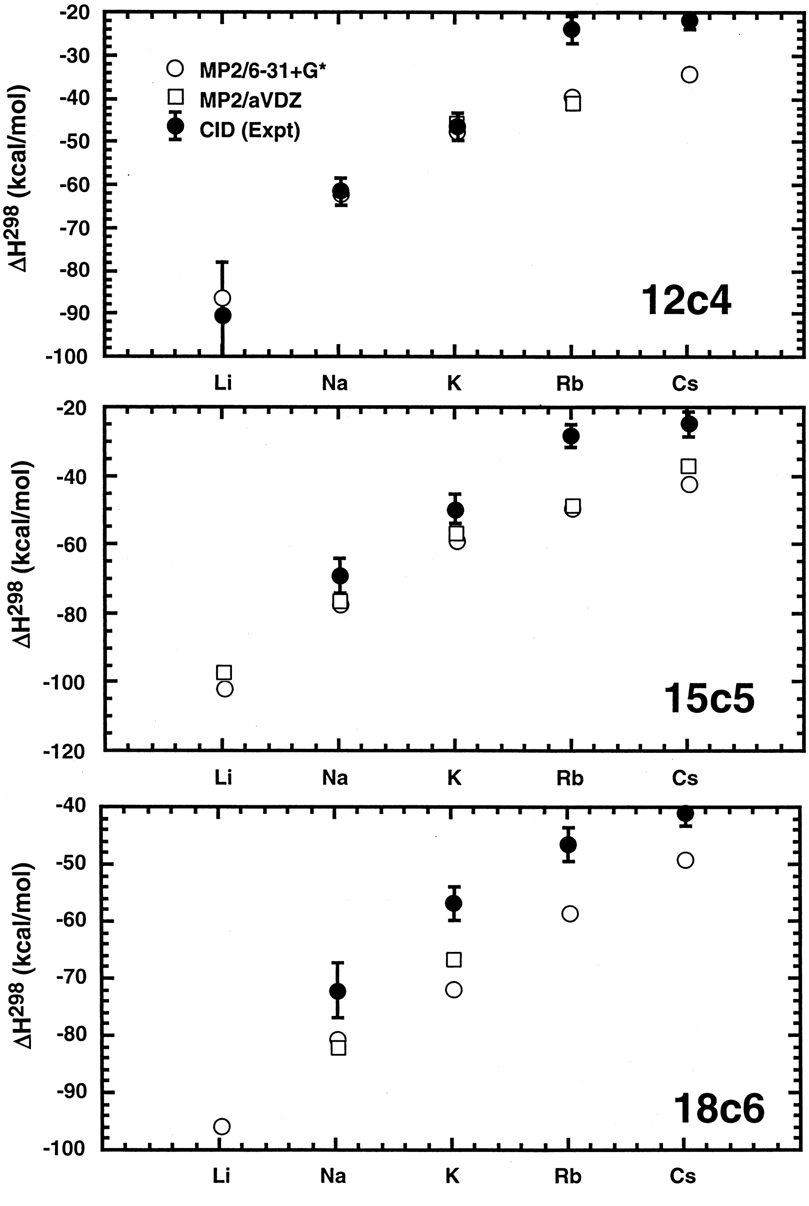

Fig. 4. A comparison of theoretical and experimental binding enthalpies $M^+ + 15c5 \rightarrow M^+/15c5$ at 298 K. A counterpoise correction has been applied to the 6-31+G* results.

degree of linear dependency in the basis set. At approximately 1000 basis functions, these were the largest calculations performed as part of the present work. In accord with the previous studies, ΔH^{298} increased in magnitude by 0.8–1.5 kcal/mol. Although quadruple zeta basis set calculations were too expensive to attempt on a system the size of $M^+/15c5$, earlier studies on M^+/DME suggests that ΔH was converged within 0.5 kcal/mol at the aVTZ level. Thus, we estimate that the actual CBS limit for the binding enthalpy is slightly larger in magnitude than the aVTZ value, but within 2 kcal/mol of the aVDZ results.

The uncertainty introduced by the use of pseudopotentials for rubidium and cesium is difficult to estimate. Fully relativistic, all-electron calculations on Rb^+/15c5 or Cs^+/15c5 are not currently feasible. For potassium, where alternative all-electron methods are possible, the pseudopotential approach produces essentially identical results when care is taken to use similar quality valence basis sets. Other evidence that pseudopotentials do not represent a significant source of error comes from comparisons between theory and experiment for complexes formed with water or smaller ethers, such as dimethyl ether. For both of these ligands, the levels of theory used in the present work yielded binding enthalpies in agreement with CID experimental values within their quoted error bars [70,71].

It has been suggested that the observed discrepancies between theoretical and CID experimental binding enthalpies are the result of populating higher energy M^+/crown conformers in the CID flow tube [2,12]. For example, the lowest energy conformer of 12c4 possesses S_4 symmetry, whereas the crown's conformation in the lowest energy forms of Rb^+/12c4 and Cs^+/12c4 is approximately C_4. If Rb^+ or Cs^+ were to approach 12c4 (S_4) with low enough kinetic energy to avoid altering the crown's conformation, it could result in metal/crown complexes that are of $\sim C_{2v}$ symmetry. Electronic structure calculations showed such structures to be 12–14 kcal/mol higher in energy than the global Rb^+/12c4 and Cs^+/12c4 minima. Although only suggestive, the C_{2v}(upper) and C_4(lowest energy) conformations were found to be connected by an intermediate C_1 symmetry structure via 11 kcal/mol linear synchronous transit barriers. The explicit identification of a continuous path linking higher-lying metastable conformations with the global minimum is a difficult problem, since it can conceivably involve locating multiple intermediate minima and their connecting transition states. Although higher energy Rb^+/15c5 and Cs^+/15c5 complexes were located during the course of this investigation, after optimization they were found to lie within 4 kcal/mol of the global minimum. Attempts to form an Rb^+/15c5 complex that was 10–20 kcal/mol higher in energy by combining Rb^+ and 15c5 (conformer **1** or **11**) proved unsuccessful. Since the crowns are asymmetric, we started these geometry optimizations with Rb^+ in both the "above" and "below" positions. Both starting points led to structures that were only 4–5 kcal/mol higher in energy, rather than the 20+ kcal/mol needed to bring theory and experiment into agreement. The limited nature of the search makes drawing a definitive conclusion impossible.

3.3. Cluster binding preferences

Gas phase 12c4, 15c5, and 18c6 bind Li^+ most strongly of the alkali metals for simple electrostatic reasons. Because Li^+ is even more strongly solvated, in aqueous solution the binding preference of the three crowns is shifted away from lithium and toward one of the larger cations. For example, 18c6 is known to prefer K^+. This behavior can be approximately reproduced in gas phase cluster calculations by considering the following cation exchange reaction:

$$K^+/18c6 + M^+(H_2O)_x \rightarrow K^+(H_2O)_x + M^+/18c6 \qquad (2)$$

or a related reaction in which the M^+/18c6 complexes are microsolvated with up to 4 hydrogen-bonded water [5]. Besides energies for the M^+/18c6 complexes, use of the analogue of Eq. (2) for 15c5 requires knowledge of the alkali cation hydration energies. In the present work, these values were taken from literature values obtained at the same level of theory [5,71]. The enthalpy change at 298 K for expression (2) is plotted in Fig. 5 versus x, the degree of hydration. At $x = 8$ there is slight preference for Na^+ and Li^+ relative to K. For 18c6, the same approach shows potassium selected by a much larger margin ($\Delta H_{r\times n} = +7.9$ kcal/mol vs Na). This weaker selectivity is in qualitative agreement with calorimetric titration studies in aqueous solution. At room temperature, potassium is preferred by 15c5 over sodium by a factor of only 1.1:1, compared to a factor of 17:1 for 18c6 [22]. Even in a nonpolar solvent, where cation solubility is lower and macrocyclic selectivity is closer to the behavior predicted with $x = 0$ in Eq. (2), the 15c5 → 18c6 trend is the same. In methanol, the respective factors are 1.9 for

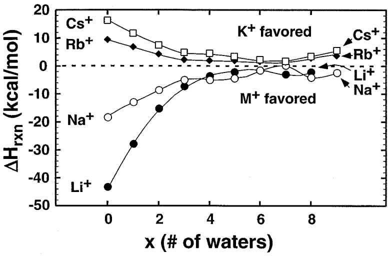

Fig. 5. The exchange reaction enthalpy for K^+ (15c5) + M^+ $(H_2O)_x \rightarrow K^+ (H_2O)_x + M^+$ (15c5) versus x, for M = Li, Na, Rb, and Cs.

15c5 and 50 for 18c6 [23]. Inclusion of microsolvating waters around the M^+/15c5 complexes may bring these cluster results into slightly better agreement with aqueous experiment, as it did in the case of 18c6. To the extent that Eq. (2) is capable of qualitatively reproducing the binding preferences in bulk phase solutions, differential entropic effects, which are completely absent in Eq. (2), appear to play a minor role.

4. Summary and conclusions

A combination of classical force field MD and electronic structure calculations with small-to-medium size basis sets have been used to identify the low-lying conformers of isolated 15c5 and metal cation complexes, i.e. M^+/15c5, where M = Li, Na, K, Rb, and Cs. The spectrum of conformation energies was found to be moderately sensitive to the level of theory applied. Depending upon the size of the metal, between 8 and 16 kcal/mol are required to reorganize the lowest energy gas phase conformer into the structures present in the complex. Small cations, such as Li^+, form stronger electrostatic bonds in roughly planar configurations, while larger cations sit atop the ring in low symmetry complexes with the ether oxygens distorted to one side of the macrocycle plane. Gas phase MP2 metal–crown binding enthalpies are in reasonable agreement with CID experimental values for Na^+/15c5 and K^+/15c5, but differ by as much as 20 kcal/mol for Rb^+ and Cs^+. Similar behavior was observed for 12c4 and 18c6. The use of much larger basis sets in the electronic structure calculations failed to resolve the differences. One possible explanation for the discrepancy assumes that the CID experiment was sampling M^+/crown complexes that were trapped in higher-lying conformations. For 12c4 a higher-lying structure formed from the lowest-energy conformation of isolated 12c4 and Rb was identified. Attempts to identify a much higher-lying structure for Rb^+/15c5 by starting from the lowest energy forms of the isolated crown were unsuccessful. The use of a gas phase cluster reaction to model the binding preference of 15c5 in solution, was found to produce results in qualitative agreement with experiments that show a lack of selective behavior on the part of 15c5 relative to that of 18c6.

The theoretical approach adopted in the present work improves upon the procedure followed in our previous studies of 12c4 and 18c6 by incorporating MP2 geometries and by reliance on extensive benchmarking of the smaller 6-31+G basis set with much larger correlation consistent sets. Despite the more extensive nature of the electronic structure calculations, changes in predicted binding energies are only on the order of a few percent.

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