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Conformational Study of the Structure of 12-crown-4−Alkali Metal Cation Complexes

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A conformational search was performed for the 12-crown-4 (12c4)−alkali metal cation complexes using two different methods, one of them is the CONFLEX method, whereby eight conformations were predicted. Computations were performed for the eight predicted conformations at the HF/6-31+G*, MP2/6-31+G*//HF/6-31+G*, B3LYP/6-31+G*, MP2/6-31+G*//B3LYP/6-31+G*, and MP2/6-31+G* levels. The calculated energies predict a C_4 conformation for the 12c4−Na$^+$, −K$^+$, −Rb$^+$, and −Cs$^+$ complexes and a C_s conformation for the 12c4−Li$^+$ complex to be the lowest energy conformations. For most of the conformations considered, the relative energies, with respect to the C_4 conformation, at the MP2/6-31+G*//B3LYP/6-31+G* are overestimated, compared to those at the MP2/6-31+G* level, the highest level of theory considerd in this report, by 0.2 kcal/mol. Larger relative energy differences are attributed to larger differences between the B3LYP and MP2 optimized geomtries. Binding enthalpies (BEs) were calculated at the above−mentioned levels for the eight conformations. The agreement between the calculated and experimental BEs is discussed.

Introduction

There has been a considerable interest in the chemistry of crown ethers due to their wide applications.[1,2] Most of these applications depend on the complexes formed between crown ethers and different metal cations. Some of the applications of crown ethers are ionophores in membrane transport,[3] column chromatography,[4] disposals of nuclear waste,[5−9] and cancer treatment.[10]

One of the smallest crown ethers is 12c4, which has been the subject of many conformational analysis reports, in the free state[11−27] and in the complexed form too.[19,20−23,25,28] In a recent publication,[27] a full conformational search of free 12c4 was reported. The energy order of the predicted conformations was determined at the MM3, HF/6-31+G*, MP2/6-31+G*//HF/6-31+G*, BLYP/6-31+G*, MP2/6-31+G*//B3LYP/6-31+G*, and MP2/6-31+G* levels of theory. Similar to the previous studies,[14,16,26,27] the study predicted that the S_4 conformation is the lowest energy conformation of 12c4. Contrary to earlier reports,[26] it was concluded that the MP2 energy is necessary to get an accurate energy order of the predicted conformations. It was also concluded, as a reflection of the closeness of the B3LYP and MP2 optimized geometries, that the relative energies at the MP2/6-31+G* and MP2/6-31+G*//B3LYP/6-31+G* levels are very close to each other, within 0.1 kcal/mol. The dependence of the conformational stability on the hydrogen bonding was discussed.

There are many reports of the conformational study of 12c4−alkali metal cation complexes, including the calculation of the structure and BEs between 12c4 and alkali metal cations.[19,20−23,25,28] The majority of these studies were done at the ab initio level by Feller and co-workers and were performed at the HF level with the correlation energy recovered at the MP2 level assuming a C_4 structure of 12c4−alkali metal cation complexes. The calculated BEs were compared with the experimental BEs determined from the collision−induced dissociation (CID) experiments.[20−23] Good agreement was found for the 12c4−Li$^+$,[20] although there was a large uncertainty in the experimental value, −Na$^+$,[21] and −K$^+$ [23] complexes but not for 12c4−Rb$^+$ and −Cs$^+$[22] complexes. It was suggested that the experimental conditions sample the 12c4−Rb$^+$ and −Cs$^+$ metal complexes in a higher energy C_{2v} conformation rather than the lowest energy C_4 conformation, as was the case for the 12c4−Li$^+$, −Na$^+$, and −K$^+$ complexes.[19,22,25] No detailed computations of this higher energy C_{2v} complex were offered. A similar case is observed for the 15-crown-5 (15c5)−alkali metal cation complexes where there is a good agreement between the experimental BEs determined by CID[29] and those calculated assuming the lowest energy complex for the 15c5−Li$^+$, −Na$^+$, and −K$^+$ complexes but not for the 15c5−Rb$^+$ and −Cs$^+$ metal complexes.[30] It was also suggested that sampling of the 15c5−Rb$^+$ and −Cs$^+$ metal complexes traps these complexes in a higher energy conformation. For 18c6, BEs are available only for the K$^+$ and Cs$^+$ metal complexes[31] and large differences between the calculated and experimental BEs of both cations are found.[32] BEs were also calculated at the HF, MP2, RI-MP2, LSDA, BLYP, and BP86 levels for the 12c4−K$^+$ complex assuming a C_4 conformation of the complex.[19] It was concluded that the MP2 method is a reliable method for the prediction of BEs and the 6-31+G* basis set is capable of reproducing the BEs within few kcal/mol of the basis set limit. The calculated BEs showed sensitivity on the basis set used. Although two C_s conformations were described as possible higher energy conformations of the 12c4−K$^+$ complex, no BEs were reported for these two conformations. Experimentally, C_4,[33−36] C_i,[37] and C_s[38] conformations were reported for 12c4−metal cation complexes.

Our main aim is the study of the vibrational spectra of free 18c6 and its cation complexes. However, it was felt that an initial conformational analysis of free 18c6 and its cation complexes is necessary. In addition, due to the large size of 18c6, our effort was directed first to the smaller 12c4 because it can be used as a model study of the larger 18c6. Conforma-

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tional analysis of free 12c4 and 18c6 were presented in two previous reports.[27,39] The aim of the current report is then to perform a conformational analysis of 12c4−alkali metal cation complexes. Conformational analysis of 18c6−alkali metal cation complexes will be presented in a separate publication.[40] Although extensive computations were reported by Feller and co-workers for 12c4−alkali metal cations, these reports concentrated mainly on the C_4 conformation of the complexes. The aim of the current report is then to extend these studies by performing a conformational analysis of 12c4−alkali metal cation complexes and to study the structure of these conformations at high levels of theory. In addition, to calculate the BEs between 12c4 and alkali metal cations assuming a structure of any of the predicted 12c4−alkali metal cation conformations.

TABLE 1: Energies (au) of the Predicted Conformations Using the First, CONFLEX, Method for the 12c4−Alkali Metal Cation Complexes at the HF/3-21G Level[a]

no.	sym	Li^{+} [a]	Na^{+}	K^{+}	Rb^{+}
1	C_4	−615.66270	−769.09681	−1204.37056	−3532.92143
2	C_1	−615.66145	−769.09404	−1204.36680	−3532.91755
3	C_s	−615.66821	−769.09284	−1204.36598	−3532.91684
4	C_{2v}	−615.66294	−769.09276	−1204.36314	−3532.91339
5	C_s	−615.66821	−769.09291	−1204.35541[a]	−3532.90697[a]
6	C_1	−615.66265	−769.08860	−1204.36126[a]	−3532.91254[a]
7	C_s	−615.67069	−769.08257	−1204.35541[a]	−3532.90697[a]

[a] Calcluated for conformations similar to those predicted for the 12c4−Na^{+} complex. See text.

Computational Details

To determine the possible conformations of 12c4−alkali metal cation complexes, two methods of conformational search were tried. The first is the CONFLEX method[41−43] used in the previous conformational search of free 12c4[27] and 18c6.[39] The details of the conformational search are similar to those used for free 12c4 and 18c6. For the additional metal cation, an ionic bond was assumed between the four oxygen atoms and the alkali metal cation and a +1 charge was placed on the alkali metal cation. The conformational search was performed at the MM3 level. Geometries of the predicted conformations were then optimized at the HF/3-21G level. The energies of the predicted conformations were compared with those predicted from the second conformational search method. The second conformational search method was tried for the 12c4−Li^{+}, −K^{+}, and −Rb^{+} metal cation complexes only and similar conformations were assumed for the other two alkali metal cation complexes, Na^{+} and Cs^{+}. In this conformational search method, the alkali metal cation was placed at the center of the molecular plane and at 0.8 Å above (and, whenever appropriate due to symmetry, below the ring plane) for 30 of some of the lowest energy conformations of free 12c4. For the K^{+} and Rb^{+} cations, due to their large size, they were positioned at 2.0 Å above or below the ring plane and computations with the metal cation positioned at the center of the ring plane were not performed. The geometries were optimized at the HF/3-21G level and conformations with imaginary vibrational frequencies were excluded.

Further computations of the predicted conformations were performed at the HF,[44] B3LYP,[45] and MP2[46] levels of theory using the 6-31+G* [47] basis set except for the K^{+}, Rb^{+}, and Cs^{+} metal cations. For these a basis set similar to that used by Feller et al.[25] in his report of 12c4−alkali metal cation complexes was used. In this basis set, the Hay and Wadt's 10-valence-electron effective core potential (ECP) with (5s4p)/[3s2p] valence basis set was used.[48] This basis set was augmented with an additional six-term d-type polarization functions with exponents of $\alpha_d = 0.48$ for K, $\alpha_d = 0.24$ for Rb, and $\alpha_d = 0.19$ for Cs. These additional functions were obtained by Glendening and co-workers through energy minimization of $M^{+}(H_2O)$ clusters,[49,50] where M^{+} refers to an alkali metal cation. For simplicity the above-mentioned basis set will be termed the 6-31+G* basis set. The additional diffuse function in the 6-31+G* basis set was used for its known necessity for the calculation of properties and structure of cation metal complexes and to minimize the basis set superposition error (BSSE).[49,50] The only difference between the basis set used in this report and that used by Feller et al.[25] is that in Feller's work, the 6-31+G* basis set was used only for the oxygen atom and the 6-31G* basis set was used for the carbon, hydrogen, lithium, and sodium atoms.

To recover part of the correlation energy at the HF and B3LYP levels, MP2 energy was calculated at the corresponding optimized geometries at these two levels using the same basis set. Those computations will be referred to as the MP2/6-31+G*//HF/6-31+G* and MP2/6-31+G*//B3LYP/6-31+G* levels, respectively. The MP2 computations were performed with the frozen core (fc) option where the core electrons were excluded from the correlation calculation.

BEs between 12c4 and alkali metal cations were calculated. As an approximation to the correction of the BSSE, the counterpoise correction of Boys and Bernardi[51] was employed. The BEs were calculated using the following explicit equation which includes the enthalpy correction[52]

$$\mathrm{BE} = E(\mathrm{complex}) - E(S_4) - E(\mathrm{CPC}) - [\mathrm{CTH(complex)} - \mathrm{CTH}(S_4) - \mathrm{CTH(metal)}]$$

where E(complex) is the energy of the 12c4 complex, $E(S_4)$ is the energy of the lowest energy S_4 conformation of free 12c4, and E(CPC) is the energy of the complex with the atoms of the 12c4 part of the complex represented as ghost atoms; all of them were calculated at the same level and basis set. CTH(complex), CTH(S_4), and CTH(metal) are the correction to enthalpy of the complex, S_4 conformation, and metal cation, respectively, all calculated at the B3LYP/6-31+G* level and at 298 K. The zero point energy correction, included in the correction to enthalpies, was not scaled because the B3LYP zero point energy scale factor is very close to one, 0.9806.[53] Notice that it was reported that the increase of the size and flexibility of the basis set more than the 6-31+G* basis set had little effect on the calculated BEs.[54] The ab initio computations were carried out using the Gaussian 98W[55] and Gaussian 03W[56] programs. In the geometry optimization step, the Gaussian program default parameters were used.

Results and Discussion

The energies of the predicted conformations by the first, CONFLEX, and second methods at the HF/3-21G level are given in Tables 1 and 2, respectively. No computations were done for the 12c4−Cs^{+} complex because the 3-21G basis set is not available for the Cs atom. As shown in Table 1, conformational search by the CONFLEX method predicted four similar conformations for each of the 12c4−K^{+} and Rb^{+} complexes with C_4, C_1, C_s, and C_{2v} symmetries. Although not listed in Table 1, similar conformations with the same symmetries were predicted for the 12c4−Cs^{+} complex at the MM3 level. For the 12c4−Na^{+} complex, seven conformations were predicted with the first four lowest energy conformations similar to those predicted for the 12c4−K^{+}, −Rb^{+}, and −Cs^{+} com-

TABLE 2: Energies (au) of the Predicted Conformations Using the Second Method for the 12c4−Alkali Metal Cation Complexes at the HF/3-21G Level[a]

no.	sym	Li$^+$	Na^{+a}	K$^+$	Rb$^+$
1	C_4	−615.66269	−769.09680	−1204.37056	−3532.92143
2	C_s	−615.66820	−769.09283	−1204.36598	−3532.91684
3	C_s	−615.66820	−769.09291	−1204.36359	−3532.91422
4	C_{2v}	−615.66293	−769.09276	−1204.36314	−3532.91339
5	C_{2v}	−615.67069	−769.07997	−1204.34816	−3532.89850

[a] Calculated for conformations similar to those predicted for the 12c4−Li$^+$ complex. See text.

plexes. A conformational search of the 12c4−Li$^+$ complex was not successful. For comparison with the conformations predicted by the second method, geometries were optimized for the 12c4−Li$^+$ complex at the HF/3-21G level for the seven conformations predicted for the 12c4−Na$^+$ complex, after replacing the Na$^+$ cation by the Li$^+$ cation. Similarly, geometries were optimized at the HF/3-21G level for the 12c4−K$^+$ and −Rb$^+$ complexes after replacing the Na$^+$ cation by the K$^+$ and Rb$^+$ cations in conformations 5, 6, and 7 predicted for the 12c4−Na$^+$ complex. In the second conformational search method, Table 2, five conformations were predicted. For comparison with conformations predicted by the first method, geometries were optimized for the 12c4−Na$^+$ complex at the HF/3-21G level for structures similar to those predicted for the 12c4−Li$^+$ complex. Vibrational frequencies were calculated for all conformations at the corresponding optimized geometries at the HF/3-21G level and none of the conformations considered had any imaginary vibrational frequency at that level.

The data in Tables 1 and 2 show that, although the MM3 method is not well parametrized for the alkali metal cations, there is a good agreement between the conformations predicted by both methods. In addition, the same conformations are predicted by the CONFLEX method for the 12c4−Na$^+$, −K$^+$, −Rb$^+$, and −Cs$^+$ complexes, that reflects the reliability of the conformational search results obtained by this method. Conformations 2 and 6 with C_1 symmetry predicted by the first method are not predicted by the second method. This indicates the difficulty of predicting conformations with this symmetry by the second method. The energies of the predicted conformations by the first method show that conformation 5 of the 12c4−K$^+$ and 12c4−Rb$^+$ complexes is same as conformation 7.

The five conformations predicted by the second method in addition to conformations 2, 6, and 7 predicted by the first method, for a total of eight conformations, were considered for computations at higher levels. These are the HF/6-31+G*, MP2/6-31+G*//HF/6-31+G*, B3LYP/6-31+G*, MP2/6-31+G*//B3LYP/6-31+G*, and MP2/6-31+G* levels. The calculated energies of conformation 1 at these five levels for the five 12c4−Li$^+$, 12c4−Na$^+$, 12c4−K$^+$, 12c4−Rb$^+$, and 12c4−Cs$^+$ alkali metal cation complexes, are shown in Table 3. The relative energies of the other seven conformations, with respect to conformation 1, at the same five levels are given in Table 4. A new conformation number is assigned to each of the eight conformations according to the MP2/6-31+G* energy and will be typed hereafter in boldface. Conformation 1 has the lowest energy for all complexes at all levels, except for the 12c4−Li$^+$ complex and is then considered as conformation **1**. The calculated BEs of the eight conformations are given in Table 5. For comparison, the experimental BEs determined by the CID method[20−23] are added to Table 5. The M−O bond lengths, where M refers to alkali metal cation, calculated at the MP2/6-31+G* level of the eight complexes are given in Table 6. Figure 1 shows the structure of 12c4−Na$^+$ and 12c4−Rb$^+$ complexes, by the side and top views, respectively, for conformations **1**−**8**, as an example of the predicted conformations of the 12c4−alkali metal cation complexes.

In the full conformational search reported for free 12c4, 180 conformations were predicted, although some of the predicted conformations were redundant.[27] In the conformational search performed in this report for the 12c4−alkali metal cation complexes a limited number of conformations were predicted although the CAChe augmented MM3 force field is not well parametrized for alkali metal cations. This is due to electrostatic attraction between the four oxygen atoms of the 12c4 ring and the alkali metal cations that limits the flexibility of the 12c4 ring. A larger number of conformations were predicted for the smaller Na$^+$ complex than for the other three larger K$^+$, Rb$^+$, and Cs$^+$ metal cation complexes. It may be rationalized that the CAChe augmented MM3 force field not being as well parametrized for the other three alkali metal cations as for the Na$^+$ cation or the smaller Na$^+$ cation does not limit the flexibility of the 12c4 ring as it does for the larger K$^+$, Rb$^+$, and Cs$^+$ cations with larger electrostatic attraction forces. Notice that due to the electrostatic attraction between the oxygen atoms and the metal cations, in the majority of the predicted conformations, conformations **1**−**8**, the oxygen atoms are oriented toward the metal cation, as shown in Figure 1.

The flexibility of the free 12c4 ring and the consequent large number of possible conformations resulted in a difficulty in matching with the experimental prediction of the conformation, or conformations, of free 12c4.[57,58] This was represented by the NMR study that indicated interconversion of free 12c4 between the C_i and C_4 conformations. A recent study of the vibrational spectra of free, or rather uncomplexed, 12c4[59] indicated that 12c4 in the solid, liquid, and solution phases exist in the C_i conformation. This conclusion was reached by the observation that IR active modes were Raman inactive and IR inactive modes were Raman active. According to the exclusion rule, the conformation assumed by free 12c4 in these phases must possess a center of inversion. From the results of a conformational search of free 12c4,[27] the only possible conformation of free 12c4 that has a center of inversion is the C_i conformation. This conclusion was further supported by comparison between the experimental and calculated vibrational spectra of free 12c4 assuming five of the important conformations of C_i, S_4, C_4, C_2 and C_s symmetries. For 12c4−alkali metal cation complexes, in the solid phase, X-ray studies have shown that 12c4−Li^{+}[33] and

TABLE 3: Energies (au) of the 12c4−Alkali Metal Cation Complexes of Conformation 1, C_4 Symmetry[a]

method	Li$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$
HF	−619.04420	−773.42679	−639.44082	−635.16636	−631.19190
MP2//HF	−620.80828	−775.18772	−641.28511	−636.97034	−633.00033
B3LYP	−622.76823	−777.52592	−643.38363	−639.10550	−635.12131
MP2//B3LYP	−620.81375	−775.19315	−641.29037	−636.97547	−633.00545
MP2	−620.81472	−775.19496	−641.29152	−636.97681	−633.00699

[a] All computations were done using the 6-31+G* basis set; see text. MP2//HF stands for the MP2/6-31+G*//HF/6-31+G* level, and MP2//B3LYP stands for the MP2/6-31+G*//B3LYP/6-31+G* level.

TABLE 4: Relative Energies (kcal/mol) of the 12C4−Alkali Metal Cation Complexes Compared to Conformation 1[a]

no.[b]	sym	level	Li$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$
2	C_1	HF	1.48	2.09	4.27	4.34	2.45
		MP2//HF	1.73	2.21	18.94	18.30	2.26
		B3LYP	1.29	1.87	7.82	8.07	2.04
		MP2//B3LYP	1.82	2.22	18.96	18.26	2.26
		MP2	1.74	2.12	18.74	18.07	1.97
3	C_s	HF	−0.43	2.91	3.12	3.16	3.15
		MP2//HF	−0.18	3.26	3.11	3.18	3.19
		B3LYP	−0.43	2.67	2.75	2.78	2.84
		MP2//B3LYP	−0.09	3.02	3.12	3.21	3.19
		MP2	−0.16	2.81	2.96	3.01	3.03
4	C_s	HF	*c*	3.35	4.11	4.02	3.72
		MP2//HF		3.56	3.65	3.80	3.82
		B3LYP		3.47	4.19	4.23	3.93
		MP2//B3LYP		3.50	3.61	3.73	3.80
		MP2		3.46	3.39	3.46	3.43
5	C_{2v}	HF	1.50	3.39	4.51	4.88	5.06
		MP2//HF	1.72	3.86	4.54	5.00	5.31
		B3LYP	1.10	3.06	3.94	4.32	4.53
		MP2//B3LYP	1.84	3.80	4.56	5.06	5.33
		MP2	1.88	3.87	4.57	5.00	5.30
6	$C_{2v}{}^{d}$	HF	1.02	11.3	13.32	13.56	13.50
		MP2//HF	1.90	13.08	13.38	13.77	14.08
		B3LYP	0.23	11.08	13.04	13.42	13.28
		MP2//B3LYP	1.90	13.18	13.38	13.81	13.96
		MP2	1.98	13.04	13.19	13.60	13.80
7	C_1	HF	2.34	5.48	7.58	7.14	4.63
		MP2//HF	2.97	5.72	22.34	21.61	5.36
		B3LYP	2.28	5.44	11.47	11.31	4.82
		MP2//B3LYP	3.08	5.68	22.18	21.51	5.27
		MP2	2.94	5.60	22.02	21.18	20.62
8	C_s	HF	5.11	8.96	10.90	10.21	9.40
		MP2//HF	6.73	9.35	26.16	25.21	24.50
		B3LYP	5.03	8.64	14.49	14.01	13.17
		MP2//B3LYP	6.87	9.27	26.00	25.11	24.37
		MP2	6.54	9.28	25.62	24.74	24.14

[a] See corresponding footnote in Table 3. [b] Conformation number. [c] Converges to conformation **2**. [d] The Li$^+$ complex has a D_{2d} symmetry.

−Na^{+}[34,35] complexes exist in the C_4 conformation. A similar methodology was used for free 12c4, in which the measurement of the vibrational spectra and comparison between the experimental and calculated vibrational spectra of the metal complexes assuming any of the possible conformations of these complexes, conformations **1**−**8**, may aid in the prediction of which conformations of 12c4−alkali metal cations exist in solution and also in the solid phases. Such an experiment is being planned in our laboratory.[60] Notice that there is a clear disagreement between the experimental and calculated BEs of 12c4−Rb$^+$ and −Cs$^+$ complexes assuming that these complexes have a C_4 structure.[25]

It was reported for free 12c4 that the difference between the relative energies at the MP2/6-31+G* and MP2/6-31+G*//B3LYP/6-31+G* levels is not larger than 0.1 kcal/mol for most of the conformations considered. This is merely a reflection of the closeness of the MP2 and B3LYP optimized geometries. For conformations with larger relative energy difference, this was attributed to a larger difference between the MP2 and B3LYP optimized geometries. The advantage of the relation between the relative energies at the MP2/6-31+G* and MP2/6-31+G*//B3LYP/6-31+G* levels is that the cheaper MP2/6-31+G*//B3LYP/6-31+G* level can be used for the determination of the energy order of the predicted conformations for larger molecules, for example, 18c6, instead of the more expensive MP2/6-31+G* level. In the conformational analysis of the large 18c6,[39] computation of the optimized geometries at the MP2 level was prohibitive, except for conformations with high symmetry, and the energy order at the MP2/6-31+G*//B3LYP/6-31+G* level was used instead. For 12c4−alkali metal cation complexes, although the number of conformations considered is small, the relative energies in Table 4 show that the difference between the MP2/6-31+G* and MP2/6-31+G*//B3LYP/6-31+G* relative energies is not larger than 0.2 kcal/mol. This is with the exception of the K$^+$, Rb$^+$, and Cs$^+$ complexes of conformation **4**, where the difference is as large as 0.37 kcal/mol. In addition, for most of the conformations, the relative energies at the MP2/6-31+G* level are smaller than those at the MP2/6-31+G*//B3LYP/6-31+G* level. The relative energies at the MP2/6-31+G*//HF/6-31+G* level are also close to those at the MP2/6-31+G* and MP2/6-31+G*//B3LYP/6-31+G* levels. This is also observed at the other computational levels, the HF/6-31+G* and B3LYP/6-31+G* levels, but the differences are less systematic.

TABLE 5: Binding Enthalpies (kcal/mol) of the 12c4−Alkali Metal Cation Complexes[a]

no.[b]	sym	level	Li$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$
		exp[c]	−90 ± 12	−61 ± 3	−46 ± 3	−23 ± 3	−21 ± 2
1	C_4	HF	−92.9	−66.2	−45.8	−38.0	−31.7
		MP2//HF	−93.4	−64.7	−48.2	−40.6	−34.9
		B3LYP	−91.2	−65.5	−45.9	−37.5	−31.2
		MP2//B3LYP	−93.2	−64.5	−47.9	−40.3	−34.6
		MP2	−93.0	−64.8	−47.6	−40.0	−34.3
2	C_1	HF	−91.5	−64.2	−41.7	−33.8	−29.4
		MP2//HF	−91.7	−62.5	−29.3	−22.4	−32.7
		B3LYP	−89.9	−63.7	−38.2	−29.5	−29.2
		MP2//B3LYP	−91.5	−62.4	−29.0	−22.1	−32.4
		MP2	−91.3	−62.8	−28.9	−21.9	−32.4
3	C_s	HF	−90.1	−61.0	−41.1	−33.3	−27.2
		MP2//HF	−90.3	−59.2	−43.4	−35.8	−30.3
		B3LYP	−88.4	−60.6	−41.5	−33.1	−27.0
		MP2//B3LYP	−90.1	−59.2	−43.1	−35.5	−29.9
		MP2	−89.9	−59.4	−42.9	−35.5	−29.8
4	C_s	HF	*d*	−60.8	−40.1	−32.5	−26.8
		MP2//HF		−59.1	−42.6	−35.2	−29.9
		B3LYP		−60.0	−40.1	−31.7	−26.0
		MP2//B3LYP		−59.0	−42.3	−34.9	−29.6
		MP2		−59.3	−42.1	−34.6	−29.5
5	C_{2v}	HF	−88.1	−60.6	−39.7	−31.5	−25.2
		MP2//HF	−88.3	−58.6	−40.0	−34.0	−28.2
		B3LYP	−86.7	−60.2	−40.3	−31.6	−25.2
		MP2//B3LYP	−88.1	−58.5	−41.7	−33.6	−27.9
		MP2	−87.8	−58.7	−41.4	−33.3	−27.3
6	$C_{2v}{}^{e}$	HF	−88.7	−53.1	−30.8	−23.0	−16.8
		MP2//HF	−88.3	−49.9	−32.6	−24.7	−19.0
		B3LYP	−87.7	−52.7	−31.2	−22.6	−16.5
		MP2//B3LYP	−88.1	−49.6	−32.1	−24.3	−18.7
		MP2	−87.8	−49.5	−31.9	−24.1	−18.5
7	C_1	HF	−90.6	−60.6	−38.2	−30.9	−27.1
		MP2//HF	−90.4	−58.8	−25.6	−19.1	−29.8
		B3LYP	−88.9	−59.9	−34.4	−26.1	−26.3
		MP2//B3LYP	−90.1	−58.7	−25.4	−18.8	−29.5
		MP2	−90.0	−59.1	−25.1	−18.5	−13.6
8	C_s	HF	−87.7	−57.0	−34.3	−27.2	−22.7
		MP2//HF	−86.5	−55.1	−21.5	−15.2	−11.4
		B3LYP	−86.0	−56.6	−30.8	−22.9	−18.4
		MP2//B3LYP	−86.3	−55.0	−21.2	−14.9	−11.2
		MP2	−86.3	−55.3	−20.9	−14.6	−10.9

[a] See corresponding footnote in Table 3. [b] Conformation number. [c] Experimental binding enthalpy, refs 20−23. [d] Converges to conformation **2**. [e] The Li$^+$ complex has a D_{2d} symmetry.

Large difference of the relative energies between that obtained at the MP2/6-31+G* level and any of the HF/6-31+G* or B3LYP/6-31+G* levels can be attributed to large difference between the optimized geometries. For example, for conformation **7** of the 12c4−Cs$^+$ complex, two of the OCCO dihedral angles are calculated to be +65.4 and −46.9° at the HF/6-31+G* level and +61.7 and −52.0° at the MP2/6-31+G* level, respectively. In addition, as was reported for free 12c4,[27] contrary to earlier reports,[26] the correlation energy is necessary

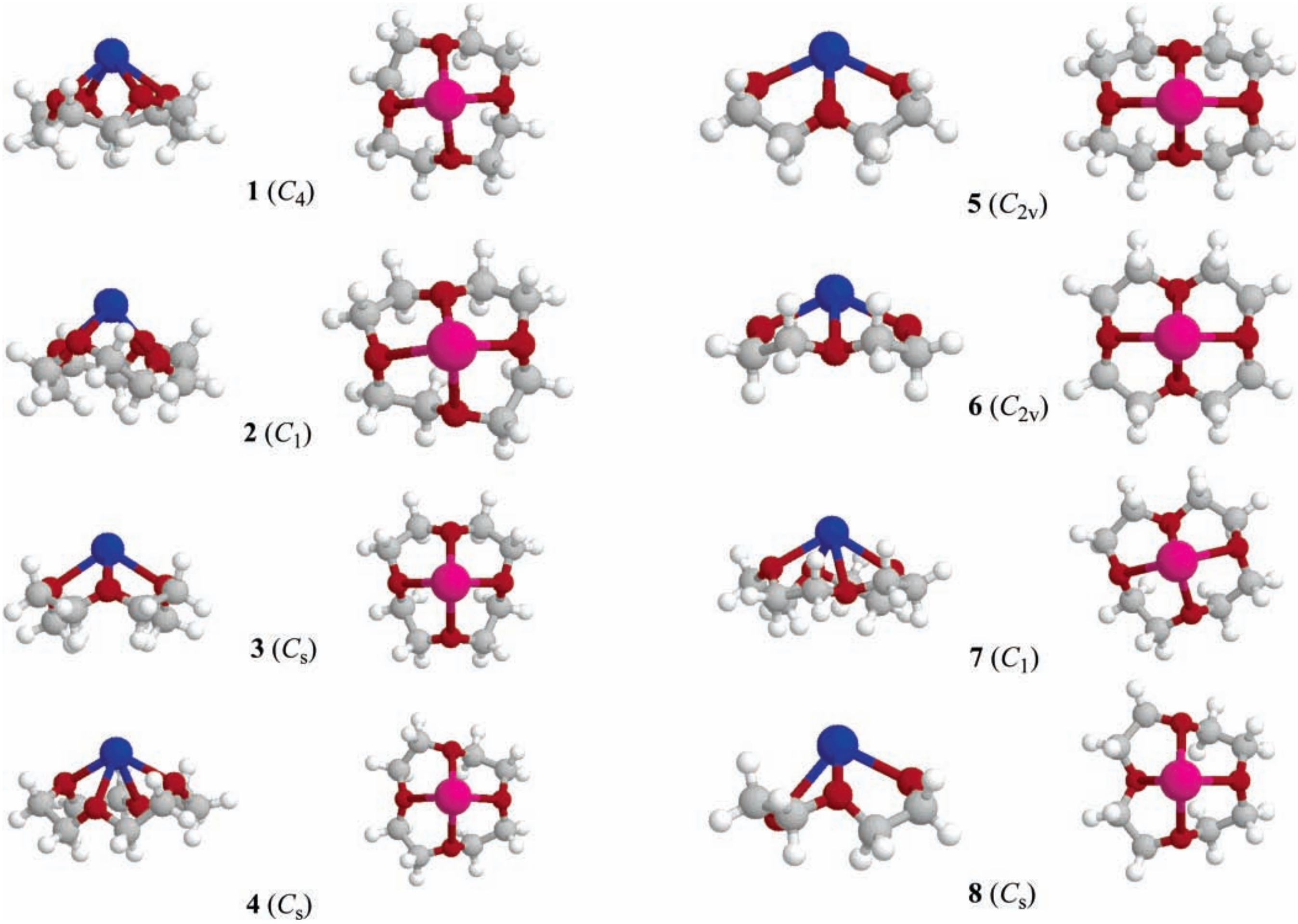

Figure 1. Structure of the 12c4−Na$^+$ (left, side view) and 12c4−Rb$^+$ (right, top view) complexes.

TABLE 6: M−O Bond Lengths (Å) of the 12c4−Alkali Metal Cation Complexes at the MP2/6-31+G* Level

no.[a]	sym	Li$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$	n[b]
1	C_4	2.018	2.394	2.707	2.930	3.144	4
2	C_1	1.984	2.367	2.678	3.017	3.246	1
		2.006	2.364	2.768	2.925	3.125	1
		2.030	2.398	2.694	2.889	3.086	1
		2.011	2.430	2.708	2.924	3.130	1
3	C_s	1.988	2.385	2.698	2.919	3.130	2
		1.968	2.441	2.768	3.008	3.240	1
		1.926	2.355	2.671	2.886	3.092	1
4	C_s	*c*	2.449	2.837	3.141	3.444	1
			2.370	2.676	2.889	3.096	2
			2.331	2.666	2.896	3.117	1
5	C_{2v}	1.978	2.412	2.771	3.024	3.274	2
		2.000	2.345	2.635	2.838	3.034	2
6	C_{2v}[d]	1.867	2.359	2.714	2.964	3.196	2
			2.348	2.692	2.929	3.158	2
7	C_1	2.007	2.420	2.766	3.001	3.235	1
		1.986	2.478	2.859	3.178	3.503	1
		1.925	2.298	2.615	2.827	3.030	1
		1.991	2.388	2.714	2.944	3.163	1
8	C_s	1.989	2.544	2.913	3.290	3.675	1
		1.896	2.275	2.582	2.790	2.985	1
		1.992	2.411	2.766	3.014	3.264	2

[a] Conformation number. [b] Number of M−O bonds due to symmetry. [c] Converges to conformation **2**. [d] The Li$^+$ complex has a D_{2d} symmetry.

for the accurate prediction of the relative energies of the predicted conformations. For example, for conformation **2** of the 12c4−K$^+$ complex, the calculated relative energies at the HF/6-31+G* and MP2/6-31+G*//HF/6-31+G* levels are 4.27 and 18.94 kcal/mol, respectively. As was mentioned above, the difference of the calculated relative energies for most of the conformations is not more than 0.5 kcal/mol.

The C_s conformation, conformation **3**, is predicted to be the lowest energy conformation, at all levels considered, for the 12c4−Li$^+$ complex, although the energy difference between this conformation and the C_4 conformation at the MP2/6-31+G* level is only 0.16 kcal/mol. In fact, conformations **1**, **2**, **4**, and **5** of the 12c4−Li$^+$ complex have energy difference of less than 2 kcal/mol, at all levels, from this lowest energy C_s conformation. Also conformations **2**−5 of all the 12c4−alkali metal cation complexes have energy differences of less than 5 kcal/mol from the C_4 lowest energy conformation. This is with the exception of conformation **2**, of C_1 symmetry, of the K$^+$ and Rb$^+$ complexes where the difference is much larger. It is clear that the correlation energy has a significant influence on the energy of this complex for the K$^+$ and Rb$^+$ cations. As was mentioned before, this indicates the importance of the inclusion of the electron correlation for the determination of the relative energies.

The calculated BE in Table 5 for the 12c4−Li$^+$ complex is in agreement with the relative energy in Table 4; that assuming conformation **3** of the 12c4−Li$^+$ complex, the best agreement between the calculated and experimental BEs is obtained. Due to the large uncertainty of the experimental BE of this complex, this excellent agreement can be fortuitous. NMR and IR studies have shown that the 12c4−Li$^+$ complex has a C_4 conformation.[33] The reason for this disagreement can be resolved by noticing that the conformation reported in ref 33 corresponds to the solid and solution phase measurements, the conformation reported in ref 20, of the BE determined experimentally, corresponds to the gas-phase measurement data, and the conformations reported in the current publication correspond to gas-phase isolated molecules at 0 K. Even with the large uncertainty of the experimental BE of the 12c4$-$Li$^+$ complex, the best agreement between the calculated and experimental BEs for the 12c4$-$Na$^+$ complex is also for conformation **3**, of C_s symmetry. This is in addition to conformation **4,** also of C_s symmetry.

For the 12c4$-$K$^+$ complex, the best agreement between the experimental and calculated BEs is for conformation **1**, of C_4 symmetry, followed by conformation **3**, of C_s symmetry. Notice that the difference between the experimental and calculated BEs of this complex for conformation **3** is within the uncertainty of the experimental BE, ±3 kcal/mol. For the Rb$^+$ and Cs$^+$ complexes, the difference between the experimental and calculated BEs at the MP2/6-31+G* level, assuming a C_4 structure of the complex, is 17 and 13 kcal/mol, respectively. The best agreement is obtained with conformation **6**, first proposed by Feller et al.[19,22,25] but no detailed structure or BEs were reported. The difference between the experimental and calculated MP2/6-31+G* BEs for the Rb$^+$ and Cs$^+$ complexes for this conformation is 1 and 3 kcal/mol, respectively. To rationalize the poor agreement between the calculated and experimental BEs assuming a C_4 conformation of the Rb$^+$ and Cs$^+$ complexes, Feller et al.[19,22,25] argued that sampling of the complexes during the spectral measurement puts these complexes in a high energy C_{2v} state, or conformation. As mentioned above this C_{2v} conformation presumably corresponds to conformation **6** in the current study. Notice that a good agreement between the calculated and experimental BEs is obtained for all $(H_2O)_n-$alkali metal cation complexes including those of the Rb$^+$ and Cs$^+$ complexes.[61]

A potential source of the disagreement between the experimental and calculated BEs for Rb$^+$ and Cs$^+$ complexes is the use of the effective core potential basis set. The optimized geometry and BE were calculated for the K$^+$ complex using the 6-31+G* basis set on all atoms, including the K atom, at the MP2 level for the C_4 conformation. No similar basis set is available in for the Rb or Cs atoms. The calculated BE and K$-$O bond length were 47.6 kcal/mol and 2.707 Å, respectively, which are quite close to those in Tables 5 and 6, respectively. In addition, the M$-$O bond lengths of the Rb$^+$ and Cs$^+$ complexes using the effective core potential basis set, listed in Table 6, are predicted in line with what is expected for the increase of the M$-$O bond length with the increase of the metal cation size.

Comparing the BEs calculated at the different levels indicates that those calculated at the MP2/6-31+G*//B3LYP/6-31+G* level are predicted to be larger than to those calculated at the MP2/6-31+G* level, the highest level of theory considered in this work, by not more than 0.3 kcal/mol. This is with the exception of those calculated for the 12c4$-$Na$^+$ complex, which are predicted to be smaller by about 0.2 kcal/mol on the average and not more than 0.4 kcal/mol at the highest. Also, for conformation **7** of the 12c4$-$Cs$^+$ complex, the difference between the MP2/6-31+G* and MP2/6-31+G*//B3LYP/6-31+G* BE is 15.9 kcal/mol. As was mentioned before, this C_1 conformation undergoes a large geometry change during the geometry optimization at the different HF, B3LYP, and MP2 levels. The same large difference is observed at the HF level for the same conformation of the 12c4$-$Cs$^+$ complex. The calculated BEs at the MP2/6-31+G*//HF/6-31+G* level, compared to those calculated at the MP2/6-31+G* level, are predicted to be larger by 0.5 kcal/mol on the average and 0.9 kcal/mol at the highest, which are larger even than those predicted at the MP2/6-31+G*//B3LYP/6-31+G* level. Similar to that at the MP2/6-31+G*//B3LYP/6-31+G* level, this is with the exception of the 12c4$-$Na$^+$ complex, which are predicted to be smaller by about 0.3 kcal/mol. The difference between the BEs calculated at both the HF or B3LYP levels and that at the MP2 level is larger without any specific level performing better.

TABLE 7: M$-$O Bond Lengths (Å) of the 12c4$-$Alkali Metal Cation Complexes for Conformation 1 at the HF, B3LYP and MP2 Levels Using the 6-31+G* Basis Set

method	Li$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$
HF	2.001	2.341	2.759	2.990	3.223
B3LYP	2.012	2.334	2.745	2.986	3.226
MP2	2.018	2.394	2.707	2.930	3.144

TABLE 8: M$-$O Bond Lengths (Å) of the 12c4$-$Alkali Metal Cation Complexes for Conformation 1 at the MP2/6-31+G* Level

method	Li$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$
MP2(fc)	2.018	2.394	2.708	2.930	3.144
MP2(full)	1.973	2.306	2.707	2.928	3.141

TABLE 9: Binding Enthalpies (kcal/mol) of the 12c4$-$Alkali Metal Cation Complexes for Conformation 1 at the MP2/6-31+G* Level

method	Li$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$
MP2(fc)	−93.0	−64.8	−47.6	−40.0	−34.3
MP2(full)	−94.2	−66.2	−47.6	−40.0	−34.3

The calculated bond lengths presented in Table 6, for the eight conformations considered, show an increase of the M$-$O bond length with the increase of the alkali metal cation size. This is reflected by the displacement of the alkali metal cation away from the center of the 12c4 ring, Figure 1. This is with the exception of the D_{2d} conformation of the Li$^+$ complex where the Li$^+$ cation is in the ring plane of the molecule. Consequently, this complex is characterized by the shortest M$-$O bond length. There are two separate reports of X-ray studies of the structure of the 12c4$-$Na$^+$ complex.[34,35] Both reports indicate a C_4 conformation of the complex. The first observes a Na$-$O bond length of 2.473$-$2.517 Å[34] and the second reports a Na$-$O bond length of 2.485 Å.[35] Both values agree well, to within 0.1 Å, to that in Table 6, at the MP2/6-31+G* level, for the same complex. Table 7 shows a comparison between the M$-$O bond lengths, where M refers to alkali metal cation, calculated at the HF, B3LYP, and MP2 levels using the 6-31+G* basis set for the C_4 conformation. It is clear that the M$-$O bond lengths calculated at the HF and B3LYP levels are close to each other to within 0.015 Å. The M$-$O bond lengths predicted at the MP2 level differ significantly from those predicted at the HF and B3LYP. This is with the exception of that for the Li$^+$ complex. While the M$-$O bond lengths calculated for the K$^+$, Rb$^+$, and Cs$^+$ complexes at the MP2 level are predicted to be up to 0.08 Å too long, that calculated for Na$^+$ complex is predicted to be 0.06 Å too short.

To investigate the effect of neglecting the core electrons on the optimized geometries and BEs predicted at the MP2 level, geometries were optimized for conformation **1** at the MP2(full)/6-31+G* level where all electrons, valence and core, are included in the correlation calculation. The calculated bond lengths and BEs are given in Tables 8 and 9, respectively. The data in Table 8 indicate that the predicted M$-$O bond lengths of the C_4 conformation at the MP2(full) and MP2(fc) levels are too close to each other to within 0.003 Å for the K$^+$, Rb$^+$, and Cs$^+$ complexes. For the Li$^+$ and Na$^+$ complexes, those calculated with the full option are predicted to be 0.045 and

0.088 Å, respectively, too short compared to those with the frozen core option. The difference between the BEs calculated at the MP2(full) and MP2(fc) levels is a reflection of the difference between the calculated M−O bond lengths, and that predicted with the full option is larger for the 12c4−Li$^+$ and −Na$^+$ complexes than for the 12c4−K$^+$, −Rb$^+$, and −Cs$^+$ complexes. Geometries were also optimized using the 6-31+G* basis set on all atoms, including the K atom, for the C_4 conformation of the 12c4−K$^+$ complex at the MP2(full) and MP2(fc) levels. The calculated K−O bond length was 2.704/2.708 Å at the MP2(full)/MP2(fc) level, which in principle agrees with what is obtained by the other basis set.

Conclusion

In this research report, more conformations of 12c4−alkali metal cation complexes were considered and at higher levels of theory too, to the best of our knowledge, than any other previous report. The calculated relative energies predict a C_4 structure for the 12c4−Na$^+$, −K$^+$, −Rb$^+$, and −Cs$^+$ complexes and a C_s structure for the 12c4−Li$^+$ complex to be the lowest energy conformations. The calculated BE of the 12c4−Li$^+$ complex supports this conclusion, although the calculated BE assuming a C_4 conformation of the complex is close to the experimental value, within the uncertainty of the BE determined experimentally. For the 12c4−Na$^+$ complex, the best agreement between the calculated and experimental BEs is for the C_s conformation, in addition to another conformation of C_s symmetry. On the other hand, the best agreement between the calculated and experimental BEs for the 12c4−K$^+$ complex is for the C_4 conformation. As is the case in the previous reports,[19,22,25] poor agreement between the calculated and experimental BEs is obtained for the Rb$^+$ and Cs$^+$ complexes assuming a C_4 structure of the complex. Instead, a good agreement is obtained assuming a C_{2v} conformation. It is hoped that measurement of the vibrational spectra, as being planned in our laboratory,[60] may resolve these conflicts.

The calculated relative energies at the MP2/6-31+G* and MP2/6-31+G*//B3LYP/6-31+G* levels are very close to each other to within 0.2 kcal/mol. This is only with minor exceptions attributed to the difference between the MP2 and B3LYP optimized geometries. Also, the calculated BEs at the MP2/6-31+G*//B3LYP/6-31+G* level are predicted to be larger compared to those obtained at the MP2/6-31+G* level by not more than 0.3 kcal/mol. This is with the exception of those calculated for the 12c4−Na$^+$ complex, which are predicted to be smaller by about 0.2 kcal/mol on the average and not more than 0.4 kcal/mol at the highest. This indicates that the cheaper MP2/6-31+G*//B3LYP/6-31+G* level can be used for the determination of the relative energies and BEs for larger molecules instead of the more expensive MP2/6-31+G* level. In fact, a similar relationship for the relative energies was reported for free 12c4 but the difference between the MP2/6-31+G* and MP2/6-31+G*//B3LYP/6-31+G* relative energies was only 0.1 kcal/mol.[27]

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