

## Non Bonded Interaction and Charge Density Analysis of Alkali Metal Cations with Crown Ethers (12c4, 15c5 and 18c6); A Nano Approach

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### Abstract

In this account 12-crown-4 (12c4), 15-crown-5 (15c5) and 18-crown-6 (18c6), their cluster complexes with  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  with general chemical formula as  $[\text{M}(\text{crown ether})]^+$  and the water solvated complexes of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  are theoretically studied. The chemical properties of crown ether complexes of Li, Na and K cations are compared with those of water-solvated complexes of these species. The B3LYP/6-31+G(d,p) level of calculation has been used for obtaining equilibrium geometries and  $\rho(r)$  functions (electron density distributions). By the aid of fundamental physical theorems implemented in the Quantum Theory of Atoms in Molecules (QTAIM), the structures and the physical nature of the chemical bonds have been determined for the abovementioned species at the B3LYP/6-31+G(d,p) computational level. These results establish the Metal-oxygen in all complexes in this work as ionic. Also  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  have coordination number of 4 with 12c4 and possess the coordination number of 5 with 15c5. But the  $\text{Li}^+$  shows the coordination number of 3 with 18c6 crown ether and  $\text{Na}^+$  and  $\text{K}^+$  exhibits the coordination number of 6.

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**Keywords:** Molecular Graph, QTAIM, Chemical Bond, Coordination, crown ether, Alkali metal, Cluster

### Introduction

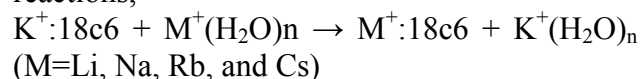
Crown ethers have received widespread attention since they were first characterized by Pedersen in 1967 [1-2]. Much of this interest comes from their ability to selectively bind to various Cations in the solution, depending in part on (1) the size of the crown ether cavity, (2) a subtle balance between Cation-ether and Cation-water interactions, (3) the presence of the substituent on the ligand backbone which alter the crown's electronic environment, (4) the type of the donor site(s) in the ring (e.g., oxygen, nitrogen, sulfur) that line the cavity, and (5) polarity of the solvent [3-7].

This crown ether/ion specificity can also serve as a simple model for understanding the host-guest recognition in enzymes [6]. Crown ethers are of particular interest to research efforts in environmental remediation. For instance, strontium-90 and cesium-137 are the two major generators of heat in nuclear waste which complicates disposal. A more thorough understanding of Cation/crown ether solution chemistry may provide the basis for rational design of new ligands useful in high level separation of these and other radionuclides from complex waste streams and hazardous waste storage facilities. One example of the use of

crown ethers for radionuclide separation is the strontium extraction (SREX) process, described by Horowitz and co-workers, [8] which uses di-tert-butylcyclohexano-18-crown-6 for recovering strontium-90 from acidic solution. Wai and co-workers [9] have also presented a wealth of data on the selective extraction and separation of the lanthanide and actinide elements using ionizable crown ethers. There is also a growing interest in the use of crown ethers, cryptands, and other ligands for radio-immunotherapy treatment of carcinomas [10]. The immunoconjugate consists of a ligand-radionuclide-cation (e.g.,  $^{224}\text{Ra}^{2+}$ ) complex that is covalently attached to a monoclonal antibody, specific for tumor antigens. The immunoconjugate selectively binds to the tumor, delivering therapeutic doses of radionuclide to the tumor site, where the subsequent decay of the radionuclide inactivates tumor cells. By directly attacking the site, this treatment spares normal tissue that is generally destroyed in conventional radiation therapy. Fluoroionophores, consisting of a fluorophore linked to an ionophore (e.g., crown ether), represent another interesting use for crown ethers and related macrocyclic ligands [11]. Measurable changes in the photophysical properties of the fluorophore upon ion binding by the ionophore may be useful for specific ion recognition in the development of sensors [6]. There is a wealth of thermodynamic [12,13] and structural data [14] for a host of crown ethers. Computational chemists have also focused their efforts on crown ethers as these molecules are perhaps the simplest that exhibit enzyme-like specificity. In particular, 18-crown-6 (18c6) has been the focus of a number of molecular mechanics, [15,16] molecular dynamics, [17-22] Monte Carlo [23,24] and electronic structure investigations [3,4,25-27]. These have provided a rather detailed description of the important conformations sampled in both gas- and condensed-phases and of the crown ether interactions with Cations and solvent molecules. Yamabe et al. [28] has reported a CNDO/2 study of the gas-phase crown ether and its interaction with  $\text{Na}^+$  and  $\text{K}^+$ . Their calculations

suggested that the charge transfer is largely responsible for the Cation crown ether interaction and that selectivity of 18c6 is strongly influenced by competition between the crown ether and the solvent molecules for the Cation. These views were subsequently corroborated by the same authors using minimal basis set ab initio methods [29]. Ha and Chakraborty [30] examined the interaction of 18c6 with ammonium Cation. Partial geometry optimizations of the crown ether and its Cation complex were performed with a density functional theory approach to generate a potential energy function for subsequent Monte Carlo simulations [24].

In two theoretical studies, the gas phase binding preferences of 18-crown-6 (18c6) for alkali metal Cations [3] and alkaline earth dications [4], were computed for the first time with correlated ab initio techniques. Contrary to experimental observations performed in aqueous solution, where potassium and barium are the preferred species, gas phase calculations show that the 18c6 binds  $\text{Li}^+$  and  $\text{Mg}^{2+}$  most strongly among the two ionic sequences ( $\text{Li}^+\text{-Cs}^+$  and  $\text{Mg}^{2+}\text{-Ra}^{2+}$ ) studied. By considering the ion exchange reactions,



or the analogous set of reactions for  $\text{Ba}^{2+}$ , the aqueous phase binding preferences were qualitatively reproduced with as few as four waters of hydration. In the next study, Feller [5] considered the consequences of (1) increasing the number of the waters (n) in order to complete the first solvation shell around  $\text{K}^+$  and  $\text{Rb}^+$  and (2) incorporating a small number of water molecules in the metal-crown complex, i.e. micro solvating the crown.

In another study, Feller and co workers [31] have investigated complexes involving the 12-crown-4 (12c4) macrocycle with alkali metal cations. Although good agreement was found in general, experimental and theoretical bond dissociation enthalpies for the heavier cations sometimes differed by as much as 14 kcal/mol or more. Higher-lying conformers of  $\text{Rb}^+(\text{12c4})$  and  $\text{Cs}^+(\text{12c4})$  were identified as possible causes

for the discrepancy between theory and experiment for these species.

Recently, The electromagnetic non-bounded interactions of the complexes inside the nano

### Methods and Computations

B3LYP/6-31+G(d,p) model were used for all steps of modeling in this work. The excellent performance of the cited model in producing the reliable molecular properties at reasonable computation time with non-expensive hardware facilities was the main reason for choosing this model. 12c4, 15c5 and 18c6 crown ethers (Figure 1) and their cluster complexes with  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  (Figures 3, 5 and 7) and also the water solvation complex of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  (Figures 2, 4 and 6) are the species used in this theoretical study. The optimized geometries have been characterized by frequency computations. The related wave function files in each case were produced at the end. The electron densities of all species, obtained from the B3LYP/6-31+G(d,p) computations, were analyzed in the framework of the Quantum Theory of Atoms in Molecules, QTAIM, [34]. All DFT computations were performed using PC GAMESS7.1 firefly [35]. The electron density analysis were done using the AIM2000 software [36].

### Results and Discussion

Since this paper is based on QTAIM methodology, some relevant important points of this theory seem worth-mentioning although, a detailed discussion may be found elsewhere [34]. By applying the Schwinger's principle of stationary action in quantum mechanics, Bader and coworkers have demonstrated that the total electron density of molecule ( $\rho(r)$ ) is divided to 3D parts with well-defined borders [34]. All these parts or fragments, obey the laws of quantum mechanics and the sum of their properties (the expectation values of Hermitian operators) produce the corresponding molecular values [34]. In brief, the theory of open quantum systems allows the division of molecule (as a system) to its fragments (as subsystems) uniquely. Therefore, this partitioning scheme does not depend on how the Schrödinger

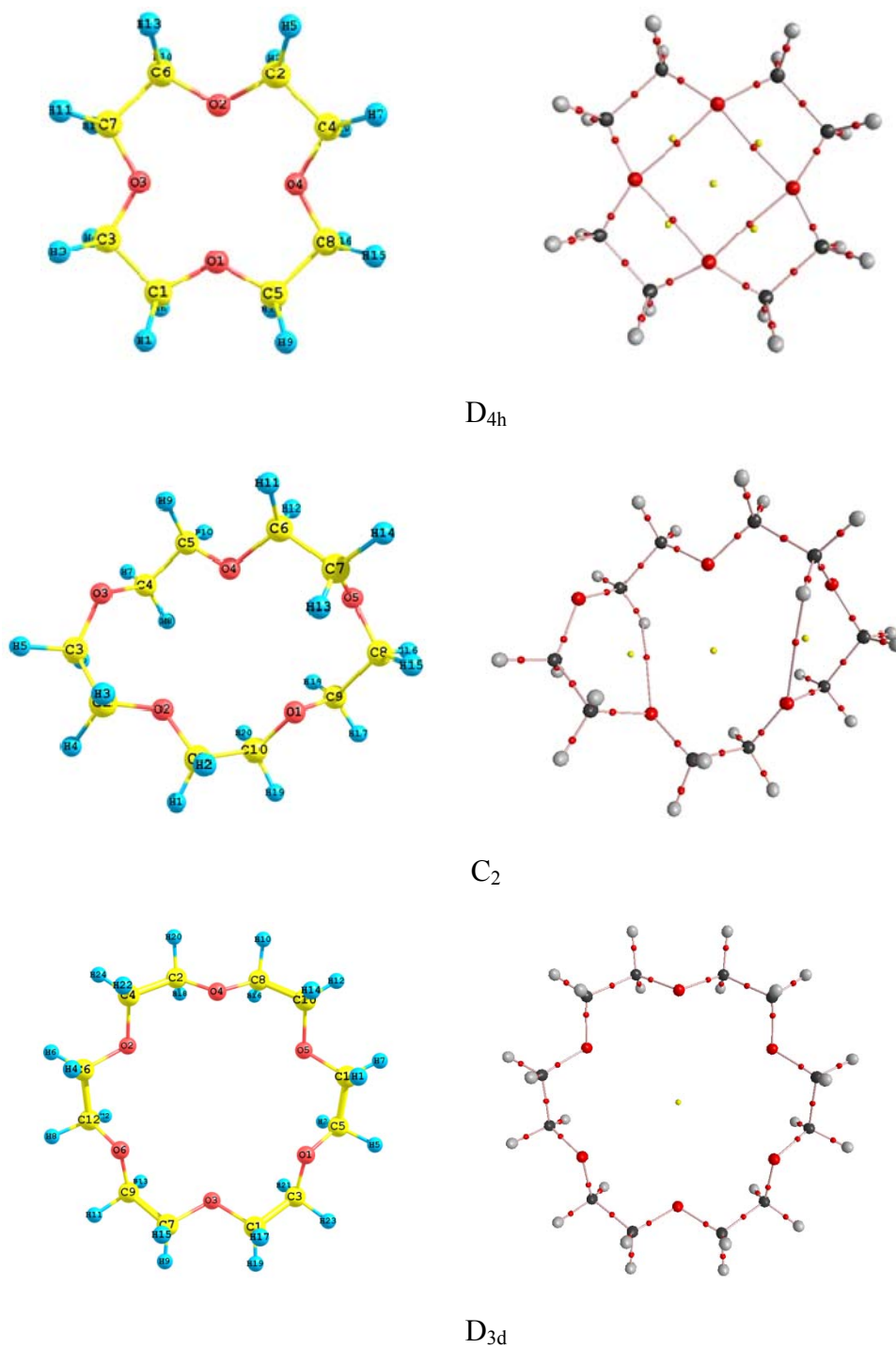
ring have been investigated in point of correlations between structural, electronic and spectral properties to identify the characteristics of hyperfine electronic structure.[32,33].

equation is solved (it is "method" independent) [34]. In comparison to known experimental facts, Bader proposed these fragments as the "chemical atoms" and the theory was called "Quantum Theory of Atoms in Molecules" [34]. Topological analysis of all complexes was first started by searching the critical points (CP) on  $\rho(r)$ . The Poincare-Hopf rule [32,35] was satisfied in all cases:

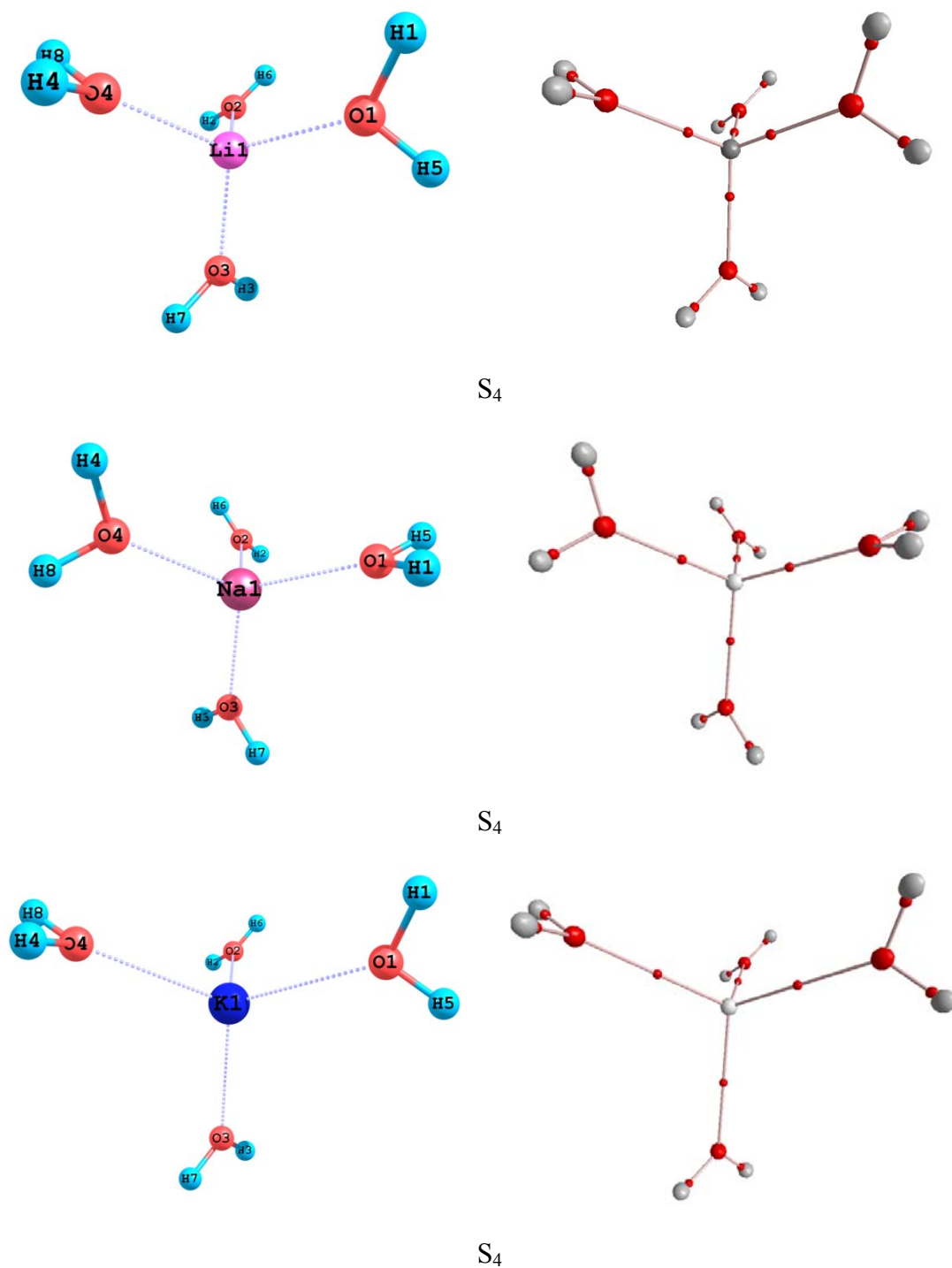
$$N-b+r-c = 1 \quad (1)$$

Where N is the number of nuclei, b is the number of bond critical points (BCPs), r is the number of ring critical points (RCPs) and c is the number of cage critical points (CCPs). The mathematical properties of the critical points of each cluster complex are listed in Tables 1-3, the corresponding molecular geometries and molecular graphs are depicted in Figures 2-6. The molecular graph provides the structure of the complex based on the network of bond paths. The molecular graphs show that  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  interact with 4 oxygen atoms in 12c4 (Figure 3) and with 5 oxygen atoms in 15c5 (Figure 5). Also the molecular graphs show that the  $\text{Li}^+$  interacts with 3 oxygen atoms while this number is 6 for  $\text{Na}^+$  or  $\text{K}^+$  (Figure 7). We examined another geometry of  $[\text{Li}(18c6)]^+$  complex in which the  $\text{Li}^+$  was kept at the center of the crown ether ring (Figure 8 and Table 4). This geometry exhibited 2 imaginary frequency at B3LYP/6-31+G(d,p) level. The molecular graph of this geometry shows the interaction of  $\text{Li}^+$  with 6 oxygen atoms (Figure 8). Usually  $\text{Li}^+$  most stable complexes are the ones having the 4 coordinated  $\text{Li}^+$ . This is consistent with the results of our topological analysis in which  $\text{Li}^+$  prefers position with low coordination number (less than 6) inside the crown ether ring.

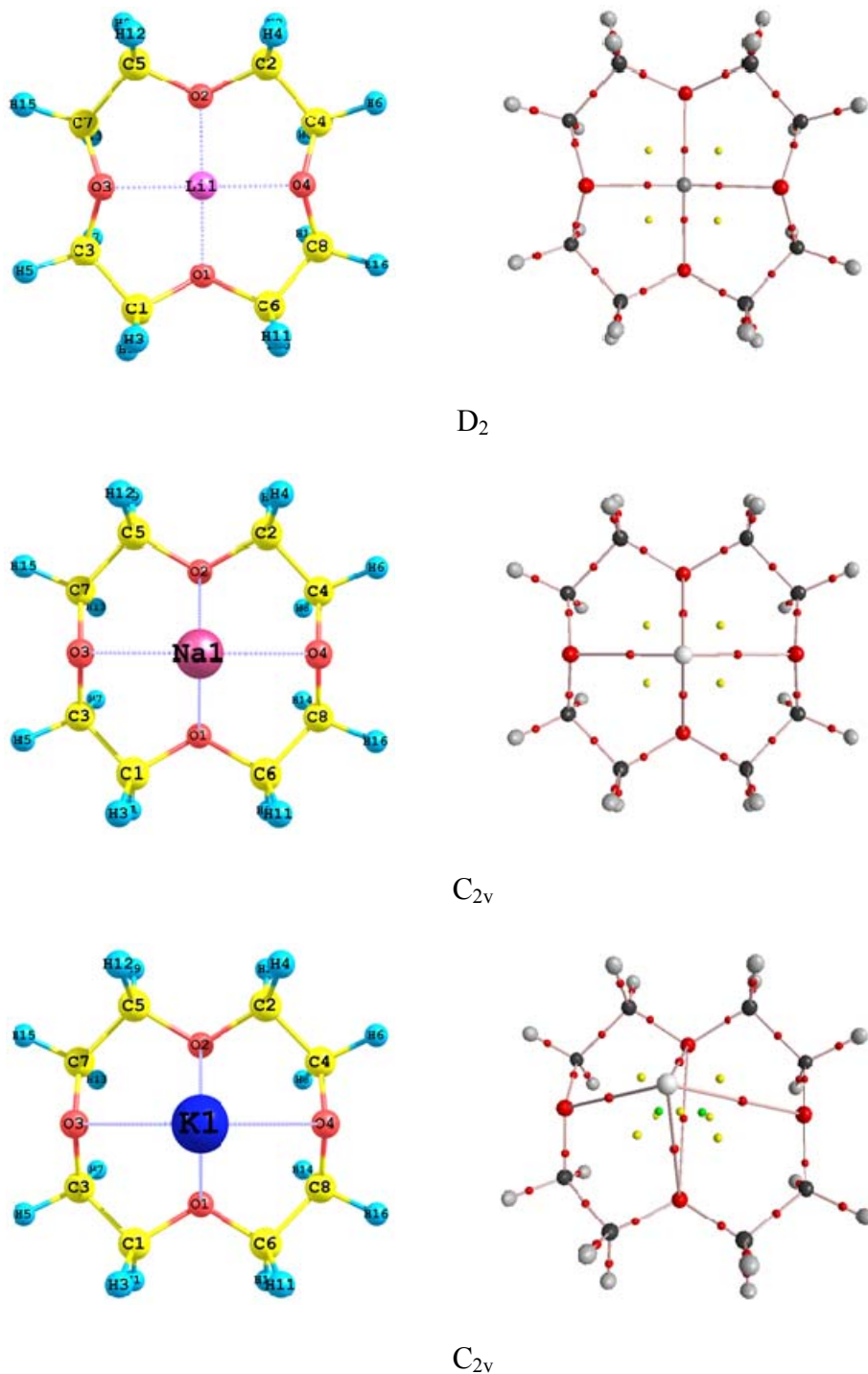
The interactions of all metal-oxygen atoms in all complexes are characterized by low values of electron density at the positions of BCPs ( $\rho$ )



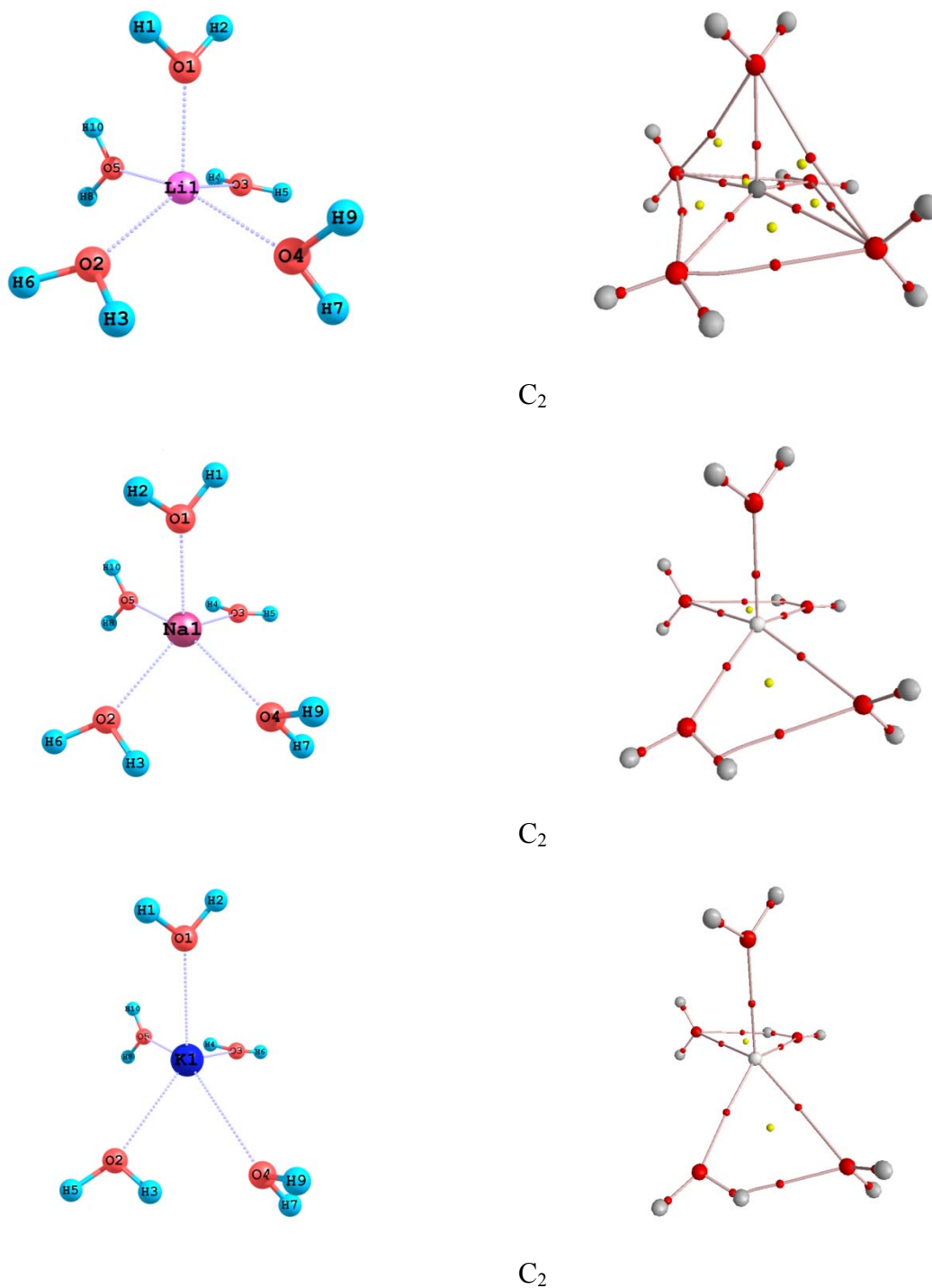
**Figure 1.** The optimized geometries (left) and the molecular graphs (right) for 12c4 (top), 15c5 (middle) and 18c6 (down) crown ethers at B3LYP/6-31+G(d,p). 12c4 have five imaginary frequencies ( $79.0$ ,  $152.1$ ,  $245.7$ ,  $245.7$  and  $298.8$   $\text{cm}^{-1}$ )



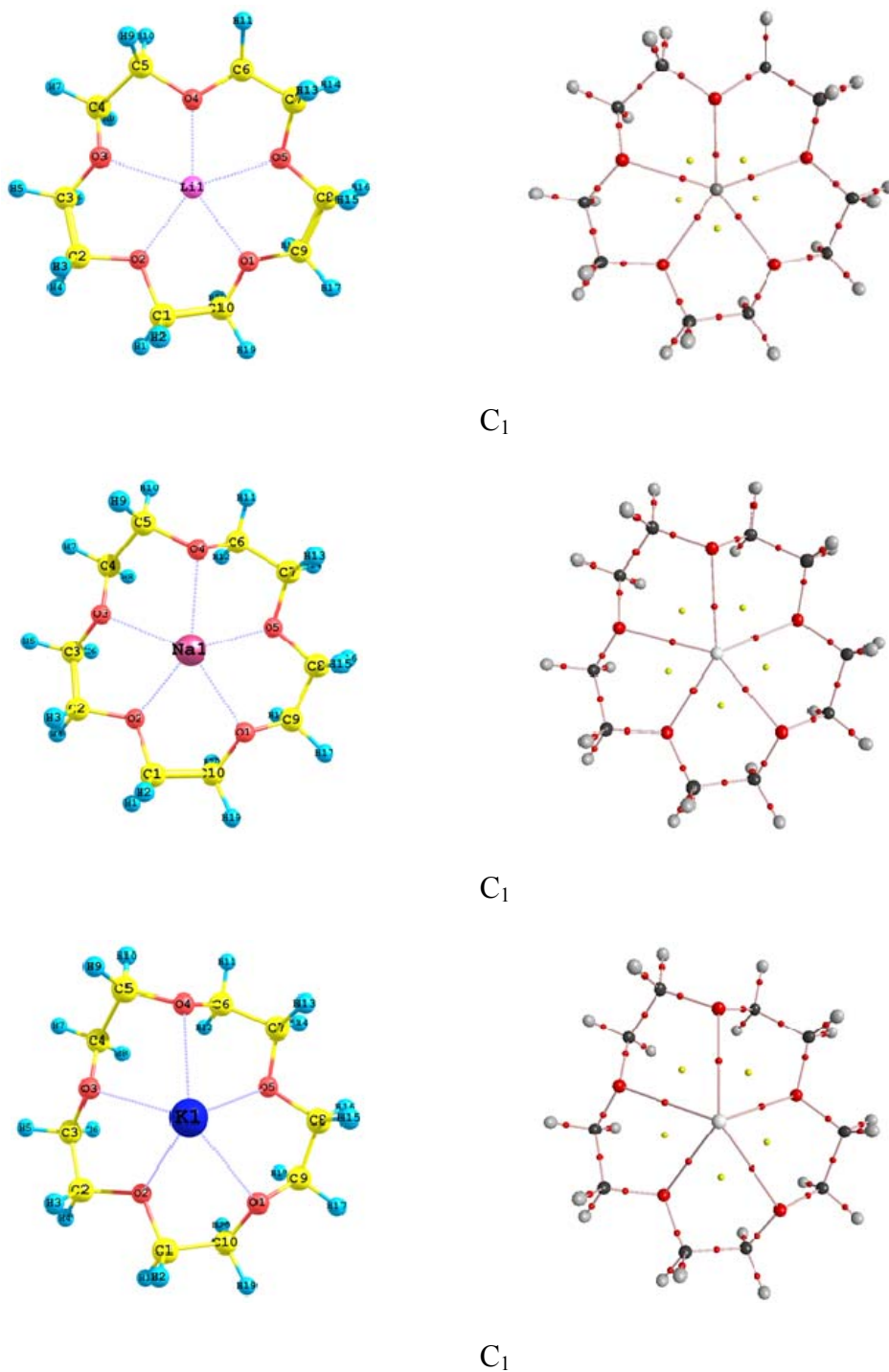
**Figure 2.** The optimized geometries (left) and the Molecular graphs (right) for  $[M(H_2O)_4]^+$  complexes ( $M=Li, Na, K$ ) at B3LYP/6-31+G(d,p)



**Figure 3.** The optimized geometries (left) and the Molecular graphs (right) for  $[M(12c4)]^+$  cluster complexes (M=Li, Na, K) at B3LYP/6-31+G(d,p).

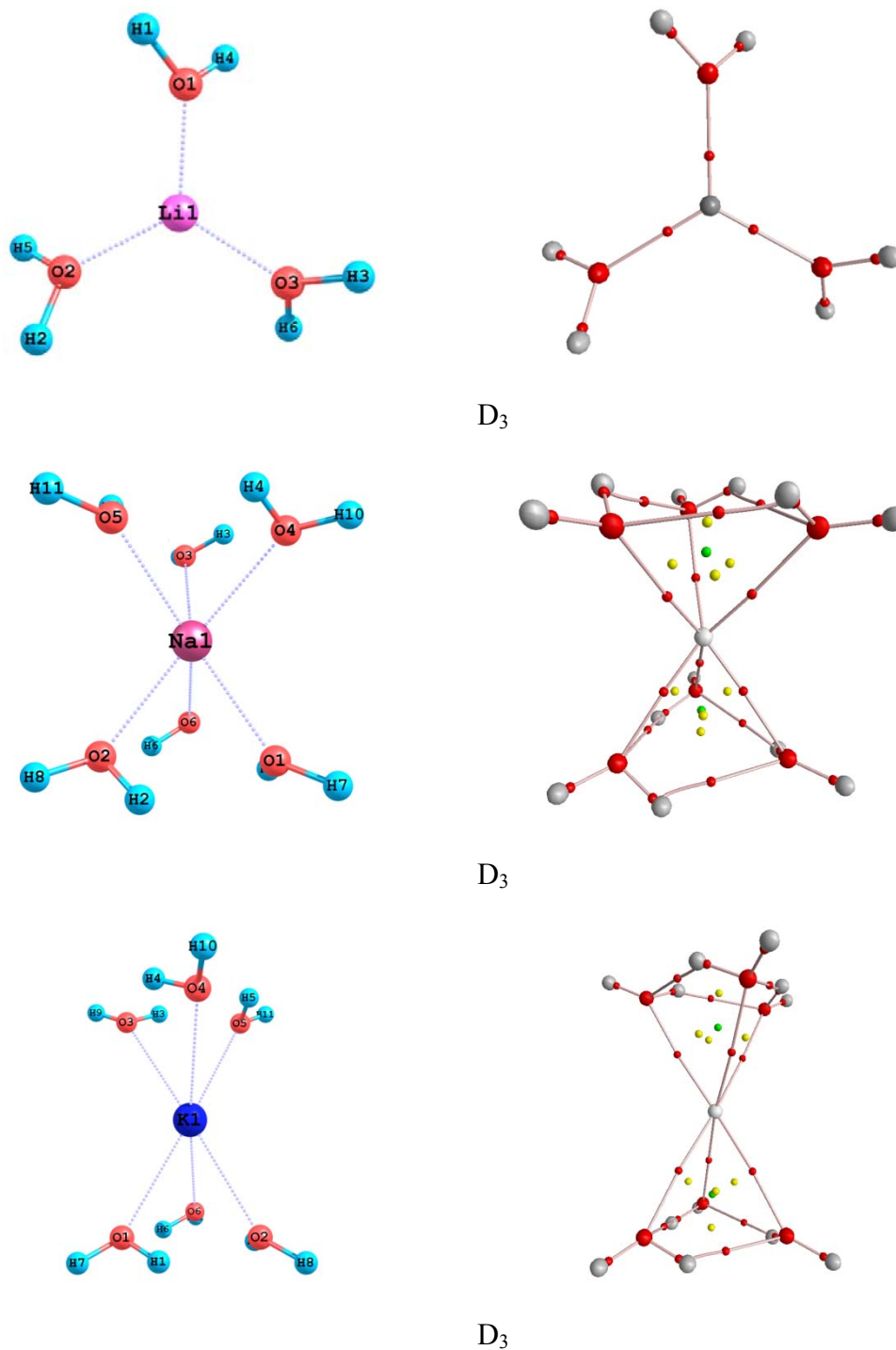


**Figure 4.** The optimized geometries (left) and the Molecular graphs (right) for  $[M(H_2O)_5]^+$  complexes (M=Li, Na, K) at B3LYP/6-31+G(d,p)

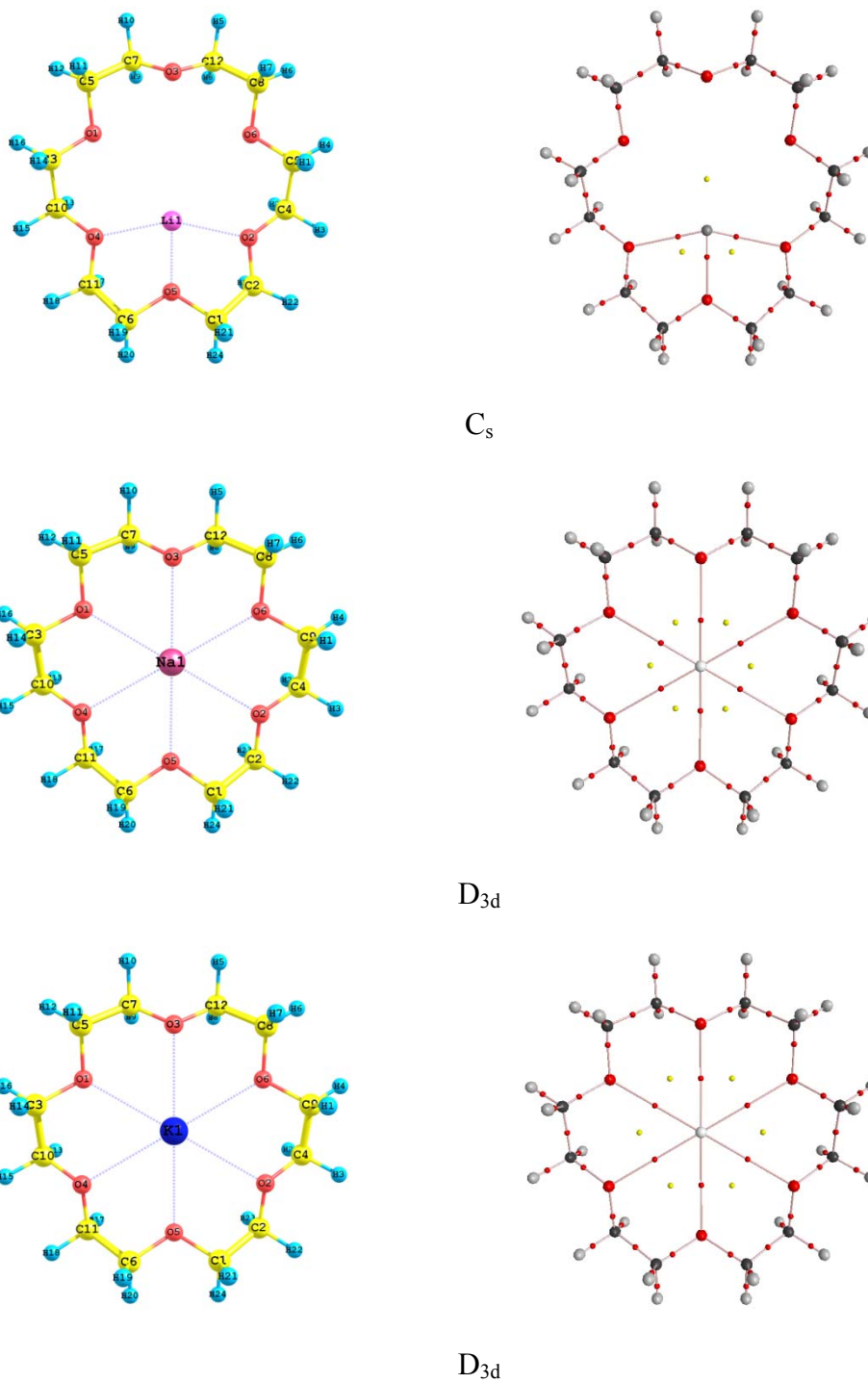


**Figure 5.** The optimized geometries (left) and the Molecular graphs (right) for  $[M(15c5)]^+$  cluster complexes (M=Li, Na, K) at B3LYP/6-31+G(d,p)

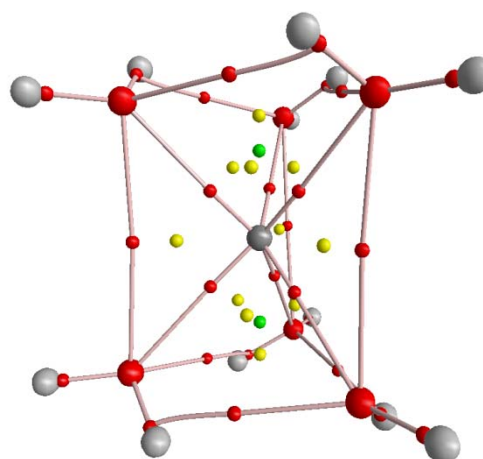
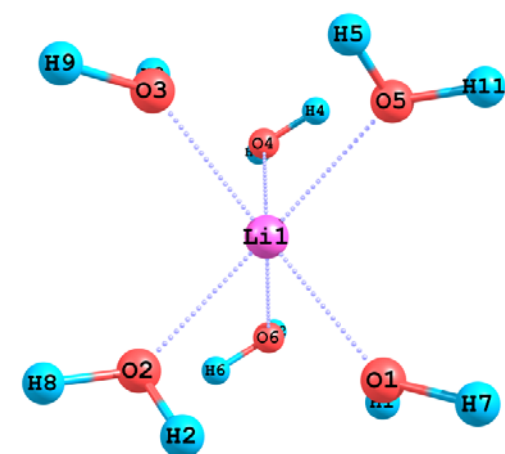
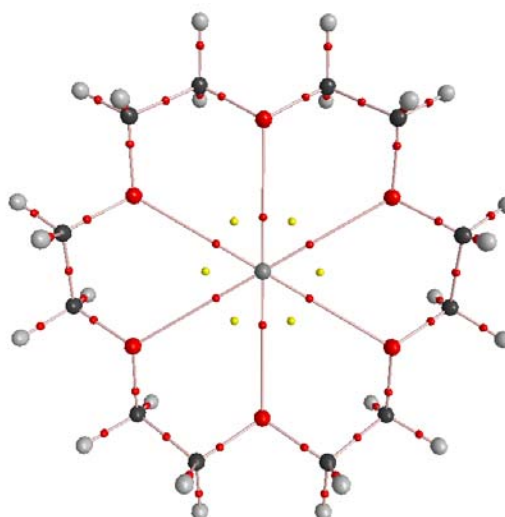
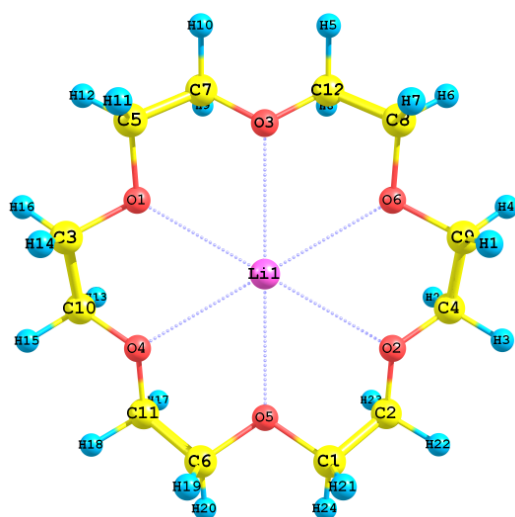




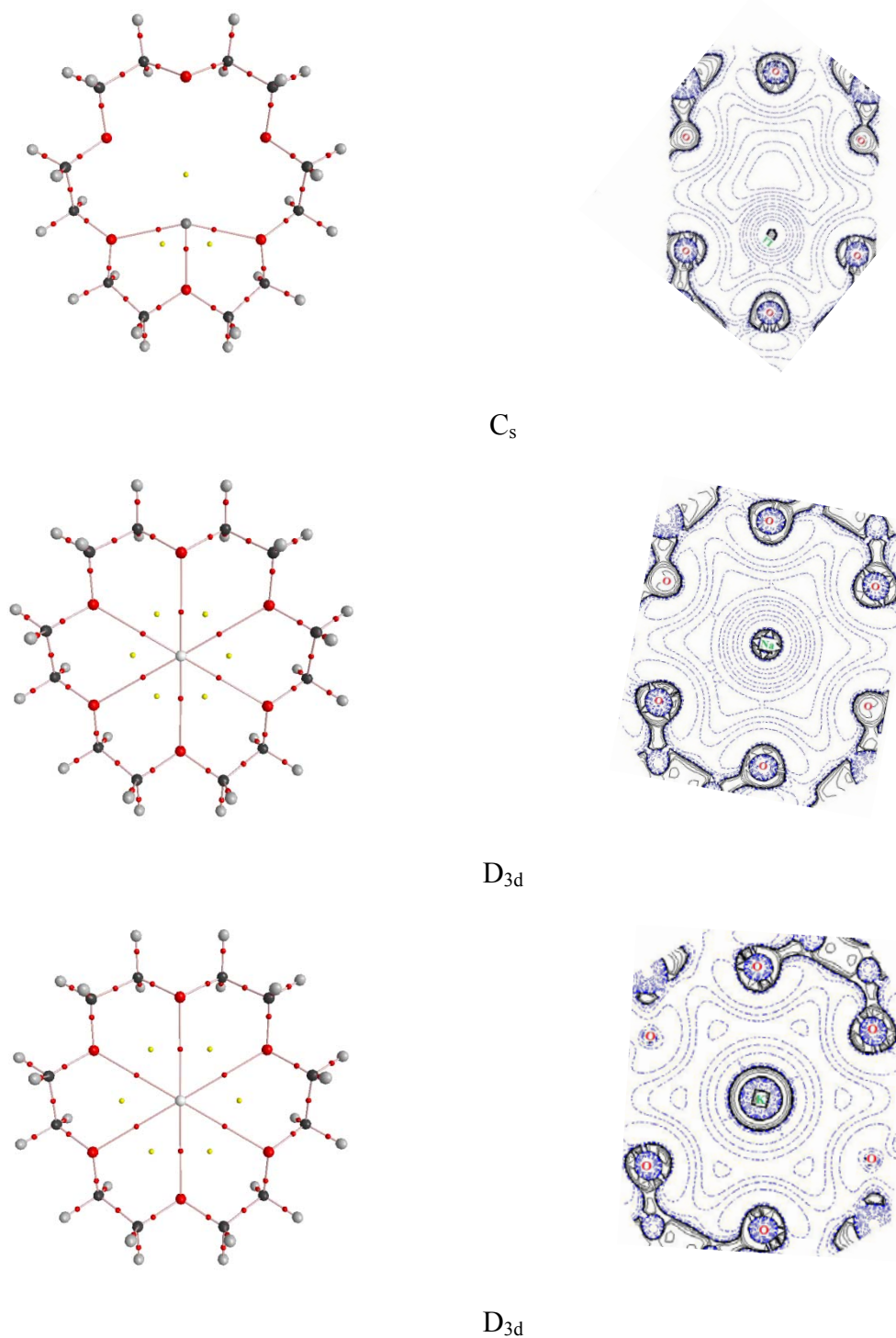
**Figure 6.** The optimized geometries (left) and the Molecular graphs (right) for  $[\text{Li}(\text{H}_2\text{O})_3]^+$  and  $[\text{M}(\text{H}_2\text{O})_6]^+$  complexes (M=Na, K) at B3LYP/6-31+G(d,p)



**Figure 7.** The optimized geometries (right) and the Molecular graphs (left) for  $[M(18c6)]^+$  cluster complexes (M=Li, Na, K) at B3LYP/6-31+G(d,p)

 $D_3$  $D_{3d}$ 

**Figure 8.** The optimized geometriy (right) and the Molecular graph (left) for  $[\text{Li}(\text{H}_2\text{O})_6]^+$  and  $[\text{Li}(18\text{c}6)]^+$  cluster complexes at B3LYP/6-31+G(d,p).  $[\text{Li}(18\text{c}6)]^+$  complex has two imaginary frequencies ( $187.2$  and  $186.3 \text{ cm}^{-1}$ )



**Figure 9.** The molecular graphs (left) and the Laplacian maps (right) for  $[M(18c6)]^+$  cluster complexes ( $M=Li, Na, K$ ) at B3LYP/6-31+G(d,p). Dashed lines are the lines of positive Laplacian.

**Table 1.** The topological mathematical characteristics ( $\rho_b$  and  $\nabla^2\rho_b$ ) at bond critical points (BCPs) for  $[\text{M}(\text{H}_2\text{O})_4]^+$  and  $[\text{M}(12\text{c}4)]^+$  cluster complexes (M=Li, Na, K) at B3LYP/6-31+G(d,p)

Complexes	Connected atoms	Inter nuclear distances (Å)	$\rho_b$ (a.u.)	$\frac{1}{4}\nabla^2\rho_b$
$[\text{Li}(\text{H}_2\text{O})_4]^+$	Li-O1	1.959	0.025	0.045
	Li-O2	1.959	0.025	0.045
	Li-O3	1.959	0.025	0.045
	Li-O4	1.959	0.025	0.045
$[\text{Li}(12\text{c}4)]^+$	Li-O1	1.872	0.036	0.065
	Li-O2	1.872	0.036	0.065
	Li-O3	1.872	0.036	0.065
	Li-O4	1.872	0.036	0.065
$[\text{Na}(\text{H}_2\text{O})_4]^+$	Na-O1	2.293	0.021	0.033
	Na-O2	2.293	0.021	0.033
	Na-O3	2.293	0.021	0.033
	Na-O4	2.293	0.021	0.033
$[\text{Na}(12\text{c}4)]^+$	Na-O1	2.296	0.023	0.035
	Na-O2	2.297	0.023	0.035
	Na-O3	2.291	0.023	0.035
	Na-O4	2.291	0.023	0.035
$[\text{K}(\text{H}_2\text{O})_4]^+$	K-O1	2.733	0.016	0.018
	K-O2	2.733	0.016	0.018
	K-O3	2.733	0.016	0.018
	K-O4	2.733	0.016	0.018
$[\text{K}(12\text{c}4)]^+$	K-O1	2.773	0.016	0.017
	K-O2	2.771	0.016	0.017
	K-O3	2.733	0.017	0.018
	K-O4	2.733	0.017	0.018

**Table 2.** The topological characteristics ( $\rho_b$  and  $\nabla^2\rho_b$ ) at bond critical points (BCPs) for  $[M(H_2O)_5]^+$  and  $[M(15c5)]^+$  cluster complexes (M=Li, Na, K) at B3LYP/6-31+G(d,p)

Complexes	Connected atoms	Inter nuclear distances (Å)	$\rho_b$ (a.u.)	$\frac{1}{4}\nabla^2\rho_b$
$[Li(H_2O)_5]^+$	Li-O1	2.011	0.022	0.038
	Li-O2	1.990	0.023	0.040
	Li-O3	1.990	0.023	0.040
	Li-O4	2.181	0.014	0.022
	Li-O5	2.181	0.014	0.022
$[Li(15c5)]^+$	Li-O1	2.207	0.015	0.021
	Li-O2	2.205	0.015	0.021
	Li-O3	2.276	0.013	0.018
	Li-O4	2.099	0.018	0.028
	Li-O5	2.280	0.013	0.017
$[Na(H_2O)_5]^+$	Na-O1	2.317	0.019	0.030
	Na-O2	2.294	0.020	0.032
	Na-O3	2.294	0.020	0.032
	Na-O4	2.433	0.015	0.022
	Na-O5	2.433	0.015	0.022
$[Na(15c5)]^+$	Na-O1	2.345	0.020	0.029
	Na-O2	2.328	0.021	0.031
	Na-O3	2.339	0.020	0.030
	Na-O4	2.342	0.020	0.030
	Na-O5	2.319	0.021	0.032
$[K(H_2O)_5]^+$	K-O1	2.738	0.016	0.018
	K-O2	2.676	0.017	0.020
	K-O3	2.676	0.017	0.020
	K-O4	3.011	0.009	0.010
	K-O5	3.011	0.009	0.010
$[K(15c5)]^+$	K-O1	2.772	0.015	0.017
	K-O2	2.739	0.017	0.018
	K-O3	2.751	0.016	0.017
	K-O4	2.713	0.018	0.019
	K-O5	2.727	0.017	0.019

**Table 3.** The topological characteristics ( $\rho_b$  and  $\nabla^2 \rho_b$ ) at bond critical points (BCPs) for  $[M(\text{H}_2\text{O})_n]^+$  and  $[M(18c6)]^+$  cluster complexes (M=Li, Na, K) at B3LYP/6-31+G(d,p)

Complexes	Connected atoms	Inter nuclear distances (Å)	$\rho_b$ (a.u.)	$\frac{1}{4}\nabla^2 \rho_b$
$[\text{Li}(\text{H}_2\text{O})_3]^+$	Li-O1	1.906	0.030	0.054
	Li-O2	1.906	0.030	0.054
	Li-O3	1.906	0.030	0.054
$[\text{Li}(18c6)]^+$	Li-O1	3.343		
	Li-O2	2.204	0.015	0.021
	Li-O3	4.098		
	Li-O4	2.207	0.015	0.021
	Li-O5	1.975	0.026	0.045
	Li-O6	3.342		
$[\text{Na}(\text{H}_2\text{O})_6]^+$	Na-O1	2.443	0.014	0.021
	Na-O2	2.443	0.014	0.021
	Na-O3	2.443	0.014	0.021
	Na-O4	2.443	0.014	0.021
	Na-O5	2.443	0.014	0.021
	Na-O6	2.443	0.014	0.021
$[\text{Na}(18c6)]^+$	Na-O1	2.758	0.007	0.010
	Na-O2	2.742	0.008	0.010
	Na-O3	2.759	0.007	0.010
	Na-O4	2.745	0.008	0.010
	Na-O5	2.738	0.008	0.010
	Na-O6	2.751	0.007	0.010
$[\text{K}(\text{H}_2\text{O})_6]^+$	K-O1	2.861	0.012	0.013
	K-O2	2.861	0.012	0.013
	K-O3	2.861	0.012	0.013
	K-O4	2.861	0.012	0.013
	K-O5	2.861	0.012	0.013
	K-O6	2.861	0.012	0.013
$[\text{K}(18c6)]^+$	K-O1	2.825	0.014	0.015
	K-O2	2.825	0.014	0.015
	K-O3	2.825	0.014	0.015
	K-O4	2.824	0.014	0.015
	K-O5	2.825	0.014	0.015
	K-O6	2.824	0.014	0.015

**Table 4.** The topological characteristics ( $\rho_b$  and  $\nabla^2\rho_b$ ) at bond critical points (BCPs) for  $[\text{Li}(\text{H}_2\text{O})_6]^+$  and  $[\text{Li}(18\text{c}6)]^+$  (with  $D_{3d}$  symmetry and two imaginary frequencies) cluster complexes (M=Li, Na, K) at B3LYP/6-31+G(d,p)

Complexes	Connected atoms	Inter nuclear distances (Å)	$\rho_b$ (a.u.)	$\frac{1}{4}\nabla^2\rho_b$
$[\text{Li}(\text{H}_2\text{O})_6]^+$	Li-O1	2.210	0.013	0.020
	Li-O2	2.210	0.013	0.020
	Li-O3	2.210	0.013	0.020
	Li-O4	2.210	0.013	0.020
	Li-O5	2.210	0.013	0.020
	Li-O6	2.210	0.013	0.020
$[\text{Li}(18\text{c}6)]^+$	Li-O1	2.724	0.004	0.006
	Li-O2	2.735	0.004	0.005
	Li-O3	2.721	0.004	0.006
	Li-O4	2.727	0.004	0.005
	Li-O5	2.734	0.004	0.005
	Li-O6	2.725	0.004	0.006

around 0.01 a.u) and positive values of the laplacian of electron density. In terms of general classification of interactions in QTAIM, these interactions are classified as closed shell interactions. Pervious topological analysis of the many ionic species has shown that the electron density at BCP point is around 0.01 a.u. generally. This also has been shown graphically by the maps of Laplacian of electron densities of  $[\text{M}(18\text{c}6)]^+$  cluster complexes in Figure 9. The outer shell of each metal-oxygen interaction is the zone of charge depletion at each complex. No charge concentration zone has been detected between central metal and oxygens. Consequently we also classify the Metal-Oxygen in all complexes in this work as ionic. Based on the properties of BCPs the degree of ionic character of metal-oxygen bonds is different among the complexes.

We also compared the BCP properties ( $\rho_b$  and  $\nabla^2\rho_b$ ) of metal-oxygen interactions with their corresponding metal-oxygen in pure hydrated cations (same number of metal-oxygen interactions) at the same level of theory (Figures 2, 4 and 6). In  $[\text{M}(\text{H}_2\text{O})_4]^+$  and  $[\text{M}(12\text{c}4)]^+$  and also in  $[\text{M}(\text{H}_2\text{O})_5]^+$  and  $[\text{M}(15\text{c}5)]^+$

(M=Li,Na,K) cluster complexes, sodium and potassium have the similar metal-oxygen interactions (Table 1 and 2). But in  $[\text{Li}(\text{H}_2\text{O})_3]^+$ ,  $[\text{M}(\text{H}_2\text{O})_6]^+$  (M=Na,K) and  $[\text{M}(18\text{c}6)]^+$  (M=Li,Na,K) only potassium containing cluster complexes showed the similar metal-oxygen interactions (Table 3).

### Conclusion

The local minimum geometries of  $\text{M}^+(12\text{c}4)$ ,  $\text{M}^+(15\text{c}5)$  and  $\text{M}^+(18\text{c}6)$  (M= Li, K, Na) were determined at B3LYP/6-31+G(d,p) level. Then Topological analysis were performed on the wavefunctions at the same Properties of electron density at the positions of BCPs have been calculated for each cluster complex. Subsequent analysis provided the molecular graphs. These graphs established the number of metal oxygen interactions.  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  is reported to have coordination number of 4 with 12c4 and possess the coordination number of 5 with 15c5 crown ether. Also  $\text{Li}^+$  is reported to have coordination number of 3 and  $\text{Na}^+$  and  $\text{K}^+$  possess the coordination number of 6. All metal-oxygen bonds were found to have ionic character. The similarities between metal-oxygen bonds in hydrated complexes and 12c4 and 15c5 cluster



complexes were found in  $\text{Na}^+$  and  $\text{K}^+$ . The similarities between metal-oxygen bonds in

hydrated complexes and 18c6 cluster complexes were just found in  $\text{K}^+$ .

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