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Topological Analysis of Theoretical Charge Density of Alkali Metal Cations (Li$^+$, Na$^+$, K$^+$)/Crown Ether (18c6) Complexes

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ABSTRACT

The [M(18c6)]$^+$ (M=Li, Na, K and 18c6=18-crown-6) complexes have been chosen as the model systems to investigate the nature of chemical bonds between alkali metal cations and large multidentate organic ligands. The B3LYP/6-31+G(d,p) level of calculation has been used for obtaining equilibrium geometries and ρ(r) functions (electron density distributions). By the aid of fundamental physical theorems implemented in Quantum Theory of Atoms in Molecules (QTAIM), the structures and the physical nature of chemical bonds have been determined for cited species at the mentioned theoretical level. These results establish the metal-oxygen in all complexes in this work as ionic. The Li$^+$ shows the coordination number of 3 with 18c6 crown ether and Na$^+$ and K$^+$ exhibits the coordination number of 6.

Keywords: Molecular graph; QTAIM; Chemical bond; Coordination; Crown ether; Alkali metal

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 various cations in 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 substituent on the ligand backbone which alter the crown's electronic environment, (4) the type of donor site 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 host-guest recognition in enzymes. 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}Ra^{2+}) complex that is

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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.

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.

Yamahe *et al.* [28] reported a CNDO/2 study of gas-phase crown ether and its interaction with Na^+ and K^+. Their calculations suggested that 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 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 18c6 binds Li^+ and Mg^{2+} most strongly among the two ionic sequences (Li^+-Cs^+ and Mg^{2+}-Ra^{2+}) studied. By considering the ion exchange reactions,

$[K(18c6)]^+ + [M(H_2O)_n]^+ \rightarrow [M(18c6)]^+ + [K(H_2O)_n]^+$ (M=Li, Na, Rb, and Cs)

or the analogous set of reactions for 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 K^+ and Rb^+ and (2) incorporating a small number of water molecules in the metal-crown complex, i.e. microsolvating 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 Rb^+(12c4) and Cs^+(12c4) were identified as possible causes for the discrepancy between theory and experiment for these species.

COMPUTATIONAL DETAILS

B3LYP/6-31+G(d,p) model was 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. The crown ether 18c6 and its complexes with Li^+, Na^+, K^+ are the species used in this theoretical study. The optimized geometries have been characterized by frequency computations (Fig. 1). The related wave function files in each case were produced at the end. All DFT computations were performed using PC GAMESS7.1 firefly [32]. The electron density analysis was done using the AIM2000 software [33].

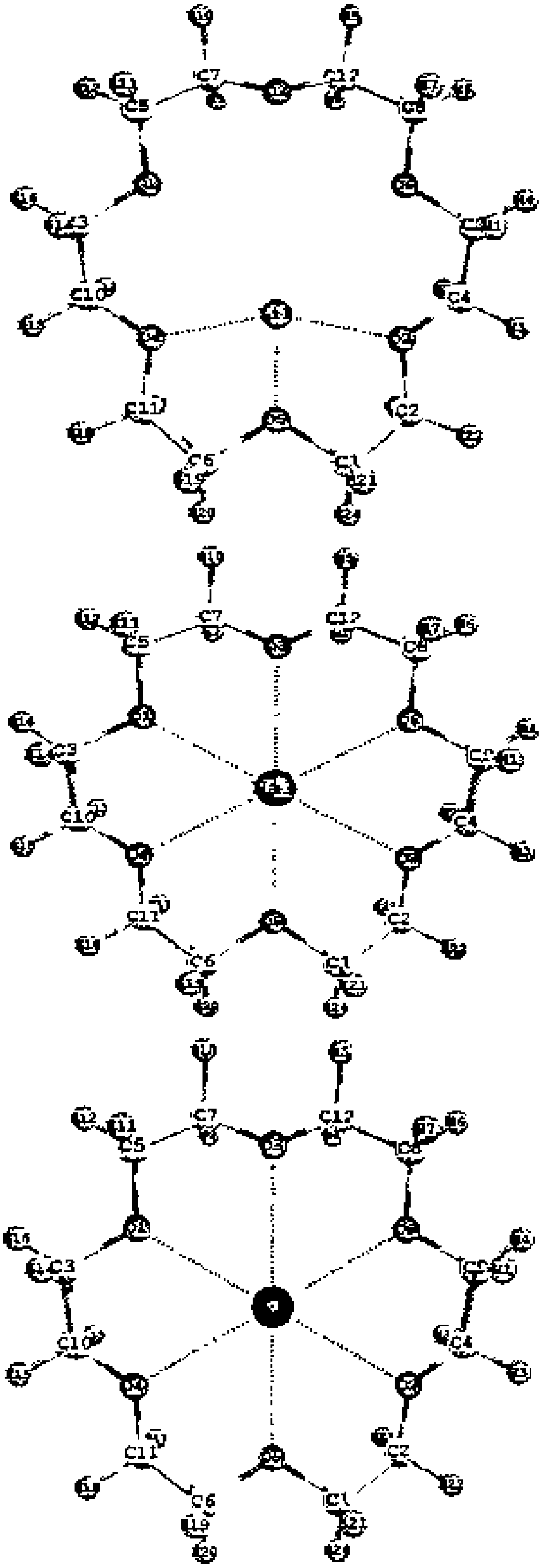

Fig. 1. The optimized geometries for $[M(18c6)]^+$ complexes (M=Li, Na, K) at B3LYP/6-31+G(d,p).

RESULTS AND DISCUSSION

Since this paper is based on the QTAIM methodology, some relevant important points of this theory seems 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 his coworkers have demonstrated that 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 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 [34, 35] was satisfied in all cases:

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

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 critical points of each complex are listed in Tables 1, the corresponding molecular geometries and molecular graphs are depicted in Fig. 1 and 2. The molecular graph provides the structure of the complex based on network of bond paths. The molecular graphs show that the Li^+ interacts with 3 oxygen atoms while this number is 6 for Na^+ or K^+. We examined another geometry of $[Li(18c6)]^+$ complex in which the Li^+ was kept at the center of the crown ether ring (Fig. 3). This geometry exhibited 2 imaginary frequency at B3LYP/6-31+G(d,p) level. The molecular graph of this geometry shows the interaction of Li^+ with 6 oxygen atoms (Fig. 3). Usually Li^+ most stable complexes are the ones having the 4 coordinated Li^+. This is consistent with the results of our topological analysis in which Li^+ prefers position with low coordination number (less than 6) inside the crown ether ring.

The interactions of all metal-oxygen in all complexes are characterized by low value of electron density at the positions of BCPs $\rho(r)$ around 0.01 a.u. (0.07 e.Å^{-3})) 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. (0.07 e.Å^{-3}) generally. This also has been shown graphically by the maps of Laplacian of electron densities of complexes in Fig. 2. 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 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. Study of this latter issue in quantitative way needs the calculation of atomic charges which will be documented in details in the subsequent work.

We also compared the BCP properties 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. Only potassium containing complexes showed the similar metal-oxygen interactions.

CONCLUSION

The local minimum geometries of $[M(18c6)]^+$ (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 complex. Subsequent analysis provides the molecular graphs. These graphs established that number of metal oxygen interactions. Li^+ is reported to have coordination number of 3 and Na^+ and 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 18C6 complexes were just found in K^+.

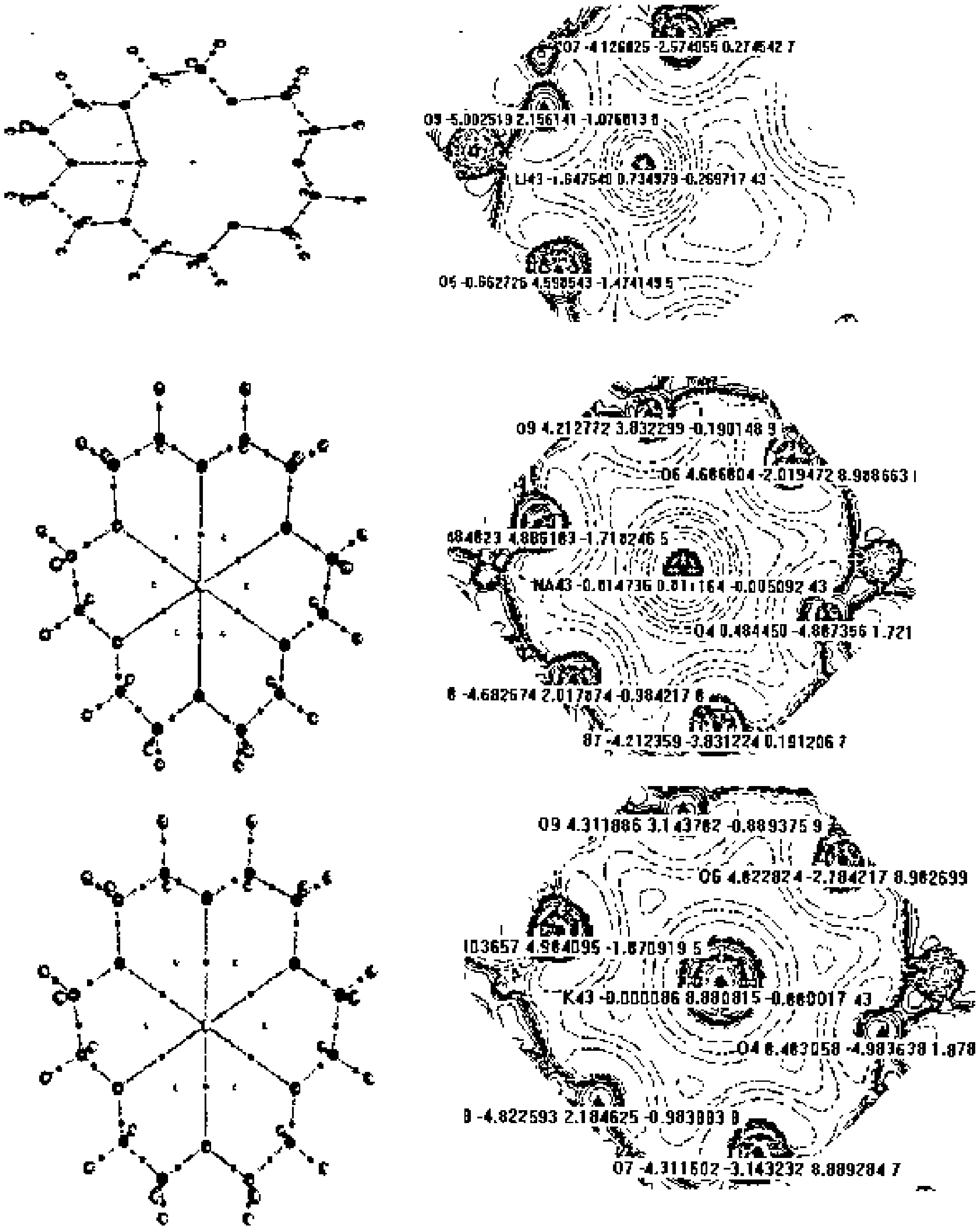

Fig. 2. The molecular graphs (right) and the Laplacian maps (left) for $[M(18c6)]^+$ complexes (M=Li, Na, K) at B3LYP/6-31+G(d,p). Dashed lines are the lines of positive Laplocian.

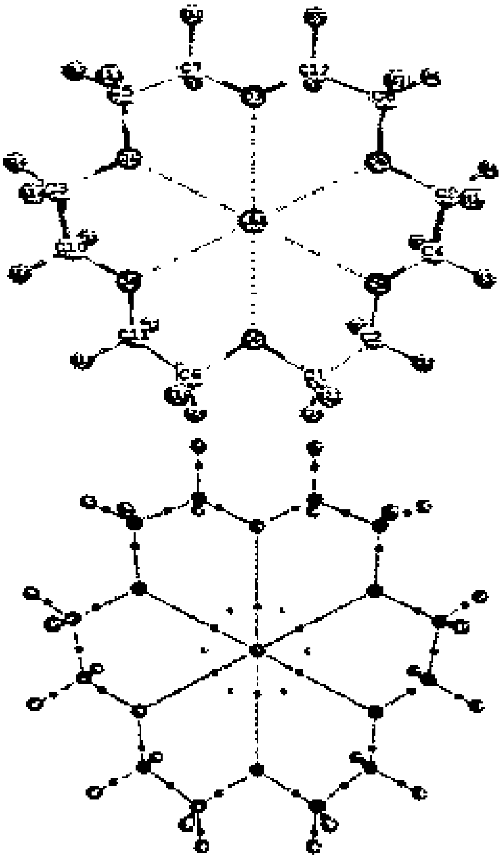

Fig. 3. The optimized geometriy (right) and the Molecular graph (left) for $[Li(18c6)]^+$ complex at B3LYP/6-31+G(d,p) with two imaginary frequencies (187.2 and 186.3 cm^{-1}).

Table 1. The mathematical caracteristics (ρ_b and $\nabla^2\rho_b$) at boad critical points (BCPs) for $[M(18c6)]^+$ complexes (M=Li, Na, K) at B3LYP/6-31+G(d,p)

Complexes	Connected atoms	Inter nuclear distances (Å)	ρ_b a.u. (e Å^{-3})	$\frac{1}{4}\nabla^2\rho_b$ a.u. (e.Å^{-5})
$[Li(18c6)]^+$	Li-O1	3.343		
	Li-O2	2.204	0.015 (0.101)	0.021 (0.507)
	Li-O3	4.098		
	Li-O4	2.207	0.015 (0.101)	0.021 (0.507)
	Li-O5	1.975	0.026 (0.176)	0.045 (1.086)
	Li-O6	3.342		
$[Na(18c6)]^+$	Na-O1	2.758	0.007 (0.047)	0.010 (0.241)
	Na-O2	2.742	0.008 (0.054)	0.010 (0.241)
	Na-O3	2.759	0.007 (0.047)	0.010 (0.241)
	Na-O4	2.745	0.008 (0.054)	0.010 (0.241)
	Na-O5	2.738	0.008 (0.054)	0.010 (0.241)
	Na-O6	2.751	0.007 (0.047)	0.010 (0.241)
$[K(18c6)]^+$	K-O1	2.825	0.014 (0.095)	0.015 (0.362)
	K-O2	2.825	0.014 (0.095)	0.015 (0.362)
	K-O3	2.825	0.014 (0.095)	0.015 (0.362)
	K-O4	2.824	0.014 (0.095)	0.015 (0.362)
	K-O5	2.825	0.014 (0.095)	0.015 (0.362)
	K-O6	2.824	0.014 (0.095)	0.015 (0.362)

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