

VIP Very Important Paper

# Record Low Ionization Potentials of Alkali Metal Complexes with Crown Ethers and Cryptands

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Electronic properties of series of alkali metals complexes with crown ethers and cryptands were studied via DFT hybrid functionals. For  $[M([2.2.2]\text{crypt})]$  ( $M=\text{Li, Na, K}$ ) extremely low (1.70–1.52 eV) adiabatic ionization potentials were found. Such low values of ionization energies are significantly lower than those of alkali metal atoms. Thus, the investigated complexes

can be defined as superalkalis. As a result, our investigation opens up new directions in the designing of chemical species with record low ionization potentials and extends the explanation of the ability of the cryptates and alkali crown ether complexes to stabilize multiple charged Zintl ions.

## 1. Introduction

Among all atoms in the periodic table, the alkali metal atoms possess the lowest ionization energies (5.39–3.89 eV).<sup>[1]</sup> However, due to collective effects, some molecules can exhibit even lower ionization potentials. Such compounds form a large class, which is called superalkali. That term was firstly introduced in 1982 by Gutsev and Boldyrev applying to  $M_{k+1}L$  family, where  $M$  is an alkali atom and  $L$  is an electronegative atom of valence  $k$ .<sup>[2]</sup> The typical examples of superalkalis are  $M_2X$  ( $M=\text{Na, Li; X}=\text{F, Cl, Br, I}$ ),  $\text{Li}_3\text{S}$ ,  $\text{Li}_4\text{N}$ ,  $\text{M}_3\text{O}$  ( $M=\text{Li, Na, K}$ ), etc.<sup>[3]</sup> Since then, a huge amount of various super alkalis has been found both theoretically<sup>[4–8,15–25]</sup> and experimentally.<sup>[9–14]</sup> The classical  $M_{k+1}L$  class has been expanded and new types of superalkalis have been developed. Those types include dinuclear<sup>[15,16]</sup> and polynuclear<sup>[17–20]</sup> superalkali species (with two or more core electronegative atoms), nonmetallic superalkalis,<sup>[21]</sup> aromatic superalkalis,<sup>[22,23]</sup> organo-zintl superalkali species<sup>[24]</sup> and organo-heterocyclic superalkalis.<sup>[25]</sup> In 2002 Cotton and coworkers synthesized in the solid state the dimetal Tungsten complex with four bulky hpp ligands (the anion of 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine) which possess ionization energy 3.514 eV.<sup>[26]</sup> As a subset of the superatoms family,<sup>[27,28]</sup> superalkalis can behave as alkali atoms forming novel materials with unique properties.<sup>[29]</sup> The idea of such solid state materials (cluster-assembled materials) was introduced by Khanna and Jena.<sup>[30]</sup> The recent review of the superatomic clusters and their use in the material design can be found in ref. [31]. In our research, we expanded the class of molecules with record low

ionization energy and introduced macrocyclic complexes as a new source of superalkali species. It should be mentioned, that after our article was submitted, a review on superalkalis was recently published.<sup>[32]</sup>

The introduction of crown ethers by Pedersen<sup>[33]</sup> and cryptands by Lehn<sup>[34]</sup> launched a new huge field of science-supramolecular chemistry. Exceptional properties of those compounds inspired researchers to create even more complex structures. Along with the unique guest particle selectivity, such compounds are widely used in the synthesis of multiply charged inorganic ions. Their large size helps to better isolate negatively charged unstable clusters. Because of the unique properties, we decided to find an answer whether these compounds are superalkalis or not. Four crown ether complexes and three [2.2.2]Cryptand complexes were considered in this work (Figure 1) as the most popular examples of alkali metal macrocyclic complexes.

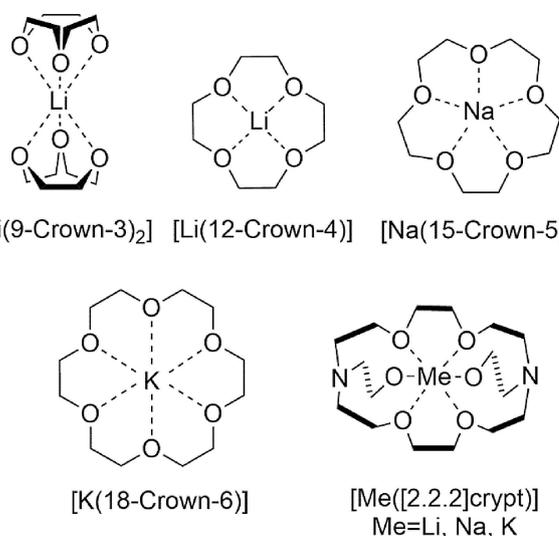


Figure 1. The structures of the investigated alkali metal complexes.

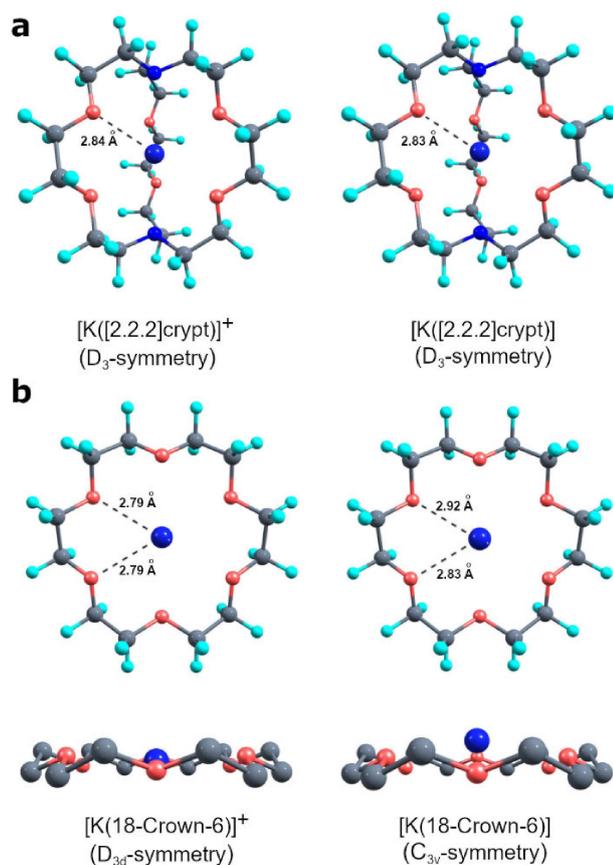
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## 2. Results and Discussion

The optimized geometries of alkali complexes possess an interesting feature. The geometries of optimized alkali-cryptand cations almost coincide with the geometries of optimized neutral species (Figure 2a). The same pattern was found for the  $C_3$ -symmetric  $[\text{Li}(9\text{-Crown-3})_2]$  complex. However, for mono-crown ether species ( $[\text{Li}(12\text{-Crown-4})]$ ,  $[\text{Na}(15\text{-Crown-5})]$ , and  $[\text{K}(18\text{-Crown-9})]$ ) slightly different geometries of cation and neutral complexes were found. Thus, for the neutral  $[\text{K}(18\text{-Crown-9})]$  the central atom is pushed out from the “plane” of crown ether ligand, reducing the symmetry from  $D_{3d}$  to  $C_{3v}$



**Figure 2.** Optimized structures of  $[\text{K}([2.2.2]\text{crypt})]^+$  and  $[\text{K}([2.2.2]\text{crypt})]$  (a). Top and side (hydrogen atoms are omitted for clarity) views of optimized  $[\text{K}(18\text{-Crown-6})]^+$  and  $[\text{K}(18\text{-Crown-6})]$  complexes (b).

(Figure 2b). The difference in the geometry is also reflected in the VIP and ADE values which differ on average by 0.2 eV for mono-crown ether species. Overall geometries of  $[\text{K}([2.2.2]\text{crypt})]$  and  $[\text{Na}([2.2.2]\text{crypt})]$  complexes are slightly distorted from the ideal  $D_3$ -group, but could be described as a macro-cycle with an alkali metal ion at the center of the structure. In turn, the radius of the lithium atom is significantly smaller than the potassium and sodium, and the  $D_3$  geometry of  $[\text{Li}([2.2.2]\text{crypt})]$  is unstable. So, the Li atom displaced from the center of the structure, reducing the symmetry to  $C_1$ . The coordination sphere of this compound can be described as a central lithium atom, one nitrogen atom and five peripheral oxygen atoms.

For all the investigated species extraordinary low ionization potentials were found (Table 1). Interestingly, that ionization potentials highly depend on the coordination sphere. Thus, for mono-crown ether species, values of AIP at the PBE0/6-311++G\*\* level of theory lay within 2.57–2.20 eV. In turn, highly coordinated cryptates and  $[\text{Li}(9\text{-Crown-3})_2]$  complex with two crown ethers exhibit lower potentials in the range 2.18–1.95 eV. Predictably, the ionization energy decreases in the row Li-Na-K. It is worth noting that with switching to a larger basis set (aug-cc-pVTZ or def2QZVP), using geometries optimized in the 6-311++G\*\* basis set, the potentials drop down to record low values 1.82–1.52 eV. The result does not depend on the DFT functional since for TPSSh method almost the same results were obtained (Table 1).

To investigate the nature of low IPs we decided to calculate the natural charge distribution of the considered structures. We found that most electronegative atoms of crown ethers and cryptand (oxygen, nitrogen) carry a significant partial negative charge (Table S2). This negative charge preserves almost the same for both neutral and cation complexes. Thus, in the case of neutral species, the destabilization of an electron with the negatively charged surrounding occurs. The decrease in ionization energy with an increase in the number of negatively charged coordination atoms illustrates that the destabilization of neutral complexes can be one of the main factors of such low IPs. Another explanation of this phenomenon is related to the electron distribution in neutral complexes. It has been shown before that the electron sitting on antibonding HOMO can cause a significant reduction in the ionization potential of the structure.<sup>[35]</sup> Entering such an antibonding orbital an electron destabilizes the neutral structure and reduces the IP. The antibonding character of the alpha HOMO for neutral

**Table 1.** Ionization potentials (in eV) of the investigated species.

Complexes	PBE0		aug-cc-pVTZ		TPSSh		aug-cc-pVTZ	
	6-311++G(3df)	VIP	AIP	VIP	6-311++G(3df)	VIP	AIP	VIP
$[\text{Li}(9\text{-Crown-3})_2]$	2.18	2.18	1.82	1.83	2.14	2.15	1.79	1.80
$[\text{Li}(12\text{-Crown-4})]$	2.57	2.73	2.15	2.30	2.50	2.65	2.10	2.22
$[\text{Na}(15\text{-Crown-5})]$	2.40	2.72	2.05	2.30	2.33	2.60	1.99	2.20
$[\text{K}(18\text{-Crown-6})]$	2.20	2.31	1.84 <sup>[a]</sup>	1.93 <sup>[a]</sup>	2.14	2.22	1.77 <sup>[b]</sup>	1.82 <sup>[b]</sup>
$[\text{Li}([2.2.2]\text{crypt})]$	2.04	2.05	1.70	1.71	1.99	2.00	1.66	1.67
$[\text{Na}([2.2.2]\text{crypt})]$	1.96	1.96	1.64	1.64	1.93	1.93	1.61	1.61
$[\text{K}([2.2.2]\text{crypt})]$	1.95	1.95	1.52 <sup>[a]</sup>	1.53 <sup>[a]</sup>	1.92	1.92	1.49 <sup>[b]</sup>	1.50 <sup>[b]</sup>

[a] Value was calculated at the PBE0/def2QZVP//PBE0/6-311++G\*\* level. [b] Value was calculated at the TPSSh/def2QZVP//TPSSh/6-311++G\*\* level.

complexes are illustrated in Figure S1 in the Supporting Information.

### 3. Conclusions

It was shown that series of cryptand and crown ether complexes of alkali metals exhibit extremely low ionization potentials, thus could be considered as superalkalis. For [K ([2.2.2]crypt)] species record low ionization potential (1.52 eV) was found. This discovery opens a new direction in designing chemical species with record low ionization potentials, as well as explains the successful use of alkali metal complexes with cryptands and crown ethers in the synthesis of multiple-charged Zintl clusters.

### Computational Details

All structures were optimized with Perdew–Burke–Ernzerhof<sup>[36]</sup> (PBE0) and Tao–Perdew–Staroverov–Scuseria<sup>[37]</sup> (TPSSH) hybrid functionals using 6-311 + +G\*\* basis set. DFT wave functions are found to be stable, so DFT approximations are valid in this case. Vertical ionization potentials (VIP) were found by calculating the energy difference between the optimized neutral complex and the cation in the geometry of the neutral complex. For the adiabatic ionization potential (AIP) the energy differences between an optimized neutral cluster and an optimized cation were found. ZPE corrections were calculated using the harmonic approximation. For the higher accuracy, single point calculations with larger basis sets were applied (aug-cc-pVTZ for structures containing Li and Na atoms; def2QZVP for structures containing the K atom). All calculations utilized the GAUSSIAN-16 program.<sup>[38]</sup> The ChemCraft 1.8 software was used to visualize geometries of investigated compounds.

### Supporting Information

Cartesian coordinates, number of imaginary frequencies, total energies, ZPE corrections of all investigated structures; partial natural charges on the selected atoms; energies and plots of alpha HOMO of all the investigated neutral complexes.

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### Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** alkali metal complexes · density functional calculations · ionization potential · superalkali · Zintl ions

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