



NBO - NEDA and AIM Studies on the Interactions between Benzocryptand [222B] and Li⁺, Na⁺, K⁺ and Ca²⁺

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ABSTRACT

Cryptands are widely studied due to their potential applications in various chemical and physical processes especial as models for biological systems. We employed B3LYP density functional theory with 6-311G* basis set to optimize the geometries and subsequently calculate binding energies (in the gas phase) of the ligand based on benzocryptand [222B] bounded to alkali metal univalent cations such as Li^+ , Na^+ , K^+ and alkaline earth divalent cation such as Ca^{2+} . Atoms in molecules (AIM) approach, natural bond orbital (NBO), and natural energy decomposition analysis (NEDA) were used to understand the nature of the host-guest interaction. From AIM theory, all interactions between donor atoms of [222B] ligand and central ions are referred to as a closed-shell based on the Laplacian data, and the interactions are totally electrostatic, based on both the Laplacian and total energy, which are positive. From NBO analysis, (L-Ca²⁺) complex has the highest the stabilization energy. Additionally, the NEDA analysis suggests that the order relative of energy for the alkali metal complexes is electrostatic > polarization > charge transfer, while that for the alkaline earth metal complex is polarization> electrostatic > charge transfer. The finding results show that all donor atoms in [222B] ligand were involved with Ca²⁺ in (L-Ca²⁺) complex, while (L-Li⁺) complex does not interact with the nitrogen and the oxygen adjacent to benzene. We proposed the alkali metal univalent cations such as lithium which has the smallest radius only draw four oxygen atoms around the cavity of the [222B] ligand, while alkaline earth metal divalent cation (calcium) with a higher charge density is able to bond with six oxygen atoms and two nitrogen atoms. Compared to the ionic radius, the charge density is a more dominant factor which governs the binding of the alkali and alkaline earth metal ions to the [222B] ligand.

Keywords: Benzocryptand, Alkali metal cations, Alkaline earth metal cation, AIM, NBO, NEDA.

INTRODUCTION

ryptands are three-dimensional analogues of crown ethers that were first synthesized by Lehn et al. in 1987¹. They are useful in many areas of organic chemistry, solvent extraction, stabilisation of uncommon or reactive oxidants, biochemistry, as well as material science²⁻⁵, due to their ability to bind selectively with metal ions and to adjust the size of the metal ion cavity^b. In addition, cryptands have the unusual property to form stable complexes with the alkali metals⁷. The interaction of a cryptand ligand with a metal ion is electrostatic and classifies as a host-guest interactions, where the formers is the host, and the latter is the guest⁸. Furthermore, these compounds are able to bind otherwise insoluble salts into organic solvents. They can also be used as phase transferring catalysts by transferring ions from one phase to another⁹.

Cryptands enabled the synthesis of alkalides and electrides. Cryptands are bis-macrocycles with various donor atoms, where nitrogen atoms are located in the bridge between the two ends of the ring. The conformation of cryptands possesses a spherical internal cavity, which is well suited for the recognition of spherical cations. Cryptands form stable and selective complexes with many metal cations^{10,11}. They form complexes with

hard cations, such as alkali and alkaline earth ions. Cryptands, compared to crown ethers, have better ion selectivity and form stronger bonds with alkali metals and alkaline earth metals. The size of cryptands cavity is vital vis-à-vis ion selectivity of complex formation. The 3-dimensional interior cavity of a cryptand provides a binding site for guest ions.

Benzocryptand [222B], with the chemical formula C22N2H36O6 and IUPAC name of 5,6-benzo-4,7,13, 16, 21, 24 -hexaoxa -1, 10 - diazabicyclo [8.8.8] hexacosan, has a benzene ring, and substituting benzene reduces the binding energy of complexes compared to cryptands. Sheme 1 shows the structures of benzocryptand [222B].



Scheme 1: The benzocryptand [222B] structure. The IUPAC name is 5, 6-benzo-4, 7, 13, 16, 21, 24-hexaoxa-1, 10-diazabicyclo [8.8.8] hexacosan.



45

Recently, density functional (DFT) studies have been performed on the complexation of cryptands and crown ethers with alkali-metal cations. Wang¹² conducted a theoretical study on the cryptand 4, 7, 13, 16, 21, 24hexaoxa-1,10- diazabicyclo [8,8,8] hexacosan (named have as [222]) and the cryptand 5, 6-benzo-4, 7, 13, 16, 21, 24-hexaoxa-1, 10-diazabicyclo [8,8, 8] hexacosan (referred to as [222B]) using DFT with at B3LYP/6-31G* level of theory in order to obtain the electronic properties and geometrical structure of the cryptands and their respective complexes with alkali metal ions such as Li⁺, Na^{\dagger} , and K^{\dagger} . Complexation study of crown ethers with cations has been a subject of several reports¹³⁻¹⁵. In this study, the electronic and the molecular structures for [222B] ligand and their respective complexes with alkali metal univalent cations like Li^{+,} Na⁺, K⁺, and alkaline earth metals divalent cation like Ca²⁺, were investigated using methods, namely density functional theory (DFT), atoms in molecules (AIM) theory, and natural bond orbital (NBO) and natural energy decomposition (NEDA) analysis. Initially, the interaction between benzocryptand with alkali metals and alkaline earth metals cations were investigated and their binding energies compared. Then, the bond critical point and the topology properties of these complexes were determined by AIM analyses. Finally, the NBO and the NEDA analyses confirmed the results from the AIM approaches to predict the strength of the donor-acceptor interactions in these complexes.

Methods and Computational Details

The primary structures of benzocryptand attached to oxygen groups at O_{13} , O_{14} , O_{15} , O_{16} , O_{25} , O_{26} and nitrogen groups at N_{17} , N_{18} positions were prepared using GaussView 5.0 software package¹⁶. The electronegative atoms, such as oxygen and nitrogen in [222B] ligand act as donors, and donate their electrons to the metal ions within the cavity. By bringing cations including Li⁺, Na⁺, K⁺ and Ca²⁺ close to the crown ether ring, we prepared four crown ether complexes.

The calculations including, the optimization of complexes, and the binding energies were performed using the-Gaussian 09 package¹⁷. All calculations at B3LYP/6-311G* were performed in windows. Both method and basis set were used for geometry optimization and frequency calculation .The DFT method is an efficient method in the study of large molecules and the B3LYP (Becke-Lee-Yang-Parr) version of DFT is the combination of Becke's three parameter non-local hybrid functional of exchange terms¹⁸ with the Lee, Yang and Parr correlation functional theorem¹⁹. All optimized structures were minimum stationary points, due to the absence of negative frequency in normal mode analyses in the gas phase. The topological parameters, such as electron densities and their Laplacians, at the bond critical point (BCP) and their molecular graph, were obtained from the Bader theory^{20,21} by the AIM 2000 software²². NBO calculations related to Li⁺, Na⁺ and Ca²⁺ complexes were performed using the NBO 3.1 version²³,

while NBO calculations related to the K⁺ complex at B3LYP/6-311G^{*} level of theory was performed with the NBO 5.0 version on a Linux system. In order to use the NBO 5.0 version for K⁺ complexes, the Avogadro software package²⁴ and MacMolPlot²⁵ were used to prepare the input file, and then re-optimized by the GAMESS 2010 software²⁶. In addition, the final optimization of the molecular structures of three complexes were drawn with ChemCraft 1.6²⁷, while HOMO and LUMO images related to K⁺ complex was drawn with Multiwfn 2.5.5²⁸.

RESULTS AND DISCUSSION

Geometric Structures

The optimized structure of complexes $[(L-Li^+), (L-Na^+), (L-K^+), (L-Ca^{2+})]$ at B3LYP/6-311G* level of theory in ground state are shown in Figure 1. Comparing the structures of $(L-Li^+)$ and $(L-Na^+)$ complexes in Figures 1.a and 1.b, cation Li^+ is able to interact with only 4 oxygen donors that are far from benzene, while cation Na^+ was able to interact with four oxygen donors that are far from benzene, as well as with two nitrogen donors. This is due to the large atomic radius of Na compared to Li atomic radius. Moreover, both cations are lack interaction with the oxygen group's adjacent benzene.

On the other hand, comparing structures such as $(L-K^{+})$ and (L-Ca²⁺) complexes, benzocryptand has the cavity size that matches the size of the atomic radius of K^+ and Ca^{2+} . Therefore, we expected these ions to be more interactive with the donors, even with oxygen groups that are bonded with benzene in benzocryptand [222B]. Although the atomic radius in K and Ca are similar, but the charge atomic in Ca being larger than K, therefore, the interaction in the $(L-Ca^{2+})$ complex exceeds the $(L-K^{+})$ complex. It is clear that, both of the $(L-K^{+})$ and $(L-Ca^{2+})$ complexes are able to interact with oxygen group's donors, which is adjacent to benzene. As a result of this, all six oxygen atoms and two nitrogen atoms donors were involved with Ca²⁺, while only five oxygen atoms donors (4 oxygen donors that are far from benzene and one oxygen donor which is adjacent to benzene) and two nitrogen atoms donors were involved with K⁺ (See Figure 1.c and 1.d).



Figure 1: The optimized structures of the [222B] complexes with alkali metal cations; Li^+ , Na^+ , K^+ and



alkaline earth metals cation; Ca^{2+} calculated with the B3LYP/6-311G.

Binding Energy

The strength of the interaction between cryptands and an ion can be predicted from the energy values in each of the ions, free ligand, and complexes.

To calculate the binding energy between the ion M^+ and the ligand L, the following relation was used.

$$\Delta E_{(ML^+)} = E_{ML^+} - E_{M^+} - E_L \quad (1)$$

The binding energy ($\Delta E_b^{ZPE+BSSE}$) was corrected using the zero-point vibrational energy (ZPE) and basis set superposition errors (BSSE).

The BSSE were eliminated by counterpoise method of Boy's and Bernardi²⁹.

The changes in the Gibbs free energy of the gas phase complexation were calculated in the following manner:

$$\Delta G^{\circ}_{(ML^{+})} = G^{\circ}_{ML^{+}} - G^{\circ}_{M^{+}} - G^{\circ}_{L}$$
(2)

Table 1 gives the electronic energy (E_{ele}), zero-point energy (ΔE_b^{ZPE}), and the binding corrected energy ($\Delta E_b^{ZPE+BSSE}$), and thermodynamic properties of complexes understudies at B3LYP/6-311G* level of theory.

A more negative value of the corrected binding energy implied the more stable formed complexes.

By comparing the binding energy of three complexes of alkali metal, it shows that the binding energy $(L-Li^{+})$ complex is more stable than other complexes. Since smaller cations are capable of having higher charge density, they are able to bond with the coordination oxygen in complexes.

This is consistent with previous studies involving cryptand in the gas phase, which it showed that the binding energy is lower for smaller sized alkali cations¹².

In addition, binding energy in (L-Na⁺) complex is slightly lower than in $(L-K^{+})$ complex, whereas the atomic radius in K is too close to Ca, but the binding energy in the (L- Ca^{2+}) is stronger and more stable compared to the other three complexes. This is because Ca has large atomic charge. On the other hand, comparing the alkali metals complexes and one of alkaline earth complex showed that the trend of the binding energies is in the order of (L- Ca^{2+} < $(L-Li^{\dagger})$ < $(L-Na^{\dagger})$ < $(L-K^{\dagger})$. Furthermore, Table 1 shows the Gibbs calculated free energies are negative, indicating that all the complexes formation in the gas phase being considered is chemically feasible. By comparing binding energy changes in alkali metal, (L-Li⁺) complex is the highest, meaning that the interaction between cation Li⁺ and ligand is stronger than cation Na⁺ and K^{+} , while it is maximum for (L-Ca²⁺) complex. These results confirm that the atomic charge is more important than the size of the ions.

Atoms In Molecules (AIM) Approach



Figure 2: Molecular graphs of the [222B] ligand with alkali metal cations like Li^+ , Na^+ , K^+ and alkaline earth metals actionlike Ca^{2+} . Small red spheres and lines correspond to the bond critical points (BCP) and the bond paths, respectively.

Analysis of the electronic charge density $\rho(r)$ and its Laplacian $\nabla^2 \rho(r)$ was proposed by Bader and coworkers³⁰. Atoms in molecules (AIM)²¹ analyses is based on the critical points (CPs) of the molecular electronic -charge density $\rho(r)$. The electron density was analyzed for two major characteristics, including the existence of critical points (CP) and bond paths³¹. The value of topology parameters, such as electron density $\rho(r)$, Laplacian $\nabla^2 \rho(r)$, electronic kinetic energy density G(r), electronic potential energy density V(r), total energy density H(r), and ellipticity (\mathcal{E}) at BCPs for all complexes being studied at B3LYP/6-311G* level of theory are tabulated in Table 2. The molecular graphs of complexes are shown in Figure 2.

The Laplacian $\nabla^2 \rho(r)$ determine the local electron density at bond critical point (BCP), and its sign is either positive or negative. If $\nabla^2 \rho(r) < 0$, it indicates that the charge density is locally concentrated, while, if $\nabla^2 \rho(r) > 0$, it indicates that the charge density is locally depleted. The interaction is called as covalent or polarized bonds, and being characteristic by large electron density $\rho(r)$ value, and $\nabla^2 \rho(r) < 0$. On the other hand, interaction is referred to as closed shell and it is characteristic of highly bonds, and hydrogen bonds or van der Walls interactions with low electron density $\rho(r)$ and $\nabla^2 \rho(r) > 0$ [19]. Moreover, the interesting parameter is ($\frac{|V|}{2G}$) which is always positive. It should also be pointed out that the interaction is characterized by H(r) > 0 and $\nabla^2\rho(r)>0$ and $(\frac{\mid V\mid}{_{2G}}<0.5$) for electrostatic interaction, while covalence interaction are for H(r) > 0 and $\nabla^2 \rho(r) < 0 \text{ and } (\frac{|v|}{2c} > 1.0), \text{ and } H(r) < 0,$ and $abla^2
ho(r)>0$ and $0.5<rac{|v|}{2G}<1.0$ are partial covalence.



Available online at www.globalresearchonline.net © Copyright protected. Unauthorised republication, reproduction, distribution, dissemination and copying of this document in whole or in part is strictly prohibited. The bond ellipticity (\mathcal{E}) provides a quantitive measure of the bond character, making it zero for C-C (σ -bond) and maximum for C=C (π -bonds).

Therefore, by comparing the values of electron density, its Laplacian, total energy density, $\frac{|V|}{2G}$, and ellipticity in Table 2, it can be concluded that all interactions between donor atoms of [222B] and central ions are referred to as a closed-shell based on Laplacian data, and the interactions are totally electrostatic, based on both Laplacian and total energy, which are positive. The ellipticity data show that these complexes possess a C-C single bond (σ -bond).

Natural Bond Orbital (NBO)

Natural bond orbital (NBO) is the calculated bonding orbital with maximum electron density. The concepts of natural orbitals was first introduced by Per-Olov Löwdin in 1955, and then developed by Weinhol and³². NBO analysis is a sufficient approach to investigate intra -and inter-molecular interaction. In this analysis, the donor-acceptor (bond-anti bond) interactions were accounted for by examining all possible interactions between filled (donor) Lewis-type NBOs and empty (acceptor) non-Lewis NBO's, and then their energies were estimated using the second-order perturbation theory. The stabilization

energy between a donor (i) and acceptor (j) is explicitly estimated using the following equation³³;

$$E^{(2)} = \Delta E_{i \to J} = q_i \frac{F^2(i, j)}{\varepsilon_j - \varepsilon_i} \quad (3)$$

where, $E^{(2)}$ is stabilization energy, q_i is the occupation number of donor orbital, ε_j and ε_i are diagonal elements (orbital energies), and $F^2(i, j)$ are off-diagonal elements of the NBO Fock matrix. The total second order perturbation stabilization energy $E^{(2)}$ was related to the donors with stronger interactions for all complexes are given in Tables 3-6.

In all cases, the donor (occupied) orbitals belong to the lone pairs (LP) of oxygen and nitrogen atoms in the cavity of the [222B] ligand, while the first empty valence (unoccupied) orbitals (LP*) ions [(orbital 2s for Li⁺), (3s for Na⁺) and (4s for K⁺, Ca⁺²)] belong to the acceptors orbitals. The sum of stabilization energy $E^{(2)}$ for oxygen and nitrogen donors in (L-Li⁺), (L-Na⁺), (L-K⁺) and (L-Ca²⁺) complexes were 128.3, 98.48, 25.55, and 201.02 (kcal/mol), respectively. As a result of this, the stabilization energy order for alkali metal and alkaline earth metal cations are in the order of Ca⁺² > Li⁺ > Na⁺ > K⁺.

Table 1: The binding energies (kcal/mol) and thermodynamic properties (kcal/mol.K) in gas phase for the complexes at the B3LYP/6-311G*.

Complexes	E _{ele}	$\Delta \mathbf{E}_{b}^{ZPE}$	$\Delta E_b^{ZPE+BSSE}$	ΔS_b°	ΔG_b°
L-Li ⁺	-896177.18	-115.86	-112.21	-30.5	-106.67
L-Na ⁺	-993298.27	-97.83	-93.51	-31.03	-87.85
L-K [⁺]	-1267915.3	-71.37	-67.14	-29.83	-62.75
L-Ca ²⁺	-1316543.5	-287.005	-282.96	-44.7	-269.82

Table 2: AIM topological parameters for complexes understudied at B3LYP/6-311G level of theory

Bonds	ε	ρ(r)	∇ ²(ρ)	G(r)	V(r)	H(r)	V 2G
(a							
(L-Li [°])							
Li [†] -015	0.0179	0.0183	0.1255	0.0254	-0.0195	0.0059	0.3841
Li ⁺ -016	0.0478	0.0156	0.1052	0.0213	-0.0163	0.005	0.3832
Li ⁺ -O25	0.09	0.0194	0.1384	0.0279	-0.0213	0.0066	0.3809
Li+-026	0.0825	0.016	0.1065	0.0216	-0.016	0.005	0.3851
(L-Na⁺)							
Na ⁺ -O15	0.0566	0.0166	0.1019	0.021	-0.0166	0.0044	0.3954
Na [⁺] -O16	0.0553	0.0176	0.1105	0.0228	-0.018	0.0048	0.395
Na⁺-N17	0.0984	0.006	0.0289	0.0058	-0.0044	0.0014	0.3788
Na⁺-N18	0.1144	0.0085	0.0411	0.0084	-0.0066	0.0018	0.3938
Na [⁺] -O25	0.063	0.0179	0.1139	0.0234	-0.0184	0.005	0.3929
Na [⁺] -O26	0.0674	0.0192	0.1232	0.0254	-0.02	0.0054	0.3941
(L-K⁺)							
K ⁺ -014	0.1643	0.0074	0.0352	0.0071	-0.0055	0.0016	0.3867
K ⁺ -O15	0.0846	0.0153	0.0746	0.0157	-0.0129	0.0028	0.4087
K ⁺ -O16	0.082	0.0193	0.0967	0.0206	-0.0171	0.0035	0.414
K ⁺ -N17	0.1174	0.0077	0.031	0.0064	-0.005	0.0014	0.3944
K ⁺ -N18	0.0082	0.014	0.0582	0.0123	-0.0101	0.0022	0.4101
K ⁺ -O25	0.062	0.0171	0.083	0.0177	-0.0146	0.0031	0.4135



International Journal of Pharmaceutical Sciences Review and Research

κ ⁺ -Ω26 0.0843 0.0194 0.0976 0.0208 -0.0172 0.0036 0.4	4145
(L-Ca ²⁺)	
Ca ²⁺ -O13 0.0806 0.0237 0.1374 0.0285 -0.0228 0.0057 0.	399
Ca ²⁺ -O14 0.0704 0.0231 0.1336 0.0277 -0.0221 0.0056 0.3	3983
Ca ²⁺ -O15 0.0858 0.0259 0.153 0.032 -0.0258 0.0062 0.4	4027
Ca ²⁺ -O16 0.075 0.0233 0.1362 0.0283 -0.0226 0.0057 0.3	3993
Ca ²⁺ -N17 0.0523 0.0116 0.0518 0.0106 -0.0082 0.0024 0.3	3884
Ca ²⁺ -N18 0.005 0.0232 0.1156 0.0245 -0.0201 0.0044 0.4	4101
Ca ²⁺ -O25 0.0858 0.0246 0.1451 0.0302 -0.0242 0.006 0.4	4005
Ca ²⁺ -O26 0.0852 0.0264 0.158 0.033 -0.0266 0.0064 0.4	4027

Table 3: NBO donors and acceptors, hybridization, occupancy and their second order perturbation energy $E^{(2)}$ for (L-Li⁺) complex at the B3LYP/6-311G^{*}. LP is valence lone pair.

Donor(i)	Acceptor(j)	Hybridization(i)	Occupancy(i)	E ⁽²⁾ (kcal/mol)
LP (1) O13	LP* Li67	n ₀₁₃ =sp ^{1.79}	1.96084	0.89
LP (2) O13	LP* Li67	n ₀₁₃ =sp ^{11.18}	1.90489	0.18
LP (1) O14	LP* Li67	n ₀₁₄ =sp ^{2.57}	1.95422	1.65
LP (2) O14	LP* Li67	n ₀₁₄ =sp ^{4.47}	1.92738	2.48
LP (1) O15	LP* Li67	n ₀₁₅ =sp ^{1.81}	1.94619	18.67
LP (2) O15	LP* Li67	n ₀₁₅ =sp ^{8.86}	1.93631	7.71
LP (1) O16	LP* Li67	n ₀₁₆ =sp ^{1.61}	1.94411	20.88
LP (2) O16	LP* Li67	n ₀₁₆ =sp ^{10.90}	1.93838	6.96
LP (1) N17	LP* Li67	n _{N17} =sp ^{10.07}	1.85996	6.61
LP (1) N18	LP* Li67	n _{N18} =sp ^{6.06}	1.86484	8.29
LP (1) O25	LP* Li67	n ₀₂₅ =sp ^{1.78}	1.949	18.19
LP (2) O25	LP* Li67	n ₀₂₅ =sp ^{10.41}	1.93719	7.36
LP (1) O26	LP* Li67	n ₀₂₆ =sp ^{2.25}	1.94375	16.88
LP (2) O26	LP* Li67	n ₀₂₆ =sp ^{5.04}	1.93516	11.55
E ⁽²⁾				128.3

Table 4: NBO donors and acceptors, hybridization, occupancy and their second order perturbation energy E⁽²⁾ for (L-Na⁺) complex at the B3LYP/6-311G^{*}. LP is valence lone pair.

Donor(i)	Acceptor(j)	Hybridization(i)	Occupancy(i)	E ⁽²⁾ (kcal/mol)
LP (1) O13	LP* Na67	n ₀₁₃ =sp ^{1.80}	1.96021	1.09
LP (2) O13	LP* Na67	n ₀₁₃ =sp ^{11.23}	1.90571	0.54
LP (1) O14	LP* Na67	n ₀₁₄ =sp ^{3.13}	1.95311	2.57
LP (2) O14	LP* Na67	n ₀₁₄ =sp ^{3.53}	1.92517	5.21
LP (1) O15	LP* Na67	n ₀₁₅ =sp ^{1.34}	1.94983	16.3
LP (2) O15	LP* Na67	n ₀₁₅ =sp ^{30.09}	1.93583	2.38
LP (1) O16	LP* Na67	n ₀₁₆ =sp ^{1.29}	1.95064	16.28
LP (2) O16	LP* Na67	n ₀₁₆ =sp ^{30.42}	1.93662	2.62
LP (1) N17	LP* Na67	n _{N17} =sp ^{10.44}	1.86570	5.05
LP (1) N18	LP* Na67	n _{N18} =sp ^{5.32}	1.87844	8.72
LP (1) O25	LP* Na67	n ₀₂₅ =sp ^{1.35}	1.95154	15.8
LP (2) O25	LP* Na67	n ₀₂₅ =sp ^{27.34}	1.93711	3.01
LP (1) O26	LP* Na67	n ₀₂₆ =sp ^{1.38}	1.95141	15.08
LP (2) O26	LP* Na67	n ₀₂₆ =sp ^{19.87}	1.93571	3.28
		E ⁽²⁾		98.4

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Table 5: NBO donors and acceptors, hybridization, occupancy and their second order perturbation energy $E^{(2)}$ for (L-K⁺) complex at the B3LYP/6-311G. LP is valence lone pair.

Donor(i)	Acceptor(j)	Hybridization(i)	Occupancy(i)	E ⁽²⁾ (kcal/mol)
LP (1) O13	LP* (1) K67	n ₀₁₃ =sp ^{1.57}	1.96230	0.35
LP (1) O14	LP* (1) K67	n ₀₁₄ =sp ^{1.91}	1.96056	2.57
LP (2) O14	LP* (1) K67	n ₀₁₄ =sp ^{11.16}	1.91585	0.73
LP (1) O15	LP* (1) K67	n ₀₁₅ =sp ^{1.18}	1.96451	4.75
LP (1) O16	LP* (1) K67	$n_{016} = sp^{1.10}$	1.96544	4.51
LP (2) O16	LP* (1) K67	$n_{016} = sp^{1.00}$	1.93907	0.13
LP (1) N17	LP* (1) K67	n _{N17} =sp ^{10.05}	1.87691	1.24
LP (1) N18	LP* (1) K67	n _{N18} =sp ^{5.76}	1.89356	2.20
LP (1) O25	LP* (1) K67	n ₀₂₅ =sp ^{1.08}	1.96611	3.99
LP (2) O25	LP* (1) K67	n ₀₂₅ =sp ^{99.99}	1.94075	0.21
LP (1) O26	LP* (1) K67	n ₀₂₅ =sp ^{1.12}	1.96539	4.81
LP* (1)O26	LP* (1) K67	n ₀₂₅ =sp ^{1.00}	1.94026	0.06
		E ⁽²⁾		25.55

Table 6: NBO donors and acceptors, hybridization, occupancy and their second order perturbation energy E ⁽²⁾ for (L-Ca²⁺) complex at the B3LYP/6-311G*. LP is valence lone pair.

Donor(i)	Acceptor(j)	Hybridization(i)	Occupancy(i)	E ⁽²⁾ (kcal/mol)
LP (1) O13	LP* Ca67	n ₀₁₃ =sp ^{1.58}	1.94499	21.54
LP (2) O13	LP* Ca67	n ₀₁₃ =sp ^{99.99}	1.89463	1.11
LP (1) O14	LP* Ca67	n ₀₁₄ =sp ^{5.49}	1.94795	12.17
LP (2) O14	LP* Ca67	n ₀₁₄ =sp ^{2.59}	1.92410	15.17
LP (1) O15	LP* Ca67	n ₀₁₅ =sp ^{3.69}	1.94507	17.35
LP (2) O15	LP* Ca67	n ₀₁₅ =sp ^{3.31}	1.94276	15.23
LP (1) O16	LP* Ca67	n ₀₁₆ =sp ^{4.25}	1.94677	13.81
LP (2) O16	LP* Ca67	n ₀₁₆ =sp ^{2.70}	1.94151	15.32
LP (1) N17	LP* Ca67	n _{N17} =sp ^{6.37}	1.88531	12.25
LP (1) N18	LP* Ca67	n _{N18} =sp ^{5.49}	1.89585	14.15
LP (1) O25	LP* Ca67	n ₀₂₅ =sp ^{3.79}	1.94673	16.02
LP (2) O25	LP* Ca67	n ₀₂₅ =sp ^{3.01}	1.94112	15.9
LP (1) O26	LP* Ca67	n ₀₂₆ =sp ^{4.43}	1.94775	13.85
LP (2) O26	LP* Ca67	n ₀₂₆ =sp ^{2.72}	1.94229	17.15
		E ⁽²⁾		201.02

Table 7: HOMO and LUMO of natural bond orbitals of calculated complexes at the B3LYP/6-311G. All orbital energies are in atomic unit (1a.u=627.5095kcal/mol).

Complexes	Energy (a.u.)	Occupancy	Hybridization
<u>L-Li⁺</u>			
НОМО	-0.3584	1.8599	$n_{N17} = sp^{10.07}$
LUMO	-0.0135	0.1207	n_{Li67}^{*} =sp ^{0.04}
<u>L-Na⁺</u>			
НОМО	-0.3596	1.8657	$n_{N17} = sp^{10.44}$
LUMO	-0.0093	0.1189	$n_{Na67}^*=sp^{0.02}$
<u>L-K</u> ⁺			



International Journal of Pharmaceutical Sciences Review and Research

НОМО	-0.3030	1.9402	$n_{026} = sp^{1.00}$
LUMO	-0.0903	0.1106	$n_{K67}^* = sp^{0.00}$
<u>L-Ca²⁺</u>			
НОМО	-0.5064	1.8853	$n_{N17} = sp^{6.37}$
LUMO	-0.1199	0.1282	$n^*_{\text{Ca67}}\text{=sp}^{0.06}$

Table 8: Natural energy decomposition analyses (NEDA) for the complexes in kcal/mol at the B3LYP/6-311G*.

Complexes	СТ	ES	POL	хс	DEF ^{lig}	DEF ^{ion}	Tot. Interaction
L-Li⁺	-75.43	-109.99	-89.03	-9.29	120.15	20.07	-143.52
L-Na ⁺	-65.89	-99.86	-73.24	-11.07	111.43	22.71	-115.92
L-K ⁺	-64.1	-92.94	-77.1	-17.35	118.15	46.24	-87.09
L-Ca ²⁺	-101.8	-254.72	-299.24	-27.97	268.99	80.52	-334.22

CT: charge transfer, ES: electrostatic, POL: polarization, DEF: deformation.

Figure 3 implies that the HOMO orbital is oriented towards the donor's ligand and LUMO orbitals being oriented toward ions.

Therefore, [222B] ligand acts as donor, and Li⁺, Na⁺, K⁺, and Ca²⁺ act as acceptor. Furthermore, energy, orbital occupation number, and hybridization related to HOMO and LUMO of complexes in B3LYP/6-311G* level of theory are reported in Table 7.

Due to charge transfer from HOMO to LUMO, the trend of occupied number and energy in LUMO for understudiesd complexes are $(L-Ca^{2+})>(L-Li^+)>(L-Na^+)>(L-K^+)$, indicating that the occupied number LUMO increased 0.1282 a.u, while the energy of LUMO decreased -0.1199 a.u. It was concluded that $(L-Ca^{2+})$ complex is the most stable complexes in alkali metals and alkaline earth metals complexes.



Figure 3: HOMO and LUMO structures of the alkali metals and alkaline earth metal complexes with the B3LYP/6-311G.

Natural Energy Decomposition Analysis (NEDA)

A scheme has been proposed for decomposing interaction energy into various components which it has been called the natural energy decomposition analysis (NEDA), [34-36]. In this method, the molecular interaction energy was partitioned into attractive terms, such as the electrostatic (ES), the polarization (POL), the charge transfer (CT), the Pauli exchange repulsion (EX), and core

repulsion (DEF) contributions. The ES and POL terms describe the static and induced interactions between two monomers, respectively. The CT term is based on interaction of filled orbitals (donors) with empty ones (acceptors) for the species involved which is the most important stabilizing component in all complexes. The EX is from exchange interactions of electrons on the adjacent fragments, and is always attractive. The DEF component is due to the deformation of wave functions of isolated fragments compared to the wave functions in the optimized complex structures. The DEF or deformation of energy is a destabilizing quantity due to it always a positive value. Unlike to the has Kitaura-Morokuma method for energy decomposition analysis³⁷, while it suffers from Pauli-exclusion principal violation in intermediate wave functions that are used for ES and POL calculations. NEDA retains antsymmetric of intermediate wave functions.

NEDA data in Table 8 shows that the CT contribution for the alkali metal complexes are 25– 27 % of the total interactions, while for ES interaction, it is 37%– 40 % (Tot interactions = CT+ES+POL+XC). In addition, POL and XC interactions for alkali metal complexes are 29%–31% and 3%–7%, respectively.

On the other hand, the CT contribution and the ES, the POL and the XC interactions for $(L-Ca^{2+})$ is 14%, 37%, 43% and 4%, respectively. Comparing the data the relative order of NEDA contributions in the intermolecular interaction for the alkali metal complexes are as ES > POL > CT > XC, while for alkaline earth metal complex are POL > ES > CT > XC.

By considering that CT is associated to the covalent delocalization, and ES is associated to the ionic interactions, it is possible to calculate the covalent character of intermolecular bonds by CT/ (CT+ES). This ratio for alkali ions (Li⁺, Na⁺ and K⁺) are similar 0.41,0.40, and 0.41, respectively, while for the alkaline ions, the ratio is reduced to 0.30. The calculated results of this study are in good agreement with finding data for the



interaction energy of aza-, diaza-, and triaza-12 crown-4(A_n -12-crown-,n=1,2,3) and Li⁺, Na⁺, and K⁺ ions³⁸.

CONCLUSION

Cryptands are more potent, selective and stronger when they bind to alkali metals and alkaline earth metals. The stability of this crown ether complexes depends on several factors. This includes relative size of cation and the macrocyclic cavity, structural flexibility, nature of the substituent, nature and number of binding sites, acid-base character of the metal ions and nature of the solvent system³⁹.

In this work, the interactions of [222B] ligand with alkali cations like $\text{Li}^{^{+}},\,\text{Na}^{^{+}},\,\text{K}^{^{+}},$ and earth alkaline cation such as Ca²⁺ have been analayzed using AIM, NBO, and NEDA methods. All calculations have been carried out by DFT method at the B3LYP using 6-311G* basis sets. The AIM analysis presents that complexes of alkali metal and alkaline earth metals have closed interaction layer and electrostatic interaction. From NBO results, the stabilization energy trend in complexes are (L-Ca2+) > (L-Li+) > (L-Na+) > (L-K+), where the stabilization energy in Ca^{2+} is the highest. The results of NEDA show that the main driving force of interactions between [222B] ligand and alkali metal univalent cations is electrostatic. In contrast, polarization interaction is more important for the complex of alkaline earth divalent cation. The results show that $(L-Ca^{2+})$ complex is the most stable complexes.

Overall, the lithium with the smallest size forms the most stable complexes, while calcium ion with two positive charges, forms a most stable complexes compared to the other three complexes. Therefore, it has been found that the selectivity of complexation depends not only on the size of cation and the crown ether cavity, but also on the ionic charge of cation is dominant over the size of ion. The stability of these complexes depends on the number of (O) atoms, geometric disposition of (O) atoms, size and shape of the ligand as well as size of the metal and metal earth ions.

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