

Theoretical study on the binding selectivity of 18-membered azacrownethers with alkaline earth metal species

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ABSTRACT

The binding selectivity of 18-membered azacrownethers (monoaza- N1, diaza- N2, triaza- N3, tetraaza- N4, pentaaza- N5, and hexaaza-18-crown-6 N6) with Ca^{2+} , Sr^{2+} , Ba^{2+} have been studied by density functional theory (DFT) calculations. The complex binding selectivity was analyzed in term of interaction energies, thermodynamic properties, second order interaction energies, and charge transfer effects. The geometrical study shows that Ca^{2+} and azacrown complexes acquire envelope like structure, leading to shorter bond lengths. As a result, these complex systems have the highest interaction energies. Theoretical study also showed that N6 complex with alkaline earth metal ion were shown to be more stable complex than those ligand with lower nitrogen number. The interaction energy order is $\text{N0} < \text{N1} < \text{N2} < \text{N3} < \text{N4} < \text{N5} < \text{N6}$. This trend shows that the presence of more nitrogen on the crown ether cavity increases the interaction energies by approx. 7.3 % in going from N0 to N6. It is clearly showed that the contribution of the number of nitrogen play a dominant role in the binding selectivity of these systems.

Keywords: DFT method, alkaline earth, aza-crown ether, metal ion, binding selectivity

INTRODUCTION

Crown ethers have received increasing interest since they were first characterized by Pedersen [1, 2]. Their ability to selectively bind metal ions has led to a wide range of applications such as sensing [3], phase-transfer catalysis [4], and extraction [5]. The selectivity of crown ethers has often been explained in terms of the fit/misfit concept between the diameter of the metal ion and the crown ether cavity, involving interaction of charge (metal ion) and dipole (arises from the donor atom in crown ether). The presence of electrostatic induction effect from electron withdrawing or donating groups, altering types of heteroatoms (O, N, S and P) within crown ether and types of solvents (solvation) plays an important role in changing the host-guest interactions and therefore control the crown ether selectivity [6-9].

The properties of crown ethers can easily be tuned by modifying the cavity size, adding substituent groups, and replacing their heteroatom (O, N, S, and P). Different heteroatoms were introduced to modify the electronic, solubility and other properties of the crown ethers. Since the synthesis of monoaza-18-crown-6 ether was reported by Greene [10], series of azacrownethers have been synthesized and their properties to bind metal ions have been described. Among azacrowns such as diaza-18-crown-6, triaza-18-crown-6, tetraza-18-crown-6, pentaaza-18-crown-6, and

hexaaza-18-crown-6 ether are the most prominent ones [11-15].

Theoretical investigations have significantly helped to explain the selectivity of crown ethers capturing metal ions [16-20]. The effect of nitrogen number on the metal binding selectivity of 12-membered crown ethers (12-crown-4, aza-12-crown-4, diaza-12-crown-4, triaza-12-crown-4, and tetraza-12-crown-4) with Be^{2+} , Li^+ or Na^+ ions have been reported employing the B3LYP/6-31+G** level of theory [21]. In another work, the structures and metal binding selectivity of complexes of 12-Crown-4 and its heterocyclic derivatives containing N, P, and S atoms have been reported at the same levels of theory [22]. The selectivity of azacrown with metal ions in term of the nitrogen position isomers of diaza-18-crown-6, diaza-15-crown-5, diaza-12-crown-4, and their complexes with Na^+ ion have been studied by the density functional theory using B3LYP/6-31+G** level of theory [23]. In this study, we explored the interaction between 18-membered azacrown ethers with the alkaline earth metal species (Ca^{2+} , Sr^{2+} , Ba^{2+}). The computational techniques were applied to investigate the structural, metal type and number of nitrogen effect on the binding selectivity of aza-18-crown-6 ethers with alkaline earth, lanthanide, and actinide metal ions.

Computational details

All calculations were conducted using density functional theory employing the hybrid B3LYP method [24, 25].

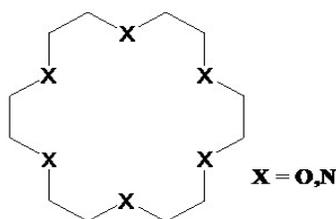
Geometry optimizations were performed without any symmetry constraints. Optimized geometries were confirmed to be minima on the potential energy surface by analyzing vibrational properties. Quasi-relativistic effective core potential developed in the Stuttgart and Dresden groups were used together with the accompanying basis function to describe the valence electron density of metal ions. For crown ether atoms (O, C, H), DZP basis sets were employed. The BSSE was eliminated with the counterpoise method proposed by Boys and Bernardi [26]. All calculations were done with the Gaussian 03 program package [27].

RESULT AND DISCUSSION

Geometrical parameters

The structures of N0 (18-crown-6), N1 (monoaza-18-crown-6), N2 (diaza-18-crown-6), N3 (triazza-18-crown-6), N4 (tetraaza-18-crown-6), N5 (pentaaza-18-crown-6), and N6 (hexaaza-18-crown-6) and their complexes with metal ions were optimized at the density functional

level of theory using the B3LYP methodology. DZP basis sets were applied for crown ether atoms, and the SDD basis for the heavier cations. We modeled a 1:1 ratio of differently azacrown ethers and one metal ion each. The nitrogen atoms were introduced to replace oxygen atoms in crown ether ring as depicted in Scheme 1. Figure 1 depicts the binding mode of M^{n+} (azacrown) complexes at B3LYP level of theory. Comparing M^{n+} -azacrown complexes, the position of these ions within the ethers' cavity is appreciably different. Figure 1 shows that because the average calculated cavity of the azacrown ether (represented by hexaazacrown, N6 = 2.60 Å) is larger than the ionic diameter of Ca^{2+} (2.00 Å) and Sr^{2+} (2.36 Å), the cavity of hexaazacrown accommodate the Ca^{2+} and Sr^{2+} . Since these ions diameter is small to fit the crown cavity, the nitrogen heteroatom of crown ether bent out of the plane, in order to form interaction with ions. In contrast, the Ba^{2+} ions are encapsulated inside the ether moiety as they perfectly fits into the cavity, their ionic diameter amounting to 2.70 Å, respectively.



Scheme 1.

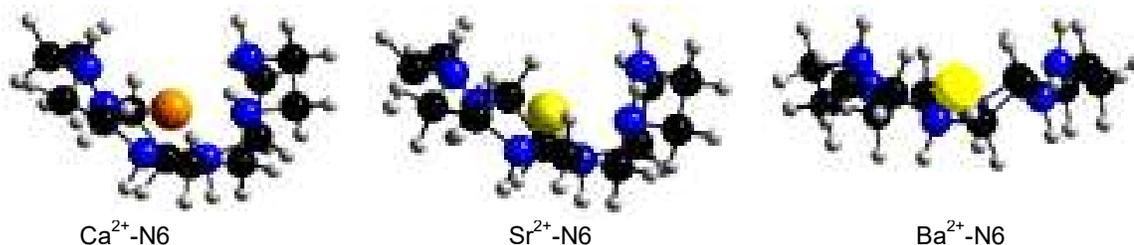


Figure. 1 The fully optimized structures of M^{n+} (hexaazacrown) complexes at B3LYP level of theory.

Table 1. Calculated distances/Å of the fully optimized structures of M^{n+} (azacrown) complexes at B3LYP level of theory.

Coordination Bond	Ionic Diameter	N0	N1	N2	N3	N4	N5	N6
Ca^{2+} -O/N	2.00	2.42 (2.41) ^a	2.44	2.41	2.43	2.44	2.42	2.52
Sr^{2+} -O/N	2.36	2.63 ((2.62) ^a	2.59	2.58	2.60	2.62	2.63	2.70
Ba^{2+} -O/N	2.70	2.77 (2.77) ^a	2.78	2.79	2.76	2.78	2.79	2.85
Cavity size free crown		2.80 (2.6-3.2)	2.68	2.78	2.42	2.55	2.54	2.60

a. Ref [28]

The selected geometric parameters of these complexes are listed in Table 1. The corresponding average bond lengths of Ca^{2+} -O/N, Sr^{2+} -O/N and Ba^{2+} -O/N in the M^{n+} -azacrown complexes increase as the ionic diameter increase. The average bond length of Ca^{2+} -N, Sr^{2+} -N and Ba^{2+} -N in the hexaazacrown complexes are

2.52 Å, 2.70 Å, and 2.85 Å, respectively. The effect of the nitrogen number dependence also exists in M^{n+} -azacrown geometrical parameters. It showed by the complex average bond length variations as the number of nitrogen atom increase. The bond length can be used as the preliminary prediction of the strength of

interaction between the metal ions and crown ethers, which are reflected in their binding properties.

Binding energies and Selectivity

Generally, the binding energy is related to the stability of the complexes. The interaction energies for the metal ion (M) and crown ether (CE) complexes were calculated as the energy difference between the complexes and their respective monomers. For the system treated, the binding energy can be expressed as follows:

$$\Delta E = (EM_{CE}) - (EM + ECE) \quad 1$$

Here, EM–CE is the complex energy, EM the energy of metal ion, and ECE the energy of crown ether. The effect of nitrogen number on the complex stability is analyzed using binding energies in the gas phase with the absence of solvent molecules (Table 2). The interaction energies were corrected for the undesirable effects of the basis set superposition error (BSSE) using the counterpoise method. Small changes between the BSSE corrected and uncorrected interaction energies indicate the suitability of the basis functions (SDD/DZP) employed. According to the calculated interaction energy data in Table 2, the interaction energy order is $Ba^{2+} < Sr^{2+} < Ca^{2+}$. Interestingly, the best fit ionic diameter encapsulation of Ba^{2+} ions in crown ether cavities less contribute to stability of the complexes.

The interaction energy also correlates with the number of nitrogen and clearly shows the preferred nitrogen heteroatom for the selectivity of the metal ion. It can be observed that the interaction energies gradually increase with the nitrogen number. This result agrees with previous studies [18, 21]. The interaction energy order is $N0 < N1 < N2 < N3 < N4 < N5 < N6$. This trend shows that the presence of nitrogen heteroatom on the crown ether cavity increases the interaction energies by approx. 7.3 % in going from N0 to N6. Apparently, the nitrogen number of the azacrown ethers plays an important role in the stability of these complexes, and leads to different metal binding energies, which perfectly means that the nitrogen number does influence their metal binding selectivity.

Thermodynamics parameters

The stability and reaction activity of complexes is further studied by thermodynamics properties of the complexes. The calculated thermodynamics properties of formation are listed in Table 3, including the enthalpy of formation ΔH_f , the thermal free energy of formation ΔG_f , and the entropy of formation ΔS_f . In general, the formation of these complexes is exothermic ($\Delta H < 0$) which causes them to be more rigid, which is probably

why the formation entropy for the coordination reaction is slightly negative (Table 3). However, the change in the enthalpy is large enough to overcome the formation entropy. In addition, the reaction equilibrium is in favor of the formation of these complexes ($\Delta G < 0$). The Gibbs free energies have a similar trend to the interaction energies, the Gibbs free energies order are $Ba^{2+} < Sr^{2+} < Ca^{2+}$. The effect of nitrogen number on the complex thermodynamic properties also has similar effect with the interaction energies. The thermodynamics parameters of formation show that these complexes are stable and easy-to-form compounds with high reactivity.

Second-order interaction energies and charge transfer

The effect of nitrogen number given above is further studied by the second-order interaction energies $E2(ij)$ trend based on the natural bond orbital (NBO) analysis. $E2(ij)$ corresponds to the intensity of interaction between Lewis donor and non-Lewis acceptor NBO. For each donor NBO (i) and acceptor NBO (j), $E2(ij)$ associated with ϵ_i and ϵ_j delocalization can be estimated as follows:

$$E2(ij) = q_i \times F(ij) / (\epsilon_i - \epsilon_j) \quad (2)$$

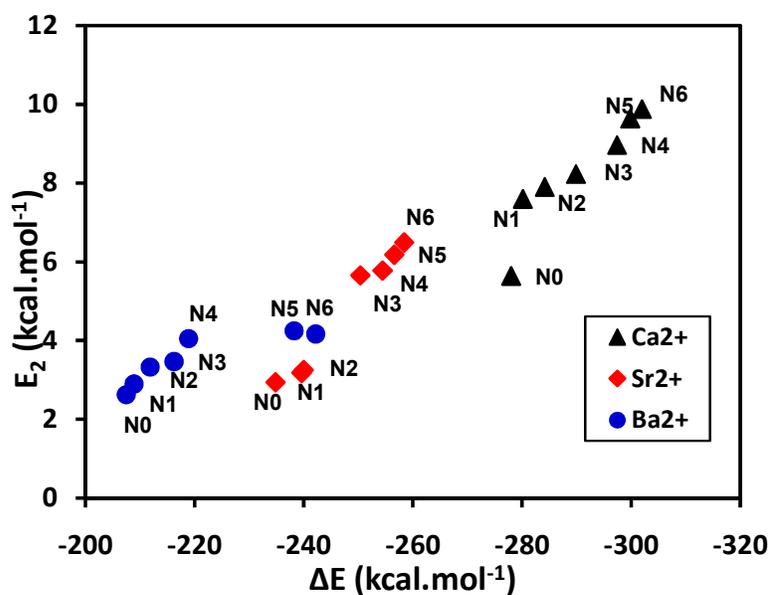
Here, q_i is the donor orbital occupancy, ϵ_i , ϵ_j are diagonal elements (orbital energies), and $F(i,j)$ are offdiagonal elements, respectively, associated with the NBO Fock matrix. A good correlation between the maximum second-order interaction energies $E2(ij)$, the interaction energies ΔE and the nitrogen number shown in Figure 2. The greater the value of second-order interaction energies, the higher the intensity of the charge transfer between the metal cations with azacrown ether so that the stronger the interaction, resulting in more stable complexes formed. The second-order interaction energies $E2(ij)$ value increases in the following order $Ba^{2+} < Sr^{2+} < Ca^{2+}$. Increasing the amount of nitrogen lead to increased value the second-order interaction energies $E2$ thus increasing the charge transfer from the metal cation to the crown ethers. The maximum value $E2$ experienced an increase of 15 kcal.mol^{-1} from N0 to N6. It can be concluded that the second-order interaction energies predict N6 to have a stronger metal interaction selectivity than the azacrown ethers, which is the same conclusion deduced by the interaction energy and thermodynamic parameters. Clearly, the effect of nitrogen number dependence is apparent in the interaction energies between the metal ions and the azacrown ether.

Table 2 Binding energies $\Delta E/\text{kcal.mol}^{-1}$, BSSE energies $E_{\text{BSSE}}/\text{kcal.mol}^{-1}$, and the interaction energies corrected for BSSE $\Delta E_{\text{BSSE}}/\text{kcal.mol}^{-1}$ of the M^{n+} (azacrown) complexes in the gas phase at 298.15 K.

Ion	R	N0	N1	N2	N3	N4	N5	N6
Ca^{2+}	ΔE	-278.04	-282.54	-285.34	-289.91	-297.42	-299.84	-302.99
	E_{BSSE}	4.94	4.54	4.53	4.65	4.78	4.82	4.98
	ΔE_{BSSE}	-273.10	-278.00	-280.81	-285.26	-292.64	-295.02	-298.01
Sr^{2+}	ΔE	-234.85	-239.64	-240.00	-250.38	-254.47	-256.59	-258.41
	E_{BSSE}	6.13	5.7	5.15	5.23	5.5	5.09	6.13
	ΔE_{BSSE}	-228.71	-233.94	-234.85	-245.14	-248.96	-251.49	-252.28
Ba^{2+}	ΔE	-207.48	-208.93	-211.87	-216.25	-218.90	-238.26	-242.21
	E_{BSSE}	4.63	4.45	5.53	5.48	5.49	5.55	5.41
	ΔE_{BSSE}	-230.96	-230.96	-225.79	-225.79	-214.62	-202.57	-202.57

Table 3. Thermodynamics enthalpy of formation $\Delta H_f/\text{kcal.mol}^{-1}$, free energy of formation $\Delta G_f/\text{kcal.mol}^{-1}$, and the entropy of formation $\Delta S_f/\text{cal.mol}^{-1}$ of the M^{n+} (azacrown) complexes in the gas phase at 298.15 K.

Ion		N0	N1	N2	N3	N4	N5	N6
Ca^{2+}	ΔH_f	-245.91	-243.30	-246.99	-243.61	-250.71	-252.03	-255.76
	ΔG_f	-234.24	-230.39	-235.09	-232.29	-238.65	-240.25	-243.9
	ΔS_f	-39.13	-43.28	-39.91	-37.97	-40.46	-39.52	-39.77
Sr^{2+}	ΔH_f	-212.54	-209.05	-208.92	-207.13	-213.12	-214.74	-211.30
	ΔG_f	-202.55	-201.50	-197.59	-195.39	-201.23	-203.22	-207.18
	ΔS_f	-33.50	-25.32	-38.00	-39.37	-39.87	-38.63	-13.81
Ba^{2+}	ΔH_f	-187.39	-187.52	-183.95	-176.68	-185.81	-181.21	-181.43
	ΔG_f	-175.37	-177.01	-175.01	-166.35	-172.6	-169.93	-168.48
	ΔS_f	-40.31	-35.29	-29.98	-34.63	-44.30	-37.82	-43.44

Figure 2. Correlation between the maximum second-order interaction energies $E_2(ij)$ (kcal.mol^{-1}) and the interaction energies ΔE (kcal.mol^{-1}) with the number of nitrogen heteroatom.

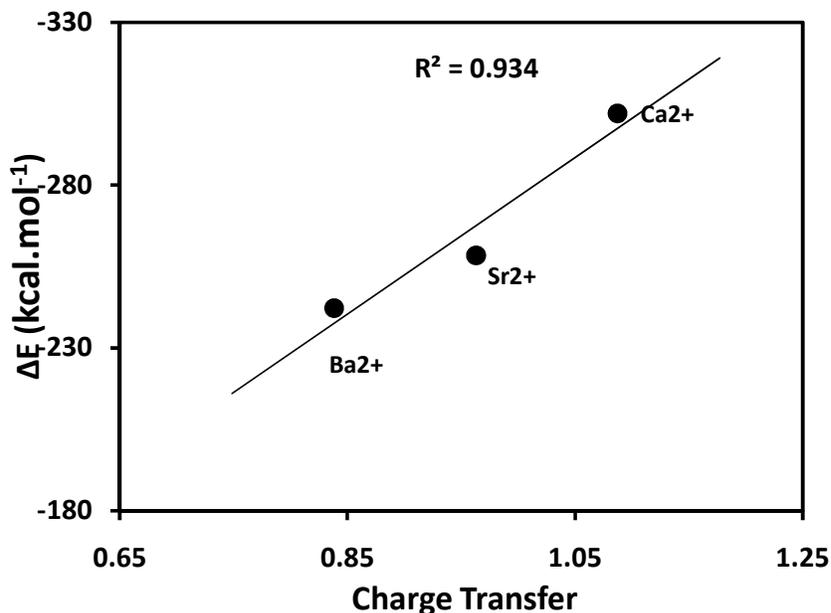


Figure 3. Correlation between the maximum the interaction energies ΔE (kcal.mol⁻¹) with the metal charge transfer in N6 complexes.

Generally, increasing in the charge transfer will result in the increase of second order interaction energy. It is also positively correlated with the rise in complex interaction energy. For the systems under consideration, the charge transfer (Qt) is defined as the charge difference between the free metal ions and its corresponding moieties in the complex. For charge transfers, unfortunately, there is no perfect method to accurately obtain the electron populations of atoms. The Mulliken population analysis was applied in the current work. The correlation between the charge transfer and energy interaction can be seen in Figure 3. It shows that the amount charge transfer from donor to acceptor linearly correlated with the energy interaction. It is found that the correlation between the maximum the interaction energies ΔE (kcal.mol⁻¹) with the metal charge transfer in N6 complexes has linearity² = 0.9341. This result agrees with many previously reported complexes [29, 30]

CONCLUSION

The binding selectivity of 18-membered azacrown ether complexes have been studied by DFT calculations. It can be concluded the number of nitrogen play important role in binding selectivity of 18-membered azacrown ethers. The interaction energy order is Ca²⁺ > Sr²⁺ > Ba²⁺. The hexaaza-18-crown-6 with the highest nitrogen number exhibits the largest metal binding capability to metal ions. The interaction energy of the complexes correlated well with the complex second order interaction energy and the amount of charge transfers. This theoretical study will contribute to the

material design of ion recognition and other related fields.

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