



Alkaline Earth Extraction by Derivatives of 15-Crown-5: A Theoretical Study

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Abstract. A theoretical study of alkaline earth extraction using a 15-crown-5 derivative has been carried out. The selectivity of the crown ether derivatives to extract alkaline earth metal cations (Be^{2+} , Mg^{2+} , Ca^{2+}) is studied by Density Functional Theory (DFT). The DFT calculations use 6-31G(d) and LANL2DZ basis set at the B3LYP level of theory. The selectivity of the 15-crown-5 derivative to bind alkaline earth metal cations is assessed based on the interaction energy (ΔE) of the addition of the substituent affecting the crown ether's selectivity. The electron donor group can increase the selectivity of the crown ether to bind the metal cations. Based on the interaction energy, charge transfer, and electron distribution in HOMO-LUMO, it can be concluded that the selectivity of the 15-crown-5 derivative to extract the metal ions increased by $\text{Be}^{2+}\text{Mg}^{2+} > \text{Ca}^{2+}$.

Keywords: Extraction · Alkaline earth · Crown ether · theoretical study

1 Introduction

Industrial development plays a very important role in boosting the national economy and is expected to be a force for the national economy [1, 2]. Alkaline earth metals have been used in industrial fields such as the nuclear power, aerospace, and cement industries. Also, there are negative impacts that can harm living things. Beryllium has toxic properties and can potentially be a carcinogenic substance that causes acute beryllium disease. Magnesium used in steel mills produces hazardous waste from explosive materials. Calcium and strontium can produce radioactive waste that causes contamination of biota and the environment. So we need a processing method that can process radioactive waste optimally so as not to contaminate the surrounding environment [3, 4].

One of the effective compounds for extracting alkaline earth elements is crown ether. Crown ether is a cyclic molecule that plays a role in the formation of a selective cation complex because of its ability to bind positive metal ions coordinated to the ring of oxygen atoms in the central cavity [5–10]. The suitability of the metal cation's diameter with the crown ether's cavities influenced the crown ether's selectivity in binding cations.

Many researchers have carried out studies on the selectivity of crown ether compounds to alkaline earth elements but only limited to certain crown ethers. Therefore, finding the best crown ether structure for extracting alkaline earth elements is necessary.

One way is to vary the structure of the crown ether by adding substituents. The addition of substituents to the crown ether structure will affect the degrees of freedom of the crown ether molecules in adjusting their conformation when interacting with metal ions. The addition of various substituent groups in the benzene ring will result in the selectivity of the crown ether, which is governed by the nature of the substituent [11–16]. The stability of the complex between crown ether and metal cations can be seen from the conformational geometry and total binding energy possessed by the crown ether complex with metal cations. Current theoretical studies focus on the selectivity test of 15-crown-5 derivatives on alkaline earth.

2 Materials and Methods

The method used in this research is the DFT method on the basis set 6-31G(d) and LANL2DZ ECP at the B3LYP theory level. This research examines the extraction of crown ether compounds against alkaline earth metals Be^{2+} , Mg^{2+} , and Ca^{2+} . The crown ether used was 15-crown-5, and the addition of various substituents used was $-\text{NO}_2$, $-\text{CH}_3$, $-\text{OH}$. The tool used in this research is software consisting of Gaussian 09 [17]. The geometric parameter aims to ensure that the basis set 6-31G(d) at the theoretical level B3LYP can be used by matching the parameters between the calculation results and the experimental single crystal structure. The calculation of the interaction energy (ΔE) aims to determine the stability of a crown metal-ether complex. The interaction energy calculation is based on the heat of formation of the heat of formation. The interaction energy of crown ether compounds with metal cations in the $[\text{Mn}^+(\text{crown ether})]$ complex is calculated by the equation: $\Delta E = E_{\text{Ecomplex}} - (E_{\text{ion}} + E_{\text{crown ether}})$. NBO analysis was used to strengthen the selectivity of crown ethers. NBO analysis was carried out by studying the interactions between alkaline earth metal ions and oxygen atoms in crown ether. In the calculation of NBO, the value of charge transfer can also be seen to explain how strong the bonds are formed between metal ions and crown ethers. Visualization of the HOMO-LUMO orbitals can explain the effect of metal ion types on the electron distribution in the complex and the selectivity of crown ethers. The distribution of electrons in the HOMO-LUMO orbitals' visualization results can be marked in the red area.

3 Results and Discussion

In computational chemistry calculations, a basis set is chosen to ensure that the structure in the calculation is in a stable state. Then the geometric parameters are obtained, which aim to ensure that the basis set of 6-31G(d) at the theoretical level of B3LYP can be used by matching the parameters between the calculated results and the experimental single crystal structure. Suppose the results between the calculations and the experimental x-ray data are similar. The DFT method with the basis set 6-31G(d) at the B3LYP theory level is appropriate for this study (Fig. 1).

The addition of substituents to the crown ether structure can affect the selectivity of a complex compound. In this study, donor groups such as $-\text{CH}_3$ and $-\text{OH}$ are added, while the withdrawal group used is $-\text{NO}_2$. A donor group is an electron-donating group

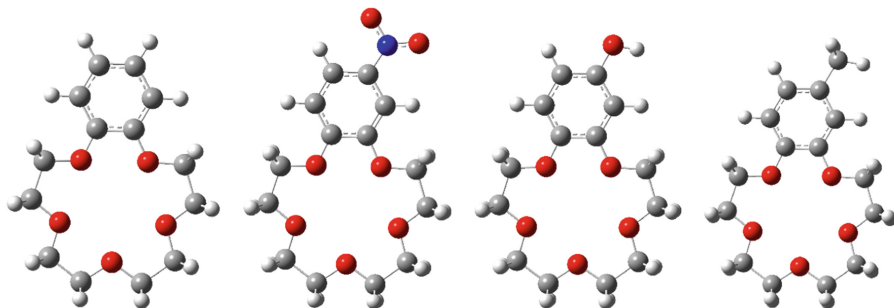


Fig. 1. Three-dimensional structure of 15-crown-5 derivative compound with substituent variation

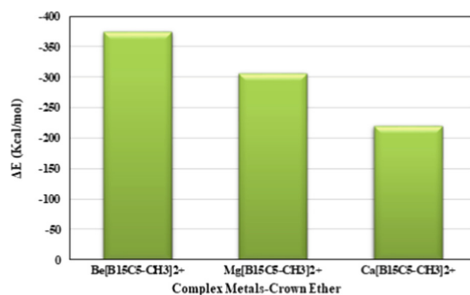


Fig. 2. Selectivity of crown ethers for alkaline earth metals

that can activate the benzene ring to become more electronegative and attract incoming electrophiles. The electronegative nature of the activated benzene ring can directly affect the crown ether derivative molecules, so the ligand's ability to bind metal cations will also increase. Adding an electron-withdrawing group such as $-\text{NO}_2$ to the benzene group will cause a deficiency of electron density in the oxygen atom of the crown ether, so it will be less effective in binding alkaline earth metal cations. The alkaline earth metal extraction process is carried out by placing the metal in the middle of the crown ether structure to form a stable complex compound and produce complex compound interaction energy, as seen in Fig. 2.

The interaction energy is the energy difference between the products and the reactants. The product is a complex compound between the 15-crown-5 derivative and a metal cation. In contrast, the reactants are crown ether derivative compounds with metal cations. Crown ether derivatives such as 15-crown-5 have structural compatibility with light metals such as alkaline earth metals. The results of energy calculations on metal cations stated that crown ether derivative complexes with alkaline earth metal cations produced the strongest interaction energy in complex compounds by adding an electron donor group, namely $-\text{CH}_3$. It can be said that the donor group has a very important role in increasing the selectivity of complex compounds, and the withdrawing group, such as $-\text{NO}_2$, can reduce the selectivity of complex compounds. The increasingly negative interaction energy indicates the strong bond between the ion and the crown ether.

Table 1. Change in charge of crown metal-ether complex based on Mulliken Population Analysis (MPA) and Natural Population Analysis (NPA)

Substituent	Be ²⁺ complexes		Mg ²⁺ complexes		Ca ²⁺ complexes	
	MPA	NPA	MPA	NPA	MPA	NPA
H	0.9411	0.5938	0.7761	0.4212	0.6021	0.3788
OH	0.9406	0.5933	0.7761	0.4209	0.6021	0.3791
NO ₂	0.9388	0.5922	0.7757	0.4202	0.6028	0.3787
CH ₃	0.9415	0.5942	0.7766	0.4213	0.6029	0.3791

Figure 2 shows that the strongest interaction energy is the Be²⁺ complex, and the weakest interaction energy is the Ca²⁺ complex.

The charge transfer that occurs in complex compounds can determine the selectivity of a complex compound. In this study, charge transfer data can be explained through two methods, namely the Mulliken Population Analysis (MPA) method, and the Natural Population Analysis (NPA) method. The natural population analysis method and the Mulliken population analysis method can explain the amount of charge transfer based on the hybridization of a compound. Table 1 shows the charge transfer values of the crown metal-ether complex compounds.

Charge transfer data obtained based on the MPA and NPA methods yielded a fairly good correlation to changes in the interaction energy of the 15-crown-5 derivative complex with alkaline earth metal cations. The smaller the value of MPA and NPA, the more charge is transferred, so the smaller the interaction energy produced. The higher the difference between the free charge of the ion and the charge of MPA and NPA, the stronger the interaction energy of the 15-crown-5 derivative complex with alkaline earth metal cations, making it more selective. Orbital visualization in the HOMO and LUMO states was carried out to explain better the bond strength that occurs in the 15-crown-5 derivative complex compound with alkaline earth metal cations. HOMO and LUMO visualizations are described in Fig. 3.

Based on the selectivity of crown ethers for alkaline earth metals, it is known that the strongest interaction energy is found in the -CH₃ substituted complex. In complex compounds the electron distribution between [Be(15C5-CH₃)]²⁺, [Mg(15C5-CH₃)]²⁺, [Ca(15C5-CH₃)]²⁺ experienced a decrease in intensity from Be²⁺ > Mg²⁺ > Ca²⁺. The distribution of electrons due to charge transfer in complex compounds is directly proportional to the strength of the bonds formed. The more the distribution of electrons, the stronger the interaction energy that occurs so that it can be said to be more selective.

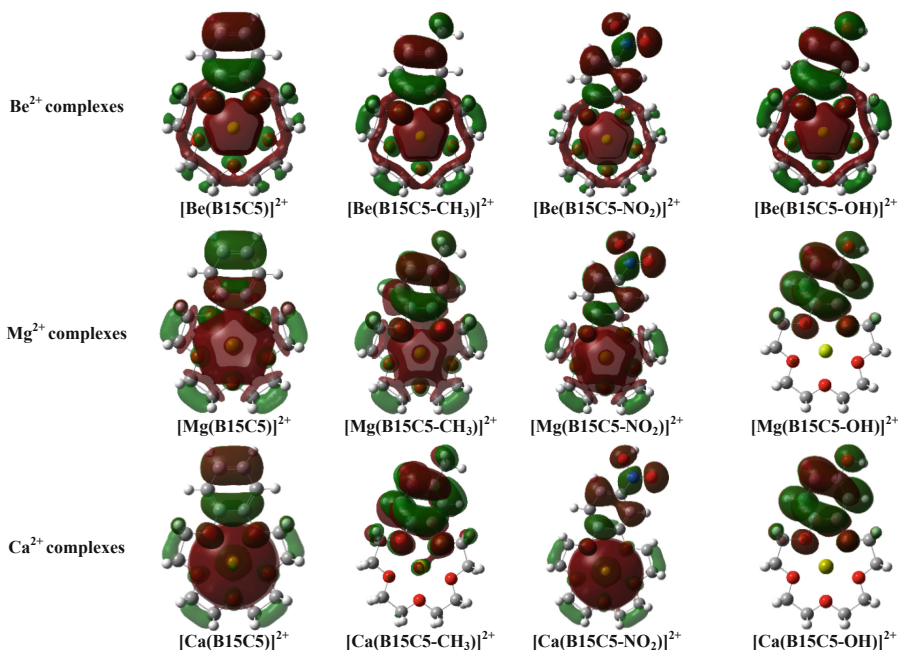


Fig. 3. Comparison of the effect of substituents on the distribution electrons of HOMO-LUMO

4 Conclusion

The DFT method using the basis set 6-31G(d) at the level of the B3LYP theory can explain the structure and energy of the compound of the crown ether derivative complex (15-crown-5) with alkaline earth metal cations (Be^{2+} , Mg^{2+} , Ca^{2+}). The selectivity of the crown ether derivatives to the alkaline earth metal cations increases from Be, Mg, and then Ca, which is based on the interaction energy value of the complex compound. The addition of electron donor substituents increases the selectivity of the crown ether shown based on peak values on the addition of the $-\text{CH}_3$ group in the Be, Mg, and Ca complex.

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