DFT Study of Selectivity of 12-Crown-4 Derivatives on Alkali Metal Ions

Saprizal Hadisaputra(✉), Husnul Khotimah, and Aliefman Hakim

Chemistry Education Program, Faculty of Teachers Training and Education, University of Mataram, Mataram, Indonesia
{rizal,aliefman}@unram.ac.id

Abstract. A theoretical study of alkaline earth extraction using 12-crown-4 derivative has been carried out. The capability of the crown ether derivative to extract alkaline metal cations (Li^+, Na^+, K^+) is studied by Density Functional Theory (DFT) Method. The DFT calculations uses 6-311G(dp) basis set at the B3LYP level of theory. The presence of electron-withdrawing substituents lowers the binding energy, while electron donors increase the binding energy. The selectivity of the crown ether to binding cations depends on the structural match between ionic radii of the crown ether cavity. The selectivity of the 12-crown-4 derivative to extract the metal ions increased by $Li^+ > Na^+ > K^+$.

Keywords: density functional study · crown ether · alkali ions

1 Introduction

The industrial sector also has a negative impact in the form of industrial waste, which, if not managed properly and properly, will cause pollution [1, 2]. Industrial growth is always accompanied by the problem of disposing of industrial waste that pollutes the environment. Industrial uses of alkali metals, such as batteries, sodium vapor lamps, and fertilizers (plant nutrition), are also used in drilling fluids in the petroleum industry. In addition to the industrial uses of alkali metals in industry, there are also negative impacts, such as B3 waste generated from lithium [3, 4]. Depending on the intensity, large amounts of external exposure can lead to burns, acute radiation sickness, and even death. Tissue that has been contaminated will be exposed to beta particles and gamma radiation which can increase cancer risk. So it is necessary to do a processing method that can process radioactive waste optimally so as not to contaminate the surrounding environment [5]. One of the effective compounds for alkaline extraction is crown ether.

Crown ethers can be used as complexing reagents for a metal cation. The ability of crown ethers as ionic complexes is related to the cavity radius of the crown ethers and the diameter of metal cations [6–10]. Diao et al. studied alkaline earth complexation with 12-crown-4 derivatives. The influence of the heteraom group affects the selectivity of the crown ether [11]. The effect of suitability of ring size with crown ethers and substituents on the selectivity of crown ethers has also been studied using theoretical studies. The more appropriate the size of the diameter of the ether crown with the metal

S. Hadisaputra et al. (Eds.): NiTRIC 2022, AHCPS 4, pp. 83–89, 2023.
https://doi.org/10.2991/978-94-6463-130-2_10

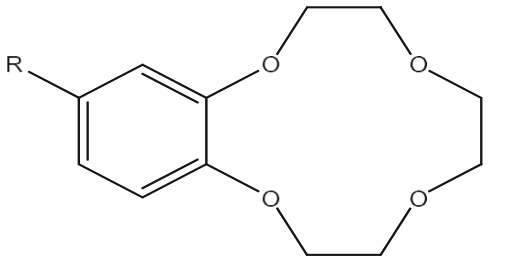


Fig. 1. Illustration of substituent replacement in benzo-12-crown-4

cations, the stronger the interaction that occurs. Furthermore, the electron donating group makes a positive contribution to the selectivity of the crown ether. In contrast, the electro wothdrawing group gives the opposite result [2–16]. This study focuses on the selectivity of 12-crown-4 extraction for cations Li+, Na+, and K+ using DFT at the theoretical level of B3LYP/^-31G(d) and LAN2DZ.

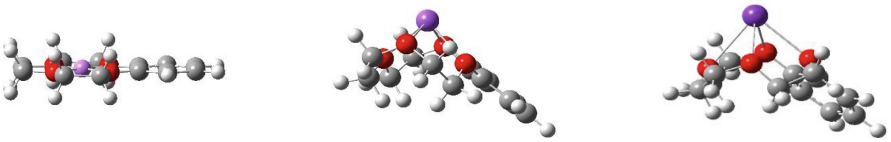
2 Computational Method

The method used in this study is the DFT method with a basis set of 6-311G(dp) and LAN2DZ ECP at the B3LYP theory level. All the calculation was conducted by Gaussian 09W [17]. The interaction energy of the alkali metal complex with the derived 12-Crown-4 crown ether. The interaction energy in the gas phase (ΔEint) of crown ether compounds with cations in the [Mn+.(crown ether)] complex is calculated by the formula: $\Delta E_{int} = E_{complex} - (E_{ion} + E_{crown\ ether})$.

3 Results and Discussion

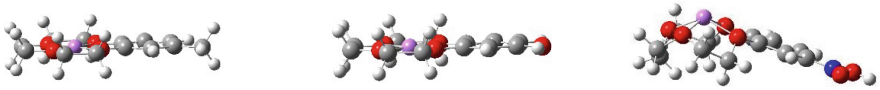
The structure of the alkali metal optimization results with 12-Crown-4 gives an illustration that the metal with crown ether is the most selective. Figure 1 shows that the $Li[B12C4]^+$ complex looks like Li^+ metal is very compatible with 12-Macrota-4 seen from the Li^+ ion, which is right in the middle of the crown ether, while in the $Na[B12C4]^+$ complex, it can be seen that the Na^+ metal slightly comes out of the crown ether. Then in the $K[B12C4]^+$ complex, K^+ metal was seen moving away from the crown ether. It indicates that the K^+ metal with 12-Crown-4 is less selective (Fig. 2).

Electron-driving groups such as -OH and $-CH_3$ activate the benzene ring, making it more electronegative and attracting incoming electrophiles. Meanwhile, electron-withdrawing groups such as $-NO_2$ can deactivate the benzene ring by withdrawing the electron density from the ring due to the induction effect. The electronegative group will reduce the benzene ring's electron density, causing a decrease in the electronegativity of the benzene ring. The substituents in the crown ether affect the degree of freedom of the crown ether structure to adjust its conformation when interacting with



(a) $Li[B12C4]^+$ (b) $Na[B12C4]^+$ (c) $K[B12C4]^+$

Fig. 2. The structures of the optimization results of alkali metals by the 12-Mahkota-4 derivative calculated on the basis set of 6-31G(d) at the theoretical level B3LYP



(a) $Li[B12C4\text{-}CH_3]^+$ (b) $Li[B12C4\text{-}OH]^+$ (c) $Li[B12C4\text{-}NH_2]^+$

Fig. 3. Three-dimension structures of the complex effect of adding substituents

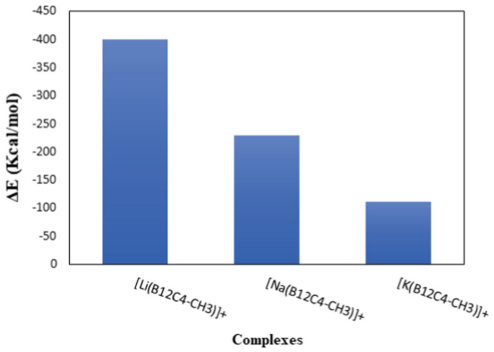


Fig. 4. Selectivity of crown ethers to alkali metals

metal ions. Figure 3 shows that the electron-pushing group is more selective than the electron-withdrawing group.

The selectivity of crown ether can be done by looking at the interaction energy of crown ether with metal ions. Determination of selectivity towards Li^+, Na^+, and K^+ ions was carried out by evaluating the interaction energy of each crown ether that had been added with electron-withdrawing and pushing groups such as $-NH_2$, -OH, and $-CH_3$. If the interaction energy is negative, the better, and if the interaction energy is positive, the group is less selective for extraction.

The selectivity of the complex was seen that the ratio of selectivity of crown ether with metal ion had a comparison of the interaction energy of crown ether with the addition of a substituent on the electron driving group, namely the $-CH_3$ group experienced an increase in the negative value of the interaction energy. The complexes that experienced an increase in the negative value of the interaction energy were the $Li[B12C4\text{-}CH_3]^+$ complex, then the $Na[B12C4\text{-}CH_3]^+$ complex, and the $K[B12C4\text{-}CH_3]^+$ complex experienced a decrease in the negative value of the interaction energy. Comparison of the

Table 1. Charge transfer of metal complexes with crown ether

Substituent	Li^+ complexes		Na^+ complexes		K^+ complexes	
	MPA	**NPA**	**MPA**	**NPA**	**MPA**	**NPA**
H	0.4372	0.3305	0.0228	0.2928	0.5405	0.4965
CH_3	0.4387	0.6634	0.0239	0.6462	0.544	0.4956
OH	0.4383	0.3306	0.0229	0.2929	0.5433	0.4949
NO_2	0.4371	0.3299	0.0187	0.2921	0.5386	0.4964

increase in the negative value of the interaction energy to the decrease in the negative value of the interaction energy can be seen in Fig. 4. That $Li[B12C4\text{-}CH_3]^+ > Na[B12C4\text{-}CH_3]^+ > K[B12C4\text{-}CH_3]^+$.

The calculation of NBO can also know the value of charge transfer which can explain how strong the bond is formed between the crown ether and metal ions. This research uses two load analysis methods: MPA *(Mulliken Population Analysis)* and NPA *(Natural Population Analysis)*. The larger the difference between MPA and NPA, the more selective it is, whereas the lower the difference between MPA and MPA less selective.

A comparison of metal cation charge and complex charge on various MPA and NPA analysis methods is shown in Table 1. It shows that MPA and NPA methods provide acceptable data. It can be seen that the addition of substituents with electron-driving groups, such as CH_3, has the highest MPA and NPA difference. In contrast, the addition of electron-withdrawing groups, such as NO_2, has the lowest MPA and NPA difference.

NBO analysis is used to determine the complex load and condition of HOMO LUMO. The study of HOMO LUMO is important to determine the reactivity of a complex or the stability of the complex. This HOMO LUMO visualization shows regions with high electron density and regions with low electron density. The complex with the highest electron density is around the point of interaction between the metal ion and the oxygen of the crown ether.

HOMO LUMO visualization of regions with high electron density and regions with low electron density. For example, complex $[Li(B12C4\text{-}CH_3)]^+$ has the highest number of electrons around the point of interaction between the cation and oxygen of the crown ether, then complex $[Na(B12C4\text{-}CH_3)]^+$ and lastly $[K(B12C4\text{-}CH_3)]^+$ has electron density. Low, which needs to be better distributed. Figure 5 can be seen that the electron with the highest interaction point is at $[Li(B12C4\text{-}CH_3)]^+ > [Na(B12C4\text{-}CH_3)]^+ > [K(B12C4\text{-}CH_3)]^+$.

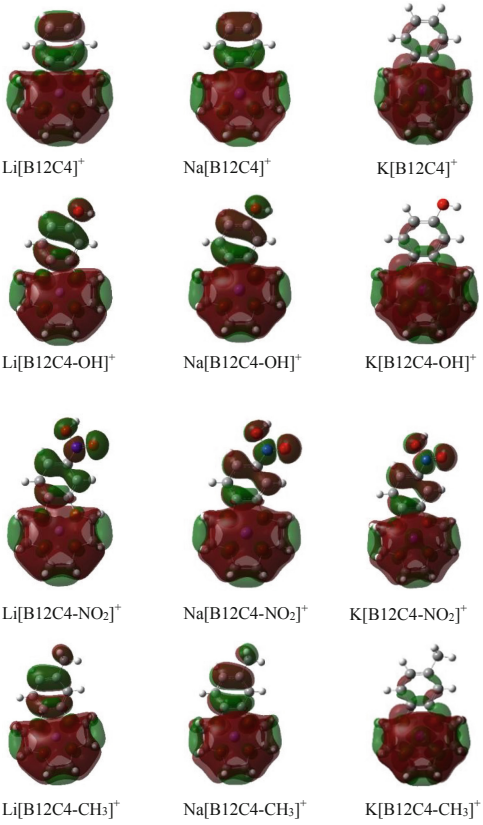


Fig. 5. Comparison of the effect of substituents on the distribution of electrons HOMO LUMO

4 Conclusion

Crown ether B12C4 has a high selectivity in binding ions Li^+ compared to binding ions Na^+ and K^+. The interaction energy shows that the donor group has better selectivity than the electron-withdrawing group. The CH_3 electron donor group is better than the NO_2 withdrawal group for selectivity of crown ether toward metal ions. The order of the interaction energies is $[Li(B12C4\text{-}CH_3)]^+ > [Na(B12C4\text{-}CH_3)]^+ > [K(B12C4\text{-}CH_3)]^+$, according to the selectivity order of the crown ethers.

References

1. Y Woodard, F. (2001). Industrial waste treatment handbook. Elsevier
2. Siddiqua, A., Hahladakis, J. N., & Al-Attiya, W. A. K. (2022). An overview of the environmental pollution and health effects associated with waste landfilling and open dumping. Environmental Science and Pollution Research, 1–23.
3. Negara, I. Z. S., Isa, M. N., Ningtyas, S. R. A., Negari, S. I. T., Kisworo, W., & Hanun, Z. (2022). The Level of Comprehension using Survey (Age 18–30 years old) about Domestic B3 Waste: Batteries. Journal of Global Environmental Dynamics, 3(2), 29–33.

4. Swain, B. (2017). Recovery and recycling of lithium: A review. Separation and Purification Technology, 172, 388–403.
5. Yang, Y., Okonkwo, E. G., Huang, G., Xu, S., Sun, W., & He, Y. (2021). On the sustainability of lithium ion battery industry–A review and perspective. Energy Storage Materials, 36, 186–212.
6. Oral, I., Tamm, S., Herrmann, C., & Abetz, V. (2022). Lithium selectivity of crown ethers: The effect of heteroatoms and cavity size. Separation and Purification Technology, 294, 121142.
7. Liang, Y., Wang, X., Zhao, S., He, P., Luo, T., Jiang, J., ... & Xu, H. (2019). A New Photoresponsive Bis (Crown Ether) for Extraction of Metal Ions. ChemistrySelect, 4(35), 10316–10319.
8. Houzar, J., Čubová, K., Semelová, M., & Němec, M. (2022). Solvent extraction of radiostrontium into ionic liquids using crown ethers. Journal of Radioanalytical and Nuclear Chemistry, 1–5.
9. Simonnet, M., Sittel, T., Weßling, P., & Geist, A. (2022). Cs Extraction from Chloride Media by Calixarene Crown-Ethers. Energies, 15(20), 7724.
10. Cheng, Q., Zhang, Y., Zheng, X., Sun, W., Li, B., Wang, D., & Li, Z. (2021). High specific surface crown ether modified chitosan nanofiber membrane by low-temperature phase separation for efficient selective adsorption of lithium. Separation and Purification Technology, 262, 118312.
11. Diao, K. S., Wang, H. J., & Qiu, Z. M. (2009). A DFT study on the metal binding selectivity of 12-crown-4 and its heterocyclic analogs. Journal of Molecular Structure: THEOCHEM, 901(1–3), 157–162.
12. Hadisaputra, S., Purwoko, A. A., Armunanto, R., & Pranowo, H. D. (2020). Theoretical Study of the Substituent and Nitrogen Number Effects on the Uranium Binding Selectivity of Crown Ethers. Acta Chimica Asiana, 3(1), 147–156.
13. Hadisaputra, S., Pranowo, H. D., & Armunanto, R. (2012). Extraction of strontium (II) by crown ether: insights from density functional calculation. Indonesian Journal of Chemistry, 12(3), 207–216.
14. Hadisaputra, S., Canaval, L. R., Pranowo, H. D., & Armunanto, R. (2014). Theoretical study of substituent effects on Cs+/Sr2+–dibenzo-18-crown-6 complexes. Monatshefte für Chemie-Chemical Monthly, 145(5), 737–745.
15. Hadisaputra, S., Canaval, L. R., Pranowo, H. D., & Armunanto, R. (2014). Theoretical Study on the Extraction of Alkaline Earth Salts by 18-Crown-6: Roles of Counterions, Solvent Types and Extraction Temperatures. Indonesian Journal of Chemistry, 14(2), 199–208.
16. 17. Hamdiani, S., Savalas, L. R. T., Purwoko, A. A., & Hadisaputra, S. (2018). Theoretical study on the binding selectivity of 18-membered azacrown ethers with alkaline earth metal species. Acta Chimica Asiana, 1(1), 17–23.
17. M. J. Frisch, G.W. Trucks, H.B. Schlegel et al., Gaussian 09 (Gaussian, Inc, Wallingford, CT, 2009)