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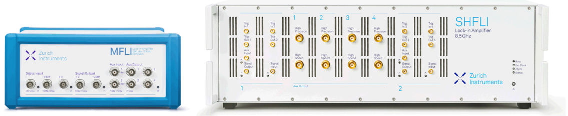

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Selectivity Study of Derivate 15-Crown-5 for Heavy Metals Extraction

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Abstract. The capability of benzo-15-crown-5 ether to form complexes with some heavy metals cation (Cd^{2+}, Hg^{2+}, and Pb^{2+}) has been investigated by the density functional theory method (DFT) using the Gaussian system. The DFT calculations were performed using 6-311G(d,p) with LANL2DZ ECP basis set at the B3LYP level of theory. The interaction energies were used to evaluate the metal binding capability of the crown ethers. The influence of adding substituents was also studied. This calculation showed that the number of ion charge transfers is proportional to the increase of the interaction energy. Furthermore, the existence of the electron donating group (EDG) affected the crown ether's ability to bind heavy metals cation. In addition, based on the extraction interaction energy, charge transfer, and the electron distribution at the HOMO-LUMO orbitals, the selectivity order of derivate 15-crown-5 is $Cd^{2+} > Hg^{2+} > Pb^{2+}$.

INTRODUCTION

In recent decades, contamination of heavy metals has been an essential part of the environmental pollution discussion. Heavy metal contamination occurs due to industrialization and urbanization, which force the number and rate of heavy metals in the environment. Heavy metals pollutant comes in many forms; cadmium, mercury, and lead are the most ones [1, 2]. Heavy metals such as cadmium and lead are widely discovered in farm products such as cereal, rice, vegetables, and fruits. At the same time, mercury was widely discovered in fisheries products [3]. Heavy metal contamination causes chronic illnesses such as brain disorder, kidney failure, neurological disorder, permanent disability even death [5, 6, 7].

There are many ways to reduce heavy metals contaminant, but it's usually done, such as ion exchange, membrane filtration, chemical precipitation, sand cap, flotation, adsorption, and photocatalysis [8, 9]. That's ways certainly have strengths and weaknesses, but adsorption is the best way based on its effectiveness and efficiency [10, 11]. Furthermore, adsorption is widely used because it is simple to reuse and recycle [11]. One of the most widely used to adsorb heavy metals is crown ether.

Crown ether has had a wide role in forming complexes [14, 15]. Crown ether can bind cation metals well by forming chelate because an oxygen group plays as an electron donor. Several factors affect the selectivity of the crown ether, such as the accuracy of the cavity size to metals cation diameter and the type of a donor group [14, 15]. Moreover, the presence of electron-donating substituent also affects the ability of crown ether to bind heavy metal cation [17, 18, 19].

Research related to crown ethers as metal complex agents has been reported in both experiment and theoretical studies. Gromov et al. Studied crown ethers such as 12-crown-4, 15-crown-5, and 18-crown-6 as a selective sorbent of radioactive and heavy metals, resulting in that 15-crown-5 is the most promising crown ether to extract heavy metals [14]. In the previous study, Harrington et al., large metals cation would be more stable in making complexes with 15-crown-5 [20]. Computationally, the selectivity of 15-crown-5 toward some metal's cation has been studied previously [21, 22]. However, crown ether modification is still needed to obtain more effective and efficient crown ethers. In this study, modification of 15-crown-5 as a heavy metal complex agent has been studied. Modification is done by adding some substitution in the benzo ring of benzo-15-crown-5.

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COMPUTATIONAL METHOD

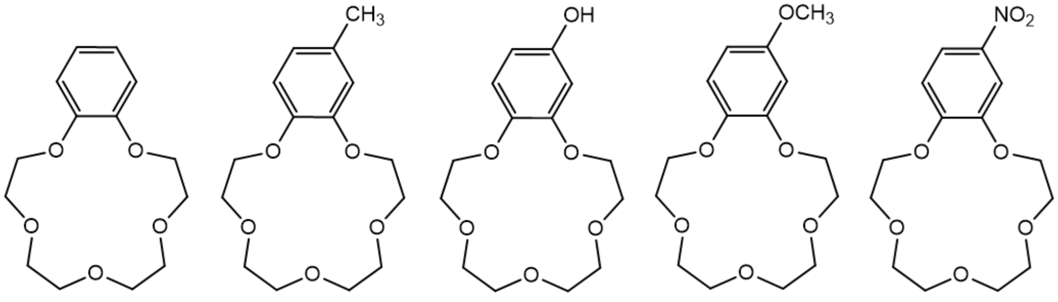
All calculation of complexes metals-crown ether is done using Density Functional Theory (DFT) at the B3LYP level of theory by using the Gaussian 09W package [23]. DFT method is selected because of the ability to calculate transition metals and heavy atoms such as ECP nicely and relatively quick. Geometric optimization of 15-crown-5 derivates with Cd^{2+}, Hg^{2+}, and Pb^{2+} performed with 6-31G(d) and LANL2DZ ECP basis set.

Geometry optimization is done to achieve the lowest energy of the molecule. Geometric optimization then continued with vibrational test with the same basis set. The optimized structure is confirmed by the absence of imaginary frequencies in the output calculation [24]. The structure is validated by comparison of the theoretical results with an X-ray crystallographic data. The smaller the difference between theoretical and experimental data, the chosen computational method is suitable for the system being studied.

Interaction energies describe the vital link between a ligand and a metal ion. Energy calculation was performed using 6-311G(d,p) and LANL2DZ ECP at the B3LYP level of theory. Both optimization and energy calculation are determined in the gas phase. The interaction energy can be calculated through equation (1).

$$\Delta E = E_{[M(B15C5-R)]^{n+}} - (E_{M^{n+}} + E_{B15C5-R}) \tag{1}$$

In addition, NBO analysis was set to calculate interaction energy to know the number of charge transfers between a ligand and a metal cation. Charge transfers are used to determine the influences of a substituent on the selectivity of 15-crown-5 derivates towards Cd^{2+}, Hg^{2+}, and Pb^{2+} [17]. The number of charge transfer are strengthened by visualizing the electron distribution at HOMO-LUMO orbitals.



B15C5 B15C5-CH_3 B15C5-OH B15C5-OCH_3 B15C5-NO_2

Scheme 1. Substituted benzo-15-crown-5 structures

RESULT AND DISCUSSION

We must compare calculation data with experimental data to validate our method and basis set. The theoretical study was a conjecture about molecular properties that come through computer calculation which needs to be proven to be accepted [25]. Figure 1 is a crystallographic reimaging of $[Cd(H_2O)_2(15\text{-Crown-}5)]^{2+}$ conducted by Bond & Rogers [19, 26]. This crystal structure can be used as a validation of theoretical data. Geometric parameter validation in Table 1, which explains the comparison between DFT calculation and experimental data. In Table 1 we also compared to ab initio calculation studied [17].

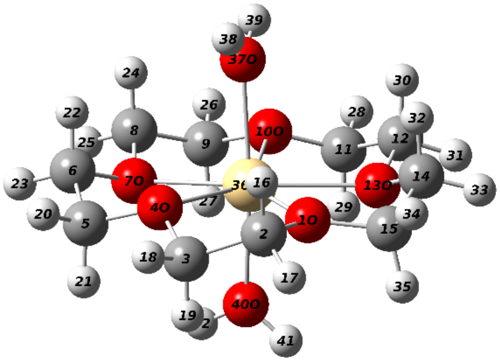


FIGURE 1. Crystal structure of the complex $[Cd(H_2O)_2(15\text{-}Crown\text{-}5)]^{2+}$

TABLE 1. Geometric parameter comparison

M-O	**Distance**		
	DFT (Å)	**ab initio (Å)**	**Exp (Å)** [19]
Cd-O1	2. 39701		2.31(2)
Cd-O4	2.33970	2.19	2.28-2.33
Cd-O7	2.33579	2.17	
Cd-O10	2.33530	2.19	
Cd-O13	2.33899	2.19	
Cd-O37 (water)	2.33913	-	2.223(6)
Cd-O40 (water)	2.33876	-	

The gap between DFT calculation and experiment data is relatively small, just around 0.03449Å while *ab initio* 0.068Å. Here the results from DFT calculations are closer to experimental observations. For transition metals and heavy atoms, DFT tends to be favored over ab initio [18].

The selectivity of the crown ether can be described through interaction energy values. The higher the interaction energy, the higher selectivity. The interaction energy of the crown ether complexes is shown in Figure 2 According to calculation data, we can see the influence of substituent on the interaction energy. Complexes with an electron-donating substituent such as OCH_3, CH_3, and OH makes higher interaction energies, while electron-withdrawing substituent such as NO_2 and H makes lower interaction energies. This trend agrees with the previous study [18].

The power of both electron donating and electron withdrawing substituent also affected the selectivity. Strong electron-donating substituents such as OCH_3 result in a massive increase in interaction energy, while weaker electron-donating substituents do not do as much as strong electron donating. But there is an exception to CH_3, which has higher interaction energy than OH, whereas CH_3 is weaker electron donating than OH. It happens because of an inductive effect in which CH_3 is more likely to donate its sigma (σ) bonds to the pi (π) bond of the benzene ring, and CH_3 is more negative than the benzene ring, so the filled sp^3 orbitals of CH_3 will overlap the empty p orbitals of benzene ring [27, 28].

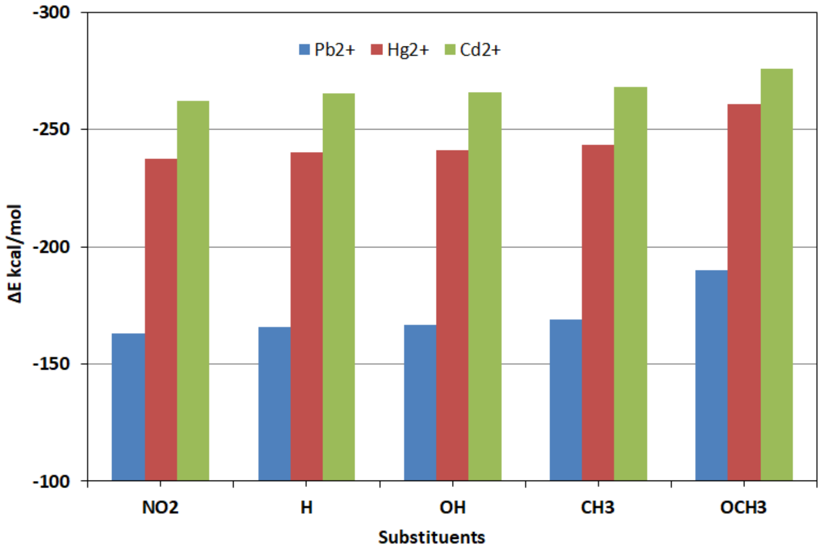


FIGURE 2. Interaction energies of metal-crown ether complexes

The charge transfer was also studied to clarify the effect of the electron-donating substituent. Generally, the number of charge transfers is proportion to the increased interaction energy. For the complexes studied, the charge transfer is defined as a gap of the ligand charge after complexation with free heavy metals cation charge values. The charge transfer was obtained based on Mulliken Population Analysis (MPA) and Natural Population Analysis (NPA). The charges transfer of complexes is listed in Table 2**.**

TABLE 2. Charge transfer within metals-crown ether complexes

Substituent	**Cd^{2+} complexes**		**Hg^{2+} complexes**		**Pb^{2+} complexes**	
	MPA	**NPA**	**MPA**	**NPA**	**MPA**	**NPA**
H	0.668926	0.42337	0.595630	0.29670	0.481037	0.46693
CH_3	0.669919	0.42399	0.597288	0.29820	0.480382	0.46784
OH	0.669272	0.42324	0.596876	0.29997	0.479663	0.46690
OCH_3	0.792190	0.41853	0.925676	0.53426	0.67891	0.36122
NO_2	0.668475	0.42399	0.593886	0.30122	0.475511	0.46618

Both MPA and NPA used hybridization to calculate the charge transfer. MPA is the most widely used method to calculate charge transfer. MPA has a lower accuracy than NPA, but both MPA and NPA have the same trend [26,27]. Based on Table 2 it is clear that the increase in charge transfer is in proportion to the increased interaction energies with the order substituent effect of OCH_3 > CH_3 > OH > H > NO_2.

The visualization of the electron distribution within complexes is shown in the HOMO-LUMO orbitals. The intensity of the electron distribution can explain to us the effect of different types of cations. The selectivity of crown ether to bind metal cation was also shown in this visualization. Electron distribution of complexes can be seen in Figure 3. Areas with a high density of electrons can be seen as red areas. Figure 3 indicates that in the same type of crown ethers, the intensity of electron distribution decreased from Cd^{2+} complexes to Hg^{2+} complexes and Pb^{2+} complexes. This distribution of electrons agrees with its interaction energies, in which the interaction energies decreased from Cd^{2+} complexes to Hg^{2+} complexes and then to Pb^{2+} too.

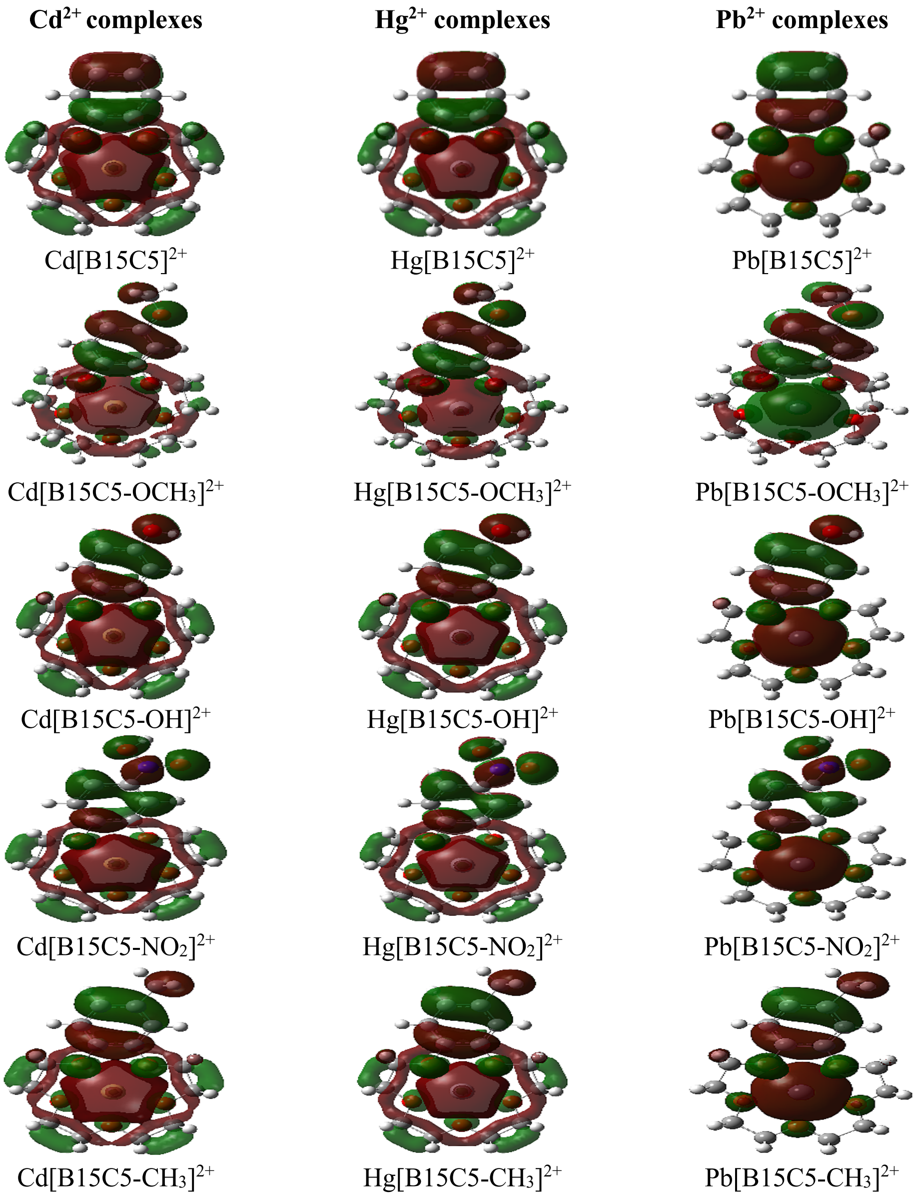


FIGURE 3. Electron distribution of complexes

CONCLUSION

The selectivity of benzo-15-crown-5 substituted to make complexes with some heavy metal's cation (Cd^{2+}, Hg^{2+}, and Pb^{2+}) has been studied by 6-311G(d,p) and LANL2DZ basis set at the B3LYP level of theory. Selectivity is predicted using interaction energies, charge transfer, and electron distribution. The results of this calculation indicated that a number of charge transfers within complexes and the presence of electron-donating substituent have a good positive relationship with interaction energies. Electron distribution in the HOMO-LUMO orbitals also takes place to define the selectivity. The computational calculation shows that the selectivity order of 15-crown-5 derivates is $Cd^{2+} > Pb^{2+} > Hg^{2+}$, while order of substituent effect is $OCH_3 > CH_3 > OH > H > NO_2$.

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