AB INITIO INVESTIGATION OF 12-CROWN-4 AND BENZO-12-CROWN-4 COMPLEXES WITH Li^+, Na^+, K^+, Zn^{2+}, Cd^{2+}, AND Hg^{2+}

Yahmin[1,*,**], Harno Dwi Pranowo[2], and Ria Armunanto[2]

[1]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang, Indonesia*

[2]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara POB.Bls. 21Yogyakarta 55281, Indonesia*

ABSTRACT

*The structure and binding energies of 12-crown-4 and benzo-12-crown-4 complexes with Li^+, Na^+, K^+, Zn^{2+}, Cd^{2+}, and Hg^{2+} were investigated with ab initio calculations using Hartree-Fock approximation and second-order perturbation theory. The basis set used in this study is lanl2mb. The structure optimization of cation-crown ether complexes was evaluated at HF/lanl2mb level of theory and interaction energy of the corresponding complexes was calculated at MP2/lanl2mb level of theory (MP2/lanl2mb//HF/lanl2mb). Interactions of the crown ethers and the cations were discussed in term of the structure parameter of crown ether. The binding energies of the complexes show that all complex formed from transition metal cations is more stable than the complexes formed from alkali metal cations.*

INTRODUCTION

Crown ethers are multidentate macrocyclic compounds with multiple oxygen heteroatoms' [1]. Their generic name originates from their molecular shape, reminiscent of a royal crown. Because of naming of crown ethers by the IUPAC nomenclature systems can be somewhat difficult and rather tedious, the abbreviated names have been proposed for these compounds. The usual abbreviated name of crown ethers is m-crown-n where m is the total number of atoms in the ring and n is the number of oxygen atoms. Other substituents are named in the usual manner. For example, the two dimensions structure of 1,4,7,10-tetraoxacyclododecane or 12-crown-4 and benzo-1,4,7,10-tetraoxacyclodo decane or benzo-12-crown-4 respectively are depicted in Fig. 1.

Since the synthesis of crown ether compound by Pedersen [2], and his observation of their ion binding properties, a great deal of interest has been focused on them. This is because of the possible chemical, biological, environmental or medical application of their unusual ion complexation, solvation and transport effect.
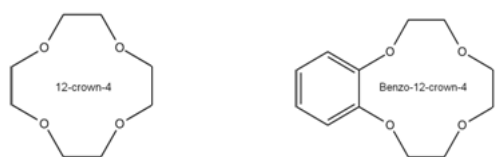
For instance, the ability of the crown ether to bind cation selectively has been used to enhance selectivity separation in chromatography [3-4], electrophoresis [5], and cation extractions [6].
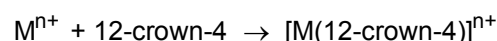
Because of the important of the application of crown ether, computational chemists have been also focusing their effort on them. One particular property of these macrocyclic which interesting to the computational chemists is their ability to select a cation which fits with the ligand size: this is also-called host-guest or best-fit concept. Although the relationship between the molecule cavity and the cation size is well known for alkali metals cation, it is nevertheless still unclear for transition metals cation and the generalization to all cation is not obvious. Free crown ethers, protonated crown ethers, and crown ethers complexes of alkali or alkaline-earth metals were rather extensively studied theoretically. Ab initio studies of these systems at various theoretical levels were reported in many articles [7-10]. Bond dissociation enthalpies of complexes of alkali metals cation with 12-crown-4 were calculated at RHF/6-31G* level [7]. The structure and binding energies of 18-crown-6 complexes with alkaline earth cations were investigated at RHF and MP2 levels of theory using 6-31+G basis set [8]. Proton affinity of some free crown ether were calculated at MP2/6-31+G** level [9]. The vibrational spectra of 12-crown-4-alkali metals complexes were evaluated at MP2 level and using 6-311++G** basis set [10].

(a) 1,4,7,10-tetraoxacyclododecane   (b) benzo-1,4,7,10-tetraoxacyclododecane

Fig 1. The IUPAC and abbreviated names of crown ethers

* Corresponding author. Email address : yahminoby@gmail.com
** Postgraduate Student of Chemistry Department, Faculty of Mathematic and Natural Sciences, Universitas Gadjah Mada

This paper is devoted to an ab initio investigation of the structure and relative stability of the small size crown ethers, in particular 12-membered ones, which have not been thoroughly studied owing to low yields in troublesome syntheses and low stability constants of the resulting complexes [11]. In this work we will use the computational technique to investigate the best-fit concept. Small size crown ethers such 12-crown-4 and benzo-12crown-4 are of interest because their rather high conformational rigidity facilitates preorganization of the donor atoms of the macrocyclic in the formation of particular complexes. Selectivity in complex formation is related to their sizes, whereas aromatic systems incorporated to the macrocyclic decrease their conformational flexibility.
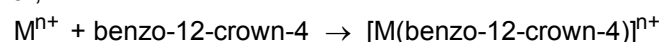
EXPERIMENTAL SECTION

For geometry optimization, all ab initio calculations were performed at the Hartree-Fock level with the lanl2mb basis. The lanl2mb basis set treated electrons near the nuclei via effective core potentials (ECPs) and also includes some relativistic effect, which are important for the transition element like Zn, Cd, and Hg. No symmetry restrictions were imposed during geometry optimization. All geometries were confirmed as minima from vibration frequency analyses.

Binding energies or relative stability were evaluated at the MP2/lanl2mb levels of theory. These quantities correspond to the energy (or enthalpy) change for the reaction:

$$M^{n+} + \text{12-crown-4} \rightarrow [M(\text{12-crown-4})]^{n+}$$

or,

$$M^{n+} + \text{benzo-12-crown-4} \rightarrow [M(\text{benzo-12-crown-4})]^{n+}$$

All the species that are involved in the reaction is at the equilibrium HF/lanl2mb geometry. The interaction energies for the complexes are therefore expressed as

$$\Delta E = E_{[M(\text{12-crown-4})]^{n+}} - E_{\text{12-crown-4}} - E_{M^{n+}}$$

or,

$$\Delta E = E_{[M(\text{benzo-12-crown-4})]^{n+}} - E_{\text{benzo-12-crown-4}} - E_{M^{n+}}$$

All the calculations are performed in Austrian-Indonesian Center for Computational Chemistry Laboratory at the Universitas Gadjah Mada Yogyakarta, Indonesia. The molecular structures of all considered systems are generated by using 150 days trial of chemcraft program [12].
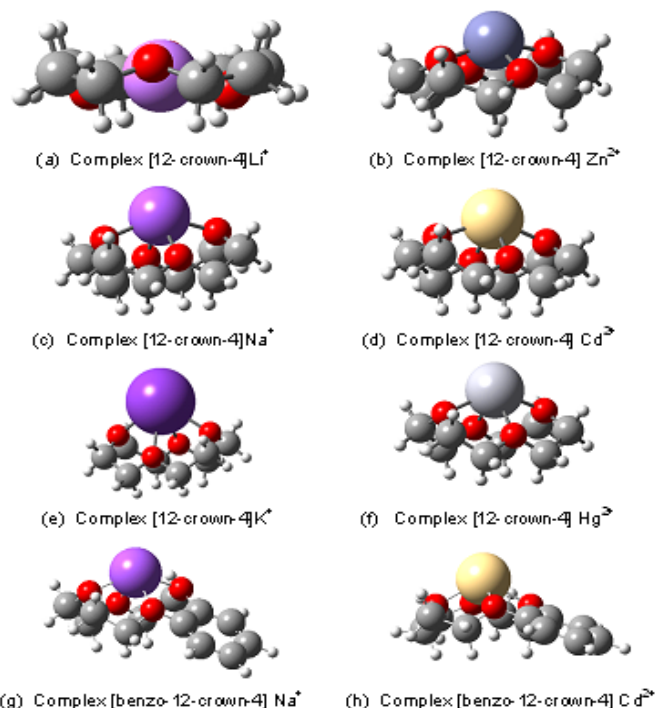

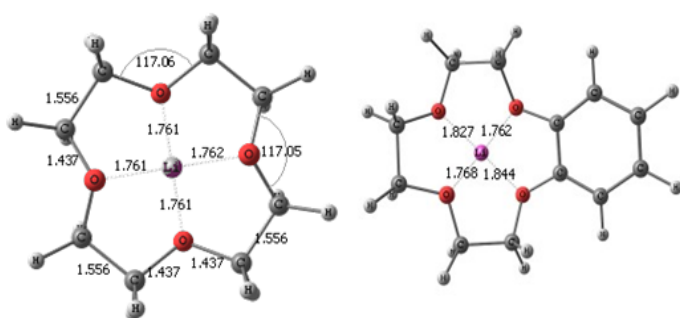**Fig 2.** Nesting and perching form of complexes calculated at HF/lanl2mb

RESULT AND DISCUSSION

Geometrical structure of the complexes

When crown ether and a cation complex occur, different types of complexes may form. The relative sizes of the cation and the crown ether cavity are important factors in determining the structure and stoichiometry of the complex. Complexation can occur in various ways which are mostly a function of the relative sizes of the cation and crown ether cavity. Typically the complex has a 1:1 ratio of crown ether and metal cation. If the cation is somewhat smaller to approximately the same size as the crown ether cavity, then a "nesting" complex is formed. If the metal cation is slightly larger than the cavity size of crown ether then a "perching" complex results. If the cation is too large compare to the cavity of crown ether, a 2:1 "sandwich" complex of crown ether cation may be formed. When the cation is much smaller than the crown ether cavity, the conformation of crown ether will change greatly so that the cation does not make interaction with all of oxygen atom of crown ether.
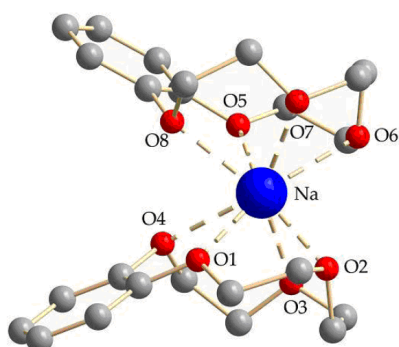
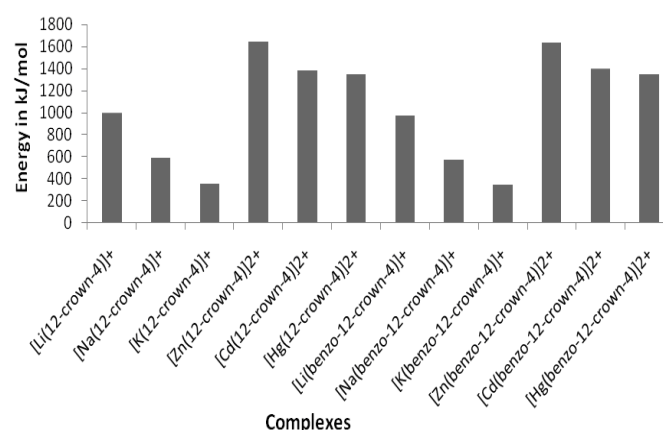**Fig 3.** Three dimension structure of [benzo-12-corwn-4]$_2$Na$^+$ complex

Table 1. Calculated M–O distance of [benzo-12-corwn-4]$_2$Na$^+$ complex

M–O distance	Calculated (Å)	Experiment[15] (Å)
Na – O1	2.34	2.47
Na – O2	2.32	2.45
Na – O3	2.32	2.43
Na – O4	2.40	2.53
Na – O5	2.31	2.40
Na – O6	2.40	2.52
Na – O7	2.34	2.50
Na – O8	2.32	2.42

(a) Complex [12-crown-4]Li$^+$ (b) Complex [benzo-12-crown-4]Li$^+$

Fig 4. Calculated structures parameters of [12-corwn-4]Li$^+$ and [benzo-12-corwn-4]Li$^+$

Fig 5. Calculated binding energies at the MP2/lanl2mb levels of theory

Table 2. Calculated M–O distance of the complexes calculated at HF/lanl2mb level

Complexes	M – O distance in angstrom			
	Value 1	Value 2	Value 3	Value 4
[Li(12-crown-4)]$^+$	1.76	1.76	1.76	1.76
[Na(12-crown-4)]$^+$	2.12	2.13	2.15	2.15
[K(12-crown-4)]$^+$	2.63	2.63	2.72	2.73
[Zn(12-crown-4)]$^{2+}$	1.94	1.94	1.96	1.96
[Cd(12-crown-4)]$^{2+}$	2.13	2.13	2.16	2.16
[Hg(12-crown-4)]$^{2+}$	2.21	2.21	2.26	2.26
[Li(benzo-12-crown-4)]$^+$	1.76	1.77	1.83	1.84
[Na(benzo-12-crown-4)]$^+$	2.12	2.13	2.16	2.16
[K(benzo-12-crown-4)]$^+$	2.67	2.69	2.70	2.72
[Zn(benzo-12-crown-4)]$^{2+}$	1.93	1.95	1.95	1.96
[Cd(benzo-12-crown-4)]$^{2+}$	2.12	2.14	2.15	2.15
[Hg(benzo-12-crown-4)]$^{2+}$	2.22	2.24	2.25	2.25

According to the experimental data, the radius size of the 12-crown-4 is 60 pm[13] and the radius size of the cations are 76, 102, 138, 74, 95, and 102 pm, for Li$^+$, Na$^+$, K$^+$, Zn^{2+}, Cd^{2+}, and Hg^{2+}, respectively [14]. All this work only considered 1:1 complex of crown ether-cation, then the structure of the complex will be nesting for lithium and zinc cation, perching for the others. Parts of these optimized structures predicted by the ab initio calculation are depicted in Fig. 2.
The optimized geometrical structures of the complexes have been calculated at Hartee-Fock levels using lanl2mb basis set. For comparing to the experimental

data, the optimization of the [Na(benzo-12-crown-4)$_2$]$^+$ has also been done at the HF/lanl2mb level. The three dimension structure of [Na(benzo-12-crown-4)$_2$]$^+$ without hydrogen atoms was shown in Fig. 3.

The corresponding M – O distance bonds of the optimized structure of [benzo-12-corwn-4]$_2$Na$^+$ complex are in a good agreement to the experimental data as given in table 1.

The optimized geometrical structure calculated at Hartee-Fock levels using lanl2mb basis set of the [Li(12-crown-4)]$^+$ and [Li(benzo-12-crown-4)]$^+$ complexes are given in Fig. 4. Among these

geometrics parameter, distance of M–O bond is most interesting because this is the indication of complex symmetry.

Symmetry is an important factor influencing the properties of cation-crown ether complexation. Benzene group incorporated to the crown ether ring result in decrease in molecular symmetry. From the Fig. 3, there is only one value for M-O distances in Li(12-crown-4)]+ and four values for [Li(benzo-12-crown-4)]+, thus Li(12-crown-4)]+ complex have a higher symmetry than [Li(benzo-12-crown-4)]+ complex. In most cases, the more symmetric complex has correlation with more stable complex. Table 2 shows all the M–O distance calculated using Hartree-Fock method with lanl2mb basis set for 12-crom-4 and benzo-12-crown complexes with metal cation considered in this work. Generally, we can say that the complexes formed from 12-crown-4 without benzene group condensed on it make more stable complexes.

Binding Energies of the complexes

According to the early concept, the 1:1 complex is more stable when the ionic diameter of the cation fits the size of the crown ether cavity; otherwise, the stability of complex is poorer. Fig. 5 shows calculated binding energy of all complexes considered in this work at HF/lanl2mb level. All calculated binding energies for the alkali metals complexes match with this concept. The benzene group attached to 12-crown-4 ring slightly decreases the binding energy in a linier manner. Thus, the relative stability complexes of alkali metal cations decrease in the following order: $[Li(12\text{-crown-4})]^+$ > $[Li(benzo\text{-}12\text{-crown-4})]^+$ > $[Na(12\text{-crown-4})]^+$ > $[Na(benzo\text{-}12\text{-crown-4})]^+$ > $[K(12\text{-crown-4})]^+$ > $[K(benzo\text{-}12\text{-crown-4})]^+$.

Binding energy of transition metal cation of group 12 (Zn, Cd, and Hg) with 12-crown-4 or benzo-12-crown-4 does not meet to the best-fit concept, primarily cadmium and mercury cations. It can be seen that all transition metal cation in this study make more stable complexes with 12-crown-4 and benzo-12crown-4, in term of binding energy. This is rather surprisingly, although it was known that many factors influence the stability of cation-crown ethers complex. The relative stability of transition metal cations decrease in the following order: $[Zn(12\text{-crown-4})]^{2+}$ > $[Zn(benzo\text{-}12\text{-crown-4})]^{2+}$ > $[Cd(benzo\text{-}12\text{-crown-4})]^{2+}$ > $[Cd(12\text{-crown-4})]^{2+}$ > $[Hg(12\text{-crown-4})]^{2+}$ > $[Hg(benzo\text{-}12\text{-crown-4})]^{2+}$.

CONCLUSION

Cavity size of crown ethers correlate generally with trapped cation radii. The benzene rings condensed to crown ethers slightly decrease the complex stability except for the cadmium complex. All the divalent cation from group 12 of transition metals formed more stable complex than the cation from the alkali metals group.

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