Theoretical Study on the Substituent and Nitrogen Number Effect of the Uranium Binding Selectivity of Crown Ethers

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ABSTRACT

The compounds, $[UO_2(dibenzo\text{-}18\text{-}crown\text{-}6)]^{2+}$ and $[UO_2(18\text{-}crown\text{-}6)]^{2+}$, as well as their related complexes: numerous disubstituted dibenzo-18-crown-6 and azacrown complexes are studied using density functional theory (DFT). Quasi-relativistic effective core potentials developed in the Stuttgart and Dresden groups was used together with the accompanying basis set for uranium and DZP basis set was used for crown ether atoms. The effects of substituent and nitrogen number on the binding selectivity were discussed in term of the structural parameter, atomic charge and interaction energy, thermodynamic parameters, and charge transfer. The electron donating substituents increase the capability of dibenzo-18-crown-6 toward UO_2^{2+} ion. In contrast, the electron withdrawing substituents have the opposite effect. It clearly shows that UO_2^{2+} prefers N donor recognition. For the systems involved, the result shows that the hexaaza-18-crown-6 exhibits the largest metal interaction capability to UO_2^{2+} ion. Some of the calculated results are in a good agreement with the experimental values.

Keywords: DFT calculation, uranium cation, crown ether, substituent effect, nitrogen effect

INTRODUCTION.

Nuclear waste has become one of the greatest environmental challenges of our time especially regarding its remediation and safety in storage. In order to solve this problem by eventual safe disposal, it is required the ability to selectively extract the radioactive actinide elements. Selective extraction is also important in the nuclear fission cycle. One of the methods proposed for nuclear waste treatment is coordination actinide ions with crown ethers [1]. Interest in crown ethers come forward due to the properties of crown ethers can easily be turned by changing the cavity size, adding substituent groups and replacing their heteroatom (O, N, S and P).

Different types of electron donating and withdrawing substituents have been incorporated into each benzo unit of dibenzo-18-crown-6. Among these substituents are alkyl groups, such as methyl, t-butyl [2,3], nitro and amine groups [4,5] and halogen [6]. They were used in the extraction of metal ions including that correlated with nuclear wastes such as cesium, strontium and lanthanide radioisotopes [7,8]. Furthermore, since the synthesis of aza-18-crown-6 was reported by Greene [9], serial azacrown ethers and diazacrown ethers have been synthesized and their properties to bind metal ions have been described [10,11]. Moreover, triazacrown ether [12,13], tetrazacrown ether [14], pentazacrown ether [15], and hexazacrown ether [16] have been reported.

Uranium inclusion complexes of macrocycles have been studied experimentally including by crown ether and azacrowns [17-20]. However, experimental processes are very time consuming and special treatment should be done in order to handle dangerous elements such as radioactive elements. Molecular modeling using computational chemistry provides solution for these difficulties and perhaps the most powerful tool for designing and studying complex molecular systems regarding their stabilities and other properties. Accurate theoretical calculations can provide ways to obtain important binding selectivity that cannot be easily obtained by experimental approaches which are time consuming, expensive and hazardous processes. The physical properties of polycyclic macromolecules like cavity of the crown ether, its structural shape and dimension, the interaction behaviors with metal ion can be confidently predicted using computational methods [21–23].

The molecular modeling investigation has been significantly helpful to explain the mechanism of selective capture metal ions by macrocyclic moiety. The structures and interaction energies of UO22+ complexes with macrocyclic such as porphyrin types compounds have been reported at B3LYP using small effective core potential (ECP) of SDD basis function and combined with 6-31G(d) basis function [24,25]. Recently, the optimized geometries and interaction energies of UO22+ complexes of 18-crown-6 and dicyclohexyl-18-crown-6 at B3LYP level of theory using large and small core ECP of SDD basis function and 6-31G(d) basis function have been investigated [26]. In the current work, we use density functional theory (DFT) to study the effect of substituents on each benzo unit of dibenzo-18-crown-6 and nitrogen number effect on the stability of the complexes of UO22+ with azacrown ethers. To the best of our knowledge, no computational investigation involving the effect of the substituents on each benzo unit of dibenzo-18-crown-6 and the effect of nitrogen number on UO22+ binding selectivity has been reported.

METHODOLOGY.

All calculations were based on approximate DFT in the form of Becke's 1988 exchange functional, combined with the Lee-Yang-Parr correlation functional in the hybrid B3LYP functional [27,28]. Geometry optimizations have been performed without any symmetry constraints. Optimized geometries are always verified as minima on the potential energy surface by calculating the harmonic vibration frequencies. Very tight criteria were used for geometry optimization and numerical DFT integration. We use relativistic small core ECP include 60 electrons in the core for uranium, leaving 32 valence electrons. SDD basis set corresponding to the ECP was used as obtained from EMSL Library and removed the most diffuse spdf functions (having an exponent of 0.005). For ligan atoms, DZP basis set was used. The basis set superposition errors (BSSE) was eliminated with the counterpoise (CP) method proposed by Boys and Bernardi [29]. All calculations were done with the Gaussian-03 program package.

RESULTS AND DISCUSSION

Geometry parameters
The quality of the computational level was assessed by optimizing the reference complex ([UO2(hexaaza-18-crown-6)]2+) at

the density functional level of theory using SDD basis function for metal ions and DZP basis function for crown ether atoms. Here, we modeled 1:1 ratio between crown ethers and metal ion in the absence of solvent molecules. The comparison between calculated bond length and the experimental X-ray results on the same structure [20] is depicted in Table 1. In Fig 1, the calculated optimized structure of [UO2(hexaaza-18-crown-6)]2+ are presented.

Figure 1 shows that uranium atom within UO22+ ion is fully encapsulated within the cavity of hexaaza-18-crown-6, mean that the 18-memberred crown ethers have matches cavity radius of Uranium in UO22+ ion. From Table 1, it can be seen that the calculated bond length and angle values show fair agreements with the X-ray results, although B3LYP (SDD/DZP) predicts UO22+-N distances that is 0.03 – 0,10 Å longer than those of the X-ray structure. This data indicates the suitable combination between the two basis fuctions and the B3LYP level of theory.
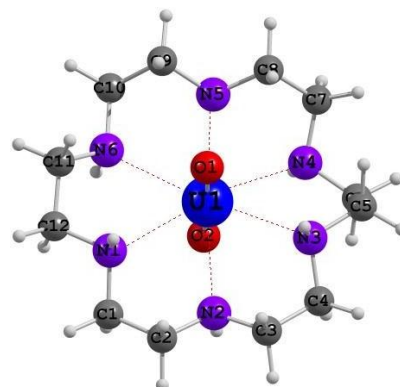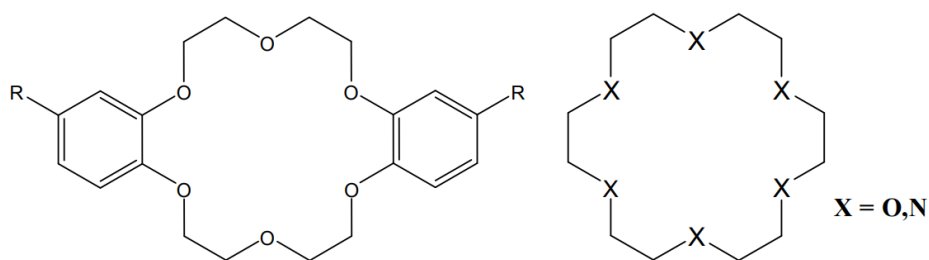

Figure 1. The fully optimized structure of the [UO2(hexaaza-18-crown-6)]2+. In order to study the geometric structures of the complexes as consequence of electron donating and withdrawing substituents (R = -CH=CH2, -OH, -CH3, -OCH3, -CHO, -COOH, -COOCH3, -COCH3) and the presence of nitrogen donors. The series of electron donating and withdrawing substituents were added into benzo unit of dibenzo-18-crown-6 and nitrogen atoms were replaced oxygen in the crown ring as depicted in scheme 1.
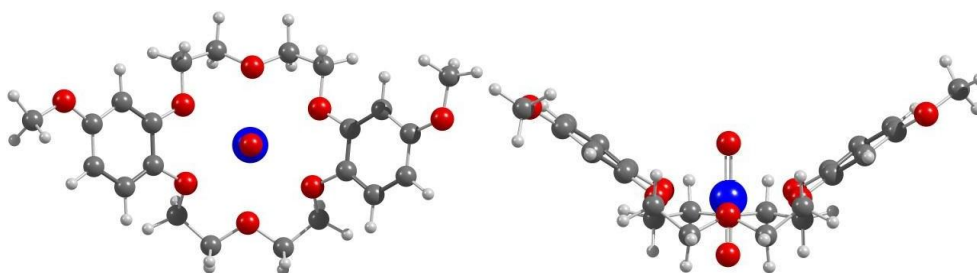
Scheme 1

Figure 2. Two projections of the optimized structure of the [UO2(dibenzo-18-crown-6(OCH3)2]2+. Oxygen (red), carbon (black), hydrogen (grey) and uranium (blue)

Table 1. Selected geometrical parameters of [UO2(hexaaza-18-crown-6)]2+: B3LYP versus X-ray Data

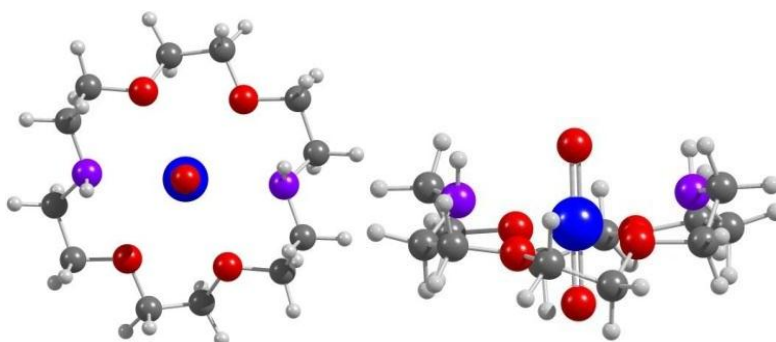| Bond	Bond Lengths B3LYP	Bond Lengths X-ray	Angle	Angle B3LYP	Angle X-ray
U=O1 (axial)	1.76	1.74	O2-U-O1	176.75	174.9
U=O2 (axial)	1.77	1.76	N2-U-O2	85.01	86.2
U-N2	2.63	2.59	N3-U-N2	63.38	64.7
U-N3	2.69	2.61	N4-U-N3	62.75	63.4
U-N4	2.73	2.70	N5-U-N4	60.01	57.7
U-N5	2.74	2.76	N6-U-N5	65.75	65.0
U-N6	2.73	2.63	N7-U-N6	62.64	61.7
U-N7	2.73	2.68	N2-U-N7	63.44	64.3

Figure 3. Two projections of the fully optimized structure of the [UO2(diaza-18-crown-6]2+. Oxygen (red), carbon (black), hydrogen (grey), nitrogen (purple) and uranium (blue)

Table 2. Selected geometrical parameters in UO2(disubstituted dibenzo-18-crown-6)2+ complexes.

-R	Min (U-O) (Å)	Max (U-O) (Å)	-R	Min (U-O) (Å)	Max (U-O) (Å)
-CHO	2.571	2.649	-CH=CH2	2.670	2.710
-COOH	2.570	2.610	-OH	2.610	2.671
-COCH3	2.577	2.661	-CH3	2.573	2.720
-COOCH3	2.610	2.671	-OCH3	2.670	2.710
-H	2.573	2.720	-H	2.573	2.720

Table 3. Selected geometrical parameters in UO2(azacrown ether)2+ complexes. a and b are the experimental values of [UO2(18-crown-6)]2+ and [UO2(18-diazacrown-6)]2+ respectively.

azacrowns	U=O1 (Å)	U=O2 (Å)	Min (U-O/N) (Å)	Max (U-O/N) (Å)
N0 (18C6)	1.751 (1.65)a	1.751 (1.64)a	2.571	2.649
N1	1.756	1.756	2.570	2.610
N2	1.757 (1.84)b	1.751 (1.84)b	2.577	2.661
N3	1.761	1.761	2.610	2.671
N4	1.764	1.767	2.573	2.720
N5	1.765	1.765	2.670	2.710

In Fig 2 and 3, the structure of both representative complexes show that since the average cavity of 18-membered crown ethers is suitable with the ionic diameter of uranium in UO22+ ion, the cavity of 18-membered crown ether are able to accommodate UO22+ ion hence it is encapsulated in the crown ether cavity. Although, in the case of [UO2(diaza-18-crown-6]2+, two nitrogen atoms are in the slightly folding structure. The selective minimum and maximum bond lengths of UO22+-O and UO22+-N in the complexes are slightly changes, 2.570 Å – 2.71 Å (Table 2 and 3). The bond length can be used as the preliminary prediction of the strength of interaction between the metal ions and crown ethers. Less difference in bond lengths may lead into closely similar interaction properties.

Interaction energies Generally, the interaction energy is related to the stability of the complexes. The interaction energies of UO22+ and crown ether (CE) monomer are calculated as the energy difference between the complexes and the UO22+ and CE monomer. For systems involved, it is defined as follows:

$$\Delta E = E = E_{UO2-CE} - (E_{UO2} + E_{CE}) \qquad (1)$$

Here, Ecomplex denotes the energy of the complexes, EUO2 the energy of UO22+ ion and ECE the energy of crown ethers. The interaction energies were also corrected for the undesirable effects of basis set superposition error (BSSE) using the counterpoise method. Small changes between the BSSE corrected and uncorrected interaction energies indicates the suitable combination of basis fuctions (SDD/DZP) for the calculation.
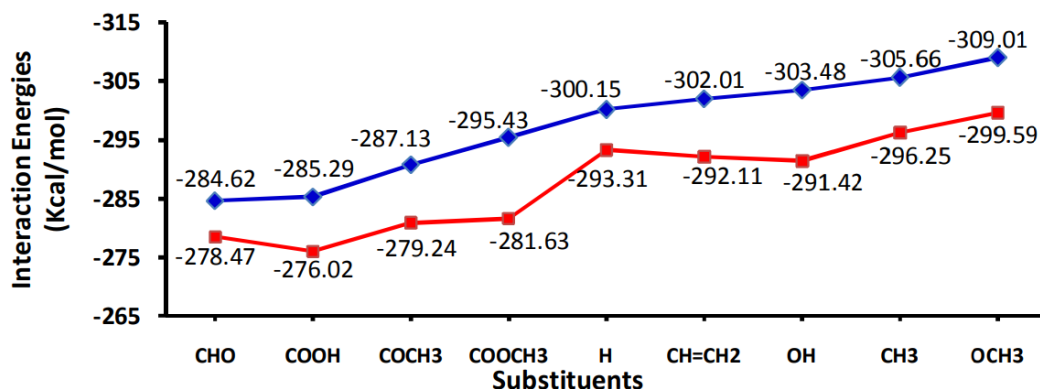
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Figure 4. The interaction energies of UO22+-DB18C6 complexes (♦ Uncorrected binding energies; ■ binding energies corrected by BSSE)
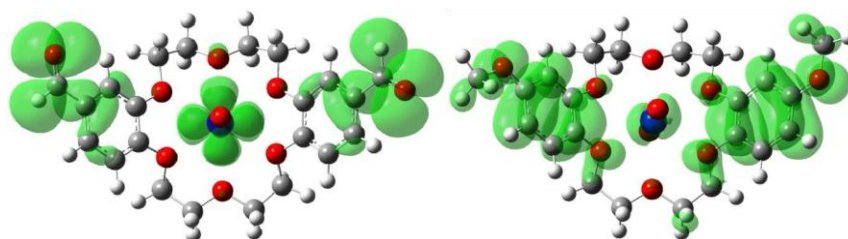

Figure 5. Molecular orbital mapped with electrostatic potential. (A) effect of electron withdrawing substituents (B) effect of electron donating substituent.

The interaction energies shows that electron donating substituents (-CH=CH2, -OH, -CH3, -OCH3) increase the interaction energies between metal ions and the studied crown ethers (2 - 9 kcal/mol), compared with the unsubstituted dibenzo-18-crown-6. In contrast, electron withdrawing substituents (-CHO, -COOH, -COOCH3, -COCH3) reduce the complex interaction energies about 5 - 15 kcal/mol from the original unsubstituted dibenzo-18-crown-6. Small differences between the interaction energies of electron donating and withdrawing complexes indicate less contribution of these substituents for the complex stability. This theoretical result shows good agreement with the previous analog experimental results with different metal ion [8, 30-31]. In order to give a clear view of the electron distribution on the complexes as a consequence of the existence of electron donating and withdrawing substituents, the molecular orbital mapped with electrostatic potential was analyzed from NBO calculation as presented in Fig 5. The

electrostatic potential demonstrates the energy of interaction of a positive point charge with the fixed charge distribution of a molecule and the nuclei [32]. The molecular isosurface of electrostatic potential indicates the electron rich region. Electrostatic potential (green surface) illustrates that electron withdrawing substituents (Fig. 5A) spread out the electron rich region of the molecule, as a result, the ability of crown ether to bind metal ion reduce. However, electron donating substituents (Fig. 5B) concentrate the electron rich region of the molecule closer into the interaction points (the oxygen atoms of crown ethers), therefore the capability of crown ether to bind ions increase.

Next, we study the effect of the nitrogen number on the interaction of UO22+ with azacrown ether. Clearly, nitrogen number dependence exists in the UO22+ crown ether complexes, which are indicated in their interaction properties (Fig. 6).
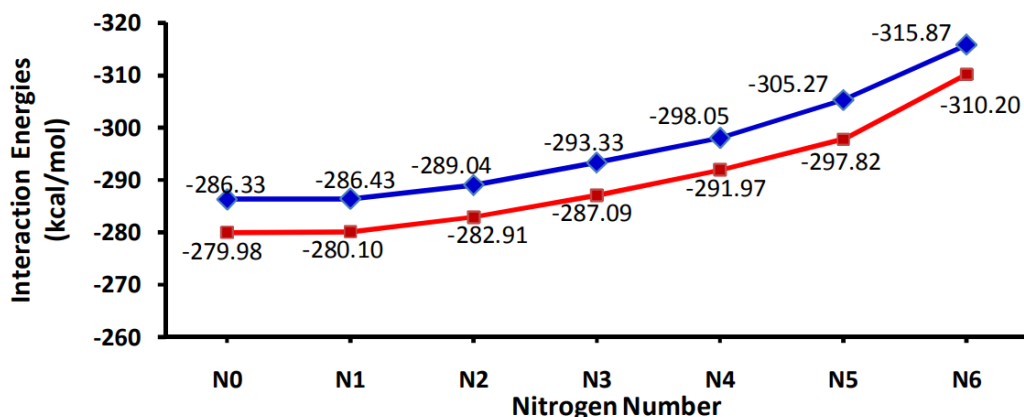
Figure 6. The interaction energies of UO22+-complexes with 18-crown-6 containing various nitrogen numbers. (♦ Uncorrected binding energies; ■ binding energies corrected by BSSE)

The interaction energy trend shows that as the nitrogen number increase in the crown system, the intreaction energies also increase gradually. From Fig 6, the interaction energy of nitrogen free complex UO2(18-crown-6)]2+ has interaction energy about -286.33 kcal/mol but than the interaction energy increase significantly about 30 kcal/mol for [UO2(hexaaza-18-crown-6)]2+ (-315.87 kcal/mol). Apparently, the nitrogen number of the 18-membered crown ether plays an important role in the stability of the complexes which perfectly means that the nitrogen number does has significant effect on the UO22+ binding selectivity.
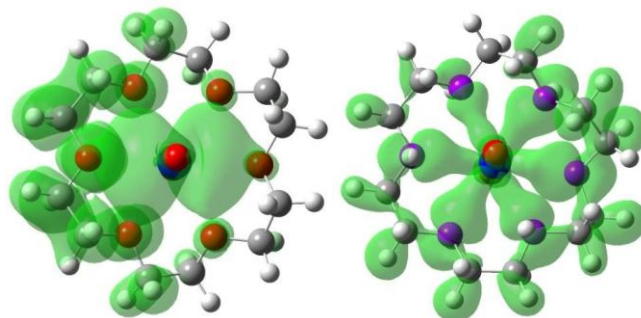

Figure 7. Molecular orbital mapped with electrostatic potential. (A) effect of without nitrogen donor (B) effect of the presence of nitrogen donor atoms.

Electrostatic potential demonstrates that without the presence of nitrogen atom in the crown system (Fig 7A), the electron rich region of the molecule spread out into the left side of the interaction points as result of less symmetrical structure of the complexes, therefore, the ability of crown ether to bind UO22+ reduce. However, as the nitrogen donor take place of oxygen atoms of crown ether, the electron rich region of the molecule (Fig 7B) concentrate into the interaction points (the uranium and nitrogen atoms of crown ethers), as a result, the capability of crown ether to bind UO22+ ion increase.

Charger Transfer
Generally, a smaller amount of atomic charge after complexation related to a larger charge transfer during coordination will result in a larger value of the relevant interaction energy. For the systems under consideration, the charge transfer is the charge difference between the free metal ion and its corresponding charge in its complex. Although, it can be observed that the amount of charge after complexation and charge transfer from donor to acceptor is not proportional with the interaction energy of few complexes. In general, the charge values follow the interaction energy trend. This can be seen from the Mulliken population analysis (Table 4).

Table 4. Atomic charges from Mulliken population analysis

Substituent	free metal ion	charge complexation	charge transfer	Nitrogen number	free metal ion	charge complexation	charge transfer
-CHO	2.000	1.581	0.419	N0	2.000	1.595	0.405
-COOH	2.000	1.582	0.418	N1	2.000	1.575	0.425
-COCH3	2.000	1.576	0.424	N2	2.000	1.556	0.444
-COOCH3	2.000	1.580	0.420	N3	2.000	1.558	0.442
-H	2.000	1.579	0.421	N4	2.000	1.526	0.474
-CH=CH2	2.000	1.564	0.436	N5	2.000	1.534	0.466
-OH	2.000	1.567	0.433	N6	2.000	1.473	0.527
-CH3	2.000	1.571	0.429				
-OCH3	2.000	1.562	0.438				
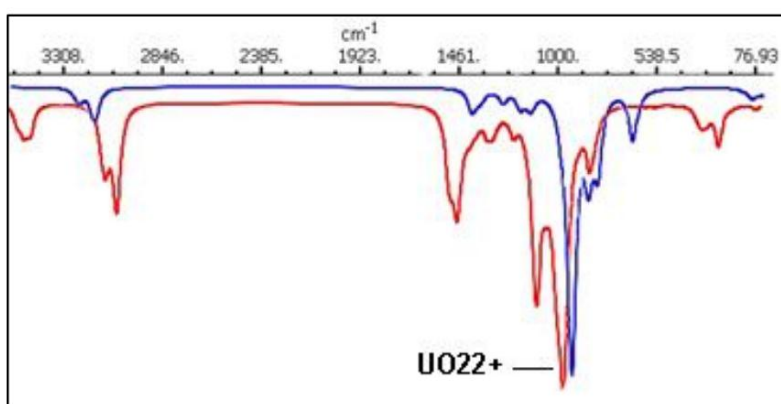
Figure 8. Calculated IR frequencies of [UO2(18-crown-6)]2+ (blue) and [UO2(hexaaza-18-crown-6)]2+ (red) complexes

In term of substituent effect, the charge of metal ion after complexation generally decrease as the substituents changes from electron withdrawing into electron donating substituents. The smallest charge after complexation means the highest charge transfer is obtained from the highest interaction energy complex (R=OCH3). Similar trend also can be found from the calculated values of Mulliken charge on UO22+ with azacrowns. The smallest charge of complexation (the highest value of charge transfer) is obtained from the highest interaction energy which is [UO2(hexaaza-18-crown-6)]2+ complexes.

Vibration Frequencies

We have calculated the vibration frequencies for all complexes considered in this work. The calculated stretching frequencies of UO2(18-crown-6)]2+ and [UO2(hexaaza-18-crown-6)]2+ as representative complexes are shown in Table 3.

All complexes are confirmed to be in minimal potential energy surface, it is indicated by no imaginary frequencies found for all species. Figure 8 clearly shows the changes of uranyl (UO22+) frequencies from UO2(18-crown-6)]2+ and [UO2(hexaaza-18-crown-6)]2+ where they are in 936,5 cm-1 and 971.5 cm-1, respectively. The calculated maximum frequencies were between 3146.518 and 3528.970 cm-1 for all complexes. Among these complexes, UO2(18-crown-6)]2+ was found to have the lowest frequency (5.934 cm-1).

CONCLUSION.

The crown ethers containing disubtituents on each benzo unit of dibenzo-18-crown-6 and azacrown and also their complexes with UO22+ have been discussed in this work. The parameters of the complexes are successfully obtained by B3LYP (SDD/DZP) level of theory. From these calculated and

analytical results, the following conclusions could be drawn.

1. Electron donating substituents increase the complexing ability of dibenzo-18-crown-6 toward UO_2^{2+}. Electron withdrawing substituents shows the opposite effect.

2. Nitrogen number has significant influence in binding stability of the crown ether toward UO_2^{2+} ion. Interaction energies indicate that hexaaza-18-crown-6 offers the highest binding capability to UO_2^{2+} ion.

3. The highest complex charge transfer is obtained from the highest complex interaction energy [UO2(hexaaza-18-crown-6)]2+

Finally, it would be a great of important to study the influence of solvent molecules for the interaction properties of these complexes. The calculation method can be used to study the behavior of other nuclear waste species.

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