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# **Dibenzo-18-crown-6 selectivity for alkali metal cations in aqueous solution**

by

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As a Requirement for Degree of B .S c . in Chemistry Science

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2016 A.C

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

يَرْفَعِ اللَّهُ الَّذِينَ آمَنُوا مِنْكُمْ وَالَّذِينَ  
أُوتُوا الْعِلْمَ دَرَجَاتٍ وَاللَّهُ بِمَا تَعْمَلُونَ  
خَبِيرٌ ۝

صدق الله العلي العظيم

سورة المجادلة الآية رقم 1

# **Acknowledgements**

**We would like to Thank Our God for this chance to get this research and we would like to thank our Supervisor, Assist. Prof Dr. Zeina M. K., and we would like to thank Chemistry Department and the head of the Department Assist. Prof Dr. Faaq . Karma, and the dean of College of Science, Qadisiaya University.**

**I would like to thank my father and my mother, and all my family.**

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# Abstract

Dibenzo-18-crown-6 (DB18C6) exhibits the binding selectivity for alkali metal cations in solution phase. In this study, we investigate the main forces that determine the binding selectivity of DB18C6 for the metal cations in aqueous solution. The solvation energy of  $M^+$ -DB18C6 in aqueous solution plays a key role in determining the binding selectivity of DB18C6. In particular, the non-electrostatic dispersion interaction between the solute and solvent, which depends strongly on the complex structure, is largely responsible for the different solvation energies of  $M^+$ -DB18C6. This study shows that the implicit solvation model like the CPCM works reasonably well in predicting the binding selectivity of DB18C6 in aqueous solution.

## Introduction

### 1-2 Supramolecular chemistry

The rapid expansion in supramolecular chemistry over the past 15 years has resulted in an enormous diversity of chemical systems, both designed and accidentally stumbled upon which they may lay some claims either in concept, origin or nature being supramolecular entity. Much of supramolecular chemistry has sprung from development in macrocyclic chemistry in the mid to late 1960's particularly the development of macrocyclic ligands for metal cations. C. J. Pederson in 1967 accidentally discovered crown ether.<sup>(1)</sup>

Crown ether is one of the most well-known host molecules, which exhibits the binding selectivity for alkali metal and alkali earth metal cations in solution phase.<sup>(1)</sup> In particular, 18-crown-6 (18C6) and DB18C6, which are the first crown ethers synthesized by Pedersen in 1967.<sup>(1)</sup> Have the strongest binding affinity to a potassium cation ( $K^+$ ) among alkali metal cations. With the similarity of the sizes between  $K^+$  and the cavity of crown ether, it had long been believed that the binding selectivity comes from the size relationship between the metal cation and the cavity.<sup>(1)</sup>

## 1-3 The macrocyclic molecules

Crown ethers are macrocyclic molecules consisting of several oxyethylene (c-c-o) units. By the simultaneous donation of ether O atoms, crown ethers can form stable complexes with metal and organic cations, neutral molecules, and even anions.<sup>(2)</sup> In addition, crown ether rings are very flexible, and they can adjust their structure to incorporate guest species with different shapes.<sup>(2,3)</sup> Because of their complex formation ability, crown ethers are used in many application such as metal cation extraction,<sup>(4)</sup> fluoroionophore,<sup>5</sup> and phase transfer catalysis.<sup>(6)</sup> It is well known that 18-crow-6 ether (18C6) forms an exceptionally stable 1: 1 complex with  $K^+$  ion is comparable with the cavity size of 18C6.<sup>2,7,8</sup> Crown ethers also show the type of encapsulation in which a guest species is enclosed by two crown ethers<sup>(9,10)</sup>, or two gusets are held by one crown ether.<sup>(11,12)</sup>

As we are interested in the formation of new materials with functional properties, especially the lower dimensional polymers.<sup>(13-16)</sup> in order to generate anisotropy, the question arose whether it was possible to stabilize one-dimensional polymers by coordination with crown ether. The potential capacity of dibenzo-crowns to form  $\pi$  interactions upon stacking appeared to us as an interesting property in this context. Indeed, we succeeded in the crystallization of a compound in which the dibenzo-18-crown-6 ligands are stacked to yield a channel in which water molecules and  $H_3O_+$  are present.<sup>(17, 18)</sup>

## 1-4 Macrocyclic molecules as a selective complexing agents

Macrocyclic compounds are commonly used as the phase transfer catalyst, in biometric studies and as specific and selective complexing agents for metals. Recently, crown ether with ethereal or anionic groups on the periphery of the macrocycles have been developed, in order to increase metal selectivity and the complex stability in analytical separations as well as in biological membranes.<sup>16</sup>

To recognise the role of solvation and thereby the origin of the binding selectivity of crown ethers in solution phase, many experimental and theoretical studies have been performed.<sup>19</sup>

## 1-5 The nomenclature of macrocyclic molecules

IUPAC nomenclature for these compounds is often cumbersome and makes key word identification impossible for computer literature searching. The regular nature of the macrocyclic structure has led to the much more useful and practical system using the x-crown-y designation. In this system, x represents the total number of atoms in the macrocyclic ring and y the number of heteroatoms. Thus Figure.(1),a. would have the IUPAC name 1,4,7,10,13,16-hexaoxaoctadecane and the common name 18-crown-6- the crown system assumes ether linkages with all other heteroatoms being specified eg . 1, 10-diaza-18-crown-6.<sup>(1, 19)</sup>

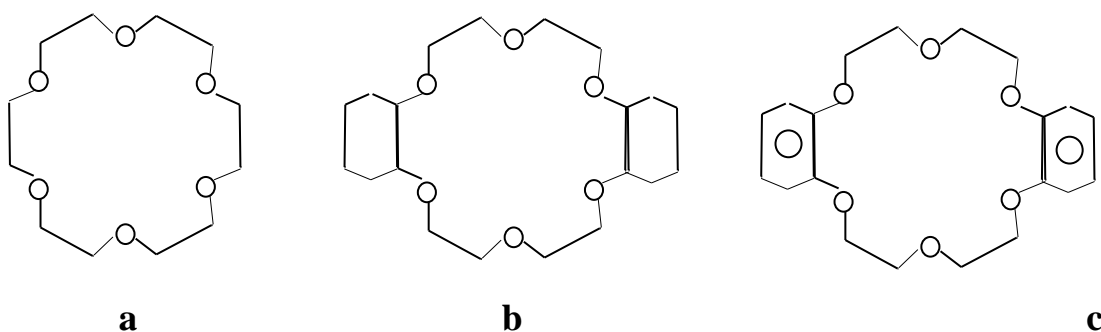


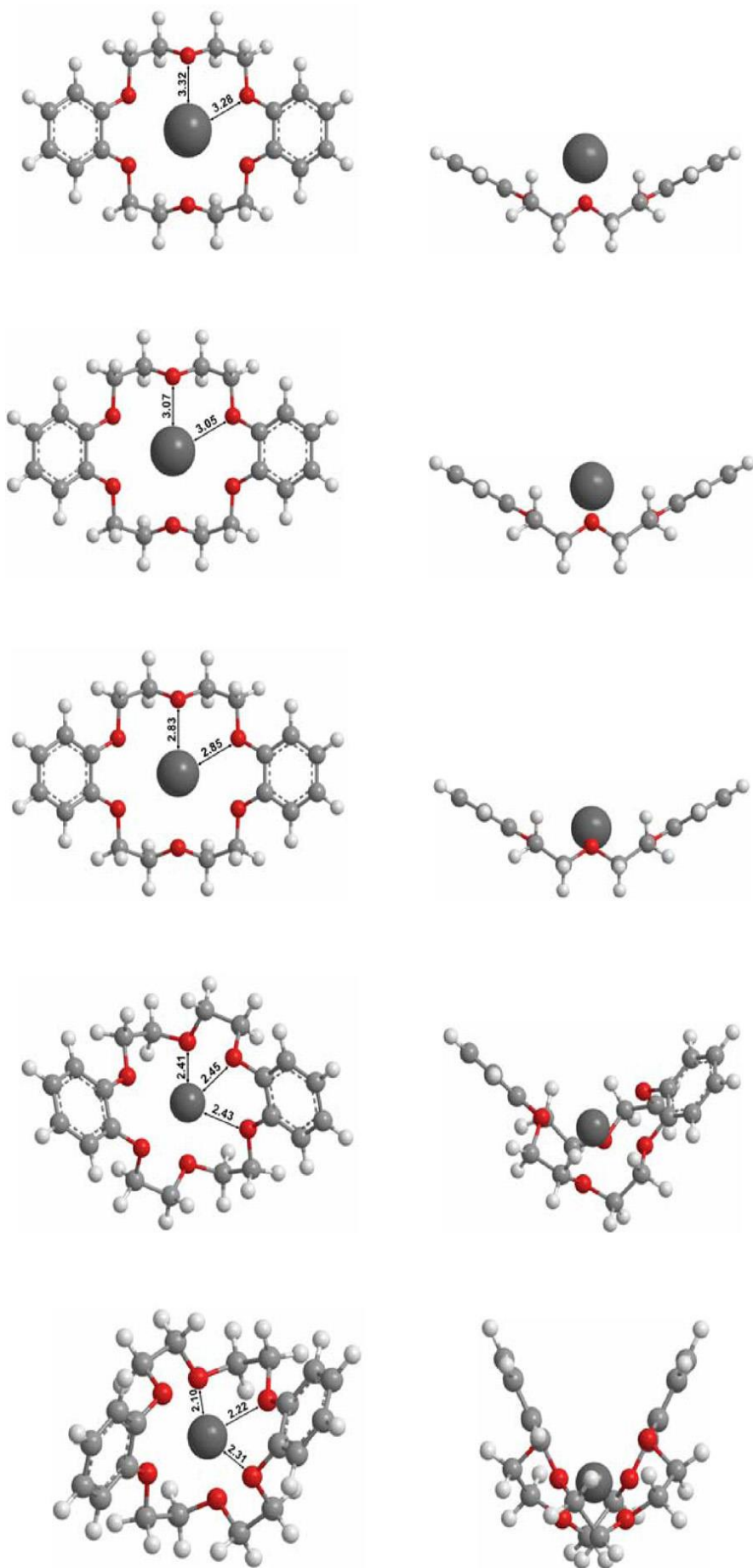
Figure.(1): Examples of crown ethers

Crown ether is one of the most well-known host molecules, which exhibits the binding selectivity for alkali metal and alkali earth metal cations in solution phase. <sup>(19, 20)</sup> In particular, 18-crown-6 (18C6) and DB18C6, which are the first crown ethers synthesized by Pedersen in 1967. <sup>(21)</sup> have the strongest binding affinity to a potassium cation ( $K^+$ ) among alkali metal cations. With the similarity of the sizes between  $K^+$  and the cavity of crown ether, it had long been believed that the binding selectivity comes from the size relationship between the metal cation and the cavity. However, it was reported that under identical experimental conditions  $K^+$  bound strongly to all crown ethers (12-crown-4 to 24-crown-8) irrespective of the ring size among other cations such as  $Na^+$ ,  $Ca^{2+}$ , and  $NH_4^+$ . <sup>(22)</sup>

This is also consistent with the fact that the structures of  $M^+-18C6(H_2O)_n$  ( $n = 1-4$ ) are not so different from those of  $M^+-18C6$ . <sup>(23, 24, 25)</sup> As a reason for those similarities, Lisy and coworkers. <sup>(23)</sup> Insisted that the 18C6.  $M^+$  interaction is so resilient and is still dominant with a few waters present.

The only exception is  $Cs^+-DB18C6$ . Although the Cs conformer (Cs-I) is the lowest energy conformer in the gas phase, the  $C_{2v}$  conformer (Cs-II) becomes the most stable conformer in aqueous solution as in Figure (2). <sup>(26)</sup>





**Figure (2): The lowest-energy structures of  $M^+$ -DB18C6 in Aqueous solution.**

## 2. Experimental Section

The conformational analysis of 18-azacrown-6 complexes with the late first transition series divalent metal ions in aqueous solution was carried out using the PCM model.<sup>(27)</sup> The K<sup>+</sup> selectivity of the [2.2.2]-cryptand in solution was also well predicted by the CPCM model.<sup>(28)</sup> The complex binding energies of [AnO<sub>2</sub> (18-crown-6)]<sup>n+</sup>, where An=U, Np, Pu and n = 1, 2, in aqueous solution were estimated using the CPCM and COSMO model.<sup>(29)</sup>

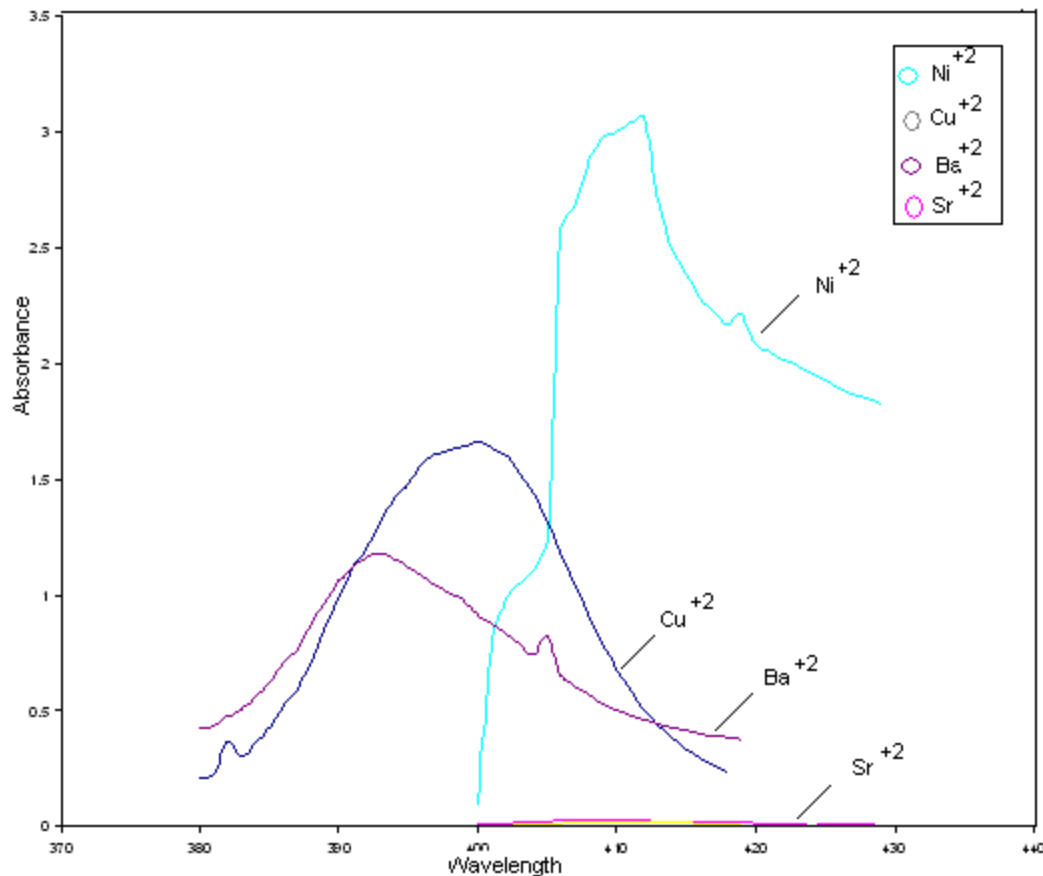
Despite those advantages and extensive uses of the continuum solvation model, only a few studies have been performed to understand the binding selectivity of crown ethers in solution phase using the continuum model.<sup>(28, 30, 31)</sup> Here, we investigate the binding selectivity of DB18C6 for alkali metal cations in aqueous solution by calculating the BDFEs of M<sup>+</sup>-DB18C6 complexes using DFT and the CPCM. DB18C6 is chosen because it has a rigid structure and exists in a small number of conformational isomers, reducing the expense of the calculation.<sup>(32)</sup> Moreover, DB18C6 complexes with alkali metal cations have recently been investigated in the gas phase using various laser spectroscopic methods.<sup>(33, 34)</sup>

Comparing the theoretical binding selectivity of DB18C6 with the experimental one, we verify the feasibility of calculations using the continuum solvation model in predicting the binding selectivity of crown ethers. On the basis of the agreements between the theory and experiment, we also determine the main forces that influence the aqueous binding selectivity of DB18C6.

## 2-1 Optical Spectral Properties:

**2-2 UV measurements:** Stock solutions of 4b ( $1 \times 10^{-4}$  M, in DMF) and metal ions such as Cu (II), Ni (II), Ba (II), Ca (II) ( $1 \times 10^{-2}$  M) in methanol were prepared to get  $1 \times 10^{-3}$  M and  $1 \times 10^{-4}$  M solutions. Aliquot of metal solution was added to the ionophore solution and the final concentrations and compositions of the solution were adjusted to the desired value by adding extra DMF. Out four metal ions only Cu (II), Ni (II) gave the satisfactory results as shown in UV-Visible spectral absorption band at 287 nm characteristics absorption band of DMF solvent.

Addition of 100-mmole equivalent of metal ions like Ca (II), Ba (II), Sr (II), Cu (II) and Ni (II) in ionophore resulted in the formation of metal complex. In case of  $\text{Cu}^{+2}$  and  $\text{Ni}^{+2}$  ions color change observed from colorless to blue and green respectively Figure (3). The shift of the absorption band from 287 nm to 400 nm and 413 nm for  $\text{Cu}^{+2}$  and  $\text{Ni}^{+2}$  respectively which indicate that there is good complexation ability of naphthaquinone derivative of dibenzo 18 crown 6 and  $\text{Cu}^{+2}$  and  $\text{Ni}^{+2}$  from that we concluded that Naphthaquinone derivative of dibenzo 18 crown 6 used as analytical probe for estimation of  $\text{Cu}^{+2}$  and  $\text{Ni}^{+2}$ .<sup>(35)</sup>



**Figure (3): The UV-Visible spectral absorption**

### **2-3 X-Ray Diffraction study:**

### **2-4 Preparation of Cu (II) complex of naphthaquinone containing dibenzo -18-crown -6:**

A solution of 0.960 g. (2 mmol) of naphthaquinone dibenzo 18 -crown 6 in ethanol (10 ml) was added in 0.344 g. (2 mmol) of Cu (NO<sub>3</sub>)<sub>2</sub> containing catalytic amount of sodium acetate 0.3 g. and stirred when the color of solution changes from colorless to greenish blue. After completion of reaction the solid formed was filtered paper, yield: 80%, m.p: above 3000C. <sup>1</sup>H NMR (300MHz, DMSO-*d*<sub>6</sub>): δ, 1.8-2.28 (m, 8H), 2.47-2.87(m, 8H), 5.34 (dd, 2H, *J*), 6.39- 6.53 (d, 3H, *J*), 6.57-6.61 (dd, 3H), 6.83-6.95(dd, 2H), 7.16-7.71(dd, 8H) ppm. IR (KBr) (cm<sup>-1</sup>): 2914, 2863, 1655, 1581, 1547, 1515.78, 1336, 1200, 1043,772. <sup>13</sup>CNMR(300MHz,DMSO): δ167,162,154,148,146,137,139,138,137,126 126,126,124,118,110,86,77,65,58,47,45,25,18,14,14

### **2-5 X-ray diffraction study of Cu (II) complex of naphthaquinone containing dibenzo 18-crown-6:**

X-ray scattering measurement was performed on a Phillips Analytical XRD spectrophotometer.

The diffractometer used for the same compound was of the type PW 3710 based. The anode tube used for the same compound was of Copper. X- ray diffraction pattern observed gave very sharp peaks indicating crystalline nature of the complex. <sup>(35)</sup>

## 3. The Discussion

### 3-1 The Application of Crown ethers

Macromolecules find their applications due to their unique chemical and biological properties.<sup>(36)</sup> Macrocyclic compounds are commonly used as the phase transfer catalyst, in biometric studies and as specific and selective complexing agents for metals. Recently, crown ether with ethereal or anionic groups on the periphery of the macrocycles have been developed, in order to increase metal selectivity and the complex stability in analytical separations as well as in biological membranes.<sup>(37- 42)</sup> Several workers have reported modified crown ethers with chromogenic groups.<sup>(43- 46)</sup> The crown ether ring or the chromophoric side arm can modify the properties of these compounds with different sensitivities and selectivity's for metal ions such as the crown ether dyes possessing a potential anionic site attached to the chromophore.<sup>(47)</sup> B.R. Pandya, Y.K. Agrawal have reported the crown ethers azo- dyes capable of fixing on the cotton fibers.<sup>(48)</sup> Macromolecules are used as PTC and reagents for extraction due to their high complexation ability and as dye intermediates and optical brighteners.<sup>(49)</sup> There has been much interest for the development of efficient and selective chromogenic and fluorogenic ionophore systems.<sup>(50)</sup>

A substantial part of research works on macrocyclic polyethers have been devoted to their complexation with alkali, alkaline earth and somewhat to transition metal ions, but a little attention has been paid to lanthanide complexation and hence, information about the coordination behavior of crown ethers towards the rare earth metal cations, is relatively scarce. Furthermore, such studies on lanthanide– crown ether complexation have been carried out in pure solvents and information in mixed solvents is very sparse.

## 3-2 The Application of the modified properties of Crown ethers

The crown ether ring or the chromophoric side arm can modify the properties of these compounds with different sensitivities and selectivities for metal ions such as the crown ether dyes possessing a potential anionic site attached to the chromophore. <sup>(51)</sup> B.R. Pandya, Y.K. Agrawal have reported the crown ethers azo- dyes capable of fixing on the cotton fibers. <sup>(52)</sup> Macromolecules are used as PTC and reagents for extraction due to their high complexation ability and as dye intermediates and optical brighteners. <sup>(53)</sup>

There has been much interest for the development of efficient and selective chromogenic and fluorogenic ionophore systems. <sup>(54)</sup> These compounds possess applications in cation recognition processes redox properties of transition metal complexes bound to the Schiff base. <sup>(55)</sup> Several workers have reported the optical and spectral properties of the crowned retinals and Bacteriorhodopsin analogs for different metal ions. <sup>(56)</sup>

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