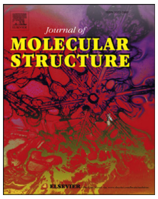
Journal of Molecular Structure 1130 (2017) 781–790

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc



Binding and selectivity of phenazino-18-crown-6-ether with alkali, alkaline earth and toxic metal species: A DFT study

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ARTICLE INFO

Article history:
Received 15 June 2016
Received in revised form
25 October 2016
Accepted 25 October 2016
Available online 3 November 2016

Keywords:
Phenazino-18-crown-6-ether
Electron affinity
Perturbation energy
Macrocyclic ligand
Dipole moment

ABSTRACT

The interactions of phenazino-crown ether ligands with alkali, alkaline earth and selected toxic species were investigated using density functional theory modelling by employing B3PW91/6-311G ++ (d, p) level of theory. The complex stability was analysed in terms of binding energies, perturbation energies, position of highest molecular orbital and energy gap values. In general, the complexes formed by P18C6-1a ligand with metal cations were found to be more stable than those with P18C6-1b. Among alkali and alkaline earth metals complexes having highest stability was observed for the complex formed by P18C6-1a with Be^{2+}. Computational calculations of P18C6 ligand with toxic metal ions reveals that the P18C6-Cr^{6+} metal complexes acquire envelop like geometry, leading to higher binding energy values. Comparing the binding energies of neutral and monocations of Ag and Hg, the former had higher value both in neutral as well as monocation state. Thus, the stability of metal complexes is determined not only by the ligand but also by the type of metal ion. In solvent systems the stability constants of metal complexes were found increasing with decreasing permittivity of the solvent. This reflects the inherited polar character of the protic solvents stabilises the cation, resulting in decrease of effective interaction of ligand with the metal ion.

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1. Introduction

The discovery of dibenzo-18-crown-6 by Pedersen attracted the attention of researchers to focus on the nature of selectivity of macrocyclic derivatives for metal cations [1]. The selectivity of macrocyclic compounds has often been explained in terms of the size-fit concept, involving either covalent interactions or non-covalent interactions [2–4]. These compounds are capable of forming complexes with alkali and alkaline earth metal ions via electrostatic attraction and encapsulation into a suitable cavity [5–7]. According to Glendening et al., and More et al., the binding energy studies between crown and alkali metal ions have shown that the enthalpic stability of the complexes in the absence of a solvent decreases monotonically with increasing size of the metal ion [8,9]. This discrepancy between the solution and gas phase results, indicates that the solvation effects strongly influence the binding selectivity of macrocyclic compounds in solution phase [7,10–12].

Crown ethers, a class of macrocyclic compounds are well-known host molecules of biological interest; playing a role in biological cation transport systems and of some antibiotics (such as valinomycin) that also bind metal cations selectively [13–18]. According to Makrlik et al., change in oxidation state of the metal inside the crown ether is useful for creating switching or photoswitching of complexes [19]. It was found that silver(I) complexes with diaza-18-crown-6-derivatives can be reduced to zero oxidation state in a solution medium. Which was used for sensing of polarizable heavy metal cations such as Ag(I) and Hg(II) [20]. Extensive theoretical studies, particularly ab initio calculations have been performed on free crown ethers, ammonium and crown ether complexes with alkali and alkaline earth metals [3,5,13,15]. Anderson et al., used Hatree-Fock and MP2 level of theory for calculating the structure and binding energies of 18-Crown-6 complexes of alkali metals [13]. According to them, the computed order of Li^+ affinities at all levels of theory is 18C6 < 15C5 < DB18C6, and that for Na^+ is 18C6 < DB18C6 < 15C5 (RHF) or 15C5<18C6< DB18C6 (MP2), in contrast to the experiments and earlier calculations. Heo [21] studied the selectivity of D18C6 ether for alkaline earth divalent cations. Based on NBO analysis, he concluded that the large binding energy is

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http://dx.doi.org/10.1016/j.molstruc.2016.10.100
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attributed to the strong polarization of the C—O bond by cation in solvent phase (aqueous). Among all dications, Mg^{2+} demonstrates the highest binding energy as compared to its lowest energy gaps in the gas phase, which may be attributed to the large hydration energy for the small size of cation in aqueous medium. Bagatur'yants et al., reported DFT calculations of the electronic and geometrical structure of 18-Crown-6, its complexes with Ag^{+}, Hg^{2+}, Ag^{0}, Hg^{+}, Hg^{0}, $AgNO_3$ [22]. According to them among all studied metal species Hg^{2+} ion is strongly bound to the crown ether. It was found that silver and mercury ions in the 18-crown-6 cavity gets reduced by capturing an electron within the complexes and nature of bonding in these complexes between the metal and the ligand is van der Waals type interaction. Structural studies on [Cd(18-crown-6)X_2] done by Yan et al. employing DFT level of theory shows that the binding of axial ligands such as water with metal ion involves ionic interaction which displays no distortion towards linear geometry of complexes. The geometry predicted for this complex shows that the Cd(II) binds to only a few of the donors of the crown ether, with short Cd—O bonds. In second case the binding of axial ligands such as Cl in the [Cd(18-crown-6)X2] complex were found more covalent in nature results in the distoration of geometry with short Cd—Cl bonds and long Cd—O bonds to the O-donors of the crown ether [2,4]. However, no theoretical investigation on structural and binding interactions has been reported on phenazino-18-crown-6-ether complexes of alkali and alkaline earth metal cations.

Phenazino-18-crown-6-ether (P18C6) (Fig. 1) is the prototype of dibenzo-18-crown-6 having phenazine instead of dibenzo, carrying one addition planar binding site for guest molecule. When substituted at C_{23} and C_{26} these are categorised under chiral crown ethers, have received much attention on account of presence of naphthalene wall, which is supportive in the enantiomeric recognition of optically active amino acids and organic ammonium ions [23–25]. Bradshaw et al., prepared a series of chiral crown ethers, aza-crown ethers, and crown ether diesters having pyridine, triazole, and pyrimidine subcyclic units to develop qualitative and quantitative relationships between molecular structural features of chiral crown ether hosts and chiral organic ammonium ion guests [23]. The log K values measured using an^{1}H NMR show that these chiral pyridino-18-crown-6 ligands have high complexing abilities. However, the investigation on geometrical parameters of pyridino-18-crown-6 ligands displays that in the lowest energy conformers the phenyl ring of the guest PhEt orients parallel and perpendicular to the pyridine ring present in chiral dimethyl-substituted ligand complexes and in chiral di-*tert*-butyl-substituted ligand complex with PhEt respectively. Various structural changes to crown ether hosts have been made in attempts to enhance their complexation stability and selectivity. Some of these modifications have involved the insertion of heterocyclic units or substitution at chiral centres of the macro-ring [24–26]. In this paper computational methods has been employed to address the structural implications and relative binding energies of alkali, alkaline earth and selective toxic metal cations (Hg, Hg^{+}, Hg^{2+}, Pb^{2+}, Pb^{4+}, Ag, Ag^{+}, As^{3+}, Cd^{2+}, Cr^{+6}) on the pore size of phenazino-18-crown-6-ether ligand.

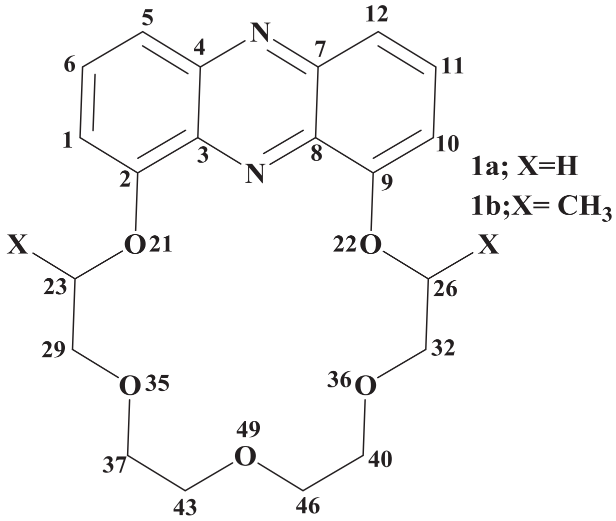

Fig. 1. Sketch of phenazino-18-crown-6-ether ligand derivatives.

2. Computational method

Calculations were performed using Gaussian 09 computational package [27]. Becke's three-parameter hybrid functional including a mixture of Hatree—Fock exchange with DFT exchange-correlation combined with Lee-Yang— Parr correlation functional (B3LYP) [28] and B3PW91 [29] were used in all calculations employing 6-311G++ (d, p) (for C, H, N, O) and LANL2DZ (Los Alamos effective core potentials) (for metal ions) basis set. B3LYP and B3PW91 are the most widely used hybrid generalized gradient approximation functional and have been demonstrated in numerous studies to be efficient and reasonably accurate in predicting interaction and binding energies of organic molecules and inorganic complexes [30–32]. Vibrational frequencies of optimised structures were calculated to identify probable imaginary frequencies of the local minimum structures. The binding energy (BE) and electron affinity (EA) were calculated by using the following equations.

$$BE = E_{Complex} - \left(E_{metal\ \ ion} + E_{Ligand}\right) \tag{1}$$

$$EA = E^{-}_{complex} - E_{complex} \tag{2}$$

To avoid a basis-set superposition error (BSSE) metal-ligand binding energies (IPBEs) were counter-poise corrected using a standard approach by Boys and Bernardi [33] The final expression for the (BE_{BSSE}) was as follows:

$$BE_{BSSE} = E_C^{CP} - E_m - E_L + \Delta ZPVE \tag{3}$$

where E_C^{CP} is the counter-poise corrected electronic energy of the complex and E_m and E_L are the electronic energies of the metal ion and the ligand in their minimum-energy geometries.

The natural bonding orbitals (NBO) calculations was performed using NBO 3.1 [34] implemented in the Gaussian 03 package. The second order perturbation energies E(2) based on the Natural Bond Orbital (NBO) analysis were calculated from analysis of Fock matrix, which corresponds to the overlap integral of orbital pair [35]. For each donor NBO (i) and acceptor NBO (j), E (2) associated with i→j delocalization is given as:

$$E_2 = \Delta E_{ij} = q_i \frac{F^2_{(i,j)}}{\varepsilon_i - \varepsilon_j} \tag{4}$$

Here, q_i is the donor orbital occupancy ε_i, ε_j are diagonal elements (orbital energies) and F(i,j) are the off diagonal elements of NBO Fock matrix.

3. Results and discussion

3.1. Geometry of ligand and metal complexes

The lowest energy structures optimised at B3PW91/6-311++G (d, p)/LANL2DZ of phenazino-18-crown-6-ether and its

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