Reduction of silver cation in the cavity of diaza-18-crown-6: a theoretical study

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The structure and stability of diaza-18-crown-6 (**1**) complex with silver cation was studied by the density functional method with the PBE functional. The reduction of the cation in the macrocycle cavity was simulated and possible stability of the resulting van der Waals complex of the crown ether **1** with silver atom was analyzed. It is shown that, after electron capture, two equilibrium conformers of $Ag^+ \cdot \mathbf{1}$ give two structures locally stable with respect to the dissociation into the silver atom and the crown ether in its nearest equilibrium conformation. One of the neutral structures, that of the C_s symmetry, corresponds to a global minimum on the potential energy surface of the Ag^0—**1** system. It ensures the thermodynamic stability of the reduced complex with respect to dissociation.

Key words: diazacrown ethers, complexes with Ag^+, reduction, quantum-chemical calculations, density functional theory, all-electron relativistic basis set.

Switching or photoswitching supramolecular systems can have a d-block metal cation, which is capable of chemical, electrochemical, or photochemical oxidation or reduction, in a macrocycle cavity as a main switching element. Hemoglobin and chlorophyll are natural analogs of these systems. The change of the oxidation number of the central ion is followed by the change in the ion binding energy in the complex as well as the change in the geometric and other characteristics of the complex. Therefore, investigations of the interaction of heavy d-block metals with crown ethers and the electron structure of the resulting crown ether complexes of heavy metals are of considerable interest.

It is reported[1,2] that Ag^+ in the cavity of a derivative of diaza-18-crown-6 (**1**) can be reduced in solution to a neutral complex with Ag^0 atom in the crown ether cavity. This complex lives rather long after reduction, ~5 мs,[2] whereupon Ag atom in the crown ether cavity enters side reactions without dissociation (mainly, aggregation processes with further loss of ligands). This system can be considered as an electron trap made of a highly polarizable heavy metal cation in a crown ether complex.

Previously,[3] we studied the complexation of 18-crown-6 (**2**) with Ag^+ and Hg^{2+} and the reduction of these ions in the macrocycle cavity. At the same time, it is interesting to analyze the possibility of interaction and the structure of the resulting complexes for the case of silver and the crown ether **1**, whose derivative was used in the experiments.[1,2]

In this paper, we theoretically studied the complexation of **1** with Ag^+ and reduction of this cation in the macrocycle cavity and compare the results with those obtained earlier[3] for the crown ether **2**. The medium, in which the processes studied in Refs 1 and 2 took place, is rather difficult for simulation, namely, it is an aqueous solution of surfactant micelles. In this case, continuum models are inapplicable, and the models explicitly taking into account the microscopic environment of the reagents are too complicated. However, we were interested only whether a stable complex of silver atom with diazacrown ether can exist in principle; therefore, we did not go beyond the gas-phase study.

Calculation Procedure

The geometry of the crown ether **1** and its complexes was fully optimized by the density functional theory (PBE[4] functional and an original all-electron relativistic L2 [5] basis set) using the PRIRODA [6] program package.

The calculated structures of various conformers of **1** and its complexes with silver cation or atom were compared with the X-ray diffraction data retrieved from the Cambridge Structural Database[7]. The energies of the conformers were calculated relative to the corresponding lowest-energy structure.

Unless otherwise indicated, the binding energy of the central atom (ion) with the macrocycle was estimated for the dissociation of the complex into the atom (ion) and molecule **1** in its lowest-energy conformation. Zero-point vibration energy (ZPE) was not taken into account, because numerous calculations

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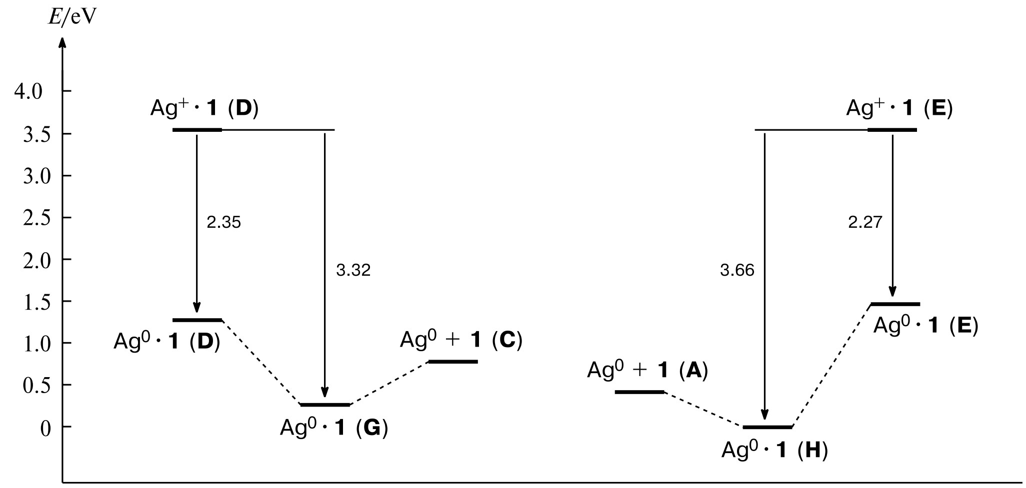


Fig. 1. Energy diagram of the Ag—**1** system. Arrows denote vertical $E_a^{(v)}$ and adiabatic $E_a^{(I)}$ electron affinity.

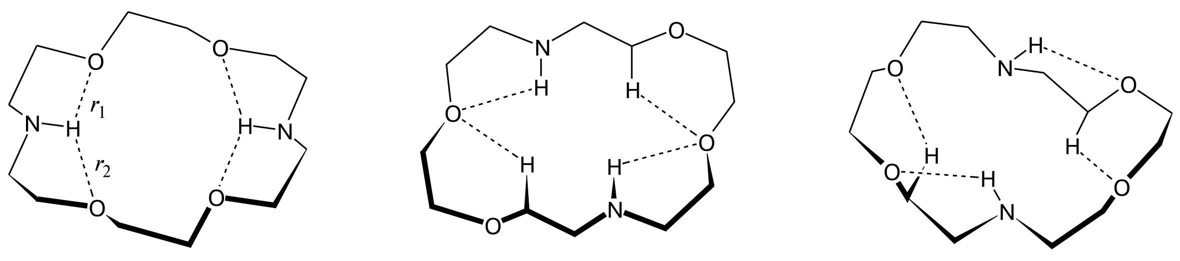
of crown ether systems showed that ZPE of different conformers of crown ethers and their complexes virtually cancel out. As a result, the energies of the conformers calculated with inclusion of ZPE are almost the same as those calculated ignoring ZPE, and the ion—ligand binding energies differ only slightly.

The vertical $E_a^{(v)}$ and adiabatic $E_a^{(I)}$ electron affinity was determined for the equilibrium structures of the cationic complexes. The $E_a^{(v)}$ value was calculated as the electron attachment energy at a fixed equilibrium geometry of the cationic complex, and the $E_a^{(I)}$ value was calculated as the electron attachment energy relative to the nearest equilibrium structure of the neutral complex obtained after geometry optimization of the cationic complex with a captured electron. We also calculated the adiabatic electron affinity ($E_a^{(II)}$) relative to the most stable structure of the complex with Ag^0. Note that, unlike the case of the ionization potential, the starting point in determining the electron affinity is the equilibrium structure of the cationic complex $Ag^+ \cdot \mathbf{1}$ (Fig. 1). At the positive electron affinity, the energy of the system with the attached electron is lower than the energy of the initial system. Vertical electron capture (without geometry relaxation) results in the energy gain $E_a^{(v)}$, and relaxation of the neutral complex $Ag^0 \cdot \mathbf{1}$ to its equilibrium geometry gives an additional energy gain equal to the relaxation energy. Hence, $E_a^{(I)} > E_a^{(v)}$ in absolute value (see Fig. 1).

Results and Discussion

Diazacrown ether 1. Unlike *N*-substituted derivatives, crown ethers without *N*-substituents prefer conformations in which the N—H bonds are directed inward the cavity and form four N—H...O contacts (Fig. 2, r_1 and r_2 distances). In the structure pre-organized for complexation the lone electron pairs (LPs) of the donor atoms should point into the cavity. These structures interconvert through the inversion of N atoms.

The geometry optimization of molecule **1** showed that the conformer of the C_{2h} symmetry (see Fig. 2, structure **A**) is the most stable, the energies of all other conformers being more than 6 kcal mol^{-1} higher. In crystals, if hydrogen bonds and other irrelevant interactions are absent, the molecules of **1** also adopt the conformation of the C_{2h} symmetry.[8—10] The geometric parameters calculated in this work (Table 1) differ from the experimental ones by at most 2%. A structure similar to **A** but with two LPs of the N atoms pointing into the cavity and the N—H bonds directed oppositely (upwards and downwards from the macrocycle) is pre-organized



A (0.0) **B** (6.2) **C** (6.4)

Fig. 2. Calculated structures of the low-lying conformers of diaza-18-crown-6 (**1**). Here and in Figs 3 and 4, figures in parentheses denote the relative energies of the conformers in kcal mol^{-1}.

Table 1. Geometric parameters of the most stable C_{2h}-symmetric conformer of diaza-18-crown-6 calculated by PBE/L2 and their error (Δ)* relative to the experiment

Bond or distance	d/Å			
	Calculation	Experiment (Δ(%))		
		See Ref. 8	See Ref. 9	See Ref. 10
C—C	1.514	1.501 (0.9)	1.497 (1.2)	1.485 (2.0)
C—O	1.420	1.421 (−0.1)	1.419 (0.0)	1.409 (0.8)
C—N	1.456	1.446 (0.7)	1.441 (1.1)	1.432 (1.7)
r_1	2.529	—	2.483 (1.9)	2.493 (1.4)
r_2	2.529	—	2.554 (−1.0)	2.524 (0.2)

* Here and in Table 2, the errors of the calculation (%) relative to the experimental data are given in parentheses.

for complexation but lies rather high in energy (11.5 kcal mol^{-1}).

We have also found a number of locally stable conformers of the C_i symmetry similar to the C_i conformer of molecule **2**, in which the N atoms occupy different positions and the N—H bonds and LPs of the N atom point in different directions (inwards or outwards the macrocycle cavity). These structures have at most two N—H...O contacts but can exhibit much weaker C—H...O contacts. These conformers (see Fig. 2, structure **B**) have the energies of at least 6.2 kcal mol^{-1}; their percentage in the equilibrium mixture at room temperature is negligible.

If one removes the cation from the most stable conformer of the $Ag^+ \cdot \mathbf{1}$ complex and optimizes the geometry of the remained diazacrown ether fragment, one obtains the conformer of the C_2 symmetry with a relative energy of 6.4 kcal mol^{-1} (see Fig. 2, structure **C**).

Therefore, at room temperature, diaza-18-crown-6 can exist as the only stable conformer of the C_{2h} symmetry not pre-organized for complexation.

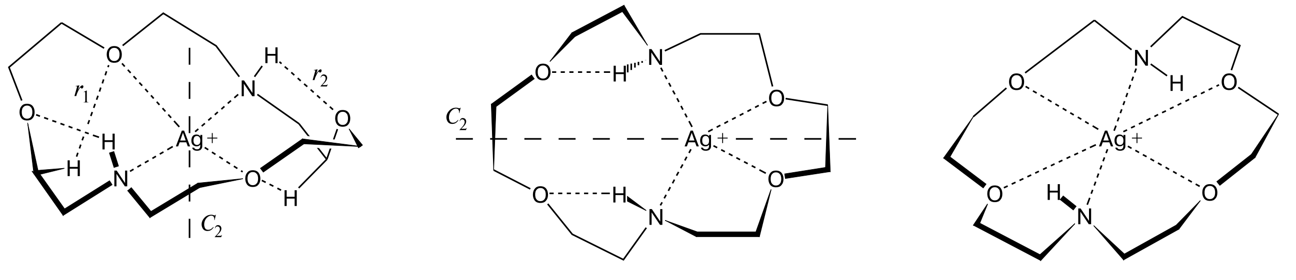
Complex of diaza-18-crown-6 with Ag^+. The complex of **1** with Ag^+ cation observed in the experiments (see Ref. 11) adopts a conformation of the C_2 symmetry stabilized by C—H...O and N—H...O contacts. In this structure, the cation is at the center of the cavity, and the C_2 axis passes through it at right angle to the lines connecting the pairs of the opposite N and O atoms (Fig. 3, structure **D**). According to our calculations, this structure has the lowest energy. Another conformer of the C_2 symmetry, in which Ag^+ is off-center, and the C_2 axis passes through Ag^+ and the centers of two opposite C—C bonds (see Fig. 3, structure **E**), lies slightly higher in energy (1.8 kcal mol^{-1}). Both conformers can exist in equilibrium with each other.

When conformers **D** and **E** of the $Ag^+ \cdot \mathbf{1}$ complex are formed, the C—C and C—O bond lengths remain virtually the same, and the C—N bonds elongate by ~0.03 Å (Table 2). Nevertheless, the macrocycle conformations in the structures **D** and **E** substantially differ from the conformation of the free crown ether.

High-lying pre-organized C_{2h} conformer of diazacrown ether forms a complex with a relative energy of 5 kcal mol^{-1}; its structure has C_{2h} symmetry (see Fig. 3, structure **F**). At room temperature, the percentage of the conformer with such a high energy in the equilibrium mixture can be neglected.

In the most stable conformer **D** of the $Ag^+ \cdot \mathbf{1}$ complex, the cation lies virtually in line with the N atoms (N—Ag—N angle is 173°) and goes out of the root-mean-square (RMS) plane of the O atoms (O—Ag—O angles are 160 and 158°). The Ag—N bonds (2.20 Å) are much shorter than the Ag—O distances (2.8 and 3.5 Å); in the latter case, it is safe to say that O—Ag bond is absent. Therefore, Ag^+ is coordinated only to the N atoms and two of the four O atoms.

In the **E** conformer of the $Ag^+ \cdot \mathbf{1}$ complex the cation lies in the RMS plane of the macrocycle on the symmetry axis. The N—Ag—N angle is 156°, and O—Ag—O angles are 164°. The Ag—N bond length is 2.23 Å, and the Ag—O distances are 2.7 and 3.4 Å. As in the case of conformer **D**, we can say that Ag^+ is only coordinated to the N atoms and two of the four O atoms, but the arrangement of the



D (0.0) **E** (1.8) **F** (5.1)

Fig. 3. Calculated structures of the low-lying conformers of $Ag^+ \cdot \mathbf{1}$ complex.

Table 2. Geometric parameters and energy characteristics of the low-lying conformers of $Ag^+ \cdot \mathbf{1}$ and $Ag^0 \cdot \mathbf{1}$ complexes calculated by the PBE/L2 method

Parameter	Calculation					Experiment[11]
	D	**E**	**F**	**G**	**H**	
E_{conf}/kcal mol^{-1}	1.8	5.1	0.0	6.1	0.0	—
E_f/kcal mol^{-1}	−110.1	−108.3	−104.9	−3.4	−9.5	—
Bond length/Å						
C–C	1.517 (1.5)	1.518	1.510	1.516	1.514	1.495
C—O	1.427 (0.4)	1.427	1.417	1.423	1.420	1.422
C—N	1.486 (0.8)	1.486	1.495	1.464	1.468, 1.457	1.475
Ag—N	2.196 (0.0)	2.234	2.316	3.53	4.16, 5.63	2.197
Ag—O	2.849 (1.7)	2.699	3.145	2.66	2.50, 6.56	2.801
	3.467 (−2.3)	3.409	3.117			3.549
(C)H...O	2.667 (1.6)	—	—	—	—	2.624
(N)H...O	2.396 (−10.7)	2.347	—	—	—	2.684

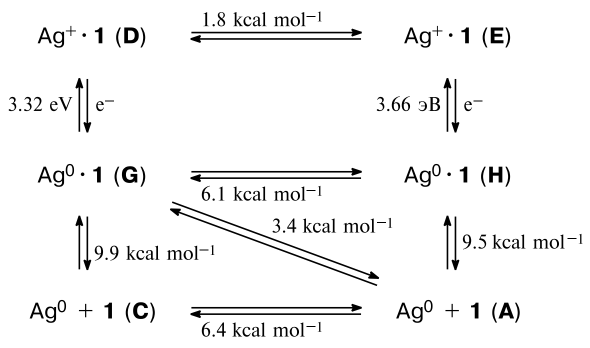
donor atoms in the coordination sphere of the cation is different.

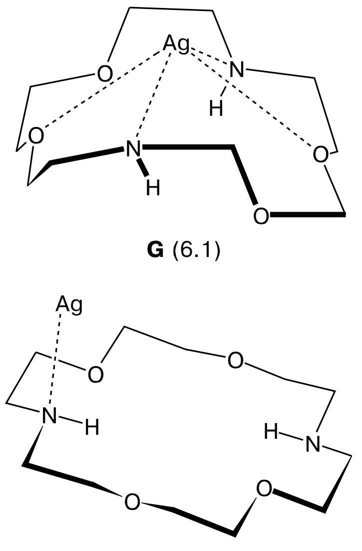
The binding energies of Ag^+ with molecule **1** in the conformers **D** and **E** are 110 and 108 kcal mol^{-1}, which is ~14 and 12 kcal mol^{-1} higher than the corresponding binding energy for molecule **2**. This high binding energy could be expected, because Ag^+ exhibits high affinity to the ligands with donor nitrogen atoms.

Reduction of Ag^+ in the cavity of diaza-18-crown-6. The possibility of the electron capture by the $Ag^+ \cdot \mathbf{1}$ complex is governed by the $E_a^{(v)}$ value equal to 2.35 (conformer **D**), 2.27 (**E**), and 2.45 eV (**F**). These values are lower than the corresponding values for the complexes of **2** with Ag^+ (see Ref. 3), which can also be attributed to the higher affinity of Ag^+ to the ligands with donor nitrogen atoms.

The evolution of the neutral complex formed upon electron capture by the $Ag^+ \cdot \mathbf{1}$ complex is of interest. Scheme 1 shows the processes that can occur in the Ag—**1** system on reduction of the cationic complex $Ag^+ \cdot \mathbf{1}$, and Fig. 1 gives the energy diagram of these processes.

Scheme 1





G (6.1)

H (0.0)

Fig. 4. Calculated structures of the low-lying conformers of $Ag^0 \cdot \mathbf{1}$ complex.

The $Ag^+ \cdot \mathbf{1}$ complex exists in solution as an equilibrium mixture of conformers **D** and **E**. Geometry optimization of the neutral complex formed upon electron attachment to the most stable conformer **D** gives the structure **G** of C_2 symmetry, in which the Ag atom goes out of the macrocycle cavity (Fig. 4). The corresponding adiabatic electron affinity is 3.32 eV. This conformer of the $Ag^0 \cdot \mathbf{1}$ complex is not the lowest-energy one and, generally speaking, can adopt a more stable conformation.

Geometry optimization of the complex resulting from electron attachment to the conformer **E** leads to the structure **H** of C_s symmetry (see Fig. 4). It can also be considered a result of attachment of the neutral Ag atom to the most stable C_{2h} conformer of the free diazacrown ether.

This structure is the most stable conformer of the neutral complex $Ag^0 \cdot \mathbf{1}$. In this structure, the Ag atom is localized near one of the N atoms above the macrocycle plane. The adiabatic electron affinity of the conformer **E** relative to this structure is 3.66 eV.

The adiabatic electron affinity $E_a^{(II)}$ of the most stable conformer **D** of the $Ag^+ \cdot \mathbf{1}$ complex calculated relative to the most stable structure **H** of the $Ag^0 \cdot \mathbf{1}$ complex is 3.58 eV.

The possibility of decomposition of the neutral $Ag^0 \cdot \mathbf{1}$ complexes (or, more precisely, their kinetic stability) is governed by the energy of the process in which the Ag atom is removed from the crown ether cavity and the crown ether fragment relaxes to the nearest equilibrium structure.

According to our calculations, the electron capture by the conformer **D** of the $Ag^+ \cdot \mathbf{1}$ complex results in the conformer **G** of the $Ag^0 \cdot \mathbf{1}$ complex (energy gain is 3.32 eV), which can dissociate to the silver atom and the conformer **C** of the crown ether without crown ether relaxation to the most stable conformation. In this case, the dissociation energy is 9.9 kcal mol^{-1} and the geometric parameters of the macrocycle relax only slightly, mainly, through shortening of the C—N bonds: 1.486 Å (**D**) > > 1.464 Å (**G**) > 1.454 Å (**C**). Further exothermic transformation of the conformer **C** to the most stable conformer **A** gives the energy gain of 6.4 kcal mol^{-1}. This process affects mainly the torsion angles and involves inversion of the N atom. Obviously, this transition is not instantaneous; therefore, the conformer **G** of the neutral complex $Ag^0 \cdot \mathbf{1}$ can be kinetically stable. The binding energy of this conformer calculated with respect to dissociation into the Ag atom and the most stable conformer **A** of the crown ether is 3.4 kcal mol^{-1}, which is 1.1 kcal mol^{-1} less than the binding energy of the neutral Ag atom in the complex with **2**.[3] This indicates rather low thermodynamic stability of the conformer **G** of the $Ag^0 \cdot \mathbf{1}$ complex with respect to dissociation into the Ag atom and the free diazacrown ether. At the same time, conformer **G** can rearrange into the more stable conformer **H**. The energy gain here is 6.1 kcal mol^{-1}.

According to our calculations, after electron capture, the conformer **E** of the $Ag^+ \cdot \mathbf{1}$ complex transforms to the conformer **H** of the $Ag^0 \cdot \mathbf{1}$ complex, which corresponds to the global minimum on the potential energy surface (PES) of the Ag^0—**1** system. The energy of its dissociation into Ag atom and the most stable conformer **A** of the crown ether is rather high (9.5 kcal mol^{-1}); therefore, this conformer of the neutral complex is thermodynamically stable with respect to dissociation.

When the conformer **E** of the $Ag^+ \cdot \mathbf{1}$ complex captures an electron, its geometry changes substantially: the Ag atom goes out of the macrocycle cavity and localizes at 2.50 Å from one of the N atoms; the C—C, C—O, and C—N bonds in the macrocycle shorten to the values characteristic of the free diazacrown ether; and the conformation of the macrocycle changes completely. The lone electron pair of the nearest N atom is donated to the Ag atom to produce an excess of electron density (0.13 e). As a result the spin density is partly localized on this N atom (0.07 e), and only 0.9 e remains on the Ag atom.

When the conformer **H** of the $Ag^0 \cdot \mathbf{1}$ complex dissociates, the macrocycle geometry changes only slightly. Only the C—N bonds involving the N atom that contacted the Ag atom shorten from 1.468 to 1.457 Å, that is, to the value characteristic of the free diazacrown ether.

Hence, on reduction of the cation, the two equilibrious conformers of the $Ag^+ \cdot \mathbf{1}$ complex give the structures that are locally stable with respect to dissociation into the Ag atom and the macrocycle in the nearest equilibrium conformation. This ensures the kinetic stability of the neutral complex. Neutral structure **H** of C_s symmetry corresponds to a rather deep global minimum on the PES of the Ag^0—**1** system and ensures the thermodynamic stability of the reduced complex with respect to dissociation. The other neutral structure (**G** of C_2 symmetry) can easily rearrange into structure **H**.

Analysis of the molecular geometry of diaza-18-crown-6 and its complex with the silver cation and atom showed that, in spite of the cavity size virtually equal to that of 18-crown-6, this macrocycle is more rigid due to the N—H...O contacts and can exist as a single stable conformer at room temperature. The structure of the complex of diaza-18-crown-6 with Ag^+ also differs substantially from the structure of the corresponding 18-crown-6 complex. At room temperature, this complex can exist as an equilibrium mixture of two conformers. The binding energy of the cation in the $Ag^+ \cdot \mathbf{1}$ complex is higher than that in $Ag^+ \cdot \mathbf{2}$, whereas the electron affinity of the former is lower.

On reduction of the cation, the equilibrious conformers **D** and **E** of the $Ag^+ \cdot \mathbf{1}$ complex give the structures locally stable with respect to dissociation into the Ag atom and the macrocycle in the nearest equilibrium conformation. A structure of the neutral complex is found that ensures its thermodynamic stability with respect to dissociation.

Therefore, the diaza-18-crown-6 complex with Ag^+ can serve as an electron trap and the resulting neutral complex is stable in agreement with experimental data.[1,2]

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