Recoordination of a metal ion in the cavity of a crown compound: a theoretical study

2.* Effect of the metal ion—solvent interaction on the conformations of calcium complexes of arylazacrown ethers**

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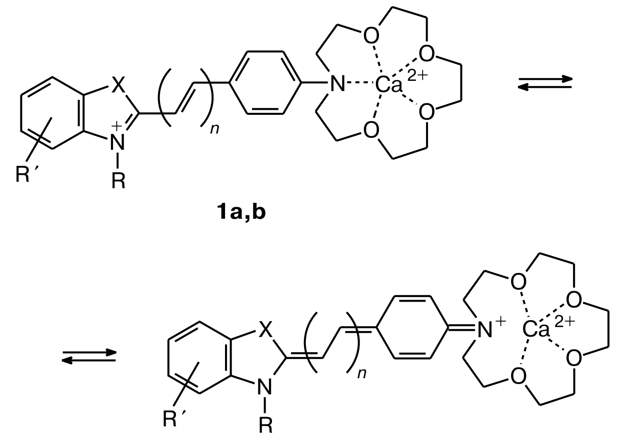
The effect of the local interaction of a metal ion with the solvent on the conformations of calcium complexes of arylazacrown ethers and an azacrown-containing dye was studied using the density functional method with the PBE and B3LYP functionals. The structures were studied and the interaction energies were determined for the calcium complexes with $n = 1—12$ water or acetonitrile molecules. It was found that the inner coordination sphere of the free Ca^{2+} cation contains six H_2O or seven MeCN molecules. The cation—acetonitrile interaction energy is higher than the cation—water interaction energy up to the moment the second solvation shell of the cation is almost complete ($n = 11$). The inner coordination sphere of Ca^{2+} in the macrocycle cavity contains at most three water molecules, while the fourth one is displaced to the second coordination sphere. Taking into account the local interaction with the solvent (H_2O or MeCN), the conformers of the calcium complexes of arylazacrown ethers and the azacrown-containing dye were studied. It was shown that the presence of two to four water molecules in the coordination sphere of the cation reduces the relative energies of the conformers with broken metal—nitrogen bond, thus favoring ground-state metal recoordination.

Key words: arylazacrown ethers, azacrown-containing dyes, complexes with Ca^{2+}, photoinduced recoordination, solvation, *ab initio* quantum chemical calculations, density functional theory.

UV absorption spectra of the alkaline-earth metal complexes of azacrown-containing dyes[1—5] recorded at a large excess of the cation ensuring the absence of the free dye in solution exhibit a long-wavelength shoulder, which cannot be attributed to the residual absorption of the free ligand. It was shown[4,5] that, in the excited state of the azacrown-containing dyes **1a,b**, the cation undergoes a photoinduced recoordination in the macrocycle cavity (Scheme 1). It was supposed that this recoordination could also occur in the ground state of the complex.

The fact that two types of cation coordination separated by an energy barrier can exist in the macrocycle cavity is nontrivial by itself. Our theoretical density functional study of the model *N*-arylaza-15-crown-5 (ArN15C5) compounds and the real dye **1a** (see Ref. 1) has demonstrated that the recoordination can occur only due to the transitions between the axial (**Ax**) and equatorial (**Eq**) forms of the arylazacrown ether complex. In the axial-type conformers, the aromatic ring axis passing through the crown ether nitrogen N_{cr} and the opposite

Scheme 1



1a: X = S, R = Et, R´ = H, $n = 1$;
1b: X = CMe_2, R = Me, R´ = 4,6-Me_2, $n = 2$

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* For Part 1, see Ref. 1.

** Dedicated to Academician A.L. Buchachenko on the occasion of his 70th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1981—1992, September, 2005.

C atom of the aromatic ring is perpendicular to the root-mean-square (RMS) plane of the crown ether*. In the equatorial-type conformers, the aromatic ring axis only slightly deflects from the RMS plane of the crown ether. In the equatorial conformers, the metal cation is immediately coordinated only to the crown ether oxygen atoms, the metal—nitrogen bond is broken, and the nitrogen atom is conjugated with the aromatic ring. In the axial conformers, the metal cation is additionally coordinated to the crown ether nitrogen, and the latter is not conjugated with the π-electron system. The corresponding changes in the π-electron system of the dye due to the recoordination manifest themselves in the UV absorption spectra.[2,3] We have shown that the presence of an acceptor group bearing a formal positive charge in the *para*-position to the crown ether nitrogen decreases the relative energy of the equatorial conformation even without solvation, which facilitates ground-state recoordination.

However, in the case of the real benzothiazolium styryl dye **1a**, in which the positively charged heterocyclic moiety is far from the crown ether moiety, the relative energy of the equatorial conformer is rather high. Therefore, the existence of the equatorial conformer of the dye complex in the ground state is hardly possible. This result is inconsistent with the conclusions made in the experimental study[2] that the form with broken metal—nitrogen bond can exist in the ground state.

Experimental data (see, *e.g.*, Ref. 6) indicate that the effects of specific solvation are important for complexation of cations with crown ethers. It was also shown theoretically[7—9] that the interaction with water could substantially alter the cation—crown ether binding energies. One can expect similar effects in the case of azacrown ethers.

The complexes of the dyes like **1** are usually studied in a polar solvating solvent, mainly, acetonitrile with trace water (<0.005%, or about 10^{-3} mol dm^{-3}).[10] The typical dye concentrations in UV spectroscopic studies of complexation are about 10^{-5} mol dm^{-3}. Therefore, comparable amounts of water and dye are present in the acetonitrile solution. It is known that excess water decomposes complexes of the crown-containing dyes with alkali and alkaline-earth cations (for example, see Ref. 3). In particular, the complexes of the dye **1** analogs ($R = (CH_2)_mSO_3^-$) with various alkali and alkaline-earth cations were titrated with water to demonstrate how water gradually decomposes the dye—cation complexes formed in acetonitrile.[10] A threshold water concentration in acetonitrile exists (about 10^{-2}—10^{-1} mol dm^{-3}), governed by the cation size and charge, at which the complex begins to decompose and hydrates begin to form. It seems not to be impossible that the intermediate step of this process involves formation of mixed aquacomplexes of the dye with the cations.

The Cambridge Structural Database[11] contains the structures of the free *N*-phenylaza-15-crown-5 ether (PhN15C5)[12] and its calcium triaquacomplex.[12] The aquacomplex incorporates three water molecules in the first coordination sphere of the cation coordinated in a half-sandwich manner (the cation and the water molecules are on the same side of the RMS plane of the macrocycle), whereas two ClO_4^- counterions are in the second coordination sphere. Therefore, at least three water molecules can enter the first coordination sphere of calcium in the cavity of PhN15C5 without destroying the complex.

Because solvation can have a substantial effect on the relative equilibrium of the two forms of the dye **1** complex, in this work we studied the ground-state recoordination of the cation in the cavity of the azacrown-containing styryl dye taking into account the inner-sphere solvation of the cation. Using model compounds and a real azacrown-containing dye, we studied the effect of the inner-sphere solvation of the cation with water and acetonitrile on the relative stability of different conformers of $[ArN15C5 \cdot Ca \cdot L_n]^{2+}$ complexes ($L = H_2O$, MeCN; $n = 1$—4). The results of our calculations were compared with the structure of *N*-phenylaza-15-crown-5 ether calcium triaquacomplex.[12]

We chose water as a main model of a solvating solvent. The water molecule is smaller than the acetonitrile molecule, which makes calculations much easier. We analyzed what changes take place on going from water to acetonitrile, because acetonitrile is the main solvent for these complexes and specific solvation of the cation with acetonitrile is also possible.

Cation—solvent interaction plays a very important role in solvation of the complexes; therefore, we first considered the interaction of the solvent (water and acetonitrile) with the free cation within the supermolecule approach.

Calculation procedure

The interaction of the free cation with the solvent was studied for $[Ca \cdot L_n]^{2+}$ complexes ($L = H_2O$, MeCN; $n = 1$—12) by filling the coordination sphere of the cation with the solvent molecules. For each n, we considered the lowest-energy structures, namely, linear for $n = 2$, trigonal for $n = 3$, tetrahedral for $n = 4$, trigonal bipyramidal for $n = 5$, octahedral for $n = 6$, and distorted pentagonal bipyramidal for $n = 7$. We also considered the structures obtained by adding solvent molecules to the outer solvation sphere of the above structures.

Full geometry optimization of the $[Ca \cdot L_n]^{2+}$ complexes studied was performed by the DFT/PBE [13] method using an original triple-zeta quality basis set (PBE/3z) implemented in

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* The root-mean-square plane of the crown ether is the least-squares fitted plane for all the crown ether atoms.

the PRIRODA program package[14]. The orbital basis sets of contracted Gaussian-type functions of the size (5s1p)/[3s1p] for H, (11s6p2d)/[6s3p2d] for C, O, and N, and (17s13p)/[12s9p] for Ca were used in conjunction with the density-fitting basis sets of uncontracted Gaussian-type functions of the size (5s1p) for H, (10s3p3d1f) for C, O, and N, and (18s3p2d) for Ca. The optimized structures corresponded to the local energy minima, which was supported by the calculations of vibrational frequencies.

For the optimum geometries of the $[\mathrm{Ca} \cdot \mathrm{L}_n]^{2+}$ complexes (L = H_2O, MeCN; n = 1—6), we calculated the energies with the hybrid density functional B3LYP and 6-311G(d) basis set using the GAUSSIAN 98 [15] program package.

The formation energies of the $[\mathrm{Ca} \cdot \mathrm{L}_n]^{2+}$ complexes were calculated from the reaction

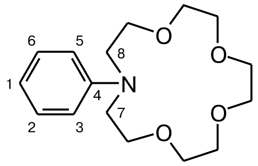
$$\mathrm{Ca}^{2+} + n\,\mathrm{L} = [\mathrm{Ca} \cdot \mathrm{L}_n]^{2+}.$$

Incremental solvation energies, or the energies of successive (stepwise) addition of the L molecules, were estimated from the reaction

$$[\mathrm{Ca} \cdot \mathrm{L}_{n-1}]^{2+} + \mathrm{L} = [\mathrm{Ca} \cdot \mathrm{L}_n]^{2+},$$

where $[\mathrm{Ca} \cdot \mathrm{L}_{n-1}]^{2+}$ is the complex with the structure most similar to $[\mathrm{Ca} \cdot \mathrm{L}_n]^{2+}$.

The structure of the solvation shells and the energy of solvation of arylazacrown ether complexes with water and acetonitrile were studied within the supermolecule approach. First, we studied the solvate complexes of the model compounds *N*-phenylaza-15-crown-5 ether **2** (13-phenyl-1,4,7,10-tetraoxa-13-azacyclopentadecane), *N*-(4-pyridyl)aza-15-crown-5 ether **3** (13-(4-pyridyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane), and *N*-(4-pyridyl)aza-15-crown-5 ether with the protonated pyridine nitrogen (4-(1,4,7,10-tetraoxa-13-azacyclopentadecyl)pyridinium) (**4**).



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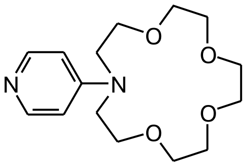

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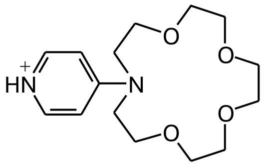

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The atoms in the structures studied are labeled as shown in structure **2**. The most important geometrical parameters of the studied complex conformers are the metal—nitrogen distance; the pyramidalization ψ of $\mathrm{N_{cr}}$ calculated as the difference between 360° and the sum of the bond angles C(7)—$\mathrm{N_{cr}}$—C(8), C(8)—$\mathrm{N_{cr}}$—C(4), and C(7)—$\mathrm{N_{cr}}$—C(4); and the angle τ between the $\mathrm{N_{cr}}$—Ca line and the normal to the C(7)C(8)C(4) plane. The angle τ characterizes the deflection of the lone electron pair (LP) at $\mathrm{N_{cr}}$ from the $\mathrm{N_{cr}}$—Ca line. We have shown in Ref. 1 that this deflection is rather large (>40°) in the structures without metal—nitrogen bond, and the $r(\mathrm{N_{cr}}\text{—Ca})$ distance is longer than 3 Å. The parameters ψ, τ, and $r(\mathrm{N_{cr}}\text{—Ca})$ correlate: longer distances usually correspond to greater deflections and smaller pyramidalization. The distance from the cation to the donor atom of the ligand (O in the water molecule or N in the acetonitrile molecule) is referred to as the cation—ligand (Ca—L) distance. The Ca—L distance to the inner-sphere ligands is usually no more than 3 Å.

We denote the solvation patterns as $c[a{:}b]d$, where a and b are the numbers of the inner-sphere water molecules on both sides of the crown ether, and c and d are the numbers of the outer-sphere water molecules on both sides of the crown ether. The experimental data (for example, see Refs. 12 and 16) and calculations[1] indicate that Ca^{2+} cation in the cavity of aza-15-crown-5 ether is located somewhat above the crown ether ring (so called half-sandwich structure). Therefore, in the models with the different number of solvent molecules below and above the macrocycle, we placed less water molecules (or no water at all) on the side of the cation covered with the macrocycle ($b + d$ = 0—2).

Different solvation patterns of the crown ether complexes were studied for L = H_2O. As mentioned above, the experimental structure of the calcium aquacomplex of crown ether **2** incorporates three water molecules. To examine whether inner coordination sphere of calcium in the macrocycle cavity can incorporate more additional ligands, we considered solvation of the complexes with four solvent molecules by positioning them in the inner coordination sphere of the cation on the one side or on the different sides of the macrocycle. We also studied the solvate complexes with fewer number of additional ligands to see how many L molecules are necessary to have any pronounced effect on the relative conformation energies of the complexes studied.

To study the solvation of the complexes with acetonitrile, we considered only [3:0]-type solvated structures of $[\mathbf{2} \cdot \mathrm{Ca}]^{2+}$, $[\mathbf{3} \cdot \mathrm{Ca}]^{2+}$, and $[\mathbf{4} \cdot \mathrm{Ca}]^{2+}$ complexes, because solvates of this type correspond to the completed coordination sphere of the cation.

The geometries of the model compounds **2**—**4**, azacrown-containing styryl dye **1a**, and their complexes with Ca^{2+} solvated by one to four water molecules or three acetonitrile molecules were fully optimized by the PBE/3z method using the PRIRODA program package[14]. We used the same Gaussian-type orbital and density-fitting basis sets as in the case of the $[\mathrm{Ca} \cdot \mathrm{L}_n]^{2+}$ complexes together with the (15s11p2d)/[10s6p2d] orbital basis set and the density-fitting basis set of uncontracted Gaussian-type functions of the size (14s3p3d1f1g) for S. We calculated vibrational frequencies for the optimized structures of the conformers of crown ether **2** and its calcium complexes and showed that the structures corresponded to the local energy minima.

The adiabatic formation energies (E_f) of the solvate complexes were calculated relative to the lowest-energy structure of the free crown ether and the optimized structure of $[\mathrm{Ca} \cdot \mathrm{L}_n]^{2+}$ from the reaction

$$[\mathrm{Ca} \cdot \mathrm{L}_n]^{2+} + \mathrm{ArN15C5} = [\mathrm{ArN15C5} \cdot \mathrm{Ca} \cdot \mathrm{L}_n]^{2+}.$$

Results and Discussion

Gas-phase formation of the calcium solvate complexes with water and acetonitrile and building of the coordination sphere

As can be easily expected, in all the calculated structures of the $[Ca \cdot L_n]^{2+}$ complexes, the donor atoms (O of the water molecules and N of the acetonitrile molecules) of the L molecule point toward the cation. The most stable structures were linear (n = 2), trigonal (n = 3), and tetrahedral (n = 4). For n = 5, the most stable structures were a tetragonal pyramid (L = H_2O) and a trigonal bipyramid (L = MeCN), and for n = 6, the most stable structure was octahedron. For n = 7, the structure of the coordination sphere differs for water and acetonitrile.

For L = H_2O, the inner coordination sphere of the cation is an octahedron, and the seventh water molecule is a bridge in the outer sphere (O atom forms two hydrogen bonds with H atoms of two adjacent water molecules in the inner sphere). The closest in energy structure, in which the seventh water molecule is in the inner coordination sphere, a pentagonal bipyramid, is 4.4 kcal mol^{-1} higher. The lowest-energy structures for n = 5—8 (L = H_2O) are shown in Fig. 1, *a*.

For L = MeCN, the inner coordination sphere is a distorted pentagonal bipyramid of seven acetonitrile molecules. The closest in energy structure, in which the seventh MeCN molecule is in the outer coordination sphere, an octahedron with one outer-sphere molecule, is 1.3 kcal mol^{-1} higher. One can see that reorganization of the inner coordination sphere in acetonitrile occurs easier. The lowest-energy structures for n = 5—8 (L = MeCN) are shown in Fig. 1, *b*. Hence, according to our calculations, the inner coordination sphere of Ca^{2+} in the $[Ca \cdot L_n]^{2+}$ complexes incorporates six water molecules arranged at the vertices of an octahedron or seven aceto-

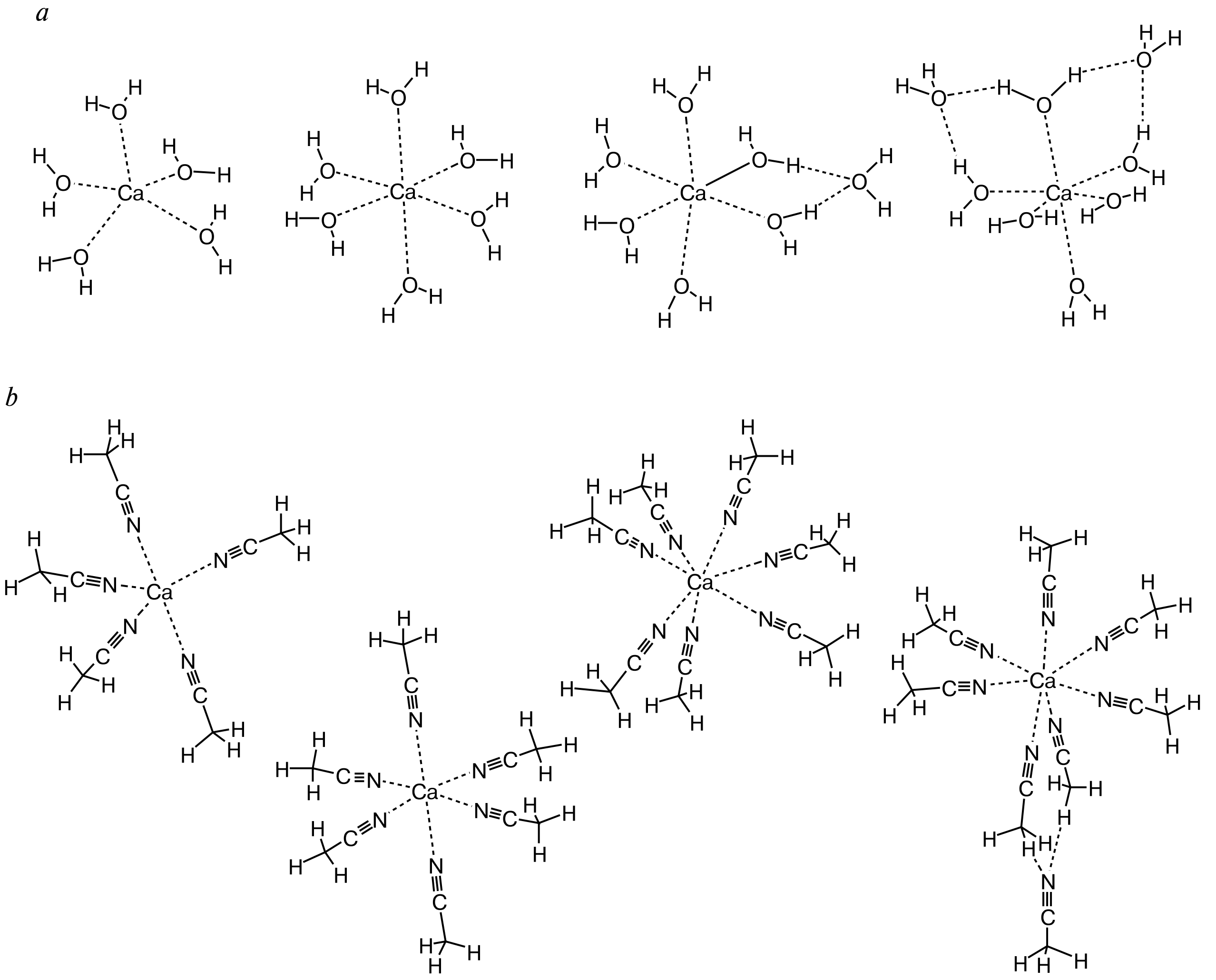

Fig. 1. Complexes $[Ca \cdot L_n]^{2+}$ for n = 5—8 and L = H_2O (*a*) and L = MeCN (*b*).

nitrile molecules arranged at the vertices of a slightly distorted pentagonal bipyramid.

Among the complexes with greater number of L molecules resulting from adding the solvent molecules to the outer sphere of the above structures, those with the bridging outer-sphere L molecules (that is, forming two hydrogen bonds with two adjacent inner-sphere L molecules) are most stable. The structures resulting from adding outer-sphere L molecules in terminal position (the outer-sphere L molecule forms a hydrogen bond with only one inner-sphere L molecule) lie higher in energy than the structures with bridging L molecules by 2 kcal mol^{-1} (L = H_2O) or 1 kcal mol^{-1} (L = MeCN). During completion of the inner sphere, the Ca—L distance in the acetonitrile complexes increases faster than in the complexes with water, which indicates that the solvation shell of calcium in acetonitrile is loose. Building up the second coordination sphere has only slight effect on the Ca—L distance for the inner-sphere molecules (Fig. 2, *a*).

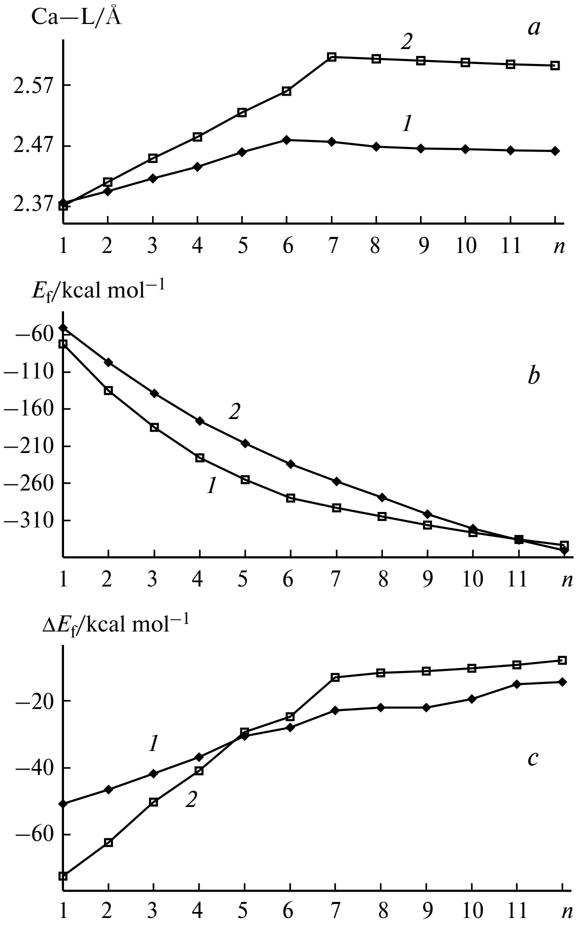

Fig. 2. Characteristics of $[Ca\cdot L_n]^{2+}$ complexes ((*1*) L = H_2O and (*2*) L = MeCN) as functions of *n*: Ca—L distance to the inner-sphere L molecules (*a*); formation energy E_f of the $[Ca\cdot L_n]^{2+}$ complex (*b*); and the energy ΔE_f of successive addition of the L molecules to the $[Ca\cdot L_{n-1}]^{2+}$ complex (*c*).

For small *n*, the overall heat of formation ($-E_f$) of the solvate complex $[Ca\cdot L_n]^{2+}$ and, therefore, the Ca—H_2O binding energy is lower than the Ca—MeCN binding energy (see Fig. 2, *b*; Table 1). This relationship of the binding energies correlates with stronger ion—dipole in-

Table 1. Binding energies for some $[Ca\cdot L_n]^{2+}$ complexes (L = H_2O or MeCN, *n* = 1—12) calculated by DFT

Complex	$-E_f$/kcal mol^{-1}	
	PBE/TZ	B3LYP/6-311G(d)
$[Ca\cdot(H_2O)]^{2+}$	50.73	65.32
$[Ca\cdot(H_2O)_2]^{2+}$	97.35	122.84
$[Ca\cdot(H_2O)_3]^{2+}$	139.09	174.86
$[Ca\cdot(H_2O)_4]^{2+}$	175.94	220.18
$[Ca\cdot(H_2O)_5]^{2+}$	206.57	256.68
$[Ca\cdot(H_2O)_6]^{2+}$	234.52	289.76
$[Ca\cdot(H_2O)_7]^{2+}$	257.52[a]	
	253.08[b]	
$[Ca\cdot(H_2O)_8]^{2+}$	279.52[c]	
	277.34[d]	
	276.01[e]	
	269.23[f]	
$[Ca\cdot(H_2O)_9]^{2+}$	301.64[g]	
$[Ca\cdot(H_2O)_{10}]^{2+}$	321.26	
$[Ca\cdot(H_2O)_{11}]^{2+}$	336.43	
$[Ca\cdot(H_2O)_{12}]^{2+}$	350.86	
$[Ca\cdot MeCN]^{2+}$	72.43	82.77
$[Ca\cdot(MeCN)_2]^{2+}$	134.69	149.04
$[Ca\cdot(MeCN)_3]^{2+}$	185.03	204.28
$[Ca\cdot(MeCN)_4]^{2+}$	225.99	248.53
$[Ca\cdot(MeCN)_5]^{2+}$	255.45	279.47
$[Ca\cdot(MeCN)_6]^{2+}$	280.24	305.55
$[Ca\cdot(MeCN)_7]^{2+}$	293.27[b]	
	291.96[a]	
	291.16[h]	
$[Ca\cdot(MeCN)_8]^{2+}$	304.97[e]	
	302.94[c]	
	301.73[i]	
$[Ca\cdot(MeCN)_9]^{2+}$	316.20[g]	
$[Ca\cdot(MeCN)_{10}]^{2+}$	326.64	
$[Ca\cdot(MeCN)_{11}]^{2+}$	336.03	
$[Ca\cdot(MeCN)_{12}]^{2+}$	343.93	

[a] Octahedron and one bridging outer-sphere L molecule.

[b] Distorted pentagonal bipyramid.

[c] Octahedron and two bridging outer-sphere L molecules.

[d] Octahedron, one bridging L molecule, and one terminal L molecule in the outer sphere.

[e] Distorted pentagonal bipyramid and one bridging outer-sphere L molecule.

[f] Square antiprism.

[g] For *n* = 9—12, only the data for the lowest-energy structures are given. These are octahedron and bridging outer-sphere molecules for water, and distorted pentagonal bipyramid and bridging outer-sphere L molecules for acetonitrile.

[h] Octahedron and one terminal L molecule in the outer sphere.

[i] Octahedron and two terminal L molecules in the outer sphere.

teraction in the case of acetonitrile, whose dipole moment is almost twice as large as the dipole moment of water. Addition of each next L molecule gives lower heat due to the ligand repulsion in the coordination sphere of the cation and weakening of the electrostatic attraction of dipole L molecules by the ion (see Fig. 2, *c*). At the early stage of building the inner coordination sphere of the cation (at small n), addition of MeCN molecule is more preferable. However, the energies of addition of the fifth L molecule become close, and for $n = 6$ addition of the next water molecule becomes more preferable. When n increases further and the inner sphere is almost complete ($n \geq 6$ for water and $n \geq 7$ for acetonitrile), the incremental solvation energy changes only slightly and approximates the energy of two hydrogen bonds of the L molecule with two inner-sphere L molecules. Water molecules in the second coordination sphere of the $[Ca \cdot (H_2O)_n]^{2+}$ complex stronger interact with the water molecules in the first coordination sphere than the acetonitrile molecules in the corresponding coordination spheres of the $[Ca \cdot (MeCN)_n]^{2+}$ complex. This stabilizes Ca^{2+} aquacomplexes at high n, when the second coordination sphere is almost complete. Therefore, at high n the overall solvation energies of Ca^{2+} with water and acetonitrile become equal (see Fig. 2, *b*).

Our theoretical finding that acetonitrile interacts with calcium cation in the gas-phase clusters stronger than water agrees with the theoretical and experimental data for related systems. For instance, MP2, RHF, and B3LYP calculations of the complexes of Li^+, Na^+, K^+, and Mg^{2+} with water and acetonitrile[7—9,17—20] also showed that for small n the cation—ligand interaction energy is higher for acetonitrile. These theoretical data agree well with the experimental gas-phase formation enthalpies of $M^+—H_2O$ [21] and $M^+—MeCN$ complexes (M = Li, Na, and K) up to $n = 6$.[22] These data indicate that the conclusion about the stronger interaction of acetonitrile with the cation is valid even for small cations.

Thus, the relative gas-phase stabilities of the crown ether complexes incorporating solvent molecules as additional ligands do not correlate with the relative stabilities of these complexes in solution. This means that the effect of solvent as a whole and the corresponding entropy factors cannot be neglected in estimating the relative stabilities of the crown ether complexes in different solvents. Nevertheless, when considering different complex structures in the same solvent, it will suffice to take into account only local cation—ligand interaction, *i.e.*, specific solvation in the supermolecule approach.

Effect of environment on the relative energies and geometries of conformers of the model crown ether complexes

The specific solvation of the model crown ether complexes with water was studied in detail. Various arrangements of up to four water molecules around the cation in the cavity of arylazacrown ether were considered. It was found that the inner solvation shell of the Ca^{2+} cation in the macrocycle cavity incorporates up to three water molecules, and the fourth one is displaced to the second coordination sphere. Therefore, calcium cation completes its coordination sphere with three water molecules. The optimized structures of the solvate complexes for $n = 4$ are shown in Fig. 3.

Adding L molecules to the cation environment results in decrease in the binding energy ($-E_f$) of the crown ether with the $[Ca \cdot L_n]^{2+}$ fragment in the $[ArN15C5 \cdot Ca \cdot L_n]^{2+}$ complexes from 190 to 95 kcal mol^{-1} in $[\mathbf{2} \cdot Ca \cdot (H_2O)_n]^{2+}$, from 180 to 85 kcal mol^{-1} in $[\mathbf{3} \cdot Ca \cdot (H_2O)_n]^{2+}$, and from 45 to –20 kcal mol^{-1} in $[\mathbf{4} \cdot Ca \cdot (H_2O)_n]^{2+}$. This weakening of the cation—macrocycle bond characterizes the effect of additional ligands L. All the complexes $[\mathbf{2} \cdot Ca \cdot (H_2O)_n]^{2+}$ and $[\mathbf{3} \cdot Ca \cdot (H_2O)_n]^{2+}$ are stable with respect to dissociation to the $[Ca \cdot (H_2O)_n]^{2+}$ fragment and the macrocycle. This dissociation is possible in the [1:1] structures of the $[\mathbf{4} \cdot Ca \cdot (H_2O)_2]^{2+}$ and in all the structures of the $[\mathbf{4} \cdot Ca \cdot (H_2O)_3]^{2+}$, $[\mathbf{4} \cdot Ca \cdot (H_2O)_4]^{2+}$, and $[\mathbf{4} \cdot Ca \cdot (MeCN)_3]^{2+}$ complexes, which have positive formation (negative binding) energies. Obviously, electrostatic repulsion between the cation and the positively charged *N*-substituent plays an important role in these complexes.

Three water molecules can be arranged in the coordination sphere of the cation in the azacrown ether cavity in a [3:0] or [2:1] fashion. Adding fourth water molecule results in 1[3:0]0, 0[3:0]1, 1[2:1]0, and 0[2:1]1 structures. The fourth water molecule can form bridging hydrogen bonds with two inner-sphere water molecules, terminal H-bonds with one inner-sphere water molecule, interact with the positive charge localized on the *N*-substituent, or build C—H...O contacts with the H atoms of the crown ether methylene groups through electrostatic interactions. Thus, the 1[3:0]0 structures are half-sandwich, the cation has the macrocycle on the one side and three water molecules on the other side, and the fourth H_2O molecule forms two bridging hydrogen bonds with two water molecules in the inner sphere. In the 0[3:0]1 structures, the fourth water molecule on the other side of the macrocycle forms C—H...O contacts the H atoms of the crown ether methylene groups. Addition of the fourth water molecule to the second solvation shell with formation of hydrogen bonds (1[3:0]0 and 1[2:1]0 structures) is more favorable than its addition on the other side of the macrocycle, where it cannot easily access the cation and can hardly form hydrogen bonds.

The effect of the solvation pattern (positioning of additional ligands on both sides or on the one side of the crown ether) on the stability of the crown ether complexes was studied.[23,24] For the cations whose size is greater or equal to the crown ether cavity (which is the

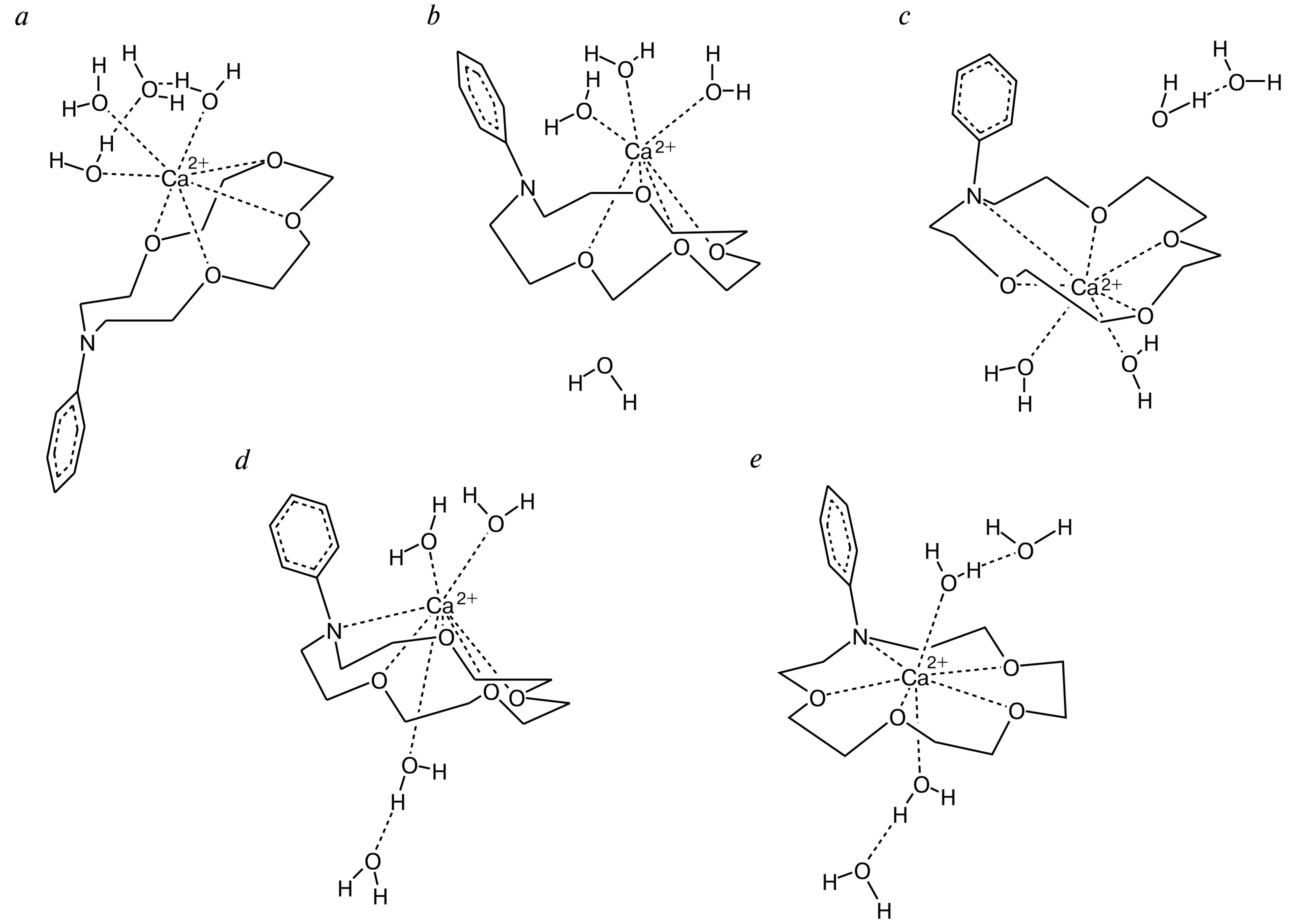

Fig. 3. Selected structures of the studied Ca^{2+} aquacomplexes with various location of four water molecules: (*a*) 1[3:0]0, (*b*) 0[3:0]1, (*c*) 0[2:0]2, (*d*) 0[2:1]1, and (*e*) 1[1:1]1.

case for Ca^{2+} and aza-15-crown-5 ether), the symmetric arrangement of the additional ligands is less preferable, because this environment forces the cation to stay at the center of the narrow cavity, which results in substantial macrocycle strain. In the asymmetric environment, the cation farther protrudes from the RMS plane of the crown ether than in the unhydrated complex, which enables donor atoms to arrange more loosely in the coordination sphere of the cation. On the contrary, in the symmetric environment ([2:1] or [1:1]), the cation lies virtually in the RMS plane, and this location increases the Pauli repulsion between the ML_n fragment and the macrocycle. In addition, *N*-arylaza-15-crown-5 ethers are asymmetric by themselves owing to the bulky *N*-substituent. Therefore, asymmetric environment of a half-sandwich structure (such as [*n*:0]) should be more preferable for these complexes.

Indeed, we found (Table 2) that at the same number of water molecules in the complex solvation shell, the structures with a more symmetric ligand arrangement have 10—20 kcal mol^{-1} higher energies than the complexes with the asymmetric ligand arrangement. This leads us to the assumption that the inner solvation shell of the calcium cation in the cavity of arylaza-15-crown-5 ether consists of three molecules of the donor solvent located on the same side of the macrocycle as the cation and completing the first coordination sphere of the cation in the half-sandwich structure (solvation pattern [3:0]). Here, the solvent molecule cannot approach the cation from the crown ether direction, and the second coordination sphere is built through hydrogen bonding with the inner-sphere solvent molecules located near the cation.

The unsolvated $[ArN15C5 \cdot Ca]^{2+}$ complex can adopt two axial (**Ax1** and **Ax2**) and two equatorial (**Eq1** and **Eq2**) conformations[1] differing in mutual arrangement of the aromatic ring and metal cation (on the one side or on the different sides of the macrocycle). $[\mathbf{2} \cdot Ca]^{2+}$ and $[\mathbf{3} \cdot Ca]^{2+}$ can adopt only the conformations **Ax1**, **Ax2,** and **Eq1**, whereas $[\mathbf{4} \cdot Ca]^{2+}$ can adopt all the four conformations. The energy of the **Eq1** conformation of $[\mathbf{2} \cdot Ca]^{2+}$ and $[\mathbf{3} \cdot Ca]^{2+}$ is ~30 kcal mol^{-1} higher than the energies of the **Ax1** and **Ax2** conformations, which makes it inaccessible in the ground state. The energies of the four conformers of $[\mathbf{4} \cdot Ca]^{2+}$ are close to one another.

Table 2. Relative energies and some geometric parameters of the conformers of $[\mathrm{ArN15C5\cdot Ca\cdot (H_2O)}_n]^{2+}$ (n = 0, 3, and 4)

Complex	Solvation type (for n = 3 and 4)	Conformer	E_{rel} /kcal mol^{-1}	$r(\mathrm{N_{cr}}—\mathrm{Ca})$ /Å	τ	ψ
					deg	
$[\mathbf{2}\cdot\mathrm{Ca}]^{2+}$	—	**Ax1**	0.00^a	2.56^a	15.1	14.8
	—	**Ax1**	0.80^a	2.58^a	15.4	15.3
	—	**Ax2**	4.05	2.54	14.5	23.7
	—	**Eq1**	32.21	3.79	83.6	4.2
$[\mathbf{2}\cdot\mathrm{Ca}\cdot(\mathrm{H_2O})_3]^{2+}$	0[3:0]0	**Ax1**	0.00	2.73	2.4	24.7
	The same	**Ax2**	1.93	2.73	17.9	26.3
	»	**Eq1**	19.05	4.12	85.9	6.4
	»	**Eq2**	13.94	3.81	54.4	11.8
	»	**Eq3**	18.65	4.17	55.4	3.4
	0[2:0]1	**Ax1**	7.50	2.69	8.4	20.5
	The same	**Ax2**	8.52	2.65	17.4	25.0
	»	**Eq1**	30.37	4.04	88.1	5.4
	0[1:1]1	**Ax1**	7.92	2.58	6.3	22.6
$[\mathbf{2}\cdot\mathrm{Ca}\cdot(\mathrm{H_2O})_4]^{2+}$	1[3:0]0	**Ax1**	0.00	2.95	5.6	24.9
	The same	**Ax2**	2.13	2.74	17.6	26.0
	»	**Eq1**	16.02	4.17	85.6	7.0
	»	**Eq2**	12.46	3.86	54.6	11.0
	»	**Eq3**	16.16	4.22	55.1	3.8
	0[3:0]1	**Ax1**	9.31	2.81	5.8	25.9
	The same	**Ax2**	11.37	2.72	16.5	26.1
	»	**Eq1**	27.55	4.12	86.2	6.0
	»	**Eq3**	26.93	4.15	54.8	2.7
	0[2:1]1	**Ax1**	13.05^a	2.65^a	11.2	28.7
	The same	**Ax1**	10.90^a	2.63^a	7.1	22.8
	1[1:1]1	**Ax1**	9.79	2.58	8.1	22.3
	0[2:0]2	**Ax1**	11.58	2.66	3.1	22.9
	The same	**Ax2**	14.62	2.64	15.7	24.9
$[\mathbf{3}\cdot\mathrm{Ca}]^{2+}$	—	**Ax1**	0.00	2.62	16.5	13.9
	—	**Ax2**	3.60	2.52	14.7	24.1
	—	**Eq1**	28.31	3.82	79.5	1.3
$[\mathbf{3}\cdot\mathrm{Ca}\cdot(\mathrm{H_2O})_3]^{2+}$	0[3:0]0	**Ax1**	0.00	2.89	4.9	24.6
	The same	**Ax2**	2.05	2.74	17.7	26.3
	»	**Eq1**	15.70	4.14	84.2	2.8
	»	**Eq2**	10.83	3.87	54.6	9.7
	0[2:0]1	**Ax1**	6.55	2.73	9.6	18.4
	The same	**Ax2**	8.52	2.66	16.7	25.2
	»	**Eq1**	27.38	4.06	86.6	3.7
	»	**Eq2**	20.68	3.81	50.2	8.8
	0[1:1]1	**Ax1**	7.55	2.60	6.6	21.9
$[\mathbf{3}\cdot\mathrm{Ca}\cdot(\mathrm{H_2O})_4]^{2+}$	1[3:0]0	**Ax1**	0.00	3.05	7.3	15.5
	The same	**Ax2**	3.21	2.76	17.3	26.1
	»	**Eq1**	13.79	4.18	82.0	2.9
	»	**Eq2**	9.62	3.94	55.6	8.6
	0[3:0]1	**Ax1**	9.99^a	3.07^a	2.7	17.6
	The same	**Ax1**	9.89^a	2.89^a	5.3	24.1
	»	**Ax2**	12.39	2.74	16.5	26.3
	»	**Eq1**	25.24	4.13	83.5	2.2
	»	**Eq2**	20.38	3.91	52.4	6.9
	»	**Eq3**	24.64	4.16	55.6	1.2
	0[2:1]1	**Ax1**	13.94^a	2.66^a	7.9	25.2
	The same	**Ax1**	11.80^a	2.65^a	6.6	22.0

(*to be continued*)

Table 2 (*continued*)

Complex	Solvation type (for n = 3 and 4)	Conformer	E_{rel} /kcal mol^{-1}	$r(N_{cr}—Ca)$ /Å	τ	ψ
					deg	
	1[1:1]1	**Ax1**	11.02	2.60	9.6	21.9
	0[2:0]2	**Ax1**	11.68	2.82	12.5	13.6
	The same	**Ax2**	14.95	2.66	17.0	25.1
[**4**·Ca]$^{2+}$	—	**Ax1**	0.45	2.96	14.8	22.8
	—	**Ax2**	6.56	2.81	29.6	25.7
	—	**Eq1**	1.81	4.22	77.6	4.6
	—	**Eq2**	0.00	4.02	59.4	0.1
[**4**·Ca·$(H_2O)_3$]$^{2+}$	0[3:0]0	**Ax1**	4.09	4.27	31.2	6.6
	The same	**Eq1**	0.97	4.45	82.3	0.0
	»	**Eq2**	0.00	4.35	64.4	1.7
	0[2:0]1	**Ax1**	13.35	4.08	29.7	7.3
	The same	**Eq1**	13.02	4.21	57.8	0.1
	»	**Eq2**	10.80	4.33	66.6	1.5
	»	**Eq2**	1.09[b]	4.16[b]	60.9	3.4
	0[1:1]1	**Ax1**	17.57	3.13	23.2	15.4
[**4**·Ca·$(H_2O)_4$]$^{2+}$	1[3:0]0	**Ax1**	3.90	4.24	30.1	6.0
	The same	**Eq1**	0.00	4.47	80.9	0.1
	»	**Eq2**	0.47	4.41	66.9	0.8
	0[3:0]1	**Ax1**	14.60	4.24	30.0	6.3
	The same	**Eq1**	12.84[c]	4.41[c]	78.0	0.1
	»	**Eq1**	12.10[c]	4.61[c]	79.9	0.0
	»	**Eq1**	10.70[c]	4.44[c]	85.6	0.0
	»	**Eq2**	9.75	4.34	65.5	1.5
	»	**Eq2**	2.06[b]	4.30[b]	63.7	2.3
	0[2:1]1	**Eq2**	19.33	4.27	66.9	1.0
	1[1:1]1	**Ax1**	21.63	3.08	25.5	15.0
	0[2:0]2	**Ax1**	20.37	4.03	32.3	6.1
	The same	**Eq1**	20.28	4.25	53.2	0.2
	»	**Eq1**	−3.10[d]			
	»	**Eq2**	18.98	4.41	73.3	0.3

[a] Conformers with the different sign of rotation of the aromatic ring relative to the macrocycle.

[b] One H_2O molecule solvates pyridinium proton.

[c] Structures with the different location of the water molecule relative to the macrocycle links.

[d] Hydrolysis of the crown ether.

For asymmetric solvation, especially when the inner coordination sphere of the cation is complete (n = 3 and 4), the energies of the equatorial conformers of the hydrated complexes are substantially lower (see Table 2). Thus, the energies of the equatorial conformers **Eq2** of the 1[3:0]0 structures of [**2**·Ca·$(H_2O)_4$]$^{2+}$ and [**3**·Ca·$(H_2O)_4$]$^{2+}$ are as low as 12 and 9 kcal mol^{-1}, respectively (*cf.* ~30 kcal mol^{-1} in the unhydrated complexes). Note that the relative energies of the conformers in the $c[a{:}b]d$ structures are close to the relative energies in the $0[a{:}b]0$ structures; that is, the effect of water molecules in the second coordination sphere on the conformation energies is negligible.

The cation—water interaction weakens its bond with the macrocycle: the distance from the cation to the RMS plane of the crown ether increases, and the distances from the cation to the donor atoms of the crown ether become longer. In the [**4**·Ca·$(H_2O)_n$]$^{2+}$ complexes, the difference between the conformers described by the τ and ψ angles and $r(N_{cr}—Ca)$ distance substantially decreases as n increases. This distance becomes longer, the pyramidalization ψ of N_{cr} decreases, and the deflection τ of the lone electron pair at N_{cr} from the N_{cr}—Ca line increases. Here, there is no distinct grouping into axial and equatorial conformers. In the [**2**·Ca·$(H_2O)_n$]$^{2+}$ and [**3**·Ca·$(H_2O)_n$]$^{2+}$ complexes, the difference between the axial and equatorial conformers also decreases, but they still can be divided into the two groups. The asymmetric environment has a more pronounced effect on these geometric parameters of the conformers than the symmetric environment. Therefore, the presence of additional ligands, especially ones located asymmetrically, weakens metal—nitrogen bonds and facilitates macrocycle rearrangement from one conformation to another.

In addition, owing to C—H...O contacts, hydration stabilizes the conformers that were not observed in the unhydrated complexes (that is, no stationary points corresponding to these conformations were found on the potential energy surface of the complex). These are, for example, the **Eq3** conformers of $[\mathbf{2}\cdot\mathrm{Ca}\cdot(\mathrm{H_2O})_n]^{2+}$ (n = 3 and 4) and $[\mathbf{3}\cdot\mathrm{Ca}\cdot(\mathrm{H_2O})_n]^{2+}$ (n = 4). This conformer is formally axial, because the aromatic ring does not lie in the RMS plane of the crown ether. However, this is caused by the severe deformation of the macrocycle rather than by the lack of planarity of the crown ether nitrogen. Anyway, the angle τ between the LP at $\mathrm{N_{cr}}$ and $\mathrm{N_{cr}}$—Ca line equal to ~55° and the $r(\mathrm{N_{cr}}$—Ca) distance equal to 4.2 Å clearly indicate that the $\mathrm{N_{cr}}$—Ca bond in the **Eq3** conformer is broken (Table 2). This conformer has virtually the same energy as **Eq1** frequently occurring in our calculations; therefore, it cannot be omitted.

Another conformer, **Eq2**, which was not found among the calculated structures of the unhydrated $[\mathbf{2}\cdot\mathrm{Ca}]^{2+}$ and $[\mathbf{3}\cdot\mathrm{Ca}]^{2+}$ complexes, appears for the 0[3:0]0 structures of the $[\mathbf{2}\cdot\mathrm{Ca}\cdot(\mathrm{H_2O})_3]^{2+}$ and $[\mathbf{3}\cdot\mathrm{Ca}\cdot(\mathrm{H_2O})_3]^{2+}$ complexes and the 0[2:0]1 structure of the $[\mathbf{3}\cdot\mathrm{Ca}\cdot(\mathrm{H_2O})_3]^{2+}$ complex for n = 3. The energies of these structures are 4—6 kcal mol^{-1} lower than the energies of the corresponding **Eq1** and **Eq3** conformers (see Table 2). The existence of the **Eq2** conformer is obviously associated with the fact that the additional ligands in the inner coordination sphere of the cation weaken the $\mathrm{N_{cr}}$—Ca interaction in the **Ax2** conformer and cause corresponding macrocycle rearrangement to the **Eq2** conformer. Additionally, extra stabilization of this structure is achieved through C—H...O contacts.

Thus, the effect of solvent on the ground-state recoordination of $[\mathrm{ArN15C5}\cdot\mathrm{Ca}\cdot\mathrm{L}_n]^{2+}$ complexes is most pronounced for the 1[3:0]0 and 0[3:0]0 solvation patterns.

The calculation data for the calcium complexes with crown ethers **2—4** solvated with acetonitrile in a [3:0] manner qualitatively agree with the results obtained for the complexes solvated with water (Table 3). As in the case of $[\mathrm{Ca}\cdot\mathrm{L}_n]^{2+}$, the cation—acetonitrile interaction energy is higher than the cation—water interaction energy. The presence of the acetonitrile molecules in the inner coordination sphere of the cation substantially reduces the energies of the equatorial conformers even for the crown ethers without positive charge in the *N*-substituent. The energies of the equatorial conformers of $[\mathbf{2}\cdot\mathrm{Ca}\cdot(\mathrm{MeCN})_3]^{2+}$ and $[\mathbf{3}\cdot\mathrm{Ca}\cdot(\mathrm{MeCN})_3]^{2+}$ are lower than the energies of the similar conformers of $[\mathbf{2}\cdot\mathrm{Ca}\cdot\cdot(\mathrm{H_2O})_3]^{2+}$ and $[\mathbf{3}\cdot\mathrm{Ca}\cdot(\mathrm{H_2O})_3]^{2+}$ because of the stronger ion—dipole interaction of acetonitrile with the cation. The changes of the geometric parameters in the complexes solvated with acetonitrile were also similar to the corresponding changes in the complexes solvated with water. Note, however, that the possibilities for hydrogen bonding and formation of C—H...N contacts in the systems including acetonitrile are limited, because the absolute values of atomic charges in the acetonitrile molecule responsible for this sort of interaction are much smaller than the atomic charges in water. Therefore, further buildup of the acetonitrile shell around the complex will result in loose weakly bound structures and prevent us from obtaining reliable data on the structure of the solvation shell of the complex by DFT.

Thus, in addition to the overall weakening of the cation—macrocycle bond, solvation reduces the relative energies of the equatorial conformers of $[\mathrm{ArN15C5}\cdot\cdot\mathrm{Ca}\cdot\mathrm{L}_n]^{2+}$ complexes and facilitates the macrocycle rearrangement to the conformation with the broken metal—nitrogen bond. This effect is most pronounced for the 1[3:0]0 and 0[3:0]0 solvation patterns, which are preferable for the complexes under study.

Table 3. Relative energies and some geometric parameters of the [3:0]-type solvated conformers of $[\mathrm{ArN15C5}\cdot\mathrm{Ca}\cdot(\mathrm{MeCN})_3]^{2+}$

Complex	Conformer	E_{rel} /kcal mol^{-1}	$r(\mathrm{N_{cr}}$—Ca) /Å	Angle/deg	
				τ	ψ
$[\mathbf{2}\cdot\mathrm{Ca}\cdot(\mathrm{MeCN})_3]^{2+}$	**Ax1**	0.00	2.94	4.0	25.2
	Ax2	0.63	2.80	18.6	25.3
	Eq1	13.65	4.31	84.6	6.4
	Eq2	9.11	3.99	57.0	9.1
$[\mathbf{3}\cdot\mathrm{Ca}\cdot(\mathrm{MeCN})_3]^{2+}$	**Ax1**	0.00	3.06	2.3	20.5
	Ax2	3.40	2.82	18.2	25.4
	Eq1	13.08	4.32	85.3	2.8
	Eq2	8.65	4.03	57.0	7.3
$[\mathbf{4}\cdot\mathrm{Ca}\cdot(\mathrm{MeCN})_3]^{2+}$	**Ax1**	5.67	4.40	31.7	5.3
	Eq1	1.40	4.55	86.5	0.0
	Eq2	0.00	4.57	70.4	0.2

Hydrated complexes of the azacrown-containing styryl dye 1a

We optimized the geometries of the [*n*:0]-type solvated **Ax1**, **Ax2**, **Eq1**, and **Eq2** conformers of $[\mathbf{1a} \cdot \mathrm{Ca} \cdot (\mathrm{H_2O})_n]^{2+}$ complexes for n = 1—4 (Fig. 4). It follows from our calculations of the model complexes that this solvation pattern provides the lowest energies.

Full geometry optimization of the **1a** complex only slightly changed the bond lengths and bond angles of the chromophore moiety as compared to their experimental values.[25] The greatest deviation of the calculated geometric parameters of the free dye from the corresponding experimental values was observed for the C=C double bond (~2%). Within the chromophore moiety, the C—N_{cr} bond length in the axial conformers of the complex undergoes the most pronounced change in complexation (up to ~0.1 Å). Essentially, "enabling" N_{cr}—Ca interaction or "disabling" it with the use of additional ligands leads to a small alternation ("benzenoid" structure) or, respectively, equalization ("quinoid" structure) of the bond lengths in the chromophore moiety as compared to the free dye.

Unlike our calculations[1] without solvent, the conformers of solvated $[\mathbf{1a} \cdot \mathrm{Ca}]^{2+}$ complexes more closely resemble the conformers of solvated $[\mathbf{4} \cdot \mathrm{Ca}]^{2+}$ complexes. The relative energies of the equatorial conformers of $[\mathbf{1a} \cdot \mathrm{Ca} \cdot (\mathrm{H_2O})_n]^{2+}$ are rather low, up to 3 kcal mol^{-1} for n = 3 and 4 (Table 4). Nevertheless, the **Ax1** conformers have the lowest energy, and the **Eq1** conformers, as usual, have the highest energy. Therefore, both axial and equatorial [*n*:0]-type solvated conformers of $[\mathbf{1a} \cdot \mathrm{Ca}]^{2+}$ can coexist in solution. Unlike the formation energies of $[\mathbf{4} \cdot \mathrm{Ca} \cdot (\mathrm{H_2O})_n]^{2+}$ (n = 3 and 4), the formation energies of $[\mathbf{1a} \cdot \mathrm{Ca} \cdot (\mathrm{H_2O})_n]^{2+}$ are negative, −(10—13) kcal mol^{-1} for n = 4; that is, the $[\mathbf{1a} \cdot \mathrm{Ca} \cdot (\mathrm{H_2O})_n]^{2+}$ complexes are stable with respect to the dissociation into the crown-containing dye and $[\mathrm{Ca} \cdot (\mathrm{H_2O})_n]^{2+}$ fragment at least up to n = 4.

As the first water molecule appears in the coordination sphere of Ca^{2+}, the $[\mathbf{1a} \cdot \mathrm{Ca}]^{2+}$ complex becomes capable of adopting the **Eq2** conformation, which was not observed in the unhydrated complex. Each additional wa-

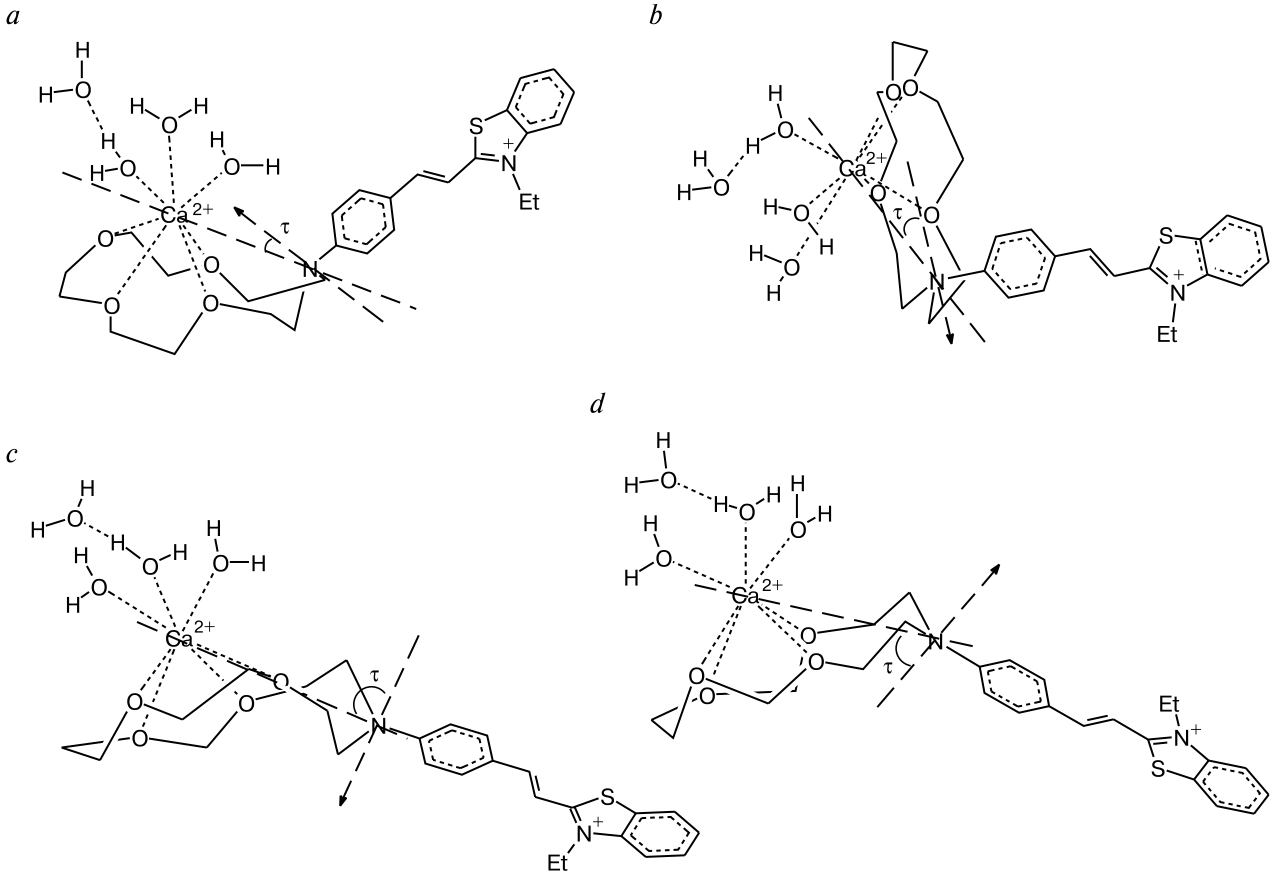

Fig. 4. 1[3:0]0 Structures of the **Ax1** (*a*) and **Ax2** (*b*) axial conformers and **Eq1** (*c*) and **Eq2** (*d*) equatorial conformers of $[\mathbf{1a} \cdot \mathrm{Ca} \cdot (\mathrm{H_2O})_4]^{2+}$ aquacomplexes of the styryl dye.

Table 4. Relative energies and some geometric parameters of the [*n*:0]-type solvated conformers of $[\mathbf{1a} \cdot Ca \cdot (H_2O)_n]^{2+}$ complexes for n = 0—4

n	Conformer	E_{rel} /kcal mol^{-1}	$r(N_{cr}$—Ca) /Å	τ	ψ
				deg	
0	**Ax1***	0.94	2.63	7.6	24.6
	Ax1*	0.00	2.62	5.4	25.7
	Ax2	2.14	2.60	21.5	25.2
	Eq1	18.10	4.00	80.3	0.9
1	**Ax1**	0.00	2.69	8.3	26.4
	Ax2	1.28	2.64	22.0	25.1
	Eq1	14.08	4.09	81.9	1.1
	Eq2	9.50	3.70	55.8	10.9
2	**Ax1**	0.00	2.79	7.8	27.0
	Ax2	1.01	2.74	22.1	25.6
	Eq1	10.11	4.21	81.4	1.3
	Eq2	6.32	3.95	60.0	7.4
3	**Ax1**	0.00	3.26	10.7	20.7
	Ax2	1.39	2.85	23.1	25.6
	Eq1	5.61	4.30	86.3	0.8
	Eq2	2.73	4.09	60.0	6.1
4	**Ax1**	0.00	3.29	11.7	20.5
	Ax2	1.77	2.87	22.9	25.5
	Eq1	2.96	4.34	84.9	1.2
	Eq2	0.53	4.16	61.1	5.0

* See note [a] to Table 2.

ter molecule reduces the relative energies of the equatorial conformers by 2—4 kcal mol^{-1} so that even the highest-lying **Eq1** conformer becomes accessible in the ground state for n = 3 and 4 (see Table 4).

Classification of the structures into axial and equatorial conformers (by $r(N_{cr}$—Ca) distance and τ and ψ angles) remains as a whole similarly to the unhydrated $[\mathbf{1a} \cdot Ca]^{2+}$ complex (see Table 4). However, the distinction between the groups becomes less pronounced. Thus, the $r(N_{cr}$—Ca) distance in the **Ax1** conformer for n = 3 and 4 increases to ~3.3 Å, although the τ and ψ angles remain within the limits corresponding to the axial conformers. This implies that N_{cr}—Ca bond in these structures is appreciably weakened. On the other hand, pyramidalization of ψ in the **Eq2** conformer of $[\mathbf{1a} \cdot Ca \cdot (H_2O)]^{2+}$ (n = 1) is ~11°, which can indicate a weak residual metal—nitrogen interaction.

Therefore, the solvent in the inner coordination sphere of the cation in the arylazacrown ether complexes weakens metal—nitrogen interaction and reduces the relative energy of the equatorial conformers with broken N_{cr}—Ca bonds. Both axial and equatorial forms of $[\mathbf{1a} \cdot Ca \cdot L_n]^{2+}$ complexes (L is a solvent, an impurity, or a counterion) contribute to the electronic absorption spectra at the corresponding wavelengths. Probably, the equatorial conformers are responsible for the long-wavelength shoulder in the spectrum, whereas axial conformers give a short-wave absorption maximum.[2,3]

* * *

Our theoretical study of microsolvation of calcium complexes with model arylazacrown ethers and an azacrown-containing dye showed that the interaction of the cation in the cavity of the crown ether with the solvent plays the most important role in the ground-state recoordination of the complexes. This interaction reduces the relative energy of the conformers with broken metal—nitrogen bonds and, in some cases, can decompose the complex. In the solvate complexes, the inner coordination sphere of the cation in the cavity of an azacrown ether incorporates at most three additional ligands. An asymmetric environment of the cation is preferable in a half-sandwich structure, where a larger number of solvent molecules is located on the same side of the macrocycle as the cation. Three solvent molecules are sufficient to reduce the energy of the conformers with broken metal—nitrogen bonds so that the ground-state recoordination can occur.

This study was financially supported by the Russian Foundation for Basic Research (Project Nos 02-03-32420-a and 03-03-32178).

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Received January 13, 2005;
in revised form June 16, 2005