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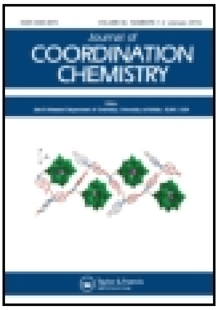

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Potentiometric and AM1d studies of the equilibria between silver(I) and diaza-15-crown and diaza-18-crown ethers with nitrogen in different positions in various solvents

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Complex formation and stability constants between typical and atypical diaza-15-crown and diaza-18-crown ethers with silver(I) were determined in methanol, acetonitrile, and propylene carbonate by the potentiometric method. In two of the diaza-crown ethers, AA-diaza-15 and AA-diaza-18-crown, two nitrogens in the macrocyclic ring replaced two consecutive oxygens instead of two opposite ones in the two other diaza-crown ethers. It was found that complexes of 1 : 1 and 1 : 2 metal-to-ligand stoichiometry were formed. The solvent composition and cavity size of crown ethers significantly influences the stability constants of complexes. AA-diaza-15 and AA-diaza-18-crown ethers were examined for comparison with diaza-15-crown and diaza-18-crown ethers. AA-diaza-crown ethers formed less stable 1 : 1 metal-to-ligand complexes with silver(I) than typical diaza-crown ethers, but their ability to form 1 : 2 metal-to-ligand complexes was stronger. The energetically most favorable structures of the 1 : 1 metal-to-ligand complexes were calculated and visualized by the AM1d method at the semiempirical level of theory.

Keywords: Azacrown ethers; Equilibrium; Silver(I)

1. Introduction

Crown ethers are efficient complexing agents for many metal ions. Numerous thermodynamic and kinetic data indicate that complexes of 1:1 metal-to-ligand stoichiometry are predominantly formed [1]. However, complexes of 1:1 metal-to-ligand stoichiometry for selected transition and alkali metal ions have also been reported [2–4]. The interactions between the macrocyclic ring and a metal ion in solution are usually analyzed in terms of the interactions with a positively charged ion that leads to the 1 : 1 inclusion complex. This is indicated by the strong effect of the macrocycle on stability constants in comparison with aliphatic amines [5]. The formation of such complexes does not necessarily imply that the metal ion is located precisely within the macrocycle cavity. For 1 : 2 type complexes, a sandwich structure in which the metal ion is located between two coronand molecules has been suggested as the most probable one [6, 7].

Interactions of aza-crown ethers with metal ions that possess a high affinity for nitrogen, such as silver(I), indicate that the number of nitrogens within the macrocyclic ring plays a

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major role in stabilization of AgL^+ complexes [7–9]. For monoaza-crown ethers, AgL^+, the Ag(I) is located within the macrocycle cavity which partially shields the metal ion from the solvent [5]. In AgL_2^+, Ag(I) forms sandwich-like structures with monoaza-crown ethers. In this case, the metal ion is completely shielded from the solvent [5]. The formation of 1 : 2 metal-to-ligand complex ions by Ag(I) and aza-crown ethers with two or more nitrogens in the macrocyclic ring is probably more complicated. Ag(I) forms linear 1 : 2 metal-to-ligand complex ions with aliphatic amines [10]. In diaza-crown ethers and AA-diaza-crown ethers, two nitrogens potentially participate in coordination with silver(I). The AA means that the two nitrogens in the macrocycle ring are separated by only one ethylene unit. Unfortunately, no crystallographic data are available for the structures of these complexes.

2. Experimental

2.1. *Materials and syntheses*

Silver(I) perchlorate (Fluka) and tetraethylammonium perchlorate (TEAP; Fluka) were purified as described previously [11]. 1,4,10-Trioxa-7,13-diazacyclopentadecane (**A$_2$15C5**, Kryptofix® 21, Merck) and 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**A$_2$18C6**, Kryptofix® 22, Merck) were used as purchased (figure 1). Propylene carbonate (PC, Merck), methanol (MeOH, Aldrich), and acetonitrile (AN, Aldrich) were of the highest purity. 2-(2-Aminoethylamino) ethanol (Aldrich) and 2-chloroethanol (Aldrich) were previously distilled. Silica gel 60 (<0.03 mm, Merck) and aluminum oxide 90 (Merck) were used for chromatography.

The syntheses of 1,4,7-trioxa-10,13-diazacyclopentadecane (AA15C5) and 1,4,7,10-tetraoxa-13,16-diazacyclopentadecane (AA18C6) were performed by a modified version of intramolecular cyclization (figure 2) [12]. To a stirred suspension of 2-(2-aminoethylamino) ethanol (208 g, 0.2 M) was added 2-chloroethanol (16.1 g, 0.2 M) and powdered sodium carbonate (16.96 g, 0.16 M). The mixture was stirred at 135 °C for 25 h. After this had been cooled to room temperature, 300 mL of MeOH was added and the mixture was filtered; the resulting solution was evaporated to yield a crude product (yellow oil), which was recrystallized twice from THF over charcoal to give **3** 12.05 g (40.7%) TLC (SiO_2) CH_2Cl_2: MeOH 2,5 : 2,5 Rf = 0.4. ^{1}H NMR: (δ, $CDCl_3$) 400 MHz: 2.78–2.84 (m; 8H), 3.66 (t; 4H). To obtain AA15C5 (4.29 g, 0.028 M), **3** (2-[2]ethanol) was dissolved in a solution of (4.40 g, 0.11 M) potassium metal in 224 mL t-butyl alcohol. To this stirred

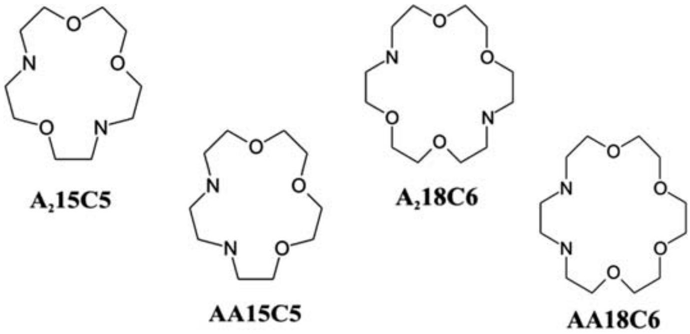


Figure 1. The structures of the diaza-crown ethers studied.

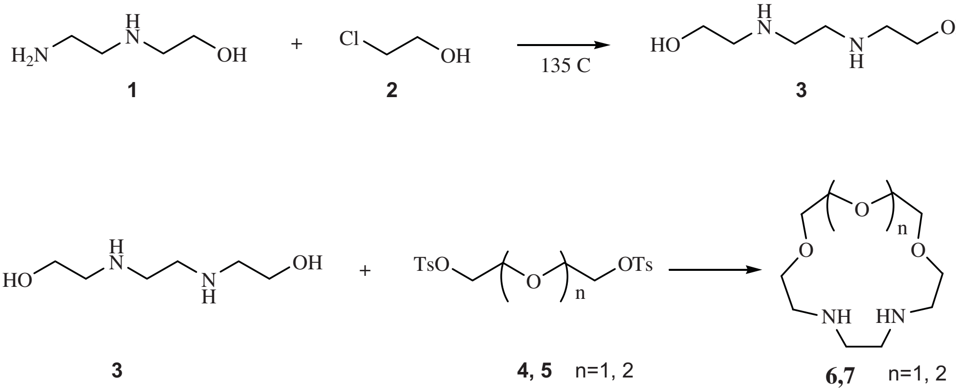


Figure 2. Synthetic scheme of AA15C5 and AA18C6.

solution, diethylene glycol bis(p-toluenesulphonate) (11.60 g, 0.028 M) in freshly distilled dioxane (84 mL) was added dropwise at 40 °C during 4 h, after which the reaction was continued for 20 h. The resulting white reaction mixture was filtered. The precipitate was rinsed with dichloromethane (3 × 100 mL) and the solvent then evaporated from the pooled rinsings. To the residue, 60 mL of water was added to the residue and the solution was extracted twice with hexane to remove by-products. It was then extracted with dichloromethane (5 × 100 mL). The dichloromethane extracts were combined and the solvent evaporated. The product was dissolved in water purified on an ion-exchange column (Dowex 50X2–100). The eluant was evaporated under reduced pressure and dried under vacuum. The crude product **6** was finally distilled in a Kugelrohr apparatus at 200 °C (0.01 hPa) to yield 3.601 g (57%) as a clear oil. TLC (SiO_2) CH_2Cl_2: MeOH 2,5 : 2,5 Rf = 0.2. ^{1}H NMR: (δ, $CDCl_3$) 500 MHz: 3.04 (s; 2H), 3.48–3.58 (m; 8H), 3.58–3.75 (m; 12H). **7** AA18C6 was obtained in a similar manner from **5** with a yield of 41% TLC (SiO_2) CH_2Cl_2: MeOH 2,5 : 2,5 Rf = 0.2. ^{1}H NMR: (δ, $CDCl_3$) 500 MHz: 2.81 (s; 2H), 3.28–3.44 (m; 8H), 3.48–3.65 (m; 16H).

2.2. *Potentiometric measurements*

Potentiometric titrations were performed at 25 °C using an OP-205 Radelkis pH-meter. Silver(I) solutions in PC, MeOH, and AN were prepared from the perchlorate salt; the concentration range was $6\text{–}9 \times 10^{-4}\,\mathrm{M\,dm^{-3}}$. Ligand concentrations were in the range $3.5\text{-}9.5 \times 10^{-3}$ mol $\mathrm{dm^{-3}}$. Measurements were performed using a 0.5 mL Hamilton syringe equipped with a Gage 30 Teflon tube; the half-cells were connected by a salt bridge filled with $0.1\,\mathrm{M\,dm^{-3}}$ TEAP dissolved in PC, MeOH, or AN. The silver concentration during the titrations was determined using silver-wire electrodes dipped in the solution. The equilibrium constants and the simulations were calculated using the STOICHIO program [13–15] based on the nonlinear least-squares Gauss–Newton–Marquardt algorithm [16].

2.3. *Semiempirical calculations*

AM1d calculations were performed using the Win Mopac 2007 program at the semiempirical level (Cache Work System Pro Version 7.5.085, Fujitsu) [17,18]. The conformers of the diaza-crown ethers and their 1 : 1 metal-to-ligand complexes were searched for simultaneously by molecular dynamics and CONFLEX® experiments. The CONFLEX® program systematically and exhaustively generates low-energy conformers of a molecule of any shape [19]. The energetically most favorable structures of the 1 : 1 metal-to-ligand complexes were found in the collection of several thousand structures optimized by the AM1d semiempirical method [20–25].

3. Results and discussion

3.1. *Potentiometric studies of formation of diaza-crown ether complexes*

On the potentiometric titration curves, there is a single potential jump for AA15C5 and AA18C6 in PC, MeOH, and AN. The largest changes in potential were observed in PC (−650 mV for AA15C5; −600 mV for AA18C6), medium in MeOH (−250 mV; −300 mV), and the lowest in AN (−150 mV; −200 mV). Therefore, the data for PC (figure 3) were used to carry out a graphical analysis of the potential of the ligands [26,27]. With the large number of experimental data, an advanced graphical and statistical analysis can be performed [26,27]. The fitting of theoretical points to experimental points does not lead to a simple equilibrium of 1 : 1 stoichiometry. It suggests that, apart from the equilibrium resulting in formation of AgL^+, other equilibria are also likely. Attempts to fit the curves to data points have shown that variations in the potential as a function of the titrant added are best represented by two equilibria:

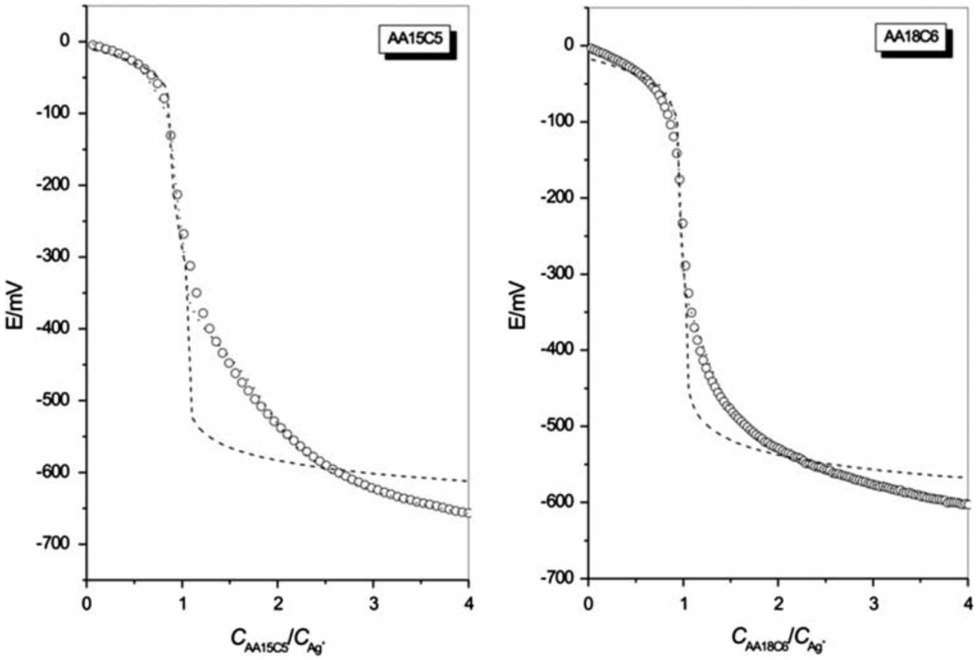


Figure 3. Graphical fitting for models 1° (-) and 2° (…) and experimental points (o) of silver(I) (6.00×10^{-4} M dm^{-3}) from potentiometric titration with AA15C5 (4.00×10^{-3} M dm^{-3}; left) and AA18C6 (4.00×10^{-3} M dm^{-3}; right) in PC at 25 °C.

$$\mathrm{Ag^+ + L = AgL^+} \qquad K_1 \tag{1}$$

$$\mathrm{AgL^+ + L = AgL_2^+} \qquad K_1 \tag{2}$$

For $A_2$15C5 and $A_2$18C6, there was a single potential in PC, MeOH, and AN. The largest changes in potential were observed in PC (−600 mV for A215C5; −750 mV for $A_2$18C6), medium in MeOH (−300 mV; −400 mV), and the lowest in AN (−200 mV; −300 mV). Therefore, the data for PC (figure 4) were used to illustrate the graphical analysis of the potentials of the ligands [26,27]. From a graphical analysis of the potential changes, one may infer that the two equilibria (1) and (2) best explain the changes in the potential, with the exception of $A_2$18C6 in PC. We have no evidence for AgL_2^+ forming in PC for $A_2$18C6. In this work, we have presented experimental data for $A_2$15C5 and $A_2$18C6, especially that there are no separate data for equilibrium (2) for $A_2$15C5 and $A_2$18C6 in MeOH and AN in the literature (with the exception of $A_2$15C5 [28]).

Additionally, in table 1, we compare the values of $\omega(x)$ and σ_E obtained from the experiment and calculated for each model. These values are lowest for model 2° which involves two equilibria leading to formation of AgL^+ and AgL_2^+. Since $\omega(x)$ and σ_E for model 2° are small, there is no need to further analyze the equilibria [26,27]. Model 2° is suitable for all the ligands and every solvent. The stability constants of all the ligands are presented in table 2 in the form of log K_1 and log K_2.

Both diaza and AA-diaza-crown ethers have two nitrogens in the macrocyclic ring. The structural differences in these macrocycles could lead to a different way of complexing the

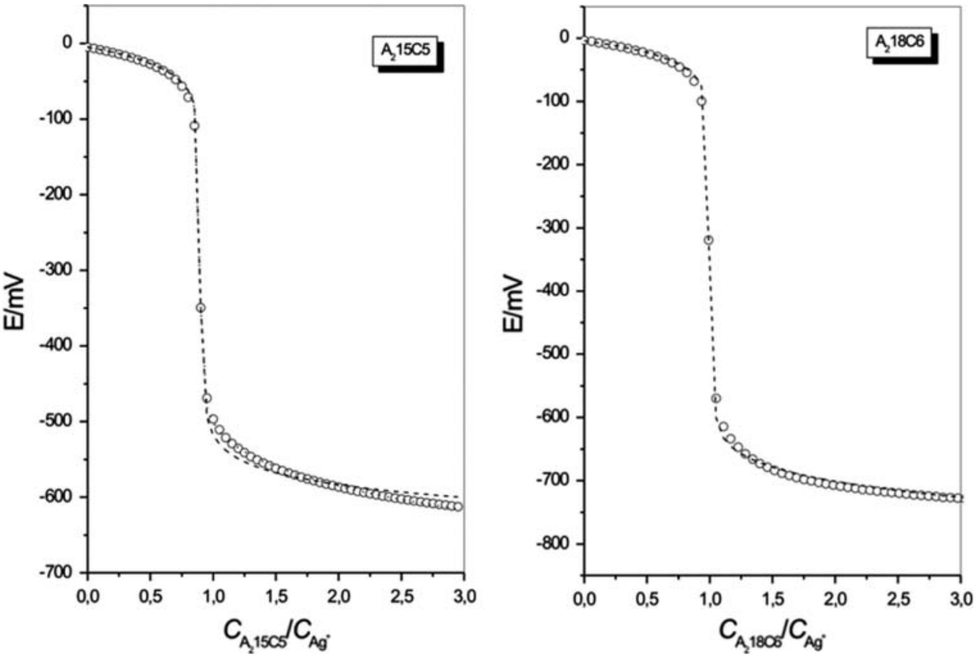


Figure 4. Graphical fitting for models 1° (-) and 2° (…) and experimental points (o) of silver(I) ($6.00 \times 10^{-4}\,\mathrm{M\,dm^{-3}}$) from potentiometric titration with $A_2$15C5 ($8.00 \times 10^{-3}\,\mathrm{M\,dm^{-3}}$; left) and $A_2$18C6 ($9.00 \times 10^{-3}\,\mathrm{M\,dm^{-3}}$; right) in PC at 25 °C.

Table 1. Comparison of statistical values for AA15C5, AA18C6, $A_2$15C5, and $A_2$18C6 with experimental points for models 1^o and 2^o; $\omega(x)$ – the sum of the squares of the differences between measured and calculated potentials and concentrations; σ_E – standard deviation of the potential.

Model of eq.	Species	$\omega(x)$ PC	σ_E	$\omega(x)$ MeOH	σ_E	$\omega(x)$ AN	σ_E
				AA15C5			
1^o	AgL^+	7.41e + 04	0.057	1.02e + 04	0.010	1.62e + 04	0.014
2^o	AgL^+, AgL_2^+	5.26e + 03	0.011	1.73e + 02	0.002	6.21e + 02	0.003
				AA18C6			
1^o	AgL^+	3.69e + 04	0.038	4.73e + 03	0.008	2.03e + 03	0.005
2^o	AgL^+, AgL_2^+	7.75e + 03	0.013	3.11e + 02	0.005	7.63e + 02	0.004
				$A_2$15C5			
1^o	AgL^+	3.32e + 04	0.029	2.80e + 02	0.003	5.87e + 02	0.003
2^o	AgL^+, AgL_2^+	9.36e + 03	0.015	1.71e + 02	0.002	3.43e + 02	0.002
				$A_2$18C6			
1^o	AgL^+	3.94e+03	0.009	1.26e+03	0.008	5.45e+02	0.004
2^o	AgL^+, AgL_2^+	–	–	2.62e+02	0.004	3.97e+02	0.003

metal ion in the macrocycle cavity (figure 1). The stability constants of formation of AgL^+ for diaza and AA-diaza-crown ethers (table 2) are larger than for monoaza-crown ethers [5]. This suggests that Ag(I) interacts with both nitrogens in the ring of these macrocycles. It is known from previous work [5] that Ag(I) fits well in the ring cavity of monoaza-15-crown and monoaza-18-crown ethers. The difference between the log K_1 and log K_2 values of typical diaza and AA-diaza-crown ethers shows that AgL^+ were predominantly formed

Table 2. Stability constants given in the form of log K_1 and log K_2 for AA15C5, AA18C6, $A_2$15C5, and $A_2$18C6 obtained from potentiometry in PC, MeOH, and AN at 25 °C.

Ligand	log K_1		log K_2
		PC	
AA15C5	11.58 ± 0.06		5.09 ± 0.11
AA18C6	12.27 ± 0.06		4.34 ± 0.10
$A_2$15C5	13.12 ± 0.05∗ [26] 13.15 ± 0.05 [8,9,26]		3.17 ± 0.09 [26] 3.11 ± 0.10 [7] 3.51 ± 0.07 [8]
$A_2$18C6	15.41 ± 0.06 14.81 ± 0.03 [7] 15.57 ± 0.01 [8]		–
		MeOH	
AA15C5	6.26 ± 0.08		4.82 ± 0.13
AA18C6	7.42 ± 0.08		4.16 ± 0.14
$A_2$15C5	7.52 ± 0.05** [28] 7.49 ± 0.01 [7,9]		2.38 ± 0.08** [28]
$A_2$18C6	9.88 ± 0.06 9.74 ± 0.08 [7]		2.60 ± 0.10
		AN	
AA15C5	5.33 ± 0.07		4.14 ± 0.11
AA18C6	5.72 ± 0.06		3.63 ± 0.11
$A_2$15C5	6.72 ± 0.04** [28] 6.43 ± 0.01 [7,29]		2.33 ± 0.09** [28]
$A_2$18C6	7.96 ± 0.05 7.75 ± 0.02 [7]		1.82 ± 0.11

*Misprint in 26 **also presented by us in 28.

and that both types of ligands are efficient complexing agents for silver(I). The difference in log K_1 between $A_2$18C6 and $A_2$15C5 is greater (2.29 in PC, 2.36 in MeOH, 1.24 in AN) than between AA18C6 and AA15C5 (0.69 in PC, 1.16 in MeOH, 0.39 in AN). This implies that the difference in the size of the macrocyclic ring influences the formation of AgL^+ more strongly in diaza-crown ethers than in AA-diaza-crown ethers. On the other hand, the two nitrogens replacing two adjacent oxygens in the macrocyclic ring weaken this influence. The data suggest that the two nitrogens, located opposite to one another in $A_2$18C6, cooperate with each other much more strongly than in $A_2$15C5.

The difference in log K_1 between $A_2$15C5 and AA15C5 is 1.54 in PC, 1.26 in MeOH, and 1.39 in AN. For $A_2$18C6 and AA18C6, the difference in log K_1 is 3.14 in PC, 2.46 in MeOH, and 2.24 in AN. The difference in log K_1 between diaza and AA-diaza-crown ethers is much greater for $A_2$18C6 which binds silver(I) more strongly. Two nitrogens replacing two adjacent oxygens in the macrocyclic ring weaken formation of AgL^+ in diaza-crown ethers.

3.2. *Formation of AgL_2^+ complexes*

Both diaza and AA-diaza-crown ethers form AgL_2^+ complex ions (table 1). Ag(I) ions form linear AgL_2^+ complexes with aliphatic amines [5,10]. Previous work [5] indicates that Ag(I) ions form sandwich-type complexes with monoaza-crown ethers with a 1 : 2 metal-to-ligand stoichiometry. The formation of linear or sandwich-type complexes has characteristic K_1/K_2 values. If the value is <4 (as opposed to crown ethers), then it is characteristic of a statistically purely linear coordination [5]. The K_1/K_2 values for crown ethers investigated in PC, MeOH, and AN are shown in table 3. These values are >4 in all cases, which confirms that the AgL_2^+ complex ion has a sandwich-type structure in all the investigated ligands in different organic solvents.

The log K_2 values of AA-diaza-crown ethers are greater than those of diaza-crown ethers (table 2), suggesting that the mechanism of formation of AgL_2^+ between AA-diaza-crown ethers and Ag(I) differs from that of typical diaza-crown ethers. In the case of AA-diaza-crown ethers, log K_2 changes from 5.09 for AA15C5 in PC to 3.63 for AA18C6 in AN. At the same time, the log K_1 values are lower than those of typical diaza-crown ethers. This observation suggests that the lower tendency of AA-diaza-crown ethers to form AgL^+ inclusion-type complex ions is suppressed by their greater tendency to form AgL_2^+. The differences of the log K_2 values are generally larger in MeOH and AN which solvate Ag(I) ions more strongly than PC. It is known from previous work on monoaza-crown ethers [5] that Ag(I) in AgL^+ is best shielded from solvent by the monoaza-18-crown. In AgL_2^+ sandwich-type complex ion, Ag(I) is well shielded from solvent by all

Table 3. Values of K_1/K_2 for silver(I) complexes with diaza and AA-diaza-crown ethers in different organic solvents.

Ligand	K_1/K_2		
	PC	MeOH	AN
AA15C5	3.09×10^6	2.75×10^1	1.55×10^1
AA18C6	8.51×10^7	1.82×10^3	1.23×10^2
$A_2$15C5	8.91×10^9	1.38×10^5	2.45×10^4
$A_2$18C6	–	1.90×10^7	1.38×10^6

monoaza-crown ethers, irrespective of the size of the macrocycle. This is due both to the high log K_1 value for monoaza-18-crown and to the log β_2 values (from log K_1 + log K_2) of all monoaza-crown ethers [5]. Similarly, we obtained high log K_1 values for the investigated ligands (table 2) and likewise, high log K_1 + log K_2 values. The log K_1 of 15.41 for $A_2$18C6 is the highest value in PC; we have no evidence that AgL_2^+ complex ion is formed in PC with this ligand. We suggest that the differences in log K_1 values and log K_2 values are due to the different extents to which the Ag(I) is shielded in AgL^+ and AgL_2^+ and are solvent-dependent.

3.3. *Discussion of structure of complexes*

Application of the Born–Haber cycle to the complex formation reactions equations (1) and (2) in two solvents (PC; S = MeOH, AN) leads to the following relationships between stability constants and free energies of transfer of the species involved in the equilibrium [30,31]:

$$-2.303RT\ \log[K_1(\mathrm{S})/K_1(\mathrm{PC})] = \Delta G_{tr}(\mathrm{AgL}^+) - \Delta G_{tr}(\mathrm{L}^+) - \Delta G_{tr}(\mathrm{Ag}^+) \tag{3}$$

$$-2.303RT\ \log[\beta_2(\mathrm{S})/\beta_2(\mathrm{PC})] = \Delta G_{tr}(\mathrm{AgL}_2^+) - 2\Delta G_{tr}(\mathrm{L}^+) - \Delta G_{tr}(\mathrm{Ag}^+) \tag{4}$$

Substitution of the free energy of transfer of Ag^+ into equations (3) and (4) gives the difference in the free energy of transfer of complexes and the corresponding ligands; the values obtained are presented in table 4. The free energy of transfer ΔG_{tr} of Ag(I) from PC to the other organic solvents presented changes in the order AN ($-42.0\,\mathrm{kJ\,M^{-1}}$) < MeOH ($-12.2\,\mathrm{kJ\,M^{-1}}$) [32]. The more the value of $\Delta G_{tr}(AgL^+)-\Delta G_{tr}(L)$ from equation (3) and of $\Delta G_{tr}(AgL_2^+)-2\Delta G_{tr}(L)$ from equation (4) approaches zero, the weaker the access of solvent to Ag(I) ion in AgL^+ or AgL_2^+ [5]. Literature data show that for the AgL^+ inclusion type complex with cryptates Ag(I) is well shielded from the solvent [7, 30, 31] like the sandwich-type AgL_2^+ with monoaza-crown ethers [5]. For the AgL^+ inclusion type complex with monoaza-crown ethers Ag(I) is shielded more strongly by the monoaza-18-crown ether than by the monoaza-15-crown ether [5].

For typical diaaza and AA-diaza-crown ethers, the values of $\Delta G_{tr}(AgL^+)-\Delta G_{tr}(L)$ obtained in AN as compared to PC are low and for $A_2$18C6 close to zero. This suggests that Ag(I) ions are not completely shielded from interaction with solvent in AgL^+, except for the complex with $A_2$18C6 in which Ag(I) ions are well shielded. Therefore, we have

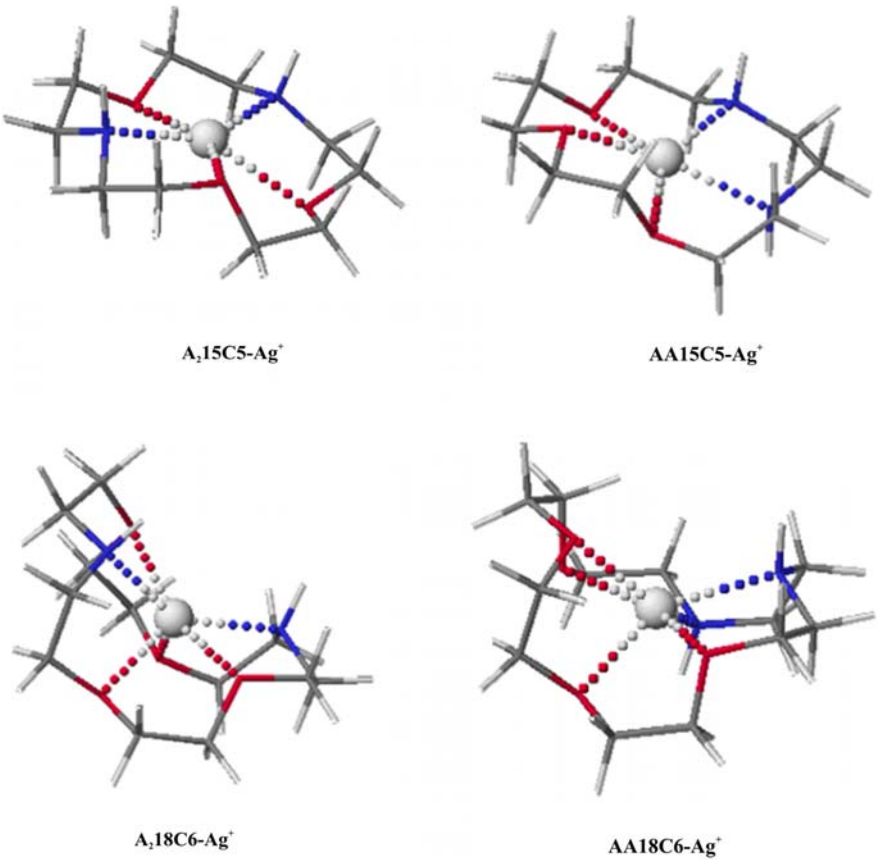
Table 4. Differences in the free energies of Ag^+ transfer from PC to MeOH and AN between Ag^+ complexes and ligand and log β_2 values (from equation. log K_1 + log K_2), with the exception of $A_2$18C6 in PC, for comparison at 25 °C.

Ligand	$\Delta G_{tr}(AgL^+)-\Delta G_{tr}(L)$		$\Delta G_{tr}(AgL_2^+)-2\Delta G\mathrm{tr}(L)$		log β_2		
	AN	MeOH	AN		AN	MeOH	AN
AA15C5	−6.4	18.2	−0.9	19.7	16.67	11.08	9.47
AA18C6	−4.6	15.5	−0.6	16.5	16.61	11.58	9.35
$A_2$15C5	−5.5	19.7	−0.7	24.3	16.29	9.90	9.05
$A_2$18C6	0.5	19.3	–	–	–	12.48	9.78

Table 5. Changes in enthalpy of formation (kcal/M) of diaza-crown ethers and their complexes with Ag$^+$ cations calculated by the AM1d method (WinMopac 2007).

Species	H_f (kcal M^{-1})	ΔH_f^*
AA15C5	−146.884	
AA15C5, Ag$^+$ uncomplexed	95.830	
AA15C5, Ag$^+$ complexed	11.822	−84.008
AA18C6	−194.561	
AA18C6, Ag$^+$ uncomplexed	48.153	
AA18C6, Ag$^+$ complexed	−40.515	−88.668
A215C5	−147.379	
A215C5, Ag$^+$ uncomplexed	95.335	
A215C5, Ag$^+$ complexed	10.589	−84.746
A218C6	−194.523	
A218C6, Ag$^+$ uncomplexed	48.191	
A218C6, Ag$^+$ complexed	−41.473	−89.664

$^*\Delta H_f = H_f$ complexed$-H_f$ uncomplexed.



$A_2$15C5-Ag$^+$

AA15C5-Ag$^+$

$A_2$18C6-Ag$^+$

AA18C6-Ag$^+$

Figure 5. The most favorable structures of the 1 : 1 metal-to-ligand complexes with Ag$^+$ cations and diaza-crown ethers.

no evidence that AgL_2^+ forms in A_218C6 in PC. The values of $\Delta G_{tr}(AgL^+)-\Delta G_{tr}(L)$ are lower than those for monoaza crown ethers (−11.5 for monoaza-15-crown; −3.5 for monoaza-18-crown 5). This means that diaza and AA-diaza-crown ethers shield silver(I) in AgL^+ better than monoaza crown ethers. For AgL_2^+ $\Delta G_{tr}(AgL_2^+)-2\Delta G_{tr}(L)$ is close to zero. This means that Ag(I) ions are well shielded from interactions with solvent; this also suggests a sandwich-like structure of AgL_2^+ complex ions.

MeOH solutions are more complex. The values of $\Delta G_{tr}(AgL^+)-\Delta G_{tr}(L)$ and $\Delta G_{tr}(AgL_2^+)-2\Delta G_{tr}(L)$ are positive for all the ligands associated with ligand protonation or hydrogen bonding by MeOH. This could be a reason for the major decrease in the stability constants of AgL^+ and AgL_2^+.

3.4. *Theoretical models of AgL^+ complexes*

Changes of the enthalpies of formation (ΔH_f) of the most favorable AgL^+ complexes of diaza-crown ethers with Ag^+ and of uncomplexed molecules calculated by the AM1d method [17,18] are listed in table 5. The conformers were selected from molecular dynamics and CONFLEX® [19] experiments and are believed to be the global minimum energy conformers in the AM1d semiempirical method. In the AA15C5-Ag^+ and A_215C5-Ag^+ structures, the silver is located in the middle of the macrocyclic ring and is shielded from further planar interactions (figure 5). For AA18C6-Ag^+ and A_218C8-Ag^+ structures, it is located in the middle of the macrocyclic ring but this is twisted over the ion which is then shielded even better. Structures of AgL_2^+ were not considered because the CONFLEX®'s algorithm does not rotate one ring over another. The theoretical structures of the AgL^+ complexes verify the conclusions drawn from experimental data.

4. Conclusion

The results obtained in this work show that controlling the size and the arrangement of nitrogens in the macrocyclic ring has a significant influence on designing chemical molecules for specific purposes. With regard to monoaza-crown ethers [5], diaza-crown ethers, and AA-diaza-crown ethers, one observes an increase in stability constants of the 1 : 1 metal-to-ligand complexes with Ag^+ in the series of monoaza-crown ethers < AA-diaza-crown ethers < diaza-crown ethers. A similar effect is observed in the series AA15C5 < AA18C6 and $A_215C5 < A_218C6$. Knowledge of how a metal ion is shielded by a molecule interacting with it is a key to understanding the role of a complexing center in larger supramolecules. The diaza-crown ethers studied here are N-substituted ligands which provide the opportunity to study more complicated interactions [27,28] between silver(I) and these specific ligands as a model of interactions in supramolecules.

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