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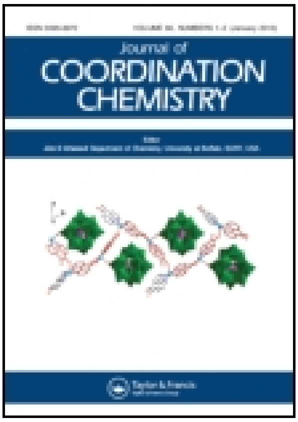

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Potentiometric and AM1d studies of the equilibria between silver(I) and monoaza, diaza, triaza and tetraaza-12-crown ethers in acetonitrile and propylene carbonate

Jaromir Kira [a] , Pawel Niedzialkowski [a] & Tadeusz Ossowski [a]
[a] Faculty of Chemistry , University of Gdansk , Gdansk , Poland

Accepted author version posted online: 21 Feb 2013.Published online: 05 Apr 2013.

To cite this article: Jaromir Kira , Pawel Niedzialkowski & Tadeusz Ossowski (2013) Potentiometric and AM1d studies of the equilibria between silver(I) and monoaza, diaza, triaza and tetraaza-12-crown ethers in acetonitrile and propylene carbonate, Journal of Coordination Chemistry, 66:7, 1220-1227, DOI: 10.1080/00958972.2013.778401

To link to this article: http://dx.doi.org/10.1080/00958972.2013.778401

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Journal of Coordination Chemistry, 2013
http://dx.doi.org/10.1080/00958972.2013.778401

Potentiometric and AM1d studies of the equilibria between silver(I) and monoaza, diaza, triaza and tetraaza-12-crown ethers in acetonitrile and propylene carbonate

JAROMIR KIRA*, PAWEL NIEDZIALKOWSKI and TADEUSZ OSSOWSKI

Faculty of Chemistry, University of Gdansk, Gdansk, Poland

(*Received 1 October 2012; in final form 29 November 2012*)

Complex formation and stability constants between monoaza, diaza, triaza and tetraaza-12-crown ethers with silver(I) were determined in acetonitrile and propylene carbonate by the potentiometric method. Complexes of 1 : 1 and 1 : 2 metal-to-ligand stoichiometry were formed. The solvent composition and number of nitrogens significantly influence the stability constants of the complexes formed. The energetically most favorable structures of the 1 : 1 metal-to-ligand complexes were calculated and visualized by the AM1d method at the semi-empirical 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, 2]. 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 [3]. Formation of such complexes does not necessarily imply that the metal ion is located precisely within the macrocycle cavity. For 1 : 2 complexes, a sandwich structure, in which the metal ion is located between two coronand molecules, has been suggested as most probable [4].

Several recent studies have reported complexation properties of aza-crown ethers with nitrogen in different positions and numbers in various solvents [3-11]. 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 major role in stabilization of AgL^+ complexes [6]. For aza-crown ethers in AgL^+ complex ions, the silver (I) is located within the macrocycle cavity which partially shields the metal ion from the solvent [3, 11]. The formation of 1 : 2 metal-to-ligand complex ions by silver(I) and aza-crown ethers with two or more nitrogens in the macrocyclic ring is more complicated. The silver(I) tends to form linear 1 : 2 metal-to-ligand complex ions with aliphatic amines [12].

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*Corresponding author. Email: jaromir@chem.univ.gda.pl

In AgL_2^+, silver(I) forms sandwich-like structures with both monoaza- and diaza-crown ethers [3, 11]. In this case, the metal ion is completely shielded from the solvent.

Recent work reported that cyclic polyamines with four or six nitrogens with pendant-arm modification and silver(I) form only AgL^+ complex ions but not AgL_2^+ [13]. *N*-substituted monoaza- and diaza-crown ethers behave differently [8, 9]. Therefore, we thought it worthwhile to investigate the stoichiometry of complexes formed by silver(I) with aza-crown ethers containing different numbers of nitrogens in the macrocyclic ring. We describe complexation properties of monoaza, diaza, triaza and tetraaza-12-crown ether with silver(I) in acetonitrile (AN) and propylene carbonate (PC). The change in the number of nitrogens in the macrocyclic ring from one to four should influence the formation of AgL^+ and AgL_2^+. Unfortunately, crystallographic data are not available for the structures of such complexes.

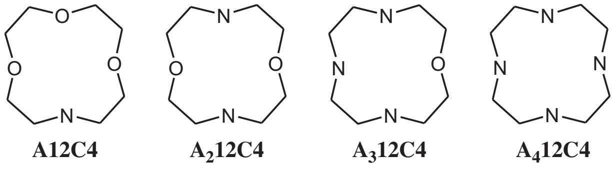
2. Experimental

2.1. *Materials and syntheses*

All solvents and reagents were analytical grade. PC (Merck) and AN (Aldrich) were of the highest purity available. 2-(2-Aminoethylamino)ethanol (Aldrich) and 2-chloroethanol (Aldrich) were previously distilled. Silver(I) perchlorate (Fluka) and tetraethylammonium perchlorate (TEAP; Fluka) were purified according to literature procedures [14]. 1,4,7-Trioxa-10-azacyclododecane (**A12C4**) was synthesized through methods reported earlier by Calverley [15]. 1,7-Dioxa-4,10-diazacyclododecane (**$A_2$12C4**) and 1-oxa-4,7,10-triazacyclododecane (**$A_3$12C4**) were purchased from Sigma-Aldrich Chemical Co. 1,4,7,10-Tetraazacyclododecane (**$A_4$12C4**) was purchased from Strem Chemicals (see figure 1).

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 $(6–9) \times 10^{-4}\,M\,dm^{-3}$. Ligand concentrations were $(3.5–9.5) \times 10^{-3}\,M\,dm^{-3}$. 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 $0.1\,M\,dm^{-3}$ tetraethylammonium perchlorate dissolved in PC or AN. The solution was flushed with argon prior and during measurements. The silver concentration during the titrations was determined using silver-wire electrodes dipped in the solution [16–21]. The equilibrium constants and simulations were calculated using the STOICHIO program [22–24] based on the nonlinear least-squares Gauss–Newton–Marquardt algorithm [25].



A12C4 **$A_2$12C4** **$A_3$12C4** **$A_4$12C4**

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

2.3. *Semi-empirical calculations*

AM1d calculations were performed using the Win Mopac 2007 program at the semi-empirical level (Cache Work System Pro Version 7.5.085, Fujitsu) [26, 27]. The conformers of the diaza-crown ethers and their 1 : 1 metal-to-ligand complexes were searched simultaneously by molecular dynamics and CONFLEX® experiments. The CONFLEX® program systematically and exhaustively generates low-energy conformers of a molecule of any shape [28]. 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 semi-empirical method [16–21].

3. Results and discussion

3.1. *Potentiometric studies on formation of aza-12-crown ether complexes*

In the potentiometric titration curves, there is a single potential jump for **A12C4** in PC and **A12C4**, **$A_2$12C4**, **$A_3$12C4**, and **$A_4$12C4** in AN and a double potential jump for **$A_2$12C4**, **$A_3$12C4**, and **$A_4$12C4** in PC (figure 2). The largest changes in potential were observed in PC (−860 mV for **$A_4$12C4**; −740 mV for **$A_3$12C4**; −585 mV for **$A_2$12C4**; −480 mV for **A12C4**) and lower in AN (−430 mV for **$A_4$12C4**; −320 mV for **$A_3$12C4**; −220 mV for **$A_2$12C4**; −80 mV for **A12C4**). With the large number of experimental points, an advanced graphical and statistical analysis can be performed [8, 9]. The fitting of theoretical points to experimental points does not lead to a simple equilibrium of 1 : 1

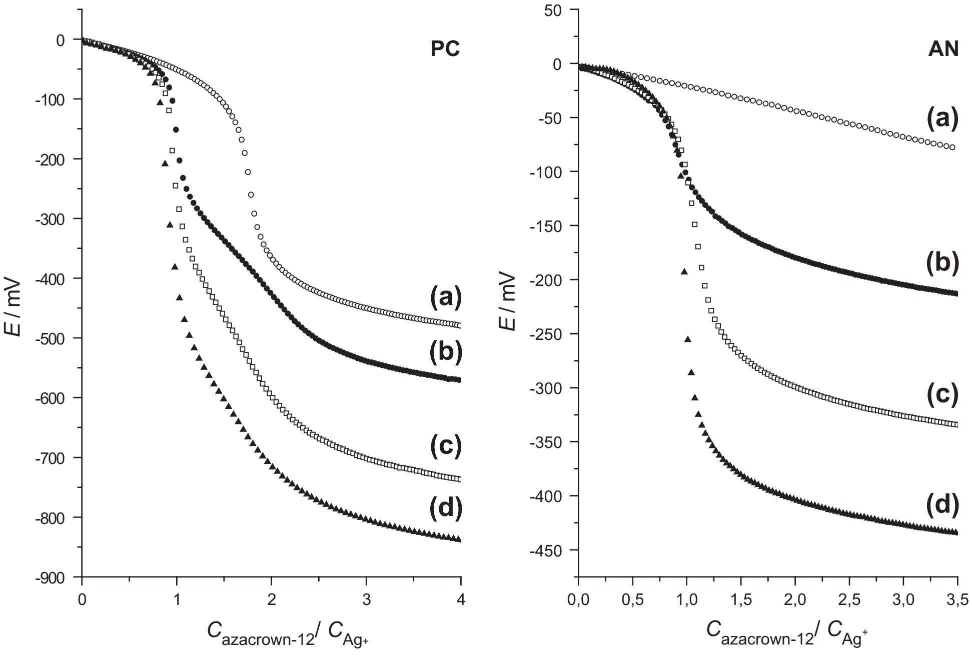


Figure 2. Changes in potential for the silver(I) (6.00×10^{-4} M dm^{-3}) from potentiometric titration with **A12C4** (○), **$A_2$12C5 (●)**, **$A_3$12C4** (□) and **$A_4$12C4** (▲) in PC and AN at 25 °C.

stoichiometry. It suggests that, apart from the equilibrium resulting in formation of AgL^+, other equilibria are also likely to occur [11]. Attempts to fit the curves to data points have shown that the variations in the potential as a function of the titrant added are best represented by a set of two equilibria:

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

$$AgL^+ + L = AgL_2^+ \quad K_2 \tag{2}$$

In addition, 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 least for Model 2° which involves two equilibria leading to the formation of AgL^+ and ${AgL_2}^+$ complex ions. Since the $\omega(x)$ and σ_E for Model 2° are small, there is no need to further analyze the equilibria [11]. 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.

Aza-12-crown ethers have from one to four nitrogens in the ring. The structural differences in these macrocycles could lead to difference in the formation of complex ions with silver(I). The stability constants of formation of AgL^+ increase in the order **A12C4** < **A$_2$12C4** < **A$_3$12C4** < **A$_4$12C4** (table 2). This suggests that the silver(I) interacts with all nitrogens in the ring of these macrocycles. For typical mono and diaza-15-crown and larger ethers, an increase in the number of nitrogens from one to two affects the log K_1 value which increases from 9.75 to 13.12 for aza-15-crown ether and from 10.17 to 15.41 for aza-18-crown ether in PC [3, 11]. This shows that the presence of a second nitrogen in these macrocycles plays a major role in formation of AgL^+. The effect is less for aza-12-crown ethers. The increase in the value of log K_1 by adding successively one nitrogen is 2.60 for **A12C4** and **A$_2$12C4**, 1.60 for **A$_2$12C4** and **A$_3$12C4**, 1.63 for **A$_3$12C4** and **A$_4$12C4** in PC. The data suggest that two and more nitrogens located in the same macrocyclic ring of aza-12-crown ethers co-operate less well than for larger rings; log K_1 values of those complexes in PC are rather large and suggest that silver(I) interacts very strongly with the aza-12-crown ethers studied. For **A$_4$12C4**, the value of log $K_1 = 14.56$ is

Table 1. Comparison of statistical values for **A12C4**, **A$_2$12C4**, **A$_3$12C4**, and **A$_4$12C4** with experimental points for Models 1° and 2°; $\omega(x)$ – the sum of the squares of the differences between measured and calculated potentials and concentrations; σ_E – standard deviation in the potential.

		$\omega(x)$	σ_E	$\omega(x)$	σ_E
Model of equation	Species	PC		AN	
		A12C4			
1°	AgL^+	2.68e+04	0.022	5.65e+02	0.006
2°	AgL^+, AgL_2^+	5.06e+02	0.003	2.72e+01	0.002
		A$_2$12C4			
1°	AgL^+	1.08e+05	0.058	8.39e+02	0.005
2°	AgL^+, AgL_2^+	8.32e+03	0.005	7.37e+01	0.002
		A$_3$12C4			
1°	AgL^+	1.96e+05	0.077	4.14e+03	0.008
2°	AgL^+, AgL_2^+	7.79e+03	0.014	2.86e+03	0.006
		A$_4$12C4			
1°	AgL^+	2.13e+05	0.083	2.49e+03	0.007
2°	AgL^+, AgL_2^+	6.32e+03	0.013	9.62e+03	0.005

Table 2. Stability constants given in the form of log K_1 and log K_2 for **A12C4**, **$A_2$12C4**, **$A_3$12C4**, and **$A_4$12C4** obtained from potentiometry in PC and AN at 25 °C.

Ligand	log K_1	log K_2
	PC	
A12C4	8.73 ± 0.07[a] [3]	5.48 ± 0.07
	8.62 ± 0.09 [7]	
$A_2$12C4	11.33 ± 0.06	4.80 ± 0.11
	11.47 ± 0.01 [10]	5.04 ± 0.03 [10]
$A_3$12C4	12.93 ± 0.11	5.70 ± 0.14
$A_4$12C4	14.56 ± 0.10	5.13 ± 0.13
	AN	
A12C4	3.50 ± 0.02[a] [3]	3.46 ± 0.04
	3.73 ± 0.04 [7]	
$A_2$12C4	6.09 ± 0.07	2.83 ± 0.11
$A_3$12C4	8.15 ± 0.07	3.33 ± 0.11
$A_4$12C4	9.75 ± 0.08	2.78 ± 0.11

[a] also presented by us [3].

close to the log K_1 values of the most strongly interacting macrocycles with silver(I) such as **$A_2$15C5** (log $K_1 = 13.12$ in PC) and **$A_2$18C6** (log $K_1 = 15.41$ in PC) [11]. This effect results in **$A_4$12C4** being a very strong complexing agent for silver(I).

We have observed previously that values of log K_1 for monoaza- and diaza-crown ethers are significantly reduced in AN in relation to PC [3, 11]. The log K_1 value for **A12C4** changes from 8.73 in PC to 3.50 in AN. This effect is due to strong solvation of silver(I) by AN. A similar effect is observed for the aza-12-crown ethers studied. The log K_1 values for **$A_2$12C4**, **$A_3$12C4**, and **$A_4$12C4** change from 11.33, 12.93, and 14.56 in PC to 6.09, 8.15, and 9.75 in AN, respectively. The log K_1 values for **$A_2$12C4**, **$A_3$12C4**, and **$A_4$12C4** are relatively high in AN (table 2).

3.2. *Formation of AgL_2^+ complexes*

Aza-12-crown ethers form AgL_2^+ in PC and AN. In previous work, we observed that silver (I) ions form a sandwich-type complex with diaza-crown ethers with a 1 : 2 metal-to-ligand stoichiometry [11]. 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 purely linear coordination [29]. The K_1/K_2 values for crown ethers investigated in PC and AN are shown in table 3. These values are >4 in all cases, with the exception of **A12C4** in AN, which confirms that the AgL_2^+ complex ion has a sandwich-type structure with almost all of the investigated ligands in PC and AN.

The log K_2 values for aza-12-crown ethers are slightly larger than those of typical monoaza- and diaza-crown ethers [3, 11]. The log K_2 changes from 5.70 for **$A_3$12C5** in PC to 2.78 for **$A_4$12C4** in AN. We have observed that values of log K_2 increase moving from diaza-crown ethers to monoaza-crown ethers, or when two nitrogens in the macrocyclic ring replace two consecutive oxygens instead of two opposite ones as for typical diaza-crown ethers [3, 11]. The effect is followed by weaker log K_1 values of the macrocyclic-type complex ions for monoaza- or AA-diaza-crown ethers [11]. In the case of aza-12-crown ethers, a similar effect is observed for **$A_2$12C4** and **A12C4** or for **$A_4$12C4** and **$A_3$12C4**.

Table 3. Values of K_1/K_2 for the silver(I) complexes with aza-12-crown ethers in PC and AN.

	K_1/K_2	
Ligand	PC	AN
A12C4	1.78×10^3	1.1
$A_2$12C4	3.39×10^6	1.82×10^3
$A_3$12C4	1.70×10^7	6.61×10^4
$A_4$12C4	2.69×10^9	9.33×10^6

3.3. *Discussion of structure of complexes*

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

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

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

Substitution of the free energy of transfer of Ag^+ into equation (3) and equation (4) gives the difference in the free energy of transfer of the complexes and corresponding ligands; the values obtained are presented in table 4. The free energy of transfer ΔG_{tr} of silver(I) from PC to AN is –42.0 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) approach zero, the weaker the access of solvent molecules to silver(I) in AgL^+ or AgL_2^+ [11]. Literature data show that for the AgL^+ inclusion-type complex with cryptates, the silver(I) is well shielded from the solvent [30, 31]. A similar effect is observed for sandwich-type AgL_2^+ complex with monoaza-crown ethers [3]. For the AgL^+ inclusion-type complex with monoaza- and diaza-crown ethers, the silver(I) shielding is weaker [11].

For aza-12-crown ethers, values of $\Delta G_{tr}(AgL^+)-\Delta G_{tr}(L)$ are more distant from zero then those for larger macrocycles such as aza-15 and aza-18 crown ethers [11]. This shows that silver(I) is less separated from solvent in AgL^+. This also suggests that silver(I) is less well adapted to the cavity of the aza-12-crown ether than to the cavity of aza-15 and aza-18 crown ethers. For AgL_2^+, the values of $\Delta G_{tr}(AgL_2^+)–2\Delta G_{tr}(L)$ are close to zero. This means that silver(I) ions are well shielded from interactions with solvent molecules, suggesting a sandwich-like structure for AgL_2^+ complex ions.

Table 4. Differences in the free energies of Ag^+ transfer from PC to AN between Ag^+ complexes and ligand and log β_2 values (from equation log K_1 + log K_2).

			log β_2	
Ligand	$\Delta G_{tr}(AgL^+)-\Delta G_{tr}(L)$	$\Delta G_{tr}(AgL_2^+)-2\Delta G_{tr}(L)$	PC	AN
A12C4	−12.1	−0.6	14.21	6.96
$A_2$12C4	−12.1	−0.8	16.13	8.92
$A_3$12C4	−14.7	−1.2	18.63	11.48
$A_4$12C4	−14.4	−0.9	19.69	12.53

3.4. *Theoretical models of AgL$^+$ complexes*

Changes of the enthalpies of formation (ΔH_f) of the most favorable AgL$^+$ complexes of the aza-12-crown ethers with Ag$^+$ and of un-complexed molecules calculated by the AM1d method [26, 27] are listed in table 5. The conformers were selected from molecular dynamics and CONFLEX® [28] experiments and are believed to be the global minimum energy conformers in the AM1d semi-empirical method. In the aza-12-crown ether-Ag$^+$ structures, silver is located in the middle over the macrocyclic ring and is shielded from further planar interactions from one side (figure 3). The silver(I) is over the cavity of the macrocycle, but interacts with all of the nitrogens and oxygens within the macrocycle's ring. Changes in enthalpy of formation ΔH_f of aza-12-crown ethers and their complexes with Ag$^+$ cations calculated by the AM1d method (table 5) follow the direction of changes of log K_1 (table 2). Structures of AgL$_2^+$ complexes were not considered because the

Table 5. Changes in enthalpy of formation (kcal M^{-1}) of aza-12-crown ethers and their complexes with Ag$^+$ cations calculated by the AM1d method (WinMopac 2007).

Species	H_f (kcal M^{-1})	ΔH_f^a
A12C4	−143.890	
A12C4, Ag$^+$ uncomplexed	98.824	
A12C4, Ag$^+$ complexed	30.233	−68.591
A$_2$12C4	−99.440	
A$_2$12C4, Ag$^+$ uncomplexed	143.274	
A$_2$12C4, Ag$^+$ complexed	73.727	−69.547
A$_3$12C4	−53.483	
A$_3$12C4, Ag$^+$ uncomplexed	189.231	
A$_3$12C4, Ag$^+$ complexed	119.345	−69.886
A$_4$12C4	−6.782	
A$_4$12C4, Ag$^+$ uncomplexed	235.932	
A$_4$12C4, Ag$^+$ complexed	164.909	−71.023

[a] $\Delta H_f = H_f$ complexed − H_f uncomplexed.

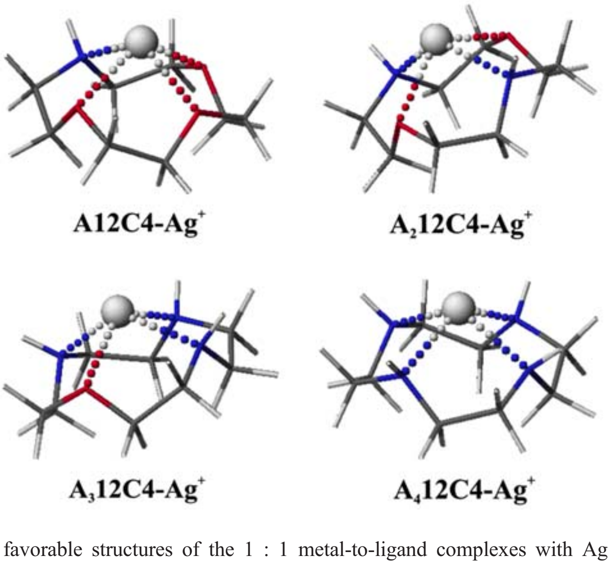


Figure 3. The most favorable structures of the 1 : 1 metal-to-ligand complexes with Ag$^+$ cations and aza-12-crown ethers.

CONFLEX®'s algorithm does not rotate one ring over another. The theoretical structures of the AgL^+ complexes verify the conclusions drawn from the experimental data.

4. Conclusion

The results obtained show that increasing the number of nitrogens in the cavity of aza-12-crown ethers increases the values of log K_1 (inclusion-type complex ions). We also showed that aza-12-crown ethers with larger numbers of nitrogens are the most strongly complexing agents for silver(I). This is implied by large values of log K_1 and relatively high values of log K_2 (sandwich-type complex ions) for aza-12-crown ethers in PC and AN.

Acknowledgements

The authors gratefully acknowledge the financial support from Grant DS/8210-4-0177-13 from the University of Gdansk and KBN NN204 122640.

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