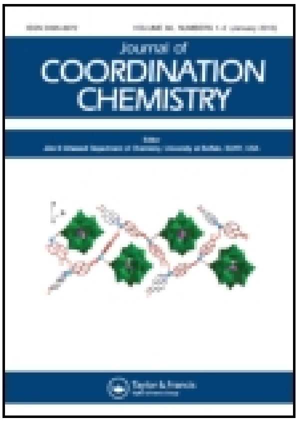
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:48
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Potentiometric, spectrophotometric, and AM1d studies of the equilibria between silver(I) ion and monoaza-crown ethers with anthraquinone in various solvents

Jaromir Kira [a] , Pawel Niedzialkowski [a] , Dorota Zarzeczanska [a] , Grzegorz Romanowski [a] & Tadeusz Ossowski [a]

[a] Faculty of Chemistry , University of Gdansk, Sobieskiego 18 , Gdansk , 80-952 , Poland

Accepted author version posted online: 29 Apr 2013.Published online: 30 May 2013.

To cite this article: Jaromir Kira , Pawel Niedzialkowski , Dorota Zarzeczanska , Grzegorz Romanowski & Tadeusz Ossowski (2013) Potentiometric, spectrophotometric, and AM1d studies of the equilibria between silver(I) ion and monoaza-crown ethers with anthraquinone in various solvents, Journal of Coordination Chemistry, 66:12, 2141-2151, DOI: 10.1080/00958972.2013.799669

To link to this article: http://dx.doi.org/10.1080/00958972.2013.799669

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Journal of Coordination Chemistry, 2013
Vol. 66, No. 12, 2141–2151, http://dx.doi.org/10.1080/00958972.2013.799669

Taylor & Francis
Taylor & Francis Group

Potentiometric, spectrophotometric, and AM1d studies of the equilibria between silver(I) ion and monoaza-crown ethers with anthraquinone in various solvents

JAROMIR KIRA*, PAWEL NIEDZIALKOWSKI, DOROTA ZARZECZANSKA,
GRZEGORZ ROMANOWSKI and TADEUSZ OSSOWSKI

Faculty of Chemistry, University of Gdansk, Sobieskiego 18, Gdansk 80-952, Poland

(*Received 14 December 2012; in final form 27 February 2013*)

Complex formation and stability constants between silver(I) and monoaza-12-crown, monoaza-15-crown, and monoaza-18-crown ethers with anthraquinone were determined in acetonitrile, methanol, and propylene carbonate by potentiometric and UV-spectrophotometric methods. Complexes of 1 : 1 and 1 : 2 metal-to-ligand stoichiometry were formed. The solvent composition and the size of the macrocyclic ring affect the stability constants of the complexes. The energetically most favorable structures of the 1 : 1 metal-to-ligand complexes were calculated and visualized by the AM1d method at a semiempirical level of theory.

Keywords: Aza-crown ethers; Equilibrium; Silver(I); Anthraquinone

1. Introduction

Numerous thermodynamic and kinetic data indicate that unsubstituted crown ethers form 1 : 1 metal-to-ligand complexes [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 lead to formation of a 1 : 1 inclusion complex. This is indicated by the strong effect of the macrocycle on stability constants in comparison with aliphatic amines [3]. 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 [4]. Interactions of aza-crown ethers with metal ions that possess a high affinity for nitrogen, such as silver(I), indicate that a nitrogen within the macrocyclic ring imparts stability to AgL^+ complexes and medium stability for AgL_2^+ complexes [3–6]. For monoaza-crown ethers in AgL^+ the silver(I) ion is located within the macrocycle cavity which partially shields the silver from solvent [3]. In AgL_2^+ silver(I) forms sandwich-like structures with monoaza-crown ethers. In this case, the metal ion is completely shielded from the solvent [3]. Formation of 1 : 1 and 1 : 2 metal-to-ligand complex ions by silver(I) and N-substituted monoaza-crown ethers is probably more

---

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

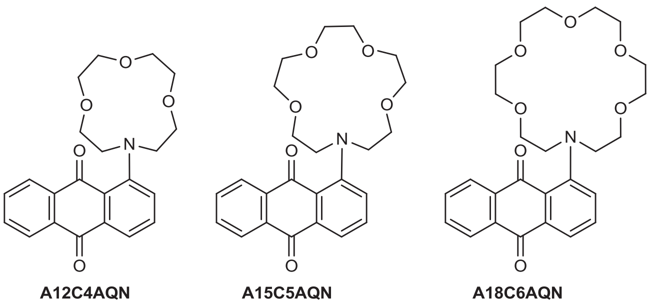


Figure 1. The structures of the monoaza-crown ethers, modified by anthraquinone.

complicated. Relatively large substituents like anthraquinone, 8-hydroxy-anthraquinone, and 8-tosyloxy-anthraquinone usually lower stability constants of AgL^+ and AgL_2^+ complexes with silver(I) ions [7]. Small substituents like benzoyl, cyanoalkyl, or methoxymethyl units slightly lower stability constants of AgL^+ [8]. Previous studies on complexation of various macrocyclic-type ligands in acetone show that small aromatic substituents insignificantly influence stability constants of AgL^+. For these complexes the most important factor is the type of macrocycle [9]. N-substitution by four or six small aromatic units lowers strongly the stability constants of AgL^+ [10]. N-substitution of aza-crown ethers of various size by 2,2′-bipyridine usually increases stability constants of both AgL^+ and AgL_2^+ [11, 12]. Therefore we thought it worthwhile to investigate the stoichiometry of complexes formed by silver(I) with monoaza-crown ethers containing anthraquinone (figure 1) in various solvents.

2. Experimental

2.1. *Materials and syntheses*

All solvents and reagents were analytical grade. Propylene carbonate (PC, Merck), methanol (MeOH, Aldrich), and acetonitrile (AN, Aldrich) were of the highest purity available. Silver(I) perchlorate (Fluka) and tetraethylammonium perchlorate (TEAP, Fluka) were purified according to literature procedures [13].

The syntheses of 1-(1,4,7,10-tetraoxa-13-azacyclopentadecan-13-yl)-9,10-anthraquinone (**A15C5AQN**) were performed according to the procedure described previously [13]. All reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) on silica plates (silica 60 F_{254}). Flash column chromatography was performed on silica gel 230–400 mesh (Merck). ^1H and ^{13}C NMR spectra were recorded on a Varian, Mercury 400 spectrometer at 400 and 100 MHz, respectively, using deuterated solvents and TMS as reference. MALDI-TOF mass spectra were recorded on a Bruker Biflex III MALDI-TOF mass spectrometer. IR spectra were recorded on a Bruker IFS66 spectrometer using KBr pellets. Elemental analyses were recorded on a Carlo-Erba CHNS-O EA1108 elemental analyzer.

The syntheses of 1-(1,4,7-trioxa-10-azacyclododecan-10-yl)-9,10-anthraquinone (**A12C4AQN**) and 1-(1,4,7,10,13-pentaoxa-16-azacyclooctadecan-16-yl)-9,10-anthraquinone (**A18C6AQN**) were performed according to analogous procedure as for A15C5AQN. For A12C4AQN to a solution of 1-fluoro-9,10-anthraquinone (710 mg, 3.138 mM) and cesium carbonate

(1.859 g, 5.706 mM) in 20 mL of toluene, 1,4,7-trioxa-10-azacyclododecane (500 mg, 2.853 mM) was added. For **A18C6AQN** to a solution of 1-fluoro-9,10-anthraquinone (473 mg, 2.090 mM) and cesium carbonate (1.238 g, 3.800 mM) in 15 mL of toluene, 1,4,7,10,13-pentaoxa-16-azacyclooctadecane (500 mg, 1.900 mM) was added. The reaction mixture was stirred at 80 °C for 24 h. The resulting mixture was cooled to room temperature, filtered, and washed with dichloromethane. The solvents were removed in vacuo and the residue was dissolved in 150 mL of dichloromethane. The solution was washed with 40% solution of tetrabutylammonium hydroxide in water (1 × 100 mL) and with water (1 × 100 mL). The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure, obtaining a red solid residue. The crude product was purified by flash chromatography (SiO_2, eluent : dichloromethane : methanol, 50 : 2 v/v) to afford 774 mg (yield : 71%) as a red solid for A12C4AQN TLC (SiO_2) CH_2Cl_2 : MeOH 25 : 1 $R_f = 0.32$; ^{1}H NMR : (δ, $CDCl_3$) 400 MHz : 3.58 (*m*; 4H), 3.74 (*m*; 8H), 3.83 (*t*; 4H), 7.48 (*dd*; 1H), 7.69 (*m*; 3H), 7.87 (*d*; 1H), 8.22 (*m*; 2H), and 723 mg (yield : 83%) as a red solid for A18C6AQN (SiO_2) CH_2Cl_2 : MeOH 25 : 1 $R_f = 0.34$; ^{1}H NMR : (δ, $CDCl_3$) 400 MHz : 3.62 (*m*; 16H), 3.71 (*m*; 8H), 7.57 (*m*; 1H), 7.72 (*m*; 4H), 8.22 (*m*; 2H).

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 $6–9 \times 10^{-4}$ mol dm^{-3}. Ligand concentrations were in the range $(3.5–9.5) \times 10^{-3}$ mol 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 mol dm^{-3} tetraethylammonium perchlorate dissolved in PC or AN. The silver concentration during the titrations was determined using silver-wire electrodes dipped in the solution [14–19]. The equilibrium constants and the simulations were calculated using the STOICHIO program [20–22] based on the non-linear least-squares Gauss-Newton-Marquardt algorithm [23].

2.3. *Spectroscopic measurements*

UV-vis spectra were recorded using a Varian CARY 3E spectrometer at 25 °C. Purity of PC, MeOH, and AN were verified by measuring the absorption spectra from 220–800 nm. Ligands were dissolved to obtain concentrations of $(1.0–2.0) \times 10^{-4}$ mol dm^{-3}. Concentrations of silver(I) were $(2.0–4.0) \times 10^{-3}$ mol dm^{-3}. The concentration of the ligand was the same in the measured solution and in the solution of silver(I). Spectroscopic measurements (magnetic stirring) were performed manually using a micro-screw with 0.5 mL Hamilton syringe equipped with a Gage 30 Teflon tube. Digital spectral data were obtained and used for graphical analysis [12, 24].

2.4. *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) [25, 26]. 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 [27]. 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 [14–19].

3. Results and discussion

3.1. *Potentiometric studies of the formation of monoaza-crown ether complexes containing anthraquinone*

Changes in potential were the largest in PC for all ligands (−250 mV for A18C6AQN; −200 mV for A15C5AQN; −120 mV for A12C4AQN). Therefore the data for PC were used to analyze changes in potential. With the large number of experimental data, an advanced graphical and statistical analysis can be performed [11, 12]. On the potentiometric titration curves there is a single potential jump for A12C4AQN, A15C5AQN, and A18C6AQN in PC (figure 2; left). The fitting of theoretical points to experimental points does not lead to a simple equilibrium of 1 : 1 stoichiometry (figure 2; right). It suggests that, apart from the equilibrium resulting in the formation of the AgL^+, other equilibria are also likely to occur [5]. 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 two equilibria:

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

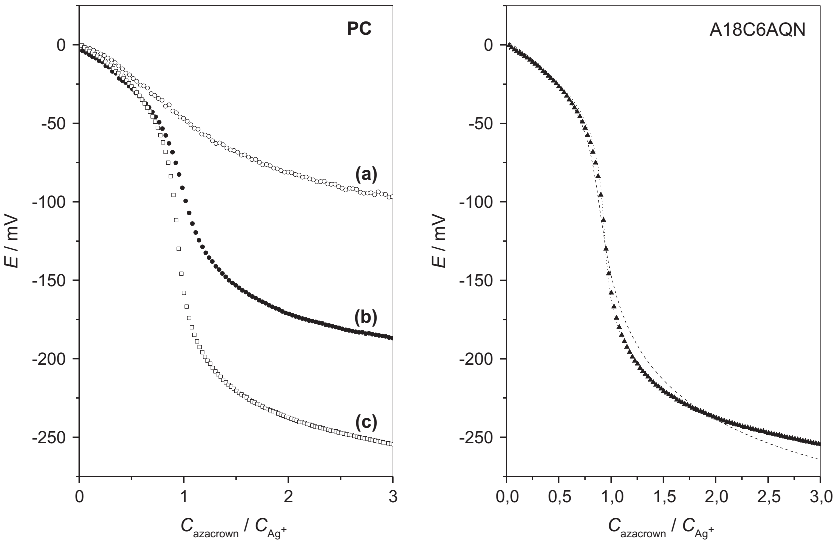


Figure 2. Changes of potential for silver(I) (6.00×10^{-4} mol*dm^{-3}) from potentiometric titration with (a) A12C4AQN (○), (b) A15C5AQN (●), and (c) A18C6AQN (□) in PC at 25 °C (left) and graphical fitting for models 1° (-) and 2° (…) and experimental points (▲) from potentiometric titration with A18C6AQN (4.00×10^{-3} mol*dm^{-3}) in PC (right).

Table 1. Comparison of statistical values for A12C4AQN, A15C5AQN, and A18C6AQN with experimental points for models 1° and 2°; $\omega(x)$ – the sum of the squares of the differences between measured and calculated potentials (or absorbances) and concentrations); σ_E – standard deviation in the potential; σ_A – standard deviation in absorbance.

Solvent	Model of eq.	Species	$\omega(x)$	σ_E	$\omega(x)$	σ_A
			A12C4AQN			
PC	1°	AgL^+	8.23e+01	0.002	8.09e+01	0.004
	2°	AgL^+, AgL_2^+	7.97e+01	0.002	1.50e+01	0.003
MeOH	1°	AgL^+	1.70e+01	0.002	1.30e+02	0.005
	2°	AgL^+, AgL_2^+	1.69e+01	0.002	2.40e+01	0.003
AN	1°	AgL^+	2.68e+01	0.002	1.11e+01	0.002
	2°	AgL^+, AgL_2^+	–	–	–	–
			A15C5AQN			
PC	1°	AgL^+	2.85e+02	0.002	6.73e+01	0.003
	2°	AgL^+, AgL_2^+	1.79e+02	0.002	5.74e+01	0.003
MeOH	1°	AgL^+	3.09e+01	0.002	8.30e+01	0.004
	2°	AgL^+, AgL_2^+	2.89e+01	0.002	1.27e+01	0.002
AN	1°	AgL^+	8.00e+01	0.002	1.08e+01	0.002
	2°	AgL^+, AgL_2^+	7.78e+01	0.002	1.07e+01	0.002
			A18C6AQN			
PC	1°	AgL^+	4.84e+02	0.004	1.38e+03	0.013
	2°	AgL^+, AgL_2^+	3.18e+02	0.003	2.39e+02	0.006
MeOH	1°	AgL^+	1.13e+02	0.002	4.63e+01	0.003
	2°	AgL^+, AgL_2^+	1.11e+02	0.002	4.10e+01	0.003
AN	1°	AgL^+	2.76e+02	0.002	3.05e+02	0.007
	2°	AgL^+, AgL_2^+	2.74e+02	0.002	1.41e+02	0.005

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

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 the least for model 2° which involves two equilibria, leading to formation of AgL^+ and AgL_2^+. Since the $\omega(x)$ and σ_E for model 2° are small, there is no need to further analyze the equilibria [5]. Model 2° is

Table 2. Stability constants given as log K_1 and log K_2 for A12C4AQN, A15C5AQN, and A18C6AQN obtained from potentiometry in PC, MeOH, and AN at 25 °C.

Ligand	log K_1	log K_2
	PC	
A12C4AQN	4.64 ± 0.06	1.81 ± 0.08
A15C5AQN	5.92 ± 0.03*	1.55 ± 0.09*
A18C6AQN	7.21 ± 0.07	2.26 ± 0.11
	MEOH	
A12C4AQN	2.47 ± 0.06	0.96 ± 0.10
A15C5AQN	3.01 ± 0.05	1.21 ± 0.08
A18C6AQN	3.84 ± 0.05	1.42 ± 0.07
	AN	
A12C4AQN	1.86 ± 0.13	–
A15C5AQN	2.36 ± 0.08	1.11 ± 0.13
A18C6AQN	2.57 ± 0.06	1.12 ± 0.11

Note: *also presented by us in [9].

suitable for all the ligands and every solvent with the exception of A12C4AQN in AN. The stability constants of all the ligands obtained from potentiometric titrations are presented in table 2 as log K_1 and log K_2.

3.2. *Spectroscopic studies of the formation of monoaza-crown ether complexes containing anthraquinone*

A12C4AQN, A15C5AQN, and A18C6AQN have similar spectra. Each spectrum from 650 to 300 nm consists of absorption for anthraquinone located near 510 nm (513 nm for A12C4AQN in PC, 511 in MeOH, 508 in AN; 511 nm for A15C5AQN in PC, 510 in MeOH, 507 in AN; 513 nm for A18C6AQN in PC, 512 in MeOH, 510 in AN). These bands changed significantly upon addition of silver(I) (figure 3). Spectral changes were the largest in PC for all bands. Therefore the data for PC were used for graphical analysis of spectra of investigated ligands [7, 11].

The formation of complexes can be analyzed by comparison of two different absorptions (figure 3) and changes of absorbance for characteristic absorption band (figure 3). The number of lines on absorbance *vs*. absorbance diagrams indicates the number of possible equilibria [12, 24] and the changes of absorbance shows the stoichiometry of the most significant complex ion [11, 12]. This indicates the possibility of formation of two complexes and the formation of the 1 : 1 metal-to-ligand complex ion. The types of complex ions can be also found from the above analysis considered together with $\omega(x)$ (the sum of

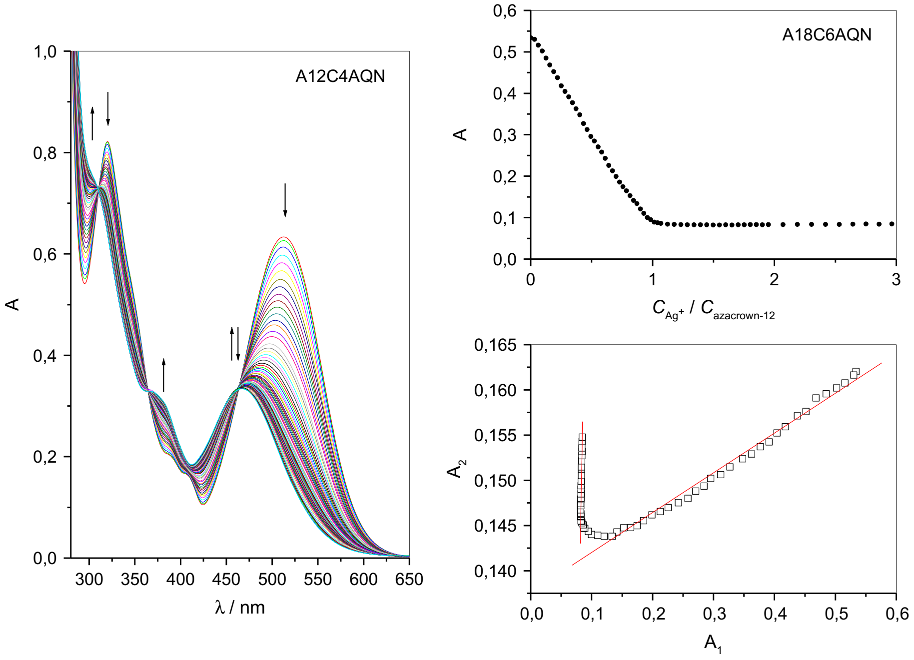


Figure 3. Changes of absorbance spectra during titration of A12C4AQN (1.50×10^{-4} mol*dm^{-3}) by silver(I) (2.70×10^{-3} mol*dm^{-3}) in PC at 25 °C (left), changes of absorbance for $\lambda = 513$ nm from spectroscopic titration with A18C6AQN (•) and silver(I) in PC (upper right) and absorbance *vs*. absorbance for two absorption bands of A18C6AQN in PC ($\lambda_1 = 513$, $\lambda_2 = 408$) (bottom right).

the squares of the differences between measured and calculated values of absorbances and concentrations) and σ_A (standard deviation in absorbance) values obtained from the experiment and calculated for each model (table 1). Graphical analysis of absorbance *vs.* absorbance diagrams and $\omega(x)$ and σ_A values indicate that changes in absorbances are best explained by two equilibria:

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

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

The stability constants of all the ligands obtained from spectroscopic titrations are presented in table 3 as log K_1 and log K_2.

3.3. *Formation of AgL^+ complexes*

Potentiometry shows concentration changes of silver(I) ions. Spectroscopy (SPE) shows changes in the spectrum of investigated ligands. Both methods indicate identical model of equilibria leading to formation of AgL^+ and $AgL_2{}^+$. Values of log K_1 and log K_2 are similar for both methods but only those obtained from potentiometry (table 2) are used for future analysis. These values will be analyzed in relation to values obtained for monoaza-crown ethers [3].

The stability constants of formation of AgL^+ with monoaza-crown ethers increase in the order A12C4 < A15C5 < A18C8 in PC and MeOH and in the order A18C6 < A12C4 < A15C5 in AN. The log K_1 values are 8.73, 9.75, and 10.17 for A12C4, A15C5, and A18C6 in PC, 3.93, 5.52, and 6.01 in MeOH and 3.50, 4.40, and 3.42 in AN, respectively [3]. Monoaza-crown ethers containing anthraquinone are characterized by lower log K_1 values than unsubstituted macrocycles. The log K_1 values are 4.64, 5.92, and 7.21 for A12C4AQN, A15C5AQN, and A18C6AQN in PC, 2.47, 3.01, and 3.81 in MeOH, 1.86, 2.36, and 2.57 in AN, respectively. This indicates that silver(I) forms weaker AgL^+ complex ions with the ligands than for monoaza-crown ethers in each case. The log K_1 values increase in the order A12C4AQN < A15C5AQN < A18C6AQN in PC, MeOH and AN, showing the same

Table 3. Stability constants given as log K_1 and log K_2 for A12C4AQN, A15C5AQN, and A18C6AQN obtained from SPE in PC, MeOH, and AN, at 25 °C.

Ligand	log K_1	log K_2
	PC	
A12C4AQN	4.67 ± 0.04	1.75 ± 0.06
A15C5AQN	5.81 ± 0.04	1.51 ± 0.06
A18C6AQN	7.14 ± 0.18	2.03
	MEOH	
A12C4AQN	2.41 ± 0.04	0.89 ± 0.07
A15C5AQN	2.92 ± 0.04	1.19 ± 0.06
A18C6AQN	3.88 ± 0.04	1.23 ± 0.06
	AN	
A12C4AQN	1.99 ± 0.10	–
A15C5AQN	2.10 ± 0.04	1.29 ± 0.06
A18C6AQN	2.53 ± 0.05	1.06 ± 0.18

direction of changes in formation of 1 : 1 metal-to-ligand complex ions as for monoaza-crown ethers. The difference in log K_1 between A15C5AQN and A12C4AQN is 1.28 in PC and is similar to 1.29, the difference in log K_1 between A18C6AQN and A15C5AQN. This describes the interaction of silver(I) with the macrocyclic ring in the 1 : 1 metal-to-ligand inclusion type complex ion. Log K_1 values change stepwise in the same manner in the order A12C4AQN < 15C5AQN < A18C6AQN in PC. This observation follows the gradual changes in construction of the macrocyclic ring itself but does not follow how the size of the silver(I) ion fits the size of A12C4 (not well matched to the size of silver(I)) and A15C5, A18C6 units (well matched to the size of silver(I)). A similar observation can be carried out for monoaza-crown ethers in PC. The difference in log K_1 between A15C5 and A12C4 is 1.02 and is similar to 0.95, the difference in log K_1 between A18C6 and A15C5 in PC. These observations are inconsistent with the results obtained for alkali ions. Disproportionate changes in log K_1 passing from 12C4 to 15C5 and 18C6 are observed for Na^+, K^+, and Rb^+ [28]. The log K_1 values strongly depend on how the size of metal ion fits the size of the macrocycle ring for these ions.

The difference in log K_1 between A15C5AQN and A12C4AQN is 0.54 in MeOH and 0.50 in AN and is not similar to 0.80 and 0.21, the difference in log K_1 between A18C6AQN and A15C5AQN in MeOH and AN, respectively. This shows that passing from A12C4AQN to A15C4AQN, and to A18C6AQN causes disproportionate changes in log K_1 values as observed for alkali ions [28]. A similar observation can be carried out for monoaza-crown ethers [3]. The difference in log K_1 between A15C5 and A12C4 is 1.59 in MeOH and 0.90 in AN and is not similar to 0.49 and −0.98, the difference in log K_1 between A18C6 and A15C5 in MeOH and AN. The increase in log K_1 is larger, passing from A12C4AQN to A15C5AQN than passing from A15C5AQN to A18C6AQN. The same is observed, passing from A12C4 to A15C5 and passing from A15C5 to A18C6 (a decrease is observed in AN). This observation follows how the size of silver(I) fits the size of A12C4 (not well matched to the size of silver(I)), A15C5, and A18C6 units (well matched to the size of silver(I)). This also confirms observations carried out for many crown ethers and metal ions of various size, which show that values of log K_1 strongly depend on how the ion fits into the cavity of the macrocycle [28]. For silver(I), this is confirmed by the stronger solvating environments such as MeOH and AN, but is not true for weakly solvating environment such as PC. This work shows that the solvent is an additional and important factor that contributes to this phenomenon.

The anthraquinone significantly reduces log K_1 values of all the monoaza-crown ethers studied. The lowering of the value of log K_1 is 4.09, 3.83, and 2.96 for A12C4AQN, A15C5AQN, and A18C5AQN in PC, 1.46, 2.51, and 2.20 in MeOH, 1.64, 2.04, and 0.85 in AN, respectively. However, comparison of log K_1 and log K_2 values (table 3) shows that AgL^+ is the most significant complex ion from the studied equilibria.

3.4. *Formation of AgL_2^+ complexes*

Monoaza-crown ethers have minor tendency to form 1 : 2 metal-to-ligand complex ions, usually with a sandwich-like structure [3, 5]. Log K_2 (from equation log β_2–log K_1) is 5.48, 4.77, and 3.37 for A12C4, A15C5, and A18C6 in PC, 3.54, 3.04, and 2.84 in MeOH, 3.46, 2.83, and 2.66 in AN, respectively [3]. Log K_2 values are very small for all investigated ligands, 1.81, 1.55, and 2.26 for A12C4AQN, A15C5AQN, and A18C6AQN in PC, 0.96, 1.21, and 1.42 in MeOH, 1.11 and 1.12 for A15C5AQN and A18C6AQN in

Table 4. Changes in enthalpy of formation (kcal/mol) of A12C4AQN, A15C5AQN, A18C6AQN and their complexes with Ag^+, calculated by the AM1d method (WinMopac [25]).

Species	H_f (kcal/mol)	ΔH_f^*
A12C4AQN	−126.698	
A12C4AQN, Ag^+ uncomplexed	116.016	
A12C4AQN, Ag^+ complexed	37.523	−78.493
A15C5AQN	−175.066	
A15C5AQN, Ag^+ uncomplexed	67.648	
A15C5AQN, Ag^+ complexed	−19.300	−86.948
A18C6AQN	−223.264	
A18C6AQN, Ag^+ uncomplexed	19.450	
A18C6AQN(1), Ag^+ complexed	−70.632	−90.082
A18C6AQN(2), Ag^+ complexed	−70.611	−90.061

Note: $^*\Delta H_f = H_f$ complexed–H_f uncomplexed.

AN, respectively. We have no evidence that AgL_2^+ is formed with A12C4AQN in AN. The log K_2 values are much lower than for monoaza-crown ethers for all investigated ligands. These data suggest that anthraquinone is a significant factor in lowering log K_2 values.

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

Changes of the enthalpies of formation (ΔH_f) of the most favorable AgL^+ complexes of the monoaza-crown ethers containing anthraquinone and of uncomplexed molecules calculated by the AM1d method [25, 26], are listed in table 4. The conformers were selected from molecular dynamics and CONFLEX® [27] experiments and are believed to be the

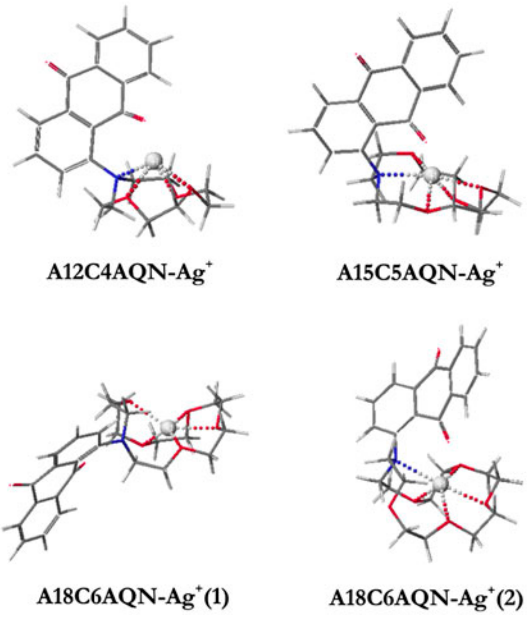


Figure 4. The most favorable structures of the 1 : 1 metal-to-ligand complexes with Ag^+ and A12C4AQN, A15C5AQN, and A18C6AQN (**1**) and the second lowest energy conformer for complexed A18C6AQN (**2**).

global minimum energy conformers in the AM1d semiempirical method. In the A12C4AQN-Ag^+ structure, silver(I) is located in the middle over the macrocyclic ring and is shielded from further planar interactions from one side (figure 4). In the A15C5AQN-Ag^+ and A18C6AQN-Ag^+(1,2) structures, the silver(I) ion is located in the middle over the macrocyclic ring and is well shielded from further interactions (figure 4). In the A12C4AQN-Ag^+ and A15C5AQN-Ag^+ structures, the anthraquinone is located over silver (I) from the side. In A18C6AQN-Ag^+(1), the anthraquinone is located on the side of the macrocyclic ring. Unexpectedly, silver(I) does not interact with nitrogen in this structure. In the second lowest energy conformer for A18C6AQN-Ag^+(2) (figure 4) the anthraquinone is located over the silver(I) as for A12C4AQN-Ag^+ and A15C5AQN-Ag^+. We searched for conformers as A18C6AQN-Ag^+(1) for A12C4AQN-Ag^+ and A15C5AQN-Ag^+, finding values of H_f = 43,406, 17,340 kcal/mol for those complexes, respectively. This suggest that the anthraquinone can freely change its location from over the silver(I) to the side of the larger macrocyclic rings. Changes in enthalpy of formation ΔH_f of monoaza-crown ethers containing anthraquinone and their complexes with Ag^+ cations calculated by the AM1d method (table 4) follow the direction of changes of log K_1 (table 2). Structures of AgL_2^+ complexes 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

Monoaza-crown ethers containing anthraquinone form more stable AgL^+ and less stable AgL_2^+ complex ions. This work shows that the anthraquinone significantly reduces both log K_1 and log K_2 values of all the monoaza-crown ethers studied and confirms observations carried out for many crown ethers and metal ions of various size which show that values of log K_1 strongly depend on how the ion fits into the cavity of the macrocycle [28]. For silver(I), this is confirmed by the stronger solvating environments such as MeOH and AN, but is not true for weakly solvating PC. This unexpected observation in PC, suggests that the solvent is a much more important factor than was previously thought. The solvent probably contributes to forming complex ions between metal ions and macrocycle-type units in the case of inclusion-type complex ions.

Theoretical models of AgL^+ complexes suggests that the anthraquinone can freely change its location from over silver(I) to the side of the macrocycle ring. This can lead to the possibility to create more complex ions between various N-substituted aza-crown ethers and silver (I) ions [7, 12].

Acknowledgments

The authors gratefully acknowledge the financial support from Grant DS 530-8210-D181-12 received from the University of Gdansk.

References

[1] R.M. Izatt, J.S. Bradshaw, S.A. Nelsen, J.D. Lamb, J.J. Christiansen. *Chem. Rev.*, **85**, 271 (1985).

[2] F. Arnaud-Neu, R. Delgado, S. Chaves. *Pure Appl. Chem.*, **75**, 71 (2003).
[3] T. Ossowski, R. Trokowski, D. Rogowska, J. Kira. *Pol. J. Chem.*, **75**, 345 (2001).
[4] A. Thaler, R. Bergter, T. Ossowski, B.G. Cox, H. Schneider. *Inorg. Chim. Acta*, **285**, 1 (1999).
[5] J. Kira, P. Niedzialkowski, T. Ossowski. *J. Coord. Chem.*, **66**, 180 (2013).
[6] J. Kira, P. Niedzialkowski, T. Ossowski. *J. Coord. Chem.*, **66**, 1228 (2013).
[7] T. Ossowski, J. Kira, D. Rogowska, H. Warmke, J. Mlodzianowski. *J. Chem. Soc., Dalton Trans.*, 689 (2000).
[8] H.J. Buschmann, E. Schollmeyer. *Transition Met. Chem.*, **27**, 295 (2002).
[9] H.J. Buschmann, E. Schollmeyer. *Mater. Sci. Eng.*, **C 23**, 509 (2003).
[10] J. Wyrwal, J. Kira, R. Pankiewicz, G. Schroeder. *Pol. J. Chem.*, **80**, 1633 (2006).
[11] J. Kira, T. Ossowski. *Pol. J. Chem.*, **82**, 1245 (2008).
[12] J. Kira, T. Ossowski. *Pol. J. Chem.*, **83**, 2067 (2009).
[13] D.D. Perrin, W.L.F. Armarego. *Purification in Laboratory Chemicals*, Pergamon Press, New York (1988).
[14] J. Kira, B. Łęska, G. Schroeder, P. Przybylski, B. Brzezinski. *J. Mol. Struct.*, **738**, 227 (2005).
[15] J. Kira, B. Łęska, O. Nevecheriya, G. Schroeder, P. Przybylski, B. Brzeziński. *J. Mol. Struct.*, **749**, 122 (2005).
[16] R. Pankiewicz, J. Kira, G. Schroeder, T. Ossowski, B. Brzeziński. *J. Mol. Struct.*, **782**, 73 (2006).
[17] G. Schroeder, J. Kira, T. Ossowski, B. Łęska, P. Przybylski, B. Brzezinski. *J. Mol. Struct.*, **788**, 184 (2006).
[18] P. Przybylski, J. Kira, G. Schroeder, B. Brzezinski, F. Bartl. *J. Phys. Chem. A*, **112**, 8061 (2008).
[19] B. Łęska, R. Pankiewicz, J. Kira, G. Schroeder. *Supramol. Chem.*, **21**, 218 (2009).
[20] P.J. Legett. *Computational Methods for the Determination of Formation Constants*, Plenum Press, New York (1985).
[21] J. Kostrowicki, A. Liwo. *Comput. Chem.*, **11**, 195 (1987).
[22] J. Kostrowicki, A. Liwo. *Comput. Chem.*, **37**, 645 (1990).
[23] D.W. Marquardt. *J. Soc. Ind. Appl. Math.*, **11**, 431 (1963).
[24] J. Polster, H. Lachman. *Spectroscopic Titration. Analysis of Chemical Equilibria*, VCH, New York (1989).
[25] Cache 7.5 WS Pro (WinMopac 2007). *User guide*, Fuitsu, Chiba (2007).
[26] J.J.P. Steward. *J. Comput. Chem.*, **12**, 320 (1991).
[27] H. Goto, E. Osawa. *J. Chem. Soc. Perkin Trans.*, **2**, 187 (1993).
[28] B.G. Cox, H. Schneider. *Coordination and Transport Properties of Macrocyclic Compounds in Solution*, Elsevier, Amsterdam (1992).