DALTON
FULL PAPER

Potentiometric and spectrophotometric studies of the equilibria between silver(I) ion and crown ethers containing chromophore substituents in propylene carbonate

Tadeusz Ossowski,[*a] **Jaromir Kira,**[*a] **Dorota Rogowska,**[a] **Hanna Warmke**[a]
and Janusz Młodzianowski[b]

[a] *Faculty of Chemistry, University of Gdańsk, Sobieskiego 18, 80-952 Gdańsk, Poland.*
E-mail: tedos@chemik.chem.univ.gda.pl; jaromir@chemik.chem.univ.gda.pl
[b] *Institute of Experimental Physics, University of Gdańsk, Wita Stwosza 57, 80-952 Poland*

Received 28th October 1999, Accepted 14th January 2000

Potentiometric and UV-spectrophotometric methods have been used to study the coordination properties of crown ethers and their derivatives containing 9,10-dioxo-1-anthryl, 8-hydroxy-9,10-dioxo-1-anthryl and 8-tosyloxy-9,10-dioxo-1-anthryl substituents with respect to the silver(I) ion in propylene carbonate. It was found that unsubstituted crown ligands were capable of forming two types of complex ion. The silver(I) ion can enter the macrocycle cavity forming 1 : 1 complexes or can coordinate externally to the nitrogen atom of a ligand as occurs for typical complexes of silver(I) with nitrogen ligands. This results in $Ag(crown)_2^+$ complexes. Introduction of chromophore groups allows investigation of the mechanism of AgL^+ and AgL_2^+ complex formation by spectrophotometric methods. Attaching a bulky chromophore to the nitrogen atom of the aza-crown makes the formation of the AgL_2^+ complexes for monoaza-crown-15 strongly restricted or impossible. For 13-(9,10-dioxo-1-anthryl)-1,4,7,10-tetraoxa-13-azacyclopentadecane *(*$A_2$15C5AQN) the presence of only one substituent leads to an increase in the stability of the external complex (AgL_2) and the formation of other complex structures $Ag_2L_3^{2+}$ and $Ag_3L_2^{3+}$.

Introduction

Crown ethers are efficient complexing agents for many metal ions. Numerous thermodynamic and kinetic data[1] indicate that complexes of 1 : 1 stoichiometry are formed predominantly. The formation of 1 : 1 metal ion–coronand complexes does not necessarily imply that the metal ion is located within the cavity of the macrocycle. The alkali metal thiocyanates of dibenzo-18-crown-6 ($B_2$18C6) were reported by Pederson *et al.*[2–4] to have metal-to-ligand ratio of 1 : 1 for potassium 1 : 1 and 1 : 2 for rubidium and 1 : 2 and 2 : 3 for caesium. A sandwich structure in which the metal ion is located between two coronand molecules was suggested as the most probable for the 1 : 2 complexes.[5,6] Similarly, the 2 : 3 complex can be visualized as being constructed of two metal ions between three coronand molecules arranged flat in their tiers.[4]

A similarly complex situation can be expected when analyzing the interactions of aza-crown ethers with metal ions that possess high affinity to nitrogen as found for silver(I) ion. Usually, the interactions between the macrocycle ring and silver ion in solution are analyzed in terms of the interactions with a positively charged ion that leads to the 1 : 1 inclusion complex. There are only few reports about more complex sandwich aggregates with the 1 : 2 (Ag^+ : ligand) stoichiometry.[7–9] The tendency of the Ag^+ ion to form linear AgL_2^+ complexes is well known in coordination chemistry.[10] Similar structures can be expected for complexes with macrocycles (examples of mono- and diaza-crown ethers complexes are shown in Fig. 1). However, further possibilities exist for extra- and intra-crown interactions (Fig. 1).

When the crown ether can form many types of complexes with ions, the introduction of a chromophore group as a side-arm fragment should result in a possibility for a step by step investigation of the complex-formation equilibrium by spectroscopic measurements, particularly for asymmetrically substituted diaza-crowns.

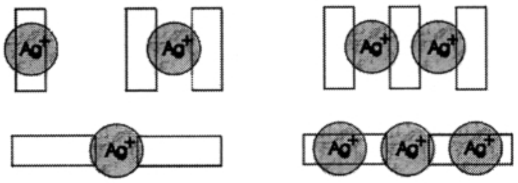


Fig. 1 Possible structures of silver–crown complexes.

Several recent studies have reported the complexation properties of differently functionalized crown ethers.[11–15] In most cases, polar side-arm groups comprise ethers, amines, amides or carbocyclic ones. Here, we describe the synthesis and some complexing properties of N-functionalized monoaza- and diaza-crown ethers containing anthraquinone, hydroxyanthraquinone and tosyloxyanthraquinone base functionalities (Fig. 2). Such groups function as spectrophotometric indicators of complex-formation equilibrium. A number of studies of crown ethers containing pendant-arm chromophore groups have been directed in order to find a sensitive and selective metal-ion detector.[16,17] Unfortunately, only in a few of these studies was the influence of side-arm groups on the stoichiometry and thermodynamics of complex formation investigated.[18] Therefore we thought it worthwhile to investigate the stoichiometry of complexes formed by the silver(I) ion with aza-crown ethers containing various side-arm groups.

Results and discussion

Spectroscopic studies

The UV–VIS spectrum of 1-amino-9,10-anthraquinone (AQN) in the visible region contains a single π→π* redox band (corresponding to charge transfer from the amino group to the anthraquinone moiety).[19,20] The band position is virtually independent of whether the chromophore fragment is attached

DOI: 10.1039/a908585h

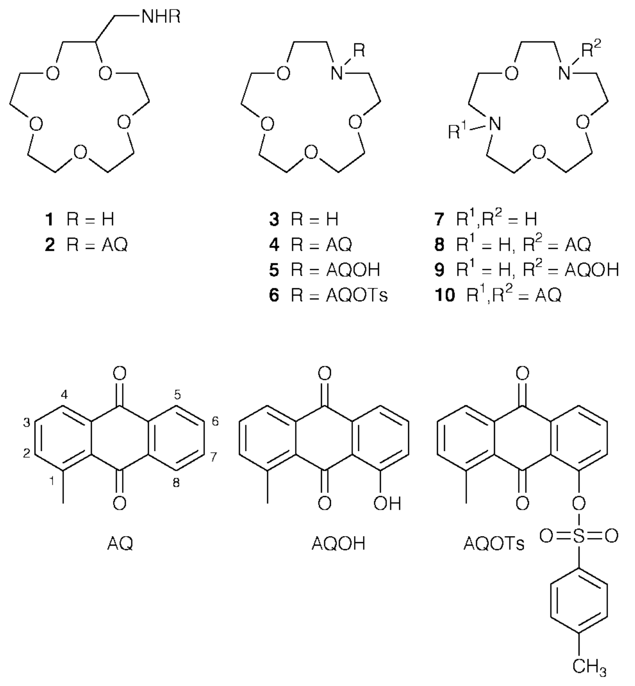


Fig. 2 Structures of ligands considered in this study.

Table 1 π→π* band position (λ/nm) and molar absorption coefficients (log ε/dm^3 mol^{-1} cm^{-1}) of 1-amino-9,10-anthraquinone and some of its derivatives and the effect of the presence of silver(I) ion in propylene carbonate solution at 25 °C

	Ligand		Ligand–silver(I)[a]	
	λ/nm	log (ε/mol^{-1} dm^3 cm^{-1})	λ/nm	log (ε/mol^{-1} dm^3 cm^{-1})
AQN	470	3.80	470	3.80
A15C5AQN **4**	510	3.60	463	3.31
A$_2$15C5AQN **8**	510	3.54	467	3.17
A$_2$15C5(AQN)$_2$ **10**	510	3.90	469	3.68
A15C5AQNOH **5**	530	3.89	462	3.69
A15C5AQNOTs **6**	506	3.64	463	3.58
A$_2$15C5AQNOH **9**	530	3.88	467	3.71
15C5meAQN **2**	510	3.70	508	3.70

[a] Concentration of ligand to silver(I) = 1 : 5.

to the macrocycle moiety by a methylene bridge (15C5meAQN **2**) {2-[*N*-(9,10-dioxo-1-anthryl)aminomethyl]-1,4,7,10,13-pentaoxacyclopentadecane} or is directly attached to the nitrogen atom (A15C5AQN **4**) [13-(9,10-dioxo-1-anthryl)-1,4,7,10-tetraoxa-13-azacyclopentadecane] (Table 1). The molar absorption coefficients of all ligands studied are constant within the concentration range considered. This demonstrates that ligand association does not play any significant role in the phenomena investigated.

When a hydroxy group is present in the molecule, a bathochromic shift of the absorption band accompanied by the increase of molar absorption coefficient is observed. The presence of two chromophore groups in the molecule doubles the intensity of the band at 510 nm. This suggests that the two chromophore groups are fully independent of each other.

The introduction of silver(I) ion to the solutions of A15C5AQN **4**, A15C5AQNOH **5** [13-(8-hydroxy-9,10-dioxo-1-anthryl-1,4,7,10-tetraoxa-13-azacyclopentadecane], A$_2$15C5-AQN **8**, A$_2$15C5AQNOH **9** [7-(8-hydroxy-9,10-dioxo-1-anthryl]-1,4,10-trioxa-7,13-diazacyclopentadecane] and A$_2$-15C5(AQN)$_2$ **10** [7,13-bis(9,10-dioxo-1-anthryl)-1,4,10-trioxa-7,13-diazacyclopentadecane] causes dramatic changes in the positions and intensities of the visible absorption bands. These changes are manifested by a blue shift of the 510 nm absorption band. At the same time, isosbestic points appear in certain ranges of the ligand : metal molar ratio. The most pronounced changes are observed for ligands containing hydroxyanthraquinone side-arm groups: A15C5AQNOH **5** and A$_2$15C5-AQNOH **9**. A typical series of UV–VIS spectra at various ligand : metal ratios is presented in Fig. 3A. Plots of absorbance *vs.* Ag$^+$: crown molar ratio indicate the formation of a single 1 : 1 complex (Fig. 3B).

A characteristic feature of the spectrophotometric titrations is that for low C_{Ag^+}/C_{ligand} molar ratios the absorbance changes are small. This effect does not depend on the concentration of ligands or silver(I) perchlorate. This type of pattern always occurs for ligands containing quinone or hydroxyquinone moieties connected directly to the nitrogen atom of the crown and is not observed if the crown moiety contains a bulky tosyloxy group (A15C5AQNOTs **6**) {13-(8-tosyloxy-9,10-dioxo-1-anthryl]-1,4,7,10-tetraoxa-13-azacyclopentadecane} (Fig. 3B). It can therefore be suggested that the introduction of a bulky tosyl group precludes the possibility of close proximity of the crown and quinone moieties. Thus, the coordination of the silver ion will lead to only minimal conformational changes. On the other hand, metal-ion coordination may cause large changes in the mutual orientation of the crown and the quinone moieties for attachment of anthaquinone and hydroxyanthaquinone moieties to the crown ether resulting in changes of the spectroscopic characteristics (Fig. 3B).

The influence of the silver(I) ion on the spectrum of 15C5meAQN is by far the weakest. The position and the intensity of the 510 nm band in the Ag$^+$–15C5meAQN system remains practically unchanged. The changes in absorbance are of the order of 0.1 log unit. Such changes are too small to be used for the analysis of coordination interactions. These results indicate that the anthraquinone moiety does not interact significantly with silver ions.

For the crown ethers for which the apparent changes in the spectra caused by the presence of the silver ion were observed, molar-ratio curves were determined.

The resulting data indicate that AgL$^+$–type complexes are the dominant forms for Ag$^+$ in propylene carbonate solution. The situation is different for mono-substituted diaza-complexes with A$_2$15C5AQN **8** and A$_2$15C5AQNOH **9**. The nature of the absorbance dependence on molar ratio for A$_2$15C5AQN **8** at 510 nm suggests that there are at least two types of complexes in propylene carbonate solution (Fig. 4B). This is manifested as inflection points that appear at $C_{Ag^+}/C_{A_215C5AQN}$ molar ratios of 1 : 1 and 1 : 1.65.

Determination of equilibrium models

For all systems, except Ag$^+$–A$_2$15C5AQN spectrophotometric and potentiometric data could be fitted assuming the formation of AgL$^+$ or AgL$^+$ and AgL$_2^+$ species. For A$_2$15C5AQN the absorbance–absorbance,[21] obtained from spectrophotometric measurements, exhibits four inflexion points and five lines as in contrast to the other systems (Fig. 5) implying more equilibria than for the other ligands.

The potentiometric titration curves of Ag$^+$ with A15C5 **3** (1,4,7,10-tetraoxa-13-azacyclopentadecane) and 15C5meNH$_2$ **1** [2-(hydroxymethyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane] in propylene carbonate exhibit characteristic inflection points indicating the coexistence of at least two equilibria. For A$_2$15C5 **7** (1,4,10-trioxa-7,13-diazacyclopentadecane), only one inflection point in the titration curve was observed as opposed to two for A15C5 **3**, within a wide range of ligand concentrations (1.00×10^{-2} mol dm^{-3}–1.00×10^{-5} mol dm^{-3}). The best-fitting equilibrium model for these ligands that contains two equilibria involves the formation of AgL$^+$ and AgL$_2^+$ complexes.

For crown ethers derived with anthraquinone, hydroxyanthraquinone and tosyloxyanthraquinone moieties similar conclusions can be drawn. The analysis of both potentiometric

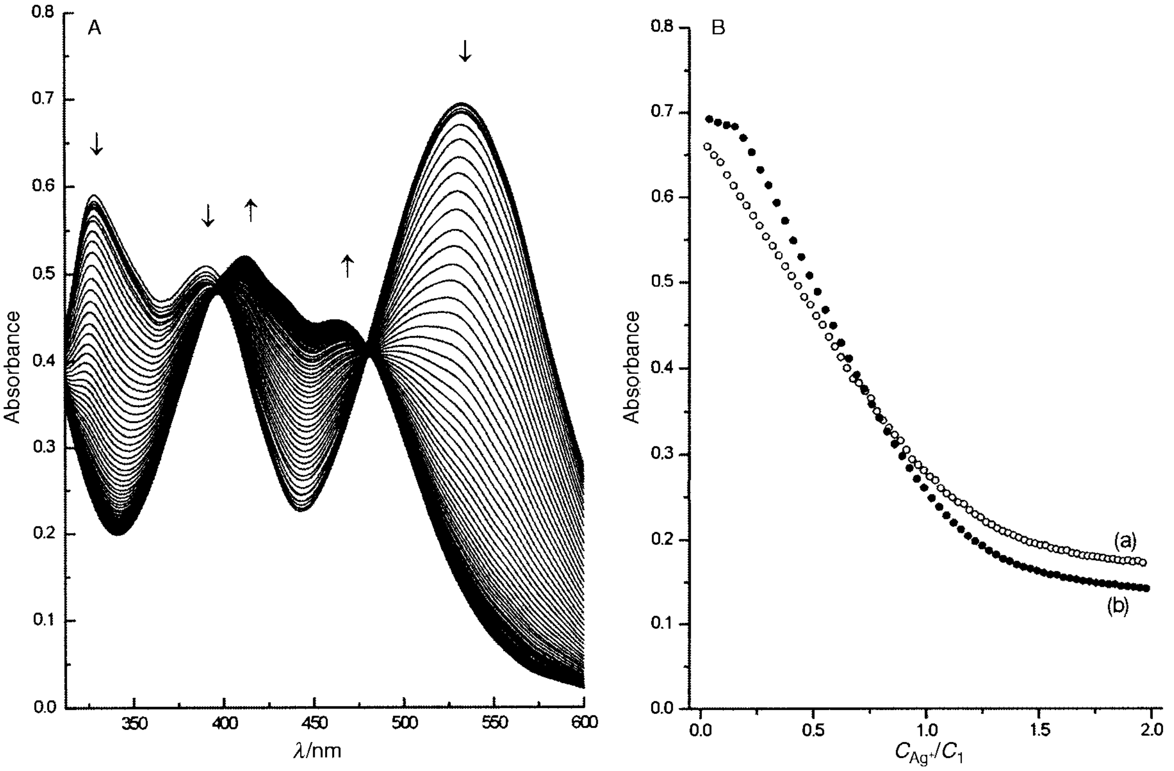


Fig. 3 A, Absorption spectra recorded in PC solution containing A15C5AQNOH **5** (9.00×10^{-5} mol dm^{-3}) and concentration of silver(I) perchlorate ($0–4.50 \times 10^{-4}$ mol dm^{-3}). B, Dependence of absorbance at 506 nm for A15C5AQNOTs **6** (a) and at 530 nm for A15C5AQNOH **5** (b) as a function of molar ratio C_{Ag^+}/C_L.

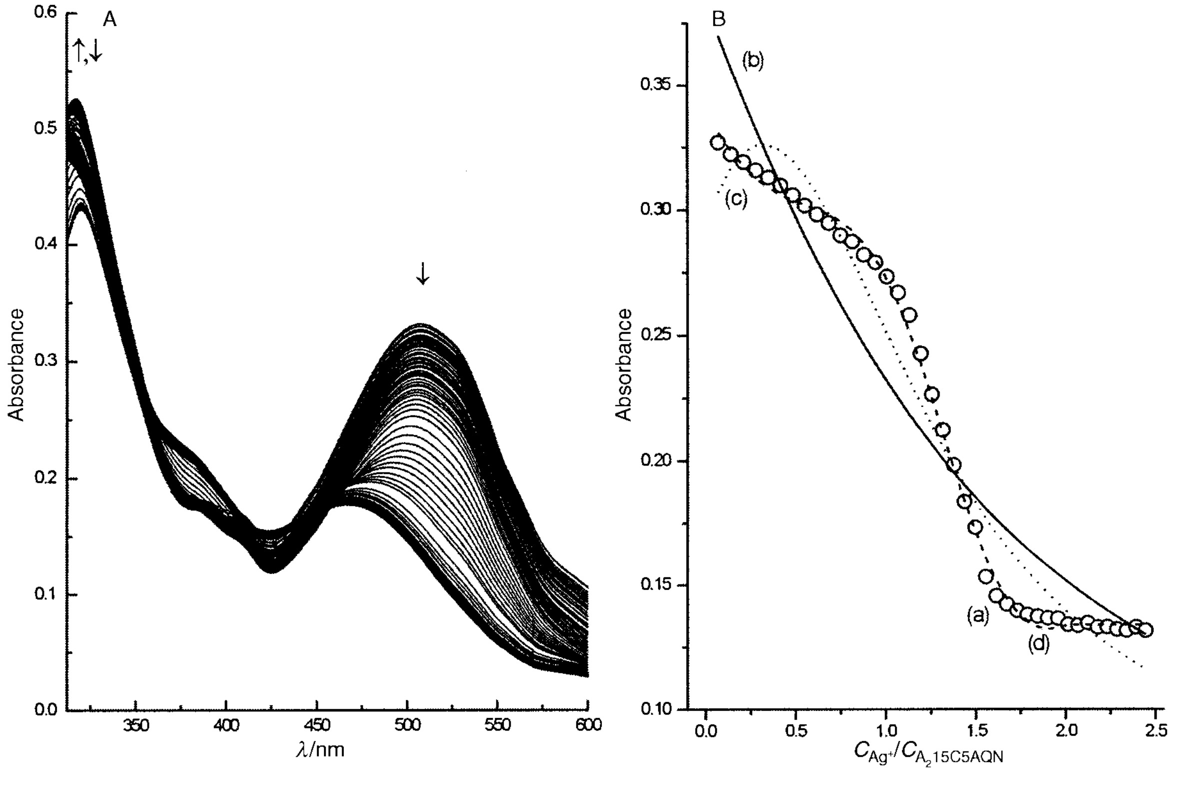


Fig. 4 A, Absorption spectra recorded in PC solutions containing $A_2$15C5AQN **8** (1.20×10^{-4} mol dm^{-3}) and concentration of silver(I) perchlorate ($0–6.00 \times 10^{-4}$ mol dm^{-3}). B, Dependence of absorbance at 510 nm for $A_2$15C5AQN **8** with silver perchlorate. The experimental points are (a) (open circles) and the fitting curves for the models are 1 (b) (line), 4 (c) (dotted line), 8 (d) (dashed line).

and spectrophotometric data leads to the conclusion that at least two equilibria exist in the solvent leading to the formation of AgL^+ or AgL^+ and AgL_2^+ complexes.

For $A_2$15C5AQN **8** the results of fitting various equilibrium models to the spectrophotometric data are summarized in Table 2. As shown, the dependence of absorbance on concentration can only be explained assuming the coexistence of three or four equilibria which involve the formation of AgL^+, $Ag_3L_2^{3+}$ and AgL_2^+ or AgL^+, $Ag_3L_2^{3+}$, $Ag_2L_3^{2+}$ and AgL_2^+ complexes. According to the F-test[22,23] the best-fitting model containing three equilibria is indistinguishable at the 90% significance level from a model in which all equilibria are included.

Table 2 Results of fitting of various equilibrium models to spectrophotometric data

Model	Species considered	σ^2[a]	F[b]	$F_{\mathrm{crit.}}$[c]	a[d]	σ_A[e]
1	AgL^+	133.8	527.65	2.26	0.01	0.022
2	AgL^+, $Ag_3L_2^{3+}$	77.4	429.80	2.30	0.01	0.016
3	AgL^+, $Ag_2L_3^{2+}$	30.9	166.62	2.30	0.01	0.010
4	AgL^+, AgL_2^+	40.6	221.52	2.30	0.01	0.012
5	AgL^+, $Ag_3L_2^{3+}$, $Ag_2L_3^{2+}$	1.7	2.62	2.34	0.01	0.002
6	AgL^+, $Ag_3L_2^{3+}$, AgL_2^+	1.5	0.33	1.61	0.10	0.002
7	AgL^+, $Ag_2L_3^{2+}$, AgL_2^+	31.8	323.56	2.34	0.01	0.010
8	AgL^+, $Ag_3L_2^{3+}$, $Ag_2L_3^{3+}$, AgL_2^+	1.5				0.002

[a] Residual variance: $\sigma^2 = \bar{\omega}(x)/(n - p)$, p is the number of parameters, n is the number of experimental points, $\bar{\omega}(x)$ is the sum of the squares of the differences between measured and calculated quantities (absorbances and concentrations). [b] F = Test value = $[\bar{\omega}(x) - \omega(x^*)](p^* - p)/[\omega(x^*)(n - p^*)]$, where $\bar{\omega}(x^*)$ and p^* correspond to the model **8** in which all the simpler models are included. [c] $F_{\mathrm{crit.}}$ = Critical F value. [d] a = Level of significance. [e] σ_A = Standard deviation in absorbance; $\sigma = (\sigma^2)^{\frac{1}{2}}$.

Table 3 Results of fitting of various equilibrium models to potentiometric data

Model	Species considered	σ^2[a]	F[b]	$F_{\mathrm{crit.}}$[c]	a[d]	σ_E[e]
1	AgL^+	455.0	940.23	1.55	0.01	40
2	AgL^+, $Ag_3L_2^{3+}$	41.9	71.78	1.55	0.01	38
3	AgL^+, $Ag_2L_3^{2+}$	72.7	170.68	1.55	0.01	15
4	AgL^+, AgL_2^+	210.2	612.18	1.55	0.01	25
5	AgL^+, $Ag_3L_2^{3+}$, $Ag_2L_3^{2+}$	64.8	287.14	1.55	0.01	14
6	AgL^+, $Ag_3L_2^{3+}$, AgL_2^+	49.8	191.26	1.55	0.01	12
7	AgL^+, $Ag_2L_3^{2+}$, AgL_2^+	22.0	14.56	1.55	0.01	6
8	AgL^+, $Ag_3L_2^{3+}$, $Ag_2L_3^{3+}$, AgL_2^+	19.9				5

[a] Residual variance: $\sigma^2 = \bar{\omega}(x)/(n - p)$, p is the number of parameters, n is the number of experimental points, $\bar{\omega}(x)$ is the sum of the squares of the differences between measured and calculated values (e.m.f. and titrant volumes). [b] F = Test value = $[\bar{\omega}(x) - \omega(x^*)](p^* - p)/[\omega(x^*)\,(n - p^*)]$, where $\bar{\omega}(x^*)$ and p^* correspond to the model **8** in which all the simpler models are included. [c] $F_{\mathrm{crit.}}$ = Critical F value. [d] a = Level of significance. [e] σ_A = Standard deviation in absorbance. [f] σ_E = Standard deviation in e.m.f.; $\sigma = (\sigma^2)^{\frac{1}{2}}$.

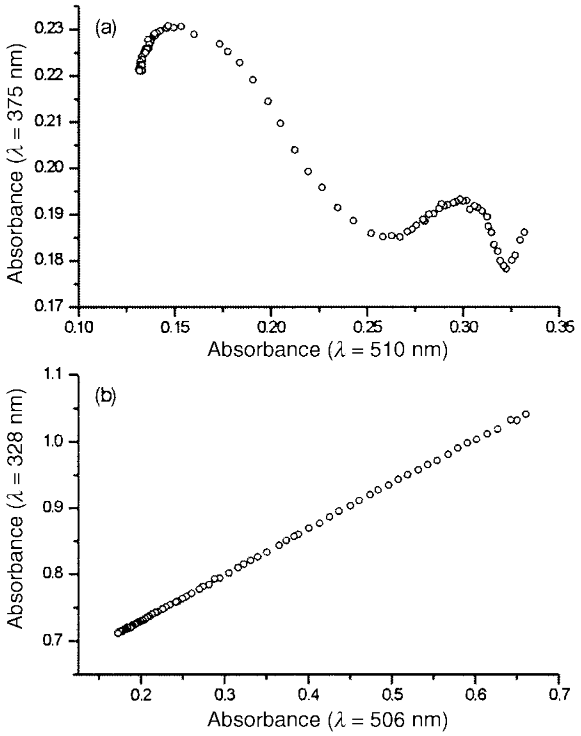


Fig. 5 Absorbance–absorbance diagrams for measurements of A_2-15C5AQN **8** (a) and A15C5AQNOTs **6** (b) with silver(I) perchlorate.

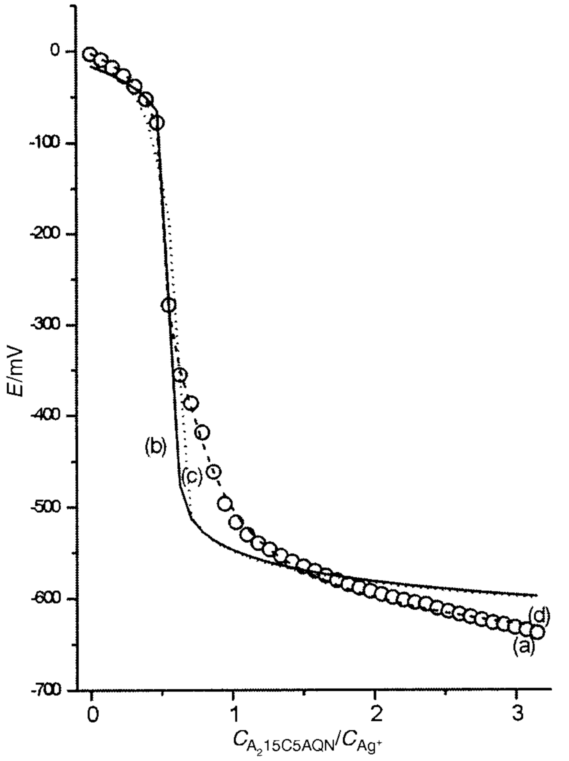


Fig. 6 Potentometric measurement of silver(I) perchlorate (6.00×10^{-4} mol dm^{-3}) with $A_2$15C5AQN **8** (0–2.00×10^{-3} mol dm^{-3}) as a function of molar ratio $C_{A215C5AQN}/C_{Ag^+}$. The experimental points are (a) (open circles) and the fitting curves for the models are 1 (b) (line), 4 (c) (dotted line), 8 (d) (dashed line).

The results of fitting various equilibrium models to the potentiometric data are summarized in Table 3. In contrast to spectrophotometry only the model of four equilibria explains the concentration dependence of the e.m.f. values in terms of the F-test all other models are distinguishable at the 90% significance level from the model containing four complexes: AgL^+, $Ag_2L_3^{2+}$, $Ag_3L_2^{3+}$ and AgL_2^+.

Based on the results of fitting of spectrophotometric (Fig. 4B) and potentiometric data (Fig. 6) it can be concluded that the minimal plausible model contains four complexes: AgL^+, $Ag_2L_3^{2+}$, $Ag_3L_2^{3+}$ and AgL_2^+. It should be noted that only three equilibria, involving AgL^+, $Ag_3L_2^{3+}$ and AgL_2^+ are needed to fit spectrophotometric data. This is caused by the fact that these

Table 4 Stability constants of silver(I) complexes with the crown ethers studied in propylene carbonate at 25 °C

Crown ether	log K_1	log K_2	log β
15C5	6.24 ± 0.03 5.67[24]	1.77 ± 0.03	
15C5meNH$_2$ **1**	9.76 ± 0.07	4.04 ± 0.05	
15C5meAQN **2**	6.08 ± 0.03	2.57 ± 0.03	
A15C5 **3**	9.75 ± 0.04 9.76 ± 0.04[25]	4.77 ± 0.08 4.75 ± 0.03[25]	
A15C5AQN **4**	5.92 ± 0.03	1.55 ± 0.09	
A15C5AQNOH **5**	5.02 ± 0.04		
A15C5AQNOTs **6**	5.90 ± 0.06		
A$_2$15C5 **7**	13.75 ± 0.04 15.6 [16]	3.17 ± 0.03	
A$_2$15C5AQN **8**	11.71 ± 0.04	4.71 ± 0.04	29.72 ± 0.33[a] 31.43 ± 0.18[b]
A$_2$15C5AQNOH **9**	4.98 ± 0.03	4.08 ± 0.03	
A$_2$15C5(AQN)$_2$ **10**	5.59 ± 0.05	1.85 ± 0.24	

[a] Determined for $Ag_3L_2^{3+}$ complex formation. [b] Determined for $Ag_2L_3^{2+}$ complex formation.

two techniques are sensitive to different parameters, *i.e.* the concentration of Ag$^+$ (potentiometry) or to the concentration of various ligand forms (spectrophotometry).

Other structurally reasonable polynuclear complexes, *e.g.* Ag_2L^{2+}, were also considered in the equilibria models but such models gave much poorer fitting than the complexes considered.

Discussion of the obtained stability constants

As indicated in Table 4, for ligand-to-metal ratio equilibrium (1) is dominant.

$$Ag^+ + L \xrightleftharpoons{K_1} AgL^+ \qquad (1)$$

The log K_1 value increases with an increase of the number of nitrogen atoms from 6.24 for 15C5 (1,4,7,10,13-pentaoxacyclopentadecane) to 9.75 (9.76) for A15C5 **3**, 9.76 for 15C5meNH$_2$ **1** and 13.75 for A$_2$15C5 **7**, respectively. It should be noted that the increase of the log K_1 value when passing from the exclusively oxygen-containing crown moiety to the aza-crown is observed regardless of whether the nitrogen atom is incorporated into the macrocycle ring or is attached as a side-arm.

For all unsubstituted crowns log K_2 values were determined for equilibrium (2).

$$AgL^+ + L \xrightleftharpoons{K_2} AgL_2^+ \qquad (2)$$

These values increase when passing from the oxygen 15C5 crown (1.77) to the aza-crown 15C5meNH$_2$ **1** (4.04) and to A15C5 **3** (4.77). For A$_2$15C5 **7**, an apparent decrease of log K_2 (3.17) is observed compared with A15C5 **3**.

Attaching an anthraquinone substituent to the nitrogen atom of A15C5 **3** results in the loss of the capability for the formation of other complexes than those of 1 : 1 type in most cases. This is confirmed not only by the shape of the potentiometric-titration curves but also by the results of spectrophotometric measurements. A bulky aromatic substituent contributes to a remarkable decrease of log K_1 from 9.75 for A15C5 **3** to 5.92 for A15C5AQN **4** which contains an anthraquinone moiety. For A$_2$15C5 **7**, the introduction of the first anthraquinone substituent has a significantly smaller effect on log K_1 compared to the hydroxyquinone substituent.

For A$_2$15C5 **7**, introduction of the anthraquinone substituent diminishes the stability constant by more than two log K_1 units. For the hydroxyanthraquinone substituent the stability constant is diminished by 8.77 logarithmic units, similarly as found for the disubstituted A$_2$15C5AQNOH crown **9**. This dramatic decrease of the stability constant can by attributed to the possibility of the formation of an intermolecular hydrogen bond between the hydroxy group of the anthraquinone moiety and the amino group of the macrocyclic ring. This is supported by the analysis of the IR spectra. For the unsubstituted A$_2$15C5 crown **7**, a sharp 3326 cm^{-1} N–H stretching band is observed. The intensity of this band decreases for A$_2$15C5AQN **8** and the band strongly broadens for A$_2$15C5AQNOH **9** suggesting the formation of an OH · · · NH hydrogen bond.

For crown ethers containing a nitrogen atom in the side chain two complexes: AgL$^+$ and AgL$_2^+$ are observed. It has been suggested that attachment of a non-coordinating side group to the crown ring diminishes the formation constant owing to steric hindrance.[26] However, for the example studied in this work (15C5meAQN **2**), it is observed that the introduction of a side chain to I5C5 only weakly diminishes log K_1 and log K_2 even increases. This suggests that even a relatively bulky anthraquinone group separated from the crown by methylene group does not significantly hinder complex formation.

For A15C5 crown **3**, the second formation constant (log K_2) decreases upon the introduction of an anthraquinone substituent in A15C5AQN **4** and for A15C5AQNOTs **6** and A15C5AQNOH **5**, AgL$_2^+$ complexes are not observed. This indicates that direct substitution of the aza-crown nitrogen by the anthraquinone moiety has a major influence on the stability of different complexes. For diaza-crown-15 the formation of 1 : 2 complexes is enhanced.

It appears that the formation of the AgL$_2^+$ complex in this case may be associated with the coordination of the secondary nitrogen atom at the macrocycle with the silver(I) ion. On the other hand, for 15C5, 15C5meAQN **2** and A15C5AQN **4**, the AgL$_2^+$ complex ion can be formed as a sandwich type complex. For such a putative sandwich structure, the formation constant is evidently smaller (2.57–1.55) compared to complexes in which silver is bonded by a secondary nitrogen atom.

For A$_2$15C5AQN **8** we have additionally observed, by spectroscopic methods, the $Ag_2L_3^{2+}$ and $Ag_3L_2^{3+}$ complexes. The equilibrium model obtained from spectrophotometric measurements has been confirmed by fitting of various models to the potentiometric and spectrophotometric data (Tables 2 and 3).

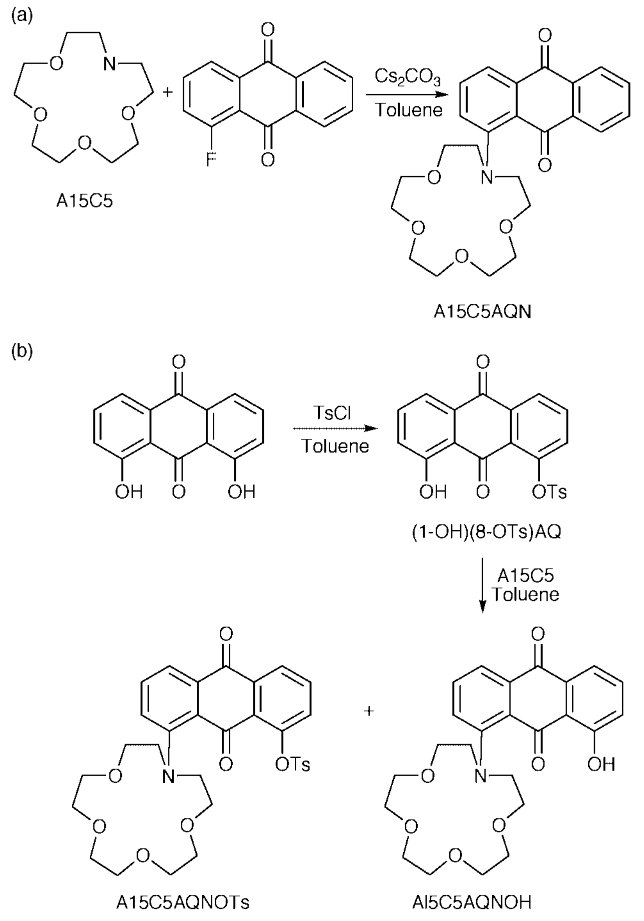
It is very important that the same conclusions regarding the correct equilibrium model have been derived from independent spectrophotometric and potentiometric measurements. Spectrophotometry results depend on the concentration of the ligand whereas potentiometry is dependent on the concentration of the silver ion. The concordance of both models is a very strong argument for the correctness of the derived equilibria.

Experimental

1,4,7,10-Tetraoxa-13-azacyclopentadecane (A15C5; Merck), 1,4,10-trioxa-7,13-diazacyclopentadecane (A$_2$15C5; Merck), 2-(hydroxymethyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (15C5meNH$_2$; Merck) and 1,4,7,10,13-pentaoxacyclopentadecane (15C5; Merck) were used as supplied without purification. Silver(I) perchlorate (Fluka) and tetraethylammonium perchlorate (TEAP; Fluka) were purified as described previously.[27] Propylene carbonate (PC; Merck) was of the highest purity available. Silica gel 60 (<0.03 mm; Merck) and aluminium oxide 90 (Merck) were used for chromatography.

Preparations

The preparation of A15C5AQN is shown in Scheme 1(a). 1-Fluoro-9,10-anthraquinone was obtained in 57% yield, according to a procedure described in the literature.[28] Treatment of this compound with the aza-crown ether A15C5 yields the 1-amino-9,10-dioxo-1-anthryl functionalized crown ether as a deep red oil. 1-Fluoro-9,10-anthraquinone can be replaced with 1-chloro-9,10-anthraquinone. However, in this



Scheme 1 Synthesis of aza-substituted crown ethers.

case the yield of the product with A15C5 is lower and more by-products are obtained. Application of a similar synthetic procedure to diaza crown ethers yields mono- and di-arm substituted crown ethers: $A_2$15C5AQN and $A_2$15C5(AQN)$_2$. Additional chromatographic purification of the crude products yields an easily soluble oil ($A_2$15C5AQN) or deep red crystals [$A_2$15C5(AQN)$_2$]. 15C5meAQN was synthesized in a similar manner from 15C5meNH$_2$ and 1-fluoro-9,10-anthraquinone. A15C5AQNOH was synthesized through the reaction of 1-tosyloxy-8-hydroxy-9,10-anthraquinone with the crown ether. The synthesis always gives two products, A15C5AQNOH as the main product (78% yield) and A15C5AQNOTs (8% yield) as the minor product [Scheme 1(b)].

The synthesis of A15C5AQNOH can also be carried out using the 1,8-ditosyl derivative of the 1,8-dihydroxyanthraquinone 1,8-(TsO)$_2$AQN. This gives A15C5AQNOTs which on hydrolysis in alcoholic KOH solution yields A15C5AQOH. However, this alternative method is less convenient and results in a lower yield of the final product.

(i) 13-(9,10-Dioxo-1-anthryl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (A15C5AQN). 1,4,7,10-Tetraoxa-13-azacyclopentadecane (A15C5) (1.0 g, 4.57 mmol), caesium carbonate (1.6 g, 4.90 mmol) and 1-fluoro-9,10-anthraquinone (1.1 g, 4.86 mmol) in 10 ml toluene were stirred and heated at 80 °C for 48 h. After cooling to the room temperature, the insoluble solid was filtered off. The solution was evaporated under vacuum, purified by column chromatography on silica gel [dichloromethane–methanol (50:2), $R_f = 0.32$] to give A15C5AQN as a red viscous oil (1.32 g, 68%) (Found: C, 67.79; H, 4.43; N, 3.23. Calc. for $C_{24}H_{27}NO_6$: C, 67.76; H, 4.32; N, 3.29%); $\delta_H(CDCl_3)$ 2.4–3.8 (24H, m) and 7.45–8.20 (7H, m).

(ii) 7-(9,10-Dioxo-1-anthryl)-1,4,10-trioxa-7,13-diazacyclopentadecane ($A_2$15C5AQN) and 7,13-bis(9,10-dioxo-1-anthryl)-1,4,10-trioxa-7,13-diazacyclopentadecane [$A_2$15C5(AQN)$_2$]. A mixture of 1 g (4.59 mmol) of 1,4,10-trioxa-7,13-diazacyclopentadecane ($A_2$15C5) 1.742 g (7.7 mmol), of 1-fluoro-9,10-anthraquinone and 2.55 g (7.8 mmol) of caesium carbonate was suspended in 15 ml of toluene, stirred and kept at 80 °C for 24 h. After cooling to the room temperature the insoluble solids were removed by filtration and the filtrate concentrated. The residual crude oil was purified by column chromatography on aluminum oxide (dichloromethane–methanol 50:4) to give $A_2$15C5(AQN)$_2$ (red solid) as the main fraction ($R_f = 0.49$, 0.068 g, 7%) (Found: C, 62.49; H, 5.48; N, 4.53. Calc. for $C_{38}H_{34}N_2O_7$: C, 62.38; H, 5.40; N, 4.44%). $\delta_H(CDCl_3)$ 3.4–3.8 (20H, m) and 7.45–8.20 (14H, m). $A_2$15C5AQN was obtained as the second fraction ($R_f = 0.22$); (0.662 g, 61%) (Found: C, 67.79; H, 6.49; N, 6.63. Calc. for $C_{24}H_{28}N_2O_5$: C, 67.92; H, 6.60; N, 6.60%). $\delta_H(CDCl_3)$ 2.9 (4H, s), 3.4–3.8 (19H, m) and 7.45–8.20 (7H, m).

(iii) 13-[8-Hydroxy-9,10-dioxo-1-anthryl]-1,4,7,10-tetraoxa-13-azacyclopentadecane (A15C5AQNOH). 1 g (4.56 mmol) of A15C5 and 2.23 g (5.65 mmol) of 1-OH(8-OTs)-AQ were dissolved in 200 ml of toluene and the mixture was heated to 80 °C for 24 h. The reaction mixture was cooled to room temperature and then concentrated *in vacuo* and the residue chromatographed on a silica gel [dichloromethane–methanol (50:1)]. A15C5AQNOH was obtained as a red solid ($R_f = 0.48$, 0.966 g, 48%) (Found: C, 65.52; H, 6.27; N, 3.15. Calc. for $C_{24}H_{27}NO_7$: C, 65.29; H, 6.16; N, 3.17%). $\delta_H(CDCl_3)$ 3.6–3.8 (20H, m), 7.4–8.0 (6H, m) and 13.0 (1H, s).

(iv) 7-(8-Hydroxy-9,10-dioxo-1-anthryl)-1,4,10-trioxa-7,13-diazacyclopentadecane ($A_2$15C5AQNOH). $A_2$15C5AQN was prepared by the same method as used for the synthesis of A15C5AQNOH. The final product was separated by a column chromatography on silica gel (dichloromethane–methanol 50:2) to give $A_2$15C5AQNOH as a red oil ($R_f = 0.15$, 21%) (Found: C, 65.51; H, 6.52; N, 6.35. Calc. for $C_{24}H_{28}N_2O_6$: C, 65.44; H, 6.40; N, 6.36%). $\delta_H(CDCl_3)$ 2.93 (4H, s), 3.4–3.8 (16H, m), 7.45–8.2 (7H, m) and 13.0 (1H, s).

(v) 13-(8-Tosyloxy-9,10-dioxo-1-anthryl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (A15C5AQNOTs). 0.56 g (2.56 mmol) of A15C5 and 1.40 g (2.56 mmol) of 1,5-(TsO)$_2$(AQN) were dissolved in 10 ml of toluene. The mixture was stirred and heated to 100 °C for 24 h. The reaction mixture was dissolved in water–dichloromethane (1:1, 100 ml). After separations, the organic phase was dried over $MgSO_4$ and the main product was purified by column chromatography on aluminum oxide [CH_2Cl_2–methanol (50:1)]. A15C5AQNOTs was obtained as a red solid ($R_f = 0.55$, 0.715 g, 47%) (Found: C, 62.72; H, 5.66; N, 2.39. Calc. for $C_{31}H_{33}NO_9S$: C, 62.51; H, 5.58; N, 2.35%). $\delta_H(CDCl_3)$ 2.4 (3H, s), 3.5–3.8 (20H, m) and 7.25–8.25 (10H, m).

(vi) 2-[*N*-(9,10-Dioxo-1-anthryl)aminomethyl]-1,4,7,10,13-pentaoxacyclopentadecane (15C5meAQN). 2-(Aminomethyl)-15-crown-5 (1 g, 4.0 mmol), 1-fluoro-9,10-anthraquinone (1.03 g, 4.56 mmol) and caesium carbonate (1.5 g, 4.6 mmol) were dissolved in 10 ml toluene and the mixture heated to 80 °C for 48 h. After cooling to room temperature the insoluble solid was removed by filtration and the filtrate was concentrated. The residue was separated by a column chromatography on aluminum oxide [dichloromethane–methanol (500:1)]. 15C5meAQN was obtained as a red solid ($R_f = 0.21$, 1.252 g, 69%) (Found: C, 65.62; H, 3.07; N, 6.42. Calc. for $C_{25}H_{29}NO_7$: C, 65.45; H, 3.09; N, 6.38%). $\delta_H(CDCl_3)$ 2.0–2.2 (2H, m), 3.2–3.8 (20H, m) and 7.45–8.2 (7H, m).

(vii) 1,8-Bis(tosyloxy)-9,10-anthraquinone (1,8-(TsO)$_2$AQN). 5.09 g (21.1 mmol) of 1,8-dihydroxy-9,10-anthraquinone and 5.32 g (27.9 mmol) of *p*-toluenesulfonyl chloride (tosyl chloride) was dissolved in 200 ml dichloromethane. 15 ml triethylamine in 100 ml dichloromethane was added dropwise to the solution over 5 h. The course of the reaction was followed by TLC [SiO_2, dichloromethane–light petroleum (bp 40–60 °C) (1 : 1)] and was complete after 5–6 h. The reaction mixture was washed with water (3 × 50 ml) and the organic phase dried with $MgSO_4$. After evaporating the solvent the residue was separated by column chromatography on silica gel [dichloromethane–light petroleum (100 : 85)]. 1,8-diOTs-AQ was obtained as orange crystals (3.29 g, 25%) (Found: C, 61.42; H, 3.69; N, 11.72. Calc. for $C_{28}H_{20}O_8S_2$: C, 61.31; H, 3.67; N, 11.69%). $\delta_H(CDCl_3)$ 2.4 (6H, s), 7.4 (8H, dd) and 7.5–8.3 (6H, m).

(viii) 1-Hydroxy-8-tosyloxy-9,10-anthraquinone (1-OH-8-TsOAQN). 5.09 g (21.1 mmol) of 1,8-dihydroxy-9,10-anthraquinone and 5.32 g (27.9 mmol) of *p*-toluenesulfonyl chloride were dissolved in 200 ml dichloromethane. 15 ml triethylamine in 100 ml dichloromethane was added dropwise to the solution over 0.5 h and the reaction continued for 20 h at a room temperature. The reaction mixture was washed with water (3 × 50 ml) and dried with $MgSO_4$. After evaporation of the solvent the residue was separated by a column chromatography on silica gel with dichloromethane–light petroleum (1 : 1) and subsequently with dichloromethane–methanol (10 : 1). 1-OH-8-OTsAQN $C_{21}H_{14}O_6S$ (MW 394.4) was obtained as a yellow solid (4.93 g, 59%). $\delta_H(CDCl_3)$ 2.40 (3H, s); 7.3–7.4 (4H, m), 7.8–8.5 (6H, m) and 12.0 (1H, s).

Potentiometric measurements

Potentiometric titrations were performed in propylene carbonate at 25 °C using an OP-205 Radelkis pH-meter linked to a personal computer *via* a PCL-838 control card. The solvent was used as purchased without further purification. Silver(I) ion solutions were prepared from the perchlorate salt with concentrations in the range 5–8 × 10^{-4} mol dm^{-3}. Concentrations of ligands were in the range 5.0 × 10^{-3}–1.0 × 10^{-2} mol dm^{-3}. Measurements were performed using a 0.5 ml Hamilton micro–syringe equipped with a Gauge 30 tin tube. The half-cells were connected by a salt bridge filled with 0.1 mol dm^{-3} tetraethylammmonium perchlorate dissolved in the solvent. The silver concentration during titrations was determined using silver-wire electrodes dipped in the solution. For poorly soluble ligands an inverted titration technique was used.[26] In this technique solutions of ligands with concentrations in the range 1–5 × 10^{-4} mol dm^{-3} and a small amount of silver ion were titrated by solutions of silver perchlorate with concentrations in the range 8 × 10^{-4}–5 × 10^{-3} mol dm^{-3}.

Stability constants for AgL^+ and AgL_2^+ complexes were determined as log K_1 and K_2 [eqns. (1) and (2)].

$$\mathrm{Ag^+ + L \overset{K_1}{\rightleftharpoons} AgL^+} \tag{1}$$

$$\mathrm{AgL^+ + L \overset{K_2}{\rightleftharpoons} AgL_2{}^+} \tag{2}$$

The equilibrium constants for the additional complexes: $Ag_3L_2{}^{3+}$ and $Ag_2L_3{}^{2+}$ were expressed as overall stability constants, [eqns. (3) and (4)]:

$$\mathrm{3Ag^+ + 2L \overset{\beta Ag_3L_2}{\rightleftharpoons} Ag_3L_2{}^{3+}} \tag{3}$$

$$\mathrm{2Ag^+ + 3L \overset{\beta Ag_2L_3}{\rightleftharpoons} Ag_2L_3{}^{2+}} \tag{4}$$

The equilibrium constants were calculated using the program STOICHIO based on the non-linear least-squares Gauss–Newton–Marquardt algorithm.[29–31]

Spectroscopic measurements

UV–VIS spectra were recorded using a Varian CARY 3E spectrometer at 25 °C. Solvents were used as purchased without further purification but their purity was verified by measuring the absorption spectra in the range 220–800 nm. Solutions of the crown ethers were prepared by solubilization of the crown ether in propylene carbonate at concentrations of 8 × 10^{-5}–4 × 10^{-4} mol dm^{-3}. Solutions of silver(I) ion were prepared from the perchlorate salt at concentrations of 8 × 10^{-4}–6 × 10^{-3} mol dm^{-3}. The concentration of the ligands was the same in both solutions. Measurements were performed manually using a micro-screw with 0.5 ml Hamilton micro-syringe equipped with a Gauge 30 tube. Magnetic stirrers employing a counter-shaft inside the spectrometer were used during measurements.

All spectra data were obtained in a digital form and subsequently transferred into a worksheet. Measurement graphs were plotted and equilibrium constants were calculated if possible.[32] The program STOICHIO[30,31] based on the non-linear least squares Gauss–Newton–Marquardt algorithm was used to fit the parameters of the equilibrium models.

Other measurements

The ^1H NMR spectra were recorded at 400 MHz using a Varian Mercury 400BB spectrometer. Chemical shifts were obtained on $CDCl_3$ solution relative to Me_4Si unless stated otherwise. IR spectra were recorded on a Bruker IFS 66 spectrometer. Spectra of solid samples were taken as Nujol and hexachlorobutadiene mulls. Elemental analysis was performed on a Carbo Erba Elemental Analyzer MOD 1106.

Acknowledgements

The authors thank Dr A. Liwo for helpful discussions concerning the modeling of equilibria. This work was supported by grants BW- 8000-5-0308-9 and PB 026/T09/97/12 from the Polish State Committee for Scientific Research (KBN).

References

1 R. M. Izatt, J. S. Bradshaw, S. A. Nelsen, J. D. Lamb and J. J. Christiansen, *Chem. Rev.*, 1985, **85**, 271.
2 C. J. Pedersen, *J. Am. Chem. Soc.*, 1970, **89**, 386.
3 C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017.
4 C. J. Pedersen and H. K. Frensdorf, *Angew. Chem.*, *Int. Ed. Engl.*, 1972, **11**, 16.
5 F. P. van Remoortere and F. P. Boerg, *Inorg. Chem.*, 1974, **13**, 2071.
6 N. S. Poonia, *J. Am. Chem. Soc.*, 1976, **96**, 107.
7 A. Thaler, R. Bergter, T. Ossowski, B. G. Cox and H. Schneider, *Inorg. Chim. Acta*, 1999, **285**, 1.
8 H.-J. Buschmann, in *Stereochemical and Stereophysical Behaviour of Macrocycles*, ed. I. Bernal, Elsevier, Amsterdam–Oxford–New York–Tokyo, 1987, vol. 2, p. 103.
9 M. Takagi, in *Cation Building by Macrocycles*, ed. Y. Inoue and G. W. Gokel, Marcel Dekker, New York, 1990, p. 464.
10 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 5th edn., 1988, p. 941.
11 T. A. Kaden, *Pure Appl. Chem.*, 1993, **65**, 1473.
12 G. W. Gokel, *Chem. Soc. Rev.*, 1992, **21**, 39.
13 H. C. Loehr and F. Voegtle, *Chem. Ber.*, 1985, **118**, 914.
14 E. Weber, in *Crown Ethers and Analogs*, ed. S. Patai and Z. Rappoport, Wiley, New York, 1989, p. 305.
15 Y. Katayama, R. Fukuda and M. Takagi, *Anal. Chim. Acta*, 1986, **185**, 295.
16 Y. Katayama, K. Nita, M. Ueda, M. Nakamura and M. Takagi, *Anal. Chim. Acta*, 1985, **173**, 193.
17 Y. Katayama, R. Fukuda, T. Iwasaki, K. Nita and M. Takagi, *Anal. Chim. Acta*, 1998, **204**, 113.
18 G. W. Gokel and I. E. Trafton, in *Cation Building by Macrocycles*, ed. Y. Inoue and G. W. Gokel, Marcel Dekker, New York, 1990, p. 253.
19 H. Inuone, T. Hoshi and Y. Tanizaki, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1018.
20 Z. Yoshiba and F. Takabyashi, *Tetrahedron*, 1968, **24**, 933.

21 J. Polster and H. Lachman, in *Spectroscopic Titration. Analysis of Chemical Equilibria*, VCH, Weinheim–Basel–Cambridge, New York, 1989.
22 J. Czerminski, in *Statistical Methods in Applied Chemistry*, Elsevier, Amsterdam–New York–Tokyo, 1990.
23 G. A. F. Seber and C. J. Wild, in *Nonlinear Regression*, Wiley, New York, 1989, p. 228.
24 M.-C. Almasio, F. Arnaud-Neu and M.-J. Swing-Weill, *Helv. Chim. Acta*, 1983, **66**, 1296.
25 T. Burchard, B. G. Cox, P. Firman and H. Schneider, *Ber. Bunsenges Phys. Chem.*, 1994, **98**, 1526.
26 B. G. Cox and H. Schneider, in *Coordination and Transport Properties of Macrocyclic Compounds in Solution*, Elsevier, Amsterdam, 1992.
27 D. D. Perrin and W. L. F. Armari, in *Purification of Laboratory Chemicals*, Pergamon Press, New York, 1988.
28 G. Valanas and H. Fopff, *J. Org. Chem.*, 1962, **27**, 3680.
29 D. W. Marquardt, *J. Soc. Ind. Appl. Math.*, 1963, **11**, 431.
30 J. Kostrowicki and A. Liwo, *Comput. Chem.*, 1987, **11**, 195.
31 J. Kostrowicki and A. Liwo, *Talanta*, 1990, **37**, 645.
32 P. J. Legett, in *Computational Methods for the Determination of Formation Constants*, Plenum Press, New York–London. 1985.

Paper a908585h