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ORIGINAL ARTICLE

Stability constants of complexes formed by new Schiff-base lariat ethers derived from 4,13-diaza-18-crown-6 with Ag^{+}, Pb^{2+}, Cu^{2+} cations determined by competitive potentiometry

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Abstract The stability of complexes formed by a series of Schiff-base lariat ethers, derived from 4,13-diaza-18-crown-6, **1** with Ag^{+}, Pb^{2+}, Cu^{2+} cations, has been comparatively determined, in methanol: dichloromethane solution. We present here the synthesis and an interesting competitive potentiometry method useful for the stability constant determination for a new family of Schiff-base bibracchial lariat ethers. The stability constants and the selectivity in competitive complexation of Ag^{+}, Pb^{2+} and Cu^{2+} cations by macrocyclic receptors **1–7** (L), can be accurately evaluated and species distribution diagrams can be calculated for individual system. In all cases further functionalization of bibracchial lariat ethers **2–7** is accompanied by an increasing of the selectivity, relative to the complexes of the initial 4,13-diaza-18-crown-6 macrocycle **1**.

Keywords Lariat-ethers · 4,13-diaza-18-crown-6 · Stability constants · Selective complexation · Competitive potentiometry

Introduction

Molecular design plays a major role in the development of a variety of host receptors, self assembled molecules, molecular devices, etc. The chemistry of macrocyclic receptors and their supramolecular complexes [1–4] has been extensively developed during last four decades with the hope of developing the "preorganization" concept for targeting inorganic and organic guests like cations, anions or molecules of specific interest [5–7]. Consequently, the design and application of new macrocyclic receptors capable of constitutional coordination of guest molecules and ions, has attracted a great deal of interest as these systems have many potential functions such as solubilization, extraction, membrane transport [8–13] with applications in separation, chromatography, electrochemistry and spectrophotometry methods [14–16]. The stability and selectivity of host-guest supramolecular complexes have been firstly obtained by dimensional complementarity between macrocyclic cavity and the diameter of complexed cation, achieved by "tail synthesis". New strategies in the design and synthesis of novel functionalized macrocyclic receptors capable of self-organization and self-assembly [17–21] have been developed with the hope of improving the recognition and selective transport functions [22–23]. Crown ethers, cyclic peptides, oligoesters, bola-amphiphiles and heteroditopic receptors have been arisen, in this context [24–31].

Gokel and co-workers made the first pioneering examples and they provided useful insights in the field of lariat crown-ethers [32–34]. Their studies are confined to the macrocyclic crown-ethers decorated with one or two-identical covalently attached sidearms.

We are interested in the possibility to use lariat crown-ethers bearing reversible connections between macrocyclic moiety and functional side arms. The Schiff-base bibracchial lariat ethers have been recently synthesized [35–37] and they provided a remarkable selectivity as for different metallic ions [38–41]. They are particularly attractive in

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view of the easy synthetic accessibility and their role and potential for application in both biological-medicinal and materials sciences. Even if several studies have shown the absence of an obvious lariat effect in complexation of metallic cations [42] their ability and selectivity in binding of cations guest have been assigned [43, 44]. We therefore decided to synthesize and to study an extended series of new Schiff-base bibracchial lariat ethers **3–7**, derived from 4,13-diaza-18-crown-6, **1** (Fig. 1) which were surveyed for their ability to complex Ag^+, Pb^{2+} and Cu^{2+} cations.

Complexation phenomena in macrocyclic chemistry can by characterized by various physical methods. They offer insights into origin of supramolecular functions and stability constant determination [45–47] and could provide useful information in order to predict potential applications such us selective transport, analytical quantification and sensing [48, 49]. In the present work, the results obtained are reported and discussed regarding the stability of complexes formed by seven receptors from that family derived from 4,13-diaza-18-crown-6, **1**. The presence of silver cation in the series of studied cations has allowed us the determination of the stability constants of the complexes by competitive potentiometry by reporting to metallic silver electrode.

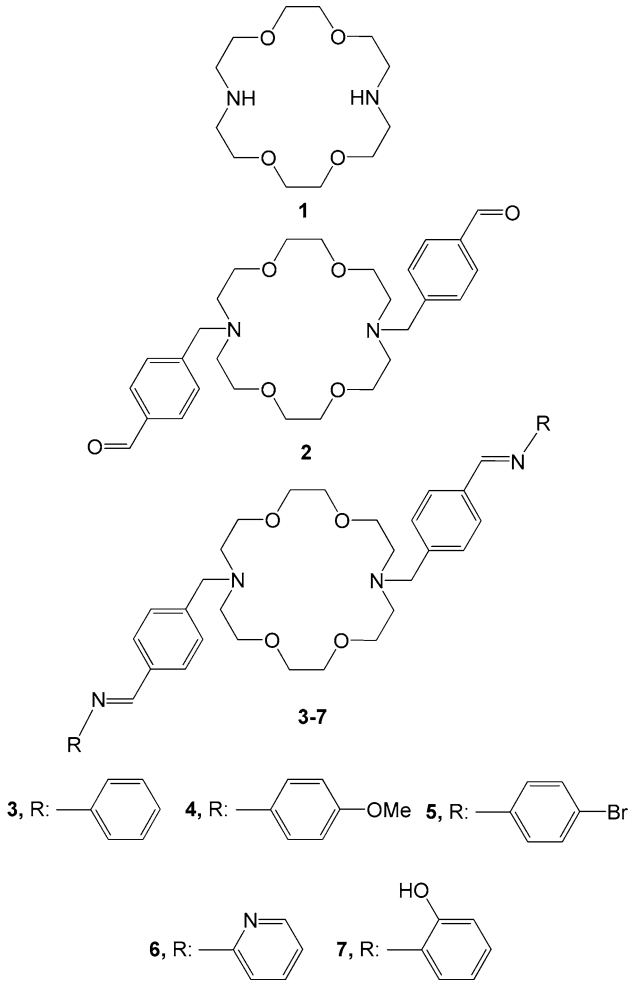

Fig. 1 Lariat ethers derived from 4,13-diaza-18-crown-6

Experimental

Methods and materials

Solvents and starting materials were obtained from commercial suppliers and used without further purification. ^{1}H NMR, ^{13}C NMR spectra were recorded at 300 MHz in $CDCl_3$ or CD_3CN on an ARX Bruker spectrometer. Mass spectrometric studies were performed in the positive ion mode using a quadrupole mass spectrometer (Micromass, Platform 2+). Samples ($\sim 10^{-4}$ M) dissolved in acetonitrile or methanol and were continuously introduced into the mass spectrometer at a flow rate of 10 mL min^{-1} through a Waters 616 HPLC pump. The temperature (60 °C) and the extraction cone voltage (V_c = 5–10 V) were usually set to avoid fragmentations.

Preparation of [*N*,*N*′-Bis(*p*-methylbenzaldehyde)-4,13-diaza-18-crown-6], **2**

4,13-diaza-18-crown-6 (0.500 g, 1.906 mmol), *p*-bromomethylbenzaldehyde (0.758 g, 3.812 mmol) and Na_2CO_3 (0.505 g, 4.765 mmol) was heated at reflux in MeCN (20 mL) for 24 h. The mixture was cooled to room temperature, filtered and concentrated in vacuum, and residue was taken up in CH_2Cl_2 (100 mL) and washed with H_2O (3 × 20 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated again in vacuum to afford an yellow oil. After 4 days a light yellow solid was isolated as a pure compound **2** (0.8554 g, 90% yield). ^{1}H-NMR ($CDCl_3$, ppm) δ = 2.8 (t, 8H, OCH_2CH_2N, ^3J = 5.4 Hz), 3.59 (m, 16H, N–CH_2–CH_2–O, OCH_2CH_2O), 3.75 (s, 4H, N–CH_2–C aryl), 7.50 (d, 4H, CH aryl, ^3J = 7.5 Hz), 7.77 (d, 4H, CH_2 aryl, ^3J = 6.9 Hz), 9.94 (s, 2H, CH=O). ^{13}C-NMR (CD_3CN, ppm) δ = 53.59, 58.70, 69.02, 69.81, 128.72, 128.88, 134.99, 147.41, 191.78; ES-MS: m/z (%): 499.36 (100) [**2**H]$^+$

General procedure for preparation of Schiff-base lariat ethers, **3–8**

The ligands **3–8** were obtained as following: Equivalent amounts of *N*,*N*′-Bis(*p*-methylbenzaldehyde)-4,13-diaza-18-crown-6 (0.100 g, 0.2 mmol) and 0.4 mmol of each different amines (0.0372 g aniline, 0.0492 g *p*-anisidine,

0.0688 g 4-bromoaniline, 0.0376 g 3-aminopyridine, 0.0436 g 2-aminophenol, 0.4 mmol) was heated at reflux in CH_3CN (8 mL) for 4 h. The mixtures were cooled and the crude products were crystallized from acetonitrile to give **3** (0.0663 g, 51% yield), **4** (0.0713 g, 50% yield), **5** (0.0400 g, 25% yield), **6** (0.0540 g, 41% yield), **7** (0.0865 g, 63%).

Compound **3** ^{1}H-NMR ($CDCl_3$, ppm) δ = 2.82 (t, 8H, OCH_2CH_2N, ^3J = 5.4 Hz), 3.62 (m, 16H, $–CH_2–CH_2–O$, OCH_2CH_2O), 3.75 (s, 4H, $N–CH_2–C$), 7.18 (m, 6H, CH), 7.37 (t, 4H, ^3J = 7.5 Hz), 7.44 (d, 4H, ^3J = 7.5 Hz), 7.815 (d, 4H, ^3J = 7.5 Hz), 8.41 (s, 2H, CH imine). ^{13}C-NMR (CD_3CN, ppm) δ = 53.47, 58.70, 68.99, 69.76, 120.33, 125.33, 128.01, 128.72, 134.66, 151.65, 159.91, 178.10, 201.31; ES-MS: m/z (%): 649.50 (100) $[\mathbf{3}^*H]^+$

Compound **4** ^{1}H-NMR ($CDCl_3$, ppm) δ = 2.82 (t, 8H, OCH_2CH_2N, ^3J = 5.4 Hz), 3.62 (m, 16H, $–CH_2–CH_2–O$, $OCH_2\ CH_2O$), 3.73 (s, 4H, $N–CH_2–C$), 3.81 (s, 6H, OCH_3), 6.91 (d, 4H, CH aryl 2, ^3J = 8.7 Hz), 7.20 (d, 4H, ^3J = 8.7 Hz), 7.43 (d, 4H, ^3J = 7.5 Hz), 7.80 (d, 4H, ^3J = 7.5 Hz), 8.44 (s, 2H, CH imine); ^{13}C-NMR (CD_3CN, ppm) δ = 48.47, 53.49, 54.63, 58.76, 68.99, 69.77, 113.88, 121.71, 27.75, 128.65, 134.95, 144.33, 157.72, 157.84, 211.79. ES-MS: m/z (%): 709.62 (100) $[\mathbf{4}^*H]^+$

Compound **5** ^{1}H-NMR ($CDCl_3$, ppm) δ = 2.82 (t, 8H, OCH_2CH_2N, ^3J = 5.4 Hz), 3.62 (m, 16H, $–CH_2–CH_2–O$, OCH_2CH_2O), 3.73 (s, 4H, $N–CH_2–C$), 7.05 (d, 4H, ^1J = 8.7 Hz), 7.48 (d, 8H, ^1J = 8.4 Hz), 7.80 (d, 4H, CH aryl 1, ^1J = 7.8 Hz), 8.38 (s, 2H, CH imine); ^{13}C-NMR (CD_3CN, ppm) δ = 51.15, 53.47, 69.55, 70.25, 118.73, 122.09, 128.36, 128.70, 129.29, 131.51, 131.69, 160.09, 206.44; ES-MS: m/z (%): 807.46 (100) $[\mathbf{5}^*H]^+$

Compound **6** ^{1}H-NMR ($CDCl_3$, ppm) δ = 2.82 (t, 8H, OCH_2CH_2N ^3J = 5.4 Hz), 3.62 (m, 16H, $–CH_2–CH_2–O$, OCH_2CH_2O), 3.73 (s, 4H, $N–CH_2–C$), 7.30 (dd, 2H, CH aryl 2, ^3J = 4.8 Hz, ^3J = 8.1 Hz), 7.49 (d, 4H, ^3J = 7.5 Hz), 7.52 (d, 2H, ^3J = 4.8 Hz), 7.84 (d, 4H, ^3J = 7.5 Hz), 8.42 (s, 2H, CH imine), 8.46 (m, 4H). ^{13}C-NMR (CD_3CN, ppm) δ = 53.52, 58.73, 68.99, 69.77, 123.33, 126.87, 128.22, 128.75, 134.33, 142.43, 146.48, 147.33, 161.85, 205.91. ES-MS: m/z (%): 651.55 (100) $[\mathbf{6}^*H]^+$

Compound **7** ^{1}H-NMR ($CDCl_3$, ppm) δ = 2.82 (t, 8H, $OCH_2CH_2N^3$ J = 5.4 Hz), 3.62 (m, 16H, $–CH_2–CH_2–O$, OCH_2CH_2O), 3.73 (s, 4H, $N–CH_2–C$), 6.88 (t, 2H, ^{3} J = 7.5 Hz), 6.99 (d, 2H, ^{3} J = 8.1 Hz), 7.17 (t, 2H, ^{3} J = 7.5 Hz), 7.26 (d, 2H, ^{3} J = 8.1 Hz), 7.47 (d, 4H, ^{3} J = 6.3 Hz), 7.825 (d, 4H, ^{3} J = 7.8 Hz), 8.65 (s, 2H, CH imine); ^{13}C-NMR (CD_3Cl, ppm) δ = 53.54, 59.34, 69.60, 70.29, 114.45, 115.35, 119.59, 128.28, 128.68, 134.16, 135.13, 143.81, 151.78, 156.54, 206.42 ES-MS: m/z (%): 681.58 (100) $[\mathbf{7}H]^+$

Stability constants β_{ML} determination by competitive potentiometry

The stability constants β_{ML} of the complexes formed by the receptors **1–7** with Ag^+, Pb^{2+} and Cu^{2+} cations, are determined by competitive potentiometry and discussed relative to the stability constants of the complexes formed by the macrocycle, 4,13-diaza-18-crown-6, **1** and the functionalized compound **2** with the same cations [48–52].

The ionic strength was kept constant at μ = 0.01 in potentiometric cells (I) and (II) by using $LiNO_3$ (Li^+ and NO_3^- ions being inactive towards all chemical species involved). The junction between the reference electrode and the studied solution was a 0.0 M $LiNO_3$ solution, that maintains the junction potential at the small values and minimize the difference, $\varepsilon_{dI} - \varepsilon_{dII}$ that can be avoided in relation (2). The metallic silver electrode (M25 Ag) and the reference electrode (Saturated calomel electrode K130) were purchased from Radiometer-Copenhagen. Both cells were kept at constant temperature by using a temperature controller FA90, Falc Instruments. The measurements of e.m.f. were carried out at 25 °C ± 0.1, by using a pH Meter, HI 931400, HANNA Instruments with a resolution of 0.1 mV and a precision of ±0.2 mV. The receptors **3–7** were dissolved in a 90:10 (V:V) methanol: dichloromethane mixture. Nitrate salts and the solvents were obtained from commercial suppliers as analytical reagents. The concentrations of stock solutions of Pb^{2+} and Cu^{2+} (5×10^{-4} M) were determined by potentiometric titration using a solution of 4,13-diaza-18-crown-6, **1**, with fixed concentration (1.25×10^{-4} M). The stock solutions freshly prepared for all receptors **3–7** are in the range 5.5×10^{-4} M–6.25×10^{-4} M and were determined by potentiometric titrations using a standard solution of $AgNO_3$ (Titrisol Merck).

Results and discussions

Synthesis of lariat ethers

Six bibracchial imino lariat ethers **2–7** were prepared for studies described here (Fig. 1). We restricted our studies to 4,13-diaza-18-crown-6, **1**, as starting macrocylic compound. The bis-aldehyde bibracchial imino-lariat ether **2** was synthesized in good yield (90%) by refluxing *p*-bromomethylbenzaldehyde and **1** in acetonitrile in the presence of anhydrous Na_2CO_3. Then, compound **2** was treated with the corresponding aromatic amines (aniline **3**, anisidine **4**, *p*-bromo-aniline **5**, pyridine **6** and *o*-aminophenol, **7**), in refluxing acetonitrile at 95 °C/4 h to afford after crystallization, macrocyclic derivatives **3–7**. The ^{1}H, ^{13}C NMR, ESI-MS spectra are in agreement with the proposed formula (see Experimental section)

Determination model for determination of stability constants by competitive potentiometry

The stability constants of the complexes AgL^+, $\beta_{AgL} = [AgL^+]/[Ag^+][L]$, were determined by potentiometric titration of a silver solution with the solutions of receptors **3–7** (L).

The stability constants of the complexes ML^{n+} were calculated based on the general exchange equilibrium of Ag^+ and M^{n+} cations by potentiometric determination of the equilibrium concentrations of Ag^+ cations in the presence of other cations, Pb^{2+} or Cu^{2+}, when a solution of receptor L was added:

$$\beta_{ML} = \frac{[ML^{n+}]}{[M^{n+}][L]}, \quad (M^{n+} = Pb^{2+}, Cu^{2+}), \qquad Ag^+ + ML^{n+} \Leftrightarrow AgL^+ + M^{n+}. \tag{1}$$

For this purpose, two potentiometric cells were used:

$$Ag|Ag^+, M^{n+}||LiNO_3||\text{Electrode of reference}; \quad (I)$$
$$Ag|Ag^+, M^{n+}, L||LiNO_3||\text{Electrode of reference}, \quad (II)$$

with the e.m.f.:

$$E_{(I)} = E_{ref} - (E^0_{Ag/Ag^+} + 0.059 \lg C_{Ag^+}) + \varepsilon_{dI};$$

$$E_{(II)} = E_{ref} - (E^0_{Ag/Ag^+} + 0.059 \lg[Ag^+]) + \varepsilon_{dII}.$$

Introducing the same total concentration C^+_{Ag} and C^{n+}_M in both of cells, the e.m.f., E(I) and E(II), at 25 °C, allowed us, to determinate the free concentration of receptor [L], by using the Olerup concentration function, Ψ_{Ag} [52] as follows:

$$\Psi_{Ag} = \frac{C_{Ag^+}}{[Ag^+]} = 10^{\frac{E_{(I)} - E_{(II)}}{0.059}} = 1 + \beta_{AgL}[L]; \tag{2}$$

$$[L] = \frac{(\Psi_{Ag} - 1)}{\beta_{AgL}}. \tag{3}$$

The mass balances of ligand, Ag^+ and M^{n+} are shown bellow:

$$C_L = [L] + [AgL^+] + [ML^{n+}]; \tag{4}$$

$$C_{Ag} = [Ag^+] + [AgL^+]; \tag{5}$$

$$C_M = [M^{n+}] + [ML^{n+}]. \tag{6}$$

Equations 2 and 3 are substituted in (4)–(6) to yield the Bjerrum concentration function $\tilde{n}_M$ [52],

$$\tilde{n}_M = \frac{[ML^{n+}]}{C_{M^{n+}}} = \frac{\beta_M[L]}{(1 + \beta_M[L])}. \tag{7}$$

Then

$$\beta_M = \frac{\tilde{n}_M}{(1 - \tilde{n}_M)[L]} \tag{8}$$

Finally, the stability constants β_M, were calculated by the appropriate computational program [53], using the relations (2)–(8).

The selectivity of receptors **1–7** in the formation of the complexes ML^{n+} can be estimated by generalizing the equilibrium (1) as follows:

$$M^{n+} + ML^{n+} \Leftrightarrow ML^{n+} + M^{n+}, \tag{1'}$$

with the equilibrium constant,

$$K_{M/M} = \frac{[ML^{n+}][M^{n+}]}{[M^{n+}][ML^{n+}]} = \frac{\beta_{ML}}{\beta_{ML}} = S_{M/M}. \tag{9}$$

The constant $K_{M/M}$ represents "the selectivity" in itself ($S_{M/M}$) of the receptor L in formation of the complexes ML^{n+} and ML^{n+} in the competitive equilibrium (1′).

The Eq. 9 is rearranged in the logarithmic form as follows:

$$\lg S_{M/M} = \lg K_{M/M} = \lg \beta_{ML} - \lg \beta_{ML}. \tag{10}$$

Using Eqs. 7 and 8 it results that the Bjerrumm function, $\tilde{n}_M$, for the 1:1 complexes, is ranged between 0 and 1, and for $\tilde{n}_M = 0.5$, $\beta_M = ([L]_{\tilde{n}=0.5})^{-1}$.

Species distribution diagrams for the complexes formed by a receptor L with a series of cations M^{n+} can simultaneously be generated by plotting $100\tilde{n}_M = f(-\lg[L])$. According to Eq. 10, they are distributed along the x axis with shift values of $\lg S_{M/M}$. Therefore, the percentage of each complex ML^{n+} formed in solution can be determined from this plot for any values of equilibrium concentration [L].

Stability constants of the complexes formed by the receptors **1–7** with Ag^+, Pb^{2+} and Cu^{2+} cations

The stability constants and the selectivity of complexation of Ag^+, Pb^{2+} and Cu^{2+} cations by macrocyclic receptors **1–7** (L), determined by potentiometric titration (AgL^+) and competitive potentiometry (PbL^{2+} and CuL^{2+}) in methanol-dichloromethane 90:10 (V/V), at 25 °C and ionic strength $\mu = 0.01$ ($LiNO_3$) are shown in Tables 1 and 2, respectively.

Species distribution diagram calculated for individual system (compound **4** and Ag^+, Pb^{2+}, Cu^{2+} cations—Fig. 2)

illustrate the effects of competing equilibria offering a suggestive image of the receptor selectivity in complexation of a series of metallic cations. The key features evident in the Fig. 2 are the prediction of the interferences that could be appears in competitive separation processes like extraction or membrane transport and the simultaneous analytical determination of M^{n+} cations.

The stability constants, reported here (Table 1) are in good agreement with directly comparable literature values for similar compounds [53–58]. They depend on the size complementarity between the cation and intermolecular cavity of 4,13-diaza-18-crown-6 macrocycle and for each studied receptors **1–7** varies in the following order: $AgL^{+} > PbL^{2+} > CuL^{2+}$. That feature termed "*macrocyclic effect*", consistent with the dimensional compatibility between the macrocycle and the size of metallic cation [55–60], is accompanied in this case by a "*coordination behaviour*" of the macrocyclic nitrogen atoms. There are some significant differences between the complexation behaviors of the starting compound **1** and the bibracchial lariat ethers **2–7**; the stability constant values are as expectedly low relative to **1**. There must be due to specific structural and sterical effects beyond secondary and less basic tertiary nitrogen atoms of the diaza-18-crown macrocyclic compounds. The available structural evidence in related systems indicate that the functionalization of the nitrogen atoms of the 4,13-diaza-18-crown-6 macrocycle **1** is a balance of low steric and electronic factors in complexation processes of metallic ions by compounds **2–7** [35–41].

However, there are important significant differences in values in the two trend directions between the stability constants (Table 1) and selectivity (Table 2):

– the imine functionalization in the side arms of bibracchial lariat ethers **3–7** is accompanied by an increasing of the stability constants, relative to the complexes of bisaldehyde ligand **2**, suggesting a secondary "*coordination behaviour*" the imino nitrogen complexation of the metallic ions, but there are not significant correlations between this behaviour and stability constants of the complexes formed by **3–7** and Ag^{+}, Pb^{2+}, Cu^{2+} cations;
– compound **7**, containing an ortho-phenolic group shows two interesting features: its stability is the highest one along the three studied Ag^{+}, Pb^{2+}, Cu^{2+} cations and in the case of Ag^{+} cation its stability increases in basic medium, becoming even more stable than the complex formed by 4,13-diaza-18-crown-6 macrocycle **1**. The net result is that the system tends to stabilize towards the "*best possible ortho-complexation behaviour*"; the available structural evidence showing optimal interactions between the ortho-substituents of the second iminoaromatic moiety [35–41]. This interactions are simply amplified in the presence of the more complexant phenolate moiety present in basic solution;
– the selectivity of the receptors **1–7** in complexation of Ag^{+}, Pb^{2+}, Cu^{2+} cations varies in order: $S_{Ag^{+}/Cu^{2+}} \gg S_{Ag^{+}/Pb^{2+}} > S_{Pb^{2+}/Cu^{2+}}$;

Table 1 Stability constants (in the increasing form) of the complexes formed by the receptors **1–7** *i*th Ag^{+}, Pb^{2+}, Cu^{2+}, in MeOH–CH_2Cl_2, 90:10 (V:V), to 25 °C and ionic strength $\mu = 0.01$ ($LiNO_3$)

Ag^{+}		Pb^{2+}		Cu^{2+}	
L	$\lg\beta_{AgL^{+}}$	L	$\lg\beta_{PbL^{2+}}$	L	$\lg\beta_{CuL^{2+}}$
2	8.60 ± 0.09	**7****	6.18 ± 0.26	**2**	5.23 ± 0.21
5	8.87 ± 0.08	**2**	6.60 ± 0.17	**4**	5.43 ±0.24
6	8.88 ± 0.09	**5**	6.79 ± 0.05	**3**	5.56 ± 0.23
3	8.97 ± 0.07	**4**	6.87 ± 0.13	**6**	5.94 ± 0.19
4	9.04 ± 0.04	**6**	6.91 ± 0.17	**5**	5.96 ± 0.13
1	9.12 ± 0.18	**3**	6.97 ± 0.07	**7***	6.07 ± 0.28
7	9.14 ± 0.12	**7**	6.98 ± 0.12	**7**	6.09 ± 0.23
7*	9.30 ± 0.06	**1**	7.72 ± 0.19	**1**	6.75 ± 0.27

* Determined in basic conditions: LiOH (10^{-3} M)

Table 2 The selectivity of complexation of Ag^{+}, Pb^{2+} and Cu^{2+} cations by macrocyclic receptors **1–7**

L	$\lg S_{Ag^{+}/Cu^{2+}}$	$\lg S_{Ag^{+}/Pb^{2+}}$	$\lg S_{Pb^{2+}/Cu^{2+}}$
1	2.37	1.4	0.97
2	3.37	2	1.37
3	3.41	2	1.41
4	3.61	2.17	1.44
5	2.91	2.08	0.83
6	2.94	1.97	0.97
7	3.05	2.16	0.89
7*	3.23	3.12	0.11

* Determined in basic conditions: LiOH (10^{-3}M)

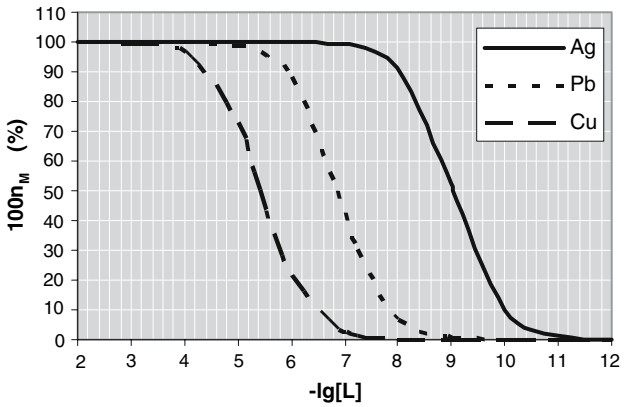

Fig. 2 The chemical speciation diagram (100 $\tilde{n}$ = f(–lg[L]) of the complexes formed by the receptor **4** with Ag^{+}, Pb^{2+}, Cu^{2+} cations

- in all cases further functionalization of bibracchial lariat ethers **2–7** is accompanied by an increasing of the selectivities (Table 2), relative to the complexes of the initial 4,13-diaza-18-crown-6 macrocycle **1**;
- for the pair of Pb^{2+}/Cu^{2+} cations, none of the **1** to **7** receptors present a significant selectivity ($lgS_{Pb^{2+}/Cu^{2+}} \approx 1$);
- for the pair of Ag^{+}/Pb^{2+} cations, only the receptor **7** has a high selectivity for silver versus lead cations ($lgS_{Ag^{+}/Pb^{2+}} = 3.12$) and for the pair of Ag^{+}/Cu^{2+} cations, all receptors **2–7**, excepting **1**, have remarkable selectivity for silver ions versus cooper cations ($lgS_{Ag^{+}/Cu^{2+}} \approx 3$), which recommends them in the further separation processes of these cations by extraction or by the membrane systems.

Conclusions

In summary, we present here the synthesis and the stability constant determination by a competitive potentiometry method for a new family of Schiff-base bibracchial lariat ethers. The stability constants and the selectivity in competitive complexation of Ag^{+}, Pb^{2+} and Cu^{2+} cations by macrocyclic receptors **1–7** (L), can be accurately determined by potentiometry and species distribution diagrams can be calculated for individual system. Our result and analysis at this stage promote the competitive potentiometry method as an interesting tool for quantification of competing species and equilibria in solution, useful for analytical and separations processes. We have emphasized the progressive structural effects affecting the stability of the resulted metal complexes. The stability constants determined in this study are nor surprising as many structural analogs are known. In all cases further functionalization of bibracchial lariat ethers **2–7** is accompanied by an increasing of the selectivity, relative to the complexes of the initial 4,13-diaza-18-crown-6 macrocycle **1**. These investigations prove an obvious lariat effect if the sidearms of the receptors bring additional binding sites for metallic cation. The Schiff-base bibracchial lariat ethers are particularly attractive compounds in view of the very wide range of structural variations available, the easy synthetic accessibility, the control through conditions of yields, rates and reversibility. New similar systems may be used in principle for comparative analytical methods and membrane transport experiments leading to more subtle analyses of these interactions and such studies are under way.

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