

A convenient synthesis of new thiaazacrown ethers and study of their complexation reactions with some transition metal cations in binary acetonitrile–chloroform mixture using the conductometric method

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Received: 9 January 2008 / Accepted: 31 March 2008 / Published online: 6 May 2008
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Abstract Three novel thiaazacrown ethers **1**, **2** and **3** were synthesized in a simple way and in high yield. The complex formation between Ag^+ , Cu^{2+} , Zn^{2+} , Pb^{2+} , Hg^{2+} and Cd^{2+} metal cations with thiaazacrown ethers **1**, **2** and **3** have been studied in acetonitrile:chloroform (1:1) binary solvent system using conductometric technique. The conductance data show that the stoichiometry of the complexes with Ag^+ , Cu^{2+} and Zn^{2+} cations is 1:1 (L:M), but in the case of Pb^{2+} and Hg^{2+} cations, a 1:2 (L:M) complex is formed in solutions. The formation constants of the resulting 1:1 complexes were determined from the molar conductance-mole ratio data at 25 °C. It was found that the stability constants of **1**- Ag^{2+} , **2**- Ag^+ and **3**- Ag^+ complexes are higher than those of their corresponding Zn^{2+} and Cu^{2+} complexes and found to vary in order **3** > **1** > **2** for Ag^+ .

Keywords Crown ethers · Thiaazacrown ethers · Transition metals · Stability constant · Conductivity

Introduction

In recent years, the importance of monitoring the levels of environmental pollutants in water and soil and the need for the recycling of resources and for waste water treatment has generated increasing interest in the designing of new extractants for toxic heavy metals [1]. The ultimate goal is to obtain more and more selective and efficient receptors. These to be used in the extraction of toxic metals from real

matrices containing alkali, alkaline earth and other metal ions that usually accompany mercury.

A number of extractants such as amines [2], trioctylphosphine oxide [3], tributylphosphate [4], octyl(phenyl) *N,N*-diisobutylcarbamoylmethylphosphine oxide [5] and calixarene derivatives [6] have been utilized for the extraction of Hg^{2+} due to its toxic impact on our environments. One of the most important extractants that have been used for extraction of metal ions is crown ethers [7].

Early workers noted that several factors affected the strength and the selectivity of crown ethers toward metal ions [8]. A match between the cavity size of the crown ether and the ionic diameter of the metal ion resulted in high extraction selectivity. Other factors that influence the extraction are the number and the nature of the hetero atoms and substituent groups on the ring [8–11]. According to the characteristics of Hg^{2+} , most of the work has been carried out with macrocyclic with N- or S-donor atoms.

This article reports the synthesis and characterization of new class of crown ether receptors containing both N- and S-donor atoms and to examine their ability to extract Hg^{2+} selectively. The stability constants of the complexes between these ligands and metal ions and their stoichiometries were determined by using the conductometric titration method.

Experimental

Melting points are uncorrected and obtained on electrothermal melting point apparatus. ^1H - and ^{13}C -NMR spectra were recorded on 200 MHz and 50 MHz NMR spectrometers, respectively. Unless otherwise noted, samples were

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dissolved in CDCl_3 . Chemical shifts are reported in ppm relative to TMS used as internal standard. All reagents were of analytical grade and used without further purification. 1,2-Ethanedithiol, 2-mercaptoethyl ether and 2-mercaptoethyl sulfide were obtained from Aldrich; salicylaldehyde was obtained from Lancaster; 1,2-dibromoethane from Merck and anhydrous potassium carbonate from Surechem. Chromatographic separations were carried out on column chromatography using silica gel columns (70–270 mesh, 60 Å) from Aldrich. The solvents were used without further purification.

The following salts were purchased from the companies indicated: AgNO_3 (Degussa), $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich), $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (Aldrich), $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich), $\text{Cd}(\text{ClO}_4)_2$ (Aldrich), $\text{Hg}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ (Aldrich). For the conductivity measurements, acetonitrile and chloroform were used after fractional distillation. The conductivity of the $\text{CH}_3\text{CN}:\text{CH}_2\text{Cl}$ (1:1) was less than $1 \times 10^{-7} \text{ S cm}^{-1}$. Solutions having metal ion concentrations of approximately ($1.00 \times 10^{-4} \text{ M}$) were prepared by dissolving a known mass of each salt in the respective solvent. These solutions were also used as solvents for preparing the crown ethers solutions with concentrations of approximately ($1.500 \times 10^{-3} \text{ M}$). The description of the conductometer and the details of the conductance measurements have been given previously [12]. Compounds **12–14** were prepared according to the literature procedures [13].

Synthesis of 3,4;15,16-dibenzo-1,18-diaza-8,11-dithia-5,14-dioxacycloicosane-1,17-diene (**1**)

In a 250 ml three-necked flask equipped with a magnetic stirrer bar and a reflux condenser, anhydrous K_2CO_3 (0.28 g, 2.00 mmol) was suspended in anhydrous CH_3CN (100 ml). To this well-stirred solution at reflux temperature was added, simultaneously, a solution of dialdehyde **12** (0.40 g, 1.03 mmol) in anhydrous CH_3CN (50 ml), and a solution of ethylene diamine (0.062 g, 1.03 mmol) in anhydrous CH_3CN (50 ml) dropwise over a period of 2 h. The reaction mixture was further refluxed with stirring for another 8 h. The reaction mixture was filtered and the filtrate was evaporated to dryness. The residue was washed with diethyl ether to give crown ether **1** as oily product, yield = 0.42 g (98%), $^1\text{H-NMR}$: $\delta = 2.95$ (s, 4H, $\text{SCH}_2\text{CH}_2\text{S}$), 3.00 (t, $J = 6 \text{ Hz}$, 4H, $\text{OCH}_2\text{CH}_2\text{S}$), 3.97 (s, 4H, $\text{NCH}_2\text{CH}_2\text{N}$), 4.30 (t, $J = 6 \text{ Hz}$, 4H, $\text{OCH}_2\text{CH}_2\text{S}$), 6.85 (d, $J = 4 \text{ Hz}$, 2H), 7.05 (t, $J = 4 \text{ Hz}$, 2H), 7.40 (t, $J = 4 \text{ Hz}$, 2H), 7.95 (d, $J = 4 \text{ Hz}$, 2H), 8.85 (s, 2H, HC=N); $^{13}\text{C-NMR}$: $\delta = 31.1$, 33.0, 64.2, 70.0, 112.5, 121.0, 125.0, 128.0, 132.0, 157.0, 160.0 (C=N); MS: m/z (%): 191.8 (100), 83.1 (98), 118.1 (10), 70.0 (6), 47.0 (85).

Synthesis of 3,4;18,19-dibenzo-1,21-diaza-8,11,14-trithia-5,17-dioxacyclotricosane-1,20-diene(**2**)

In a 100 ml one-necked flask equipped with a magnetic stirrer bar and a reflux condenser, the dialdehyde **13** (0.52 g, 1.10 mmol), ethylene diamine (0.08 g, 1.10 mmol) and anhydrous K_2CO_3 (0.30 g, 2.10 mmol) were mixed in anhydrous CH_3CN (50 ml). The mixture was refluxed for 24 h. The mixture was filtered and the filtrate was evaporated to dryness. The residue was washed with diethyl ether to give crown ether **2** as pale yellow solid, yield = 0.51 g (98%), mp 74 °C; $^1\text{H-NMR}$: $\delta = 2.85$ –3.00 (br, 8H, $\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{S}$), 2.75 (t, $J = 6 \text{ Hz}$, 4H, $\text{OCH}_2\text{CH}_2\text{S}$), 3.97 (s, 4H, $\text{NCH}_2\text{CH}_2\text{N}$), 4.30 (t, $J = 6 \text{ Hz}$, 4H, $\text{OCH}_2\text{CH}_2\text{S}$), 6.85 (d, $J = 4 \text{ Hz}$, 2H), 7.05 (t, $J = 4 \text{ Hz}$, 2H), 7.40 (t, $J = 4 \text{ Hz}$, 2H), 7.95 (d, $J = 4 \text{ Hz}$, 2H), 8.80 (s, 2H, HC=N); $^{13}\text{C-NMR}$: $\delta = 31.1$, 33.0, 34.0, 63.4, 70.2, 111.5, 121.0, 125.0, 128.0, 132.0, 157.0, 158.0 (C=N); MS: m/z (%): 355.9 (5), 281.7 (5), 221.6 (5), 167.4 (5), 149.4 (12), 129.4 (2), 83.3 (7), 73.2 (19).

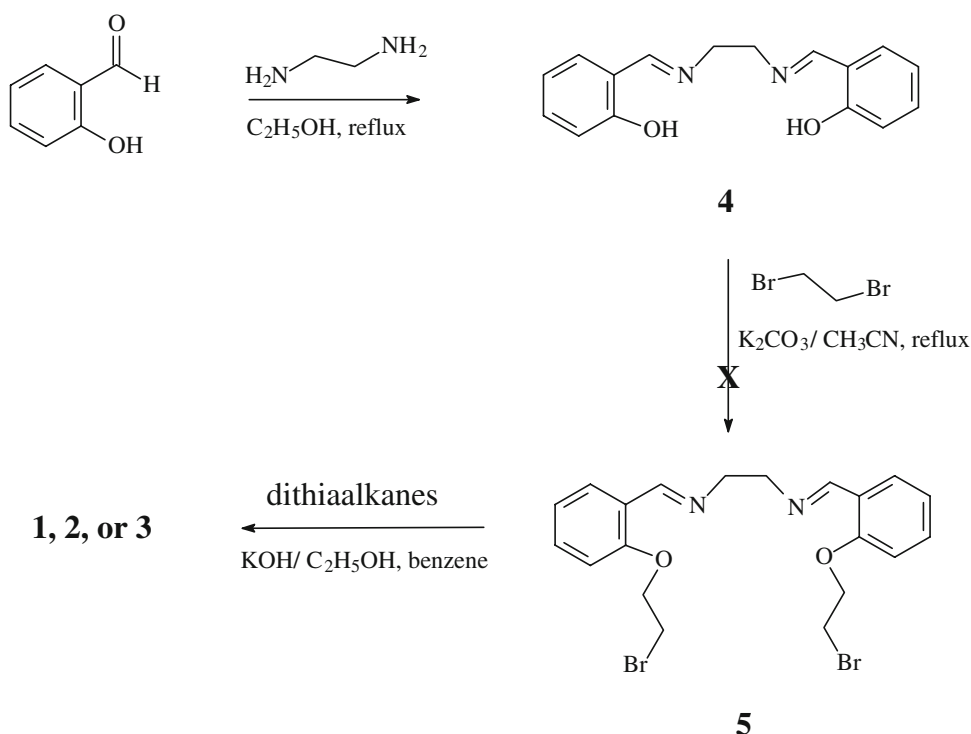
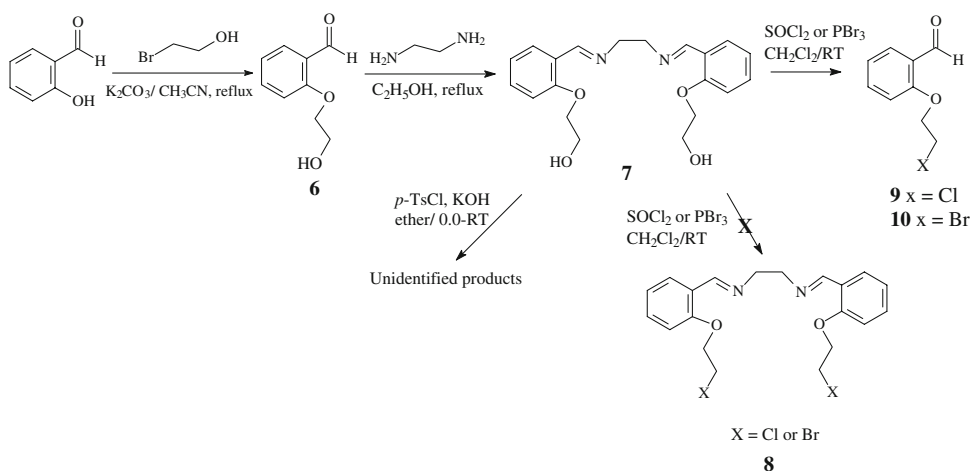
Synthesis of 3,4;18,19-dibenzo-1,21-diaza-8,14-dithia-5,11,17-trioxacyclotricosane-1,20-diene(**3**)

In a 100 ml one-necked flask equipped with a magnetic stirrer bar and a reflux condenser, the dialdehyde **14**, (0.32 g, 0.74 mmol), ethylene diamine (0.044 g, 0.74 mmol) and anhydrous K_2CO_3 (0.12 g, 0.87 mmol) were mixed in anhydrous CH_3CN (50 ml). The mixture was refluxed for 48 h. The mixture was filtered and the filtrate was evaporated to dryness. The residue was washed with diethyl ether to give crown ether **3** as oily product, yield = 0.30 g (75%); $^1\text{H-NMR}$: $\delta = 2.85$ (t, $J = 4 \text{ Hz}$, 4H, $\text{OCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OAr}$), 2.95 (t, $J = 4 \text{ Hz}$, 4H, $\text{OCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OAr}$), 3.65 (t, $J = 4 \text{ Hz}$, 4H, $\text{OCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OAr}$), 3.97 (s, 4H, $\text{NCH}_2\text{CH}_2\text{N}$), 4.25 (t, $J = 4 \text{ Hz}$, 4H, $\text{OCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OAr}$), 6.87 (d, $J = 4 \text{ Hz}$, 2H), 7.05 (t, $J = 4 \text{ Hz}$, 2H), 7.40 (t, $J = 4 \text{ Hz}$, 2H), 7.95 (d, $J = 4 \text{ Hz}$, 2H), 8.80 (s, 2H, HC=N); $^{13}\text{C-NMR}$: $\delta = 31.1$, 33.0, 62.0, 70.0, 72.0, 112.0, 121.0, 125.0, 128.0, 132.0, 158.0, 159.0 (C=N); MS: m/z (%): 256.9 (2), 213.7 (1), 185.6 (2), 167.5 (4), 149.4 (8), 120.3 (9), 83.2 (100).

Results and discussions

Synthesis

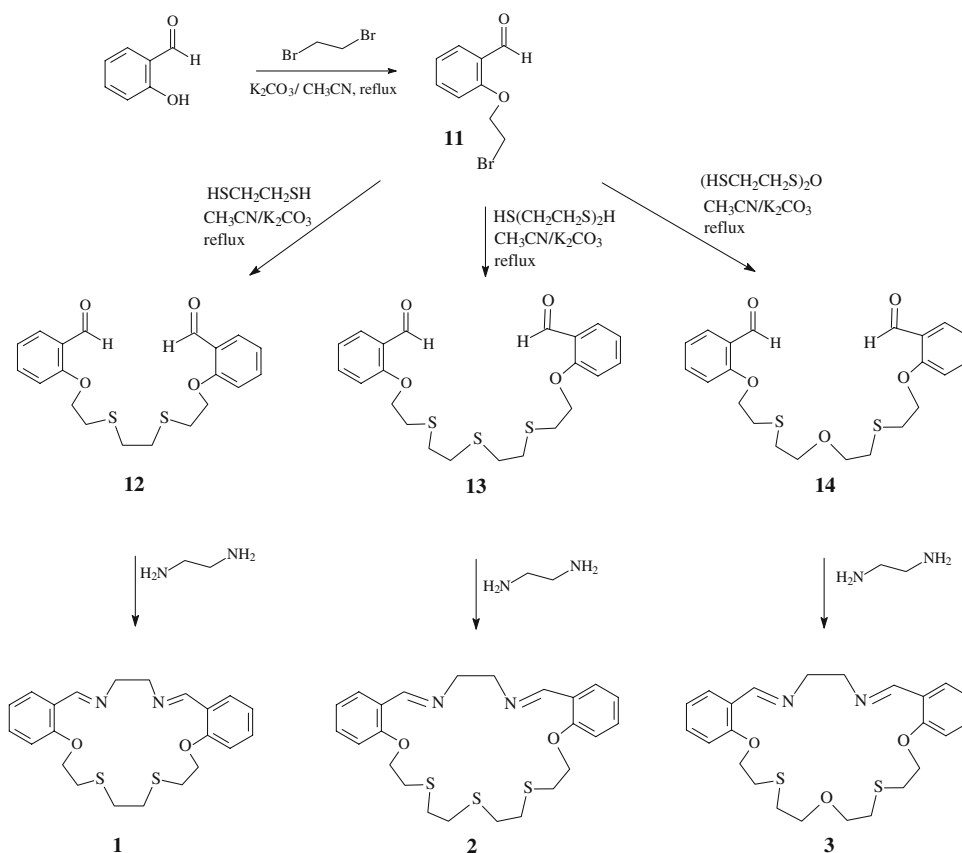
The first synthetic approach investigated toward **1**, **2**, or **3** is outlined in Scheme 1. Diimine **4** was envisioned as being

Scheme 1 Reaction route for preparation of crowns **1**, **2** and **3** via compound **5****Scheme 2** Reaction route for preparation of crowns **1**, **2** and **3** via compound **7**

suitable target precursor compound. However, all attempts at synthesizing **5** by condensation **4** with excess 1,2-dibromoethane were failed to recover only the starting material **4**. Thus, an alternative route (Scheme 2) was applied to prepare the diimine **8** via introducing the hydroxyethyl group first at the phenolic oxygen atom of salicylaldehyde followed by condensation of **6** with ethylenediamine to give **7**. Unfortunately, treatment of **7** with either SOCl_2 or PBr_3 in order to give **8**, produced instead, *o*-(2-chloroethoxy)- or *o*-(bromoethoxy)-1-benzaldehyde **9** and **10**, respectively. Also, treatment of **7** with *p*-toluenesulfonylchloride using KOH or pyridine produced unidentified products. Therefore, a different route to **1**, **2** or

3 was evaluated as shown in Scheme 3. When *o*-(bromoethoxy)-1-benzaldehyde **11** was treated with 1,2-ethanedithiol or 2-mercaptoethyl sulfide or 2-mercaptoethyl ether afforded dialdehyde dimers **12**, **13** and **14**, respectively in very good yields. Fortunately, when these dialdehydes condensed with ethylenediamine in CH_3CN at reflux temperature produced the corresponding target crown ethers **1**, **2** and **3** in excellent yields. Compounds **1**, **2** and **3** were fully characterized, and established to be in cyclic form by the presence of two designated singlet signals in their $^1\text{H-NMR}$ spectra at about δ 4.00 ppm and at δ 8.85 ppm due to $(=\text{NCH}_2\text{CH}_2\text{N}=\text{N})$ and to $(\text{ArCH}=\text{N})$, respectively.

Scheme 3 Preparation of crowns **1**, **2** and **3** via condensation of compounds **12**, **13** and **14** with ethylenediamine



Complexation studies

In principle, measurements of the variation of electrical conductance with the concentration of metal salts and receptors can determine the strength, stoichiometry and stability constants of complex formation and to assess the nature of the interactions taking place. We employed such measurements to establish the stoichiometry of the complexes formed between several individual metal cations and compound **1**, **2**, **3** and also to determine the stability constants of these complexes.

The variation of molar conductivity (Λ) with $[L]_T/[M]_T$ for complexation of crowns **1**, **2** and **3** with Cu^{2+} , Cd^{2+} , Zn^{2+} , Pb^{2+} , Hg^{2+} and Ag^+ cations in acetonitrile:chloroform (1:1) solvent system were studied at 25 °C. $[L]_T$ and $[M]_T$ denoting total concentrations of crown ethers and metal cations, respectively. The resulting molar conductance–mole ratio plots are shown in Figs. 1–3.

It is obvious from Figs. 1–3 that the addition of thiazacrown ether **1**, **2**, or **3** to Ag^+ , Cu^{2+} or Zn^{2+} metal solutions causes a decrease in the molar conductance which begins to level off at a mole ratio of 1:1 crown-to-metal indicating the formation of a stable 1:1 complex. This decreasing indicates that the complex has lower mobility than the free solvated metal ions. On the other hand Figs. 1–3 show that addition of thiazacrown ether **1**, **2** or **3**

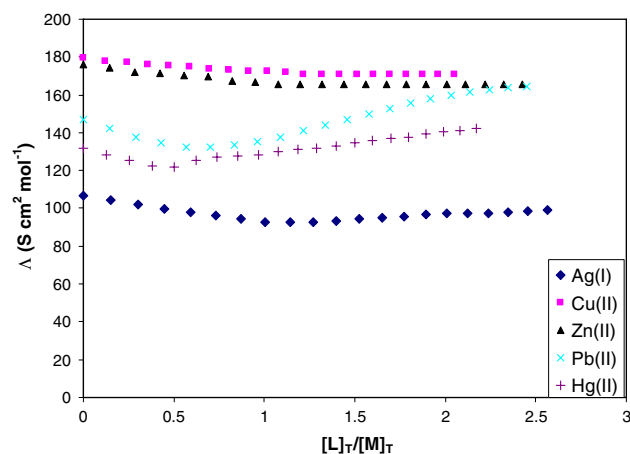


Fig. 1 Molar conductance–mole ratio plots for **1** and metal cations in $\text{CH}_3\text{CN}:\text{CHCl}_3$ (1:1) at 25 °C

to Hg^{2+} or Pb^{2+} perchlorate salt solution show that changes in the slope of the conductometric titration curves are observed at a ligand:metal ratio of 0.5 indicating the formation of 1:2 complexes. No detectable changes in molar conductance were found when a solution of **1**, **2** or **3** was added to Cd^{2+} solution (not shown in Figs. 1–3). This may indicate either no complexation is taking place between this metal cation and the ligands or the mobility of the complex is almost similar to the mobility of the free ions.

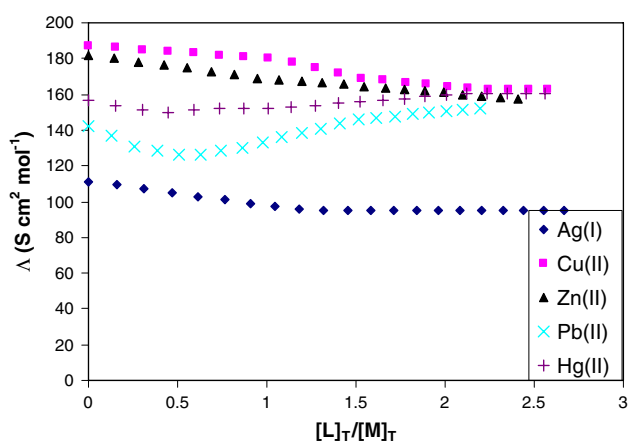


Fig. 2 Molar conductance–mole ratio plots for **2** and metal cations in $\text{CH}_3\text{CN}:\text{CHCl}_3$ (1:1) at 25 °C

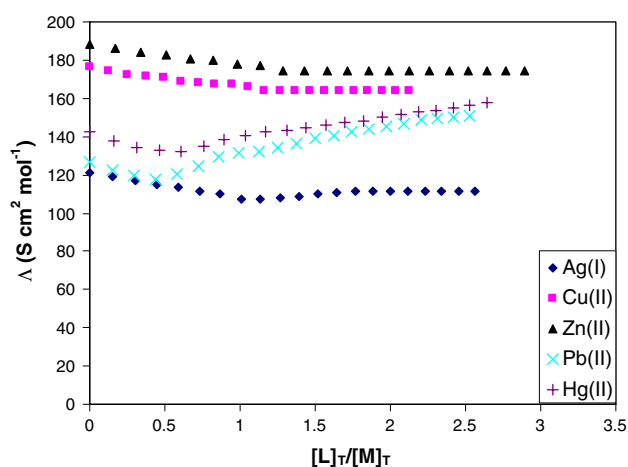


Fig. 3 Molar conductance–mole ratio plots for **3** and metal cations in $\text{CH}_3\text{CN}:\text{CHCl}_3$ (1:1) at 25 °C

It is important to mention that in most of the cases the degree of curvature of the $\Delta:[L]_T/[M]_T$ plot is related to the strength of the interaction between metals and ligands, and to the K values. As shown in Table 1, the stability constants of **1**- Ag^{2+} , **2**- Ag^+ and **3**- Ag^+ complexes are higher than those of their corresponding Zn^{2+} and Cu^{2+} complexes. This can be explained on the term of “*macrocyclic effect*” which refers to the dimensional compatibility between the macrocycle and the size of metallic cation. So, the higher values obtained for the stability constants for Ag^+ may be related to its bigger ionic radius which allows a better fit to the crowns cavity. It is noteworthy that the order of the stability constants of crown- Ag^+ complexes is in the order **3** > **1** > **2**. This indicates that the cavity size of compound **3** is the most compatible one with the ionic radius of Ag^+ .

It should be noted that in the procedure of calculation of stability constants of the complexes, the calculations were

Table 1 Log K_{assoc} for complexation of Ag^+ , Cu^{2+} , Zn^{2+} with crowns **1**, **2** and **3** in $\text{CH}_3\text{CN}:\text{CHCl}_3$ (1:1) at 25 °C

Compound	Ag^+	Cu^{2+}	Zn^{2+}
1	6.71 ± 0.17	2.75 ± 0.12	3.13 ± 0.13
2	5.33 ± 0.13	1.52 ± 0.04	3.48 ± 0.10
3	7.29 ± 0.18	3.24 ± 0.13	3.90 ± 0.12
I ^a	1.60^b		
II ^a	5.27^b (4.34 ^c)		
III ^a	7.80^b		
IV ^a	5.36^b		

^a Measurements done in H_2O

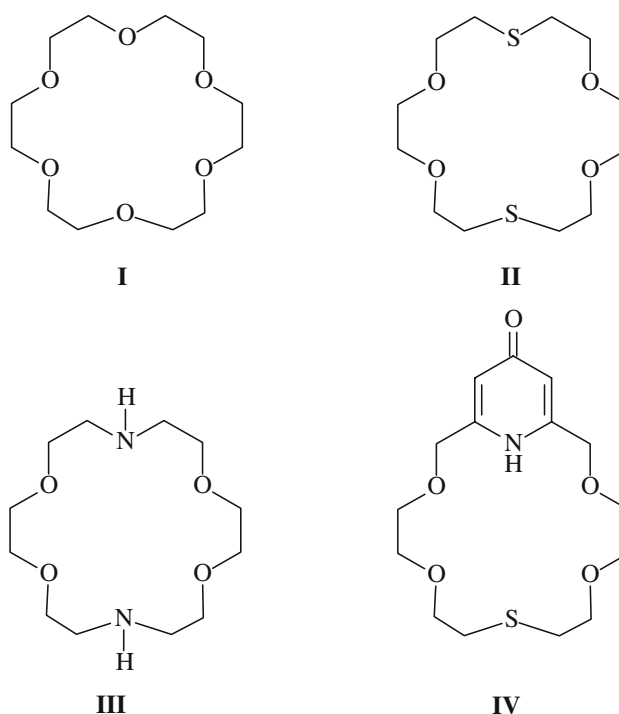
^b Reference [14]

^c Reference [15]

done for a 1:1 crown-to-cation due to the limited capability of our program.

For comparison purposes, the stability constants of some crown ethers **I–IV** (Scheme 4) with Ag^+ were incorporated (Table 1). The stability constants of these crown ethers with Ag^+ are almost the same as crowns **1–3**.

In order to achieve better understanding of the thermodynamic of the complexation reactions, it will be useful to consider the enthalpic and entropic contributions to these reactions. This study will be reported in due course.



Scheme 4 Selected some crown ethers from literature to compare their stability constants with prepared crowns **1**, **2** and **3**

Conclusion

Three new thiaazacrown ethers **1**, **2** and **3** have been synthesized in a simple way and in a very good yield. These ligands showed complexation ability for Ag^+ , Cu^{2+} , Zn^{2+} , Hg^{2+} and Pb^{2+} . The stoichiometry of the complexes with Ag^+ , Cu^{2+} or Zn^{2+} cations is 1:1 (L:M), but in the case of Pb^{2+} and Hg^{2+} cations, a 1:2 (L:M) complex is formed in solutions.

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