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ORIGINAL ARTICLE

Syntheses and cations complexation properties of novel thiacalix[4]-1,3-aza-crown and bisthiacalix[4]-1,3-aza-crown

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Abstract By reacting thiacalix[4]arene with *N*,*N*′-bis(2-chloracetamide)ethylene in Na_2CO_3/toluene or K_2CO_3/toluene system, novel thiacalix[4]-1,3-aza-crown **3** and mono-bridged bisthiacalix[4]-aza-crown **4** were selectively synthesized in "1 + 1" cyclocondensation or "1 + 2" condensation in moderate yields. Novel bis-bridged bisthiacalix[4]-1,3-aza-crown **5** was prepared by further condensating compound **4** with *N*,*N*′-bis(2-chloracetamide)ethylene in Na_2CO_3/toluene. The non-competitive and competitive liquid–liquid extraction experiments showed that new hosts possessed good extraction capabilities for soft cations. Hosts **3** and **5** showed good extraction selectivities for Ni^{2+} and Ag^{+}, respectively. The ^1H NMR titration experiment showed 1:1 stoichiometry of the complex between host **5** and Ag^{+}.

Keywords Thiacalix[4]crown · Bisthiacalix[4]crown · Aza · Synthesis · Complexation

Introduction

Thiacalixarenes attracted much research interests recently because the presence of sulfur atoms in calixarene skeleton results in many novel features compared with "classical" calixarenes, such as easy chemical modification, different size and more flexible conformational behavior, different complexation ability with sulfur contribution [1]. Among all kinds of thiacalixarene derivatives, bridging thiacalix[4]arene attracted much attentions due to the bridging chains not only anchor the conformation effectively but also construct new *tri*-dimensional cavities which usually exhibit excellent recognizing abilities for guests. In 2002, Vicens and Coworkers [2] and Bitter and Coworkers [3] synthesized the first example of bridging calix[4]arene: thiacalix[4]crowns. From then on, a series of full-oxygen thiacalix[4]crowns and their binding properties for metal cations were reported [4–8]. Narumi et al. [9] also reported a thiacalix[4]crown carboxylic acid with recognition abilities for enantiomeric primary amines and amino esters. In 2005, Lhoták and coworkers [10] synthesized the first thiacalix[4]-1,2-3,4-*aza*-biscrowns in cone conformation, and Csokai et al. [11] reported an inherently chiral thiacalix[4]arene derivatives capped by carboxamide bridges, but no complexation properties of them were presented. On the other hand, several bis-bridged bisthiacalix[4]arenes were synthesized with normal crown ether linkages and diimime linkages [12–14]. Our groups also reported a series of thiacalix[4]-aza-crowns lately [15–17]. Nevertheless, comparing with "classical" calix[4]arene, many research fields of thiacalix[4]crowns and bisthiacalix[4]arene are still unknown. In this paper, we wish to report the selective synthesis of novel thiacalix[4]-aza-crown **3**, the first example of mono-bridged bisthiacalix[4]-aza-crown **4** and novel bis-bridged bisthiacalix[4]-aza-crown **5**. Also, their cation complexation properties were presented.

Experimental

Melting points were uncorrected. ^1H NMR spectra were recorded in $CDCl_3$ on a Bruker-ARX 500 instrument, using

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TMS as reference. ESI–MS spectra were obtained from DECAX-30000 LCQ Deca XP mass spectrometer. Elemental analyses were performed at Vario EL III Elemental Analyzer. The UV–Vis measurements were performed on Varian UV–Vis spectrometer. Cation concentrations in competitive extracting experiments were measured with Thermo Intrepid XSP Radial ICP-OES. Toluene was dried by sodium. K_2CO_3 and Na_2CO_3 were toasted at 600 °C for 2 h. The picrate salts were prepared according to literatures [18, 19]. The organic and inorganic reagents were analytical grade or chemical grade without further purification.

Synthesis of thiacalix[4]-1,3-aza-crown **3**

Under N_2 atmosphere, a mixture of *p-tert*-butylthiacalix[4]arene **2** (0.50 g, 0.7 mmol), *N*,*N*′-bis(2-chloracetamide)ethylene **1** (0.15 g, 0.7 mmol), Na_2CO_3 (0.5 g, 4.7 mmol) and NaI (0.3 g, 2 mmol) were stirred and refluxed in 50 mL dry toluene. TLC analysis revealed that after 12 h all the starting materials reacted. After distilling off the solvent by reduced pressure, the residue was purified by chromatographic column (50 cm × 3 cm, SiO_2 100–200 mesh, acetone/CH_2Cl_2(1:1, v/v) as eluant, 500 mL), then compound **3** was obtained as white powder in yield of 32%. Compound **3**: mp. 265–268 °C,^{1}H NMR (500 MHz, $CDCl_3$)δ: 1.21(s, 18H, $C(CH_3)_3$), 1.24(s, 18H, $C(CH_3)_3$), 3.70(s, 4H, NCH_2CH_2N), 4.62 (s, 4H, OCH_2CO), 7.65 (s, 4H, ArH), 7.68(s, 4H, ArH), 8.59 (bs, 2H, OH), 8.81 (s, 2H, NH). ESI–MS m/z (%): 861.2 (M^+, 100). Anal calcd for $C_{46}H_{56}N_2O_6S_4$: C, 64.17; H, 6.56; N, 3.25; found: C, 64.27; H, 6.64; N, 3.36.

Synthesis of mono-bridged bisthiacalix[4]-aza-crown **4**

Under N_2 atmosphere, a mixture of *p-tert*-butylthiacalix[4]arene **2** (0.50 g, 0.7 mmol), *N*,*N*′-bis(2-chloracetamide)ethylene **1** (0.08 g, 0.37 mmol), K_2CO_3 (0.3 g, 2.2 mmol) and KI (0.13 g, 0.78 mmol) were stirred and refluxed in 50 mL dry toluene. TLC analysis revealed that after 24 h all the starting materials reacted. After distilling off the solvent by reduced pressure, the residue was purified by chromatographic column (50 cm × 3 cm, SiO_2 100–200 mesh, acetone/CH_2Cl_2 (1:2, v/v) as eluant, 800 mL). Then compounds **3** and **4** were obtained as white powder in yield of 9 and 53%, respectively. Compound **4**: mp. 236–239 °C, ^{1}H NMR (500 MHz, $CDCl_3$,)δ: 1.23 ~ 1.10 (bs, 54H, $C(CH_3)_3$), 1.28 (s, 18H, $C(CH_3)_3$), 3.97 (m, 4H, NCH_2CH_2N), 4.82 (m, 4H, OCH_2CO), 7.27 (m, 8H, ArH), 7.52(bs, 2H, ArH), 7.59(bs, 4H, ArH), 7.66 (bs, 2H, ArH), 9.19 (s, 2H, OH), 9.30 (s, 4H, OH), 9.52 (s, 2H, NH); ESI–MS m/z (%): 1582.1 (M^+, 100); Anal. calcd for $C_{86}H_{104}N_2O_{10}S_8$: C, 65.30; H, 6.63; N, 1.77; found C, 65.21; H, 6.70; N, 1.84.

Synthesis of bis-bridged bisthiacalix[4]-1,3-aza-crown **5**

Under N_2 atmosphere, a mixture of compound **4** (0.30 g, 0.19 mmol), *N*,*N*′-bis(2-chloracetamide)ethylene **1** (0.04 g, 0.19 mmol), Na_2CO_3 (0.2 g, 1.9 mmol) and NaI (0.07 g, 0.46 mmol) were stirred and refluxed in 50 mL dry toluene. TLC analysis revealed that after 48 all the starting materials reacted. After distilling off the solvent by reduced pressure, the residue was purified by chromatographic column ((50 cm × 3 cm, SiO_2 100–200 mesh, acetone/CH_2Cl_2 (1:3, *v*) as eluant, 800 mL). Then compound **5** was obtained as white powder in yield of 14%. Compound **5**: mp. 286–289 °C,^{1}H NMR (500 MHz, $CDCl_3$)δ: 1.20(s, 36H, $C(CH_3)_3$), 1.25(s, 36H, $C(CH_3)_3$), 3.72(s, 8H, NCH_2CH_2N), 4.66 (s, 8H, OCH_2CO), 7.65 (s, 8H, ArH), 7.67(s, 8H,ArH), 8.58 (s, 4H, OH), 8.87 (s, 4H, NH). ESI–MS m/z (%): 1722.2 (M^+, 100). Anal calcd for $C_{92}H_{112}N_4O_{12}S_8$: C, 64.17; H, 6.56; N, 3.25; found: C, 64.25; H, 6.60; N, 3.38.

Noncompetitive extracting experiment of metallic picrates

According to the reported method [16], 3 mL of chloroform solution containing calixarene derivatives (2.0×10^{-5} M) and 3 mL of aqueous solution containing a metallic picrate (2.0×10^{-5} M) were placed in a flask. The mixture was shaken for 5 min and stored for 2 h at room temperature. The extraction ability was not affected by further shaking, indicating that the equilibrium had been attained within 2 h. The aqueous phase was separated and subjected to the analysis by UV absorption spectrometry in near 357 nm. The extracting percentage (E%) was determined by the decrease of the picrate concentration in the aqueous phase: $E\% = \{([Pic]_{blank} - [Pic]_{water})/[Pic]_{blank}\} \times 100$, where $[Pic]_{blank}$ denoted the picrate concentrations in the aqueous phase after extraction with pure chloroform, and $[Pic]_{water}$ denoted the picrate concentrations in the aqueous phase after extraction with chloroform solution containing calixarene derivatives as extractants. Average of two independent experiments was carried out. Control experiments showed that no picrate extraction occurred in the absence of the calixarene derivatives.

Competitive extracting experiments of metallic cations

Competitive extraction experiments were performed with equal volumes (10 mL) of an aqueous solution of an equimolar mixture of picrate salts (Na^+, K^+, Cs^+, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, $Hg^{2+}$and Ag^+, 2.0×10^{-5} M each) and a $CHCl_3$ solution (10 mL) of the hosts

(2.0×10^{-5} M) were mixed in a stoppered flask and vigorously shaken for 15 min. The solution was stored for 2 h. This was repeated three times. Then the solutions were left standing for 24 h until phase separation was complete. The relative concentrations of the cations in the aqueous phase were determined by ICP-OES. Quantification was made by using a standard solution containing a mixture of picrate salts ((Na^+, K^+, Cs^+, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, $Hg^{2+}$and Ag^+). Blank experiments without added hosts were carried out under same experimental conditions.

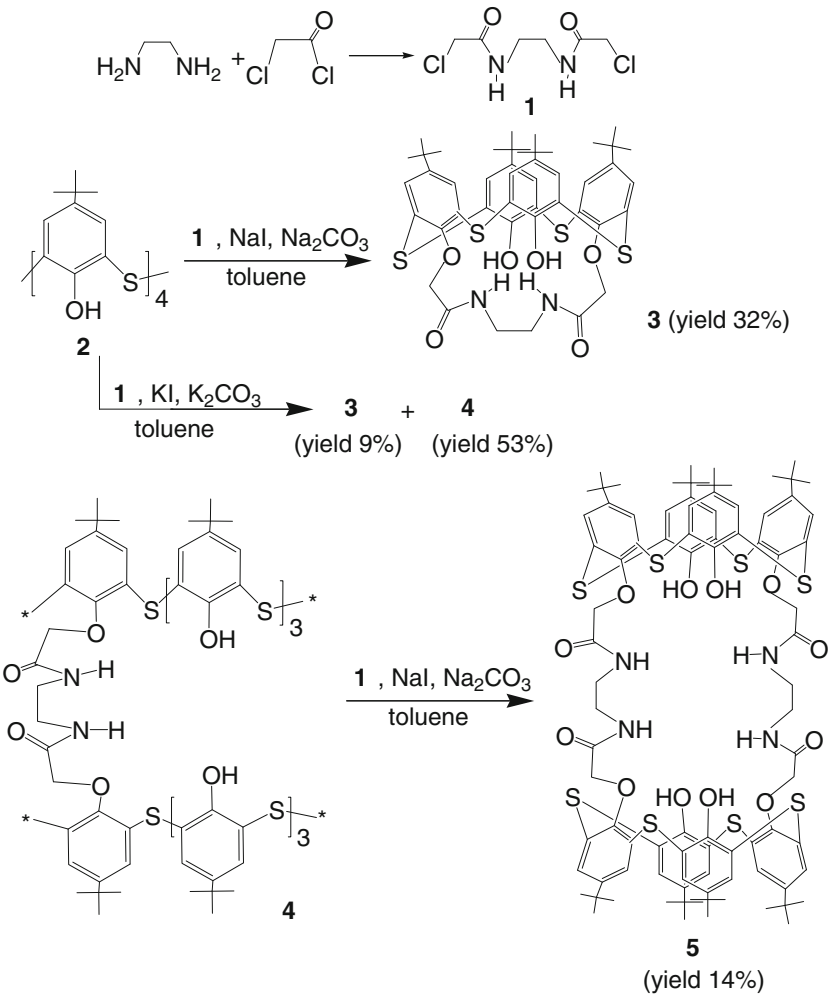
^{1}H NMR complexation experiments

Solution of receptor **5** was prepared at a concentration of 5×10^{-4} M in $CDCl_3$-CD_3OD (9:1). And aliquots of Ag^+ (ClO_4^-) in the same solvent, were added by a microsyringe from a solution made such that from 0 molar equiv. to 2.0 molar equiv. were added in 20 μL, and the ^{1}H NMR spectra were recorded.

Results and discussion

Synthesis of novel thiacalix[4]-aza-crown derivatives **3**, **4** and **5**

The synthetic route is shown in Scheme 1. It was found that the reacting results of *p-tert*-butylthiacalix[4]arene **2** with *N*, *N*'-bis(2-chloracetamide)ethylene **1** were greatly influenced by the reaction conditions. The thiacalix[4]-1,3-aza-crown **3** was conveniently prepared in Na_2CO_3/toluene in yield of 32% after separation with chromatographic column. However, when using K_2CO_3/toluene, mono-bridged bisthiacalix[4]-aza-crown **4** was obtained as main product in yield of 53%, and compound **3** was only obtained as by-product in yield of 9%. Indeed, this condensation reaction were investigated in the other reaction systems, such as Na_2CO_3(or K_2CO_3)/acetone, Na_2CO_3(or K_2CO_3)/MeCN, Na_2CO_3(or K_2CO_3)/DMF, but the experiments results were complicated and no pure products were separated. These results might reveal that toluene was an ideal solvent for



Scheme 1 The synthetic routes of compounds **3**, **4** and **5**

syntheses of bridging thiacalix[4]arene, which were accord with the literature [14]. It was unexpected that this reaction preferred to intramolecular bridging when using Na_2CO_3 as bases, but intermolecular bridging when using K_2CO_3 as bases. These results could be explained by cations template effects. Akdas et al. had reported the thiacalix[4]arene preferred to maintaining cone conformation when using Na_2CO_3 as bases, but partial cone and alternate conformation were obtained by using K_2CO_3 as bases [20]. In this reaction, using Na_2CO_3 as bases preferred to cone conformation, which was favorable for intramolecular bridging. On the other hand, the thiacalix[4]arene was difficult to maintain cone conformation with K_2CO_3 as bases, so that the intramolecular bridging was restrained and intermolecular bridging was mainly obtained. The yield of intermolecular mono-bridged bisthiacalix[4]-aza-crown **4** was as high as 53% under optimized reaction condition. It was disappointing that no bis-bridged bisthiacalix[4]-aza-crown **5** was obtained in this reaction. However, compound **5** could be obtained by further reacting compound **4** with *N*,*N*′-bis(2-chloracetamide)ethylene **1** in Na_2CO_3/toluene in yield of 14%. The low yield of compound **5** might be attributed to compound **4** possess mixed conformations (partial cone or alternate conformations) which were not favorable for synthesizing compound **5**. Although the thiacalix[4]-1,2-3,4-aza-biscrown were reported by reacting cone conformational thiacalix[4]arene tetraethyl acetate derivative with α,ω-diamine [10], our experiments provided new synthetic routes to afford thiacalix[4]-aza-crown by directly condensating tihacalix[4]arene with bridging chains. To the best of our knowledge, compound **3**, **4** and **5** were the first examples of 1,3-bridged thiacalix[4]-aza-crown, mono-bridged bisthiacalix[4]-aza-crown and 1,3-bis-bridged bisthiacalix[4]-aza-crown.

Structures and conformations of novel thiacalix[4]-aza-crown derivatives **3**, **4** and **5**

The structures of new compounds **3**, **4** and **5** were characterized by ESI–MS spectra, elemental analyses, ^{1}H NMR spectra. The ESI–MS spectra of compounds **3**, **4** and **5** showed clearly molecular base peak(M^+) at 861.2, 1582.1 and 1722.2, respectively, which indicated the "1 + 1", "1 + 2", "2 + 2" intermolecular condensation were accomplished utterly. The ^{1}H NMR spectrum of compound **3** showed two singlets for the *tert*-butyl groups, two singlets for the aromatic protons and a singlet for OCH_2CO, which were similar to the ^{1}H NMR signals of reported normal full-oxygen thiacalix[4]-1,3-crown with cone conformations [2–8]. Also, due to compound **3** was prepared by Na_2CO_3 system as discussed above, it was reasonable to deduce compound **3** was in cone conformation. As to the ^{1}H NMR spectrum of compound **4**, it was difficult to deduce its conformation due to the overlapped signals, which might indicate that it possessed mixed conformations (including cone, partial cone and alternate conformations) attributed to the influence of K_2CO_3 as bases. The ^{1}H NMR spectrum of bisthiacalix[4]crown **5** showed similar signals to that of compound **3** and the other reported bisthiacalix[4]arene with cone conformation [12–14], so it was reasonable to deduce that compound **5** also adopted cone conformation, which was accordance to Na_2CO_3 system.

Complexation studies for cations

It is well known that the cavity of calix-*aza*-crowns could bind soft metal cations according to the "soft and hard acids and bases" concept. The noncompetitive complexation abilities of compounds **3**, **4** and **5** towards a series of metal cations were studied by two phase extraction experiment ($H_2O/CHCl_3$) of metal cation picrate salts. The results were summarized in Figure 1. It could be seen that all new hosts exhibited good extraction percentage for cations, especially for soft cations, which were accordance with the "soft and hard acids and bases" concept. Hosts **3** and **5** showed higher extraction selectivities for soft cations than that of host **2**. These extraction results might be explained by that hosts **3** and **5** possessed stable cone conformations which were pre-organized structures and favorable for producing extraction selectivity. The highest Ag^+ and Ni^{2+} extraction percentage of host **5** and **3** was as high as 68.8% and 60.6%, respectively.

To assess the competitive extraction selectivities of compounds **3**, **4** and **5**, competitive solvent extractions experiments from aqueous solutions into chloroform were performed. The extraction percentages (%E) were summarized in Table 1. It can be seen that the extraction

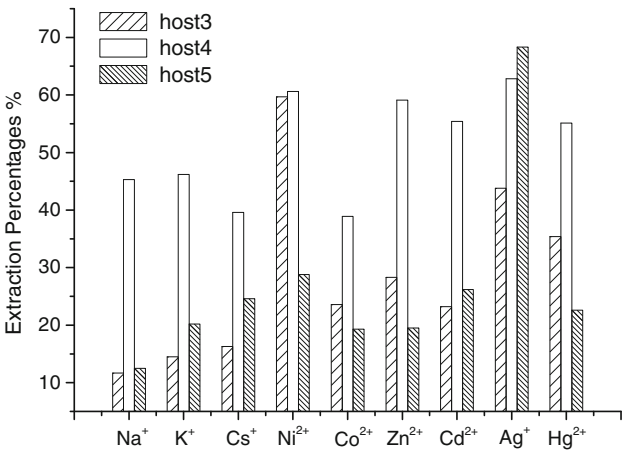


Fig. 1 The extraction percentages of hosts **3**, **4** and **5** for metallic cations

Table 1 Competitive extracting percentages (%E) of compounds **3, 4** and **5** for picrate salts from water into $CHCl_3$

Cations	Na^+	K^+	Cs^+	Ni^{2+}	Co^{2+}	Zn^{2+}	Cd^{2+}	Ag^+	Hg^{2+}
3	0.6	1.0	1.4	23.6	5.2	2.4	1.9	9.6	4.7
4	1.8	1.6	1.2	15.7	6.2	6.5	4.3	8.2	7.9
5	0.9	1.1	1.6	8.4	2.5	2.7	1.8	34.8	5.2

abilities towards the competing metallic ions showed similar capability order of noncompetitive extraction experiment: soft metallic cations> hard metallic cations. Moreover, similar to noncompetitive extraction results, hosts **3** and **5** with stable cone conformations showed higher extraction abilities and higher extraction selectivities than that of host **4** with mixed conformations. On the other hand, although the extraction percentages were lower than that of noncompetitive extraction experiment, however, the extraction selectivities in competition experiments were far higher than that of noncompetitive experiment. For example, the Ag^+/Na^+ extraction percentage of hosts **3** and **5** were as high as 39.3 and 38.7, respectively. From the noncompetitive and competitive extraction results, it could be concluded that both the conformation and the functional groups influenced the complexation ability and complexation selectivity greatly. Hosts **3** and **5** exhibited good complexation abilities and selectivities for Ni^{2+} and Ag^+, respectively.

In order to investigate the complex mechanism of new hosts for cations, the complex ^1H NMR spectra of compound **5** for Ag^+ were studied. Figure 2 showed the partial ^1H NMR spectra of compound **5** and compound **5** with Ag^+ (1.0 equiv.). The protons shift of NH moved from 8.87 ppm to 8.92 ppm and the other protons signals almost kept immovability. These results suggested that Ag^+ was binded in the cavity composed of amido groups, not in the cavities of calixarene skeleton. Figure 3 showed the change of the chemical shift of NH groups plotted against the amount of Ag^+ (ClO_4^-) added. The $\Delta\delta$ value increased in

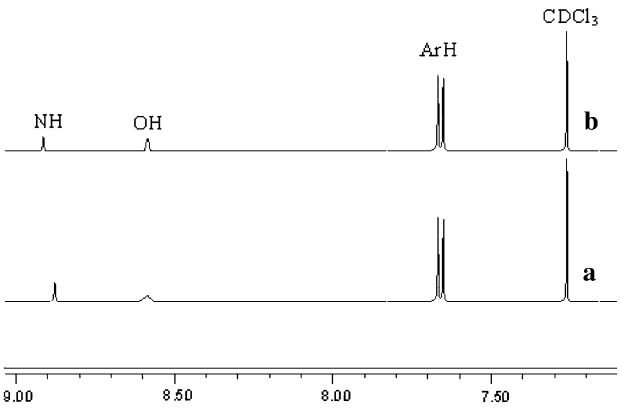


Fig. 2 ^1H NMR shift of compound **5**(a) and compound **5** with Ag^+(1.0 equiv.)(b)

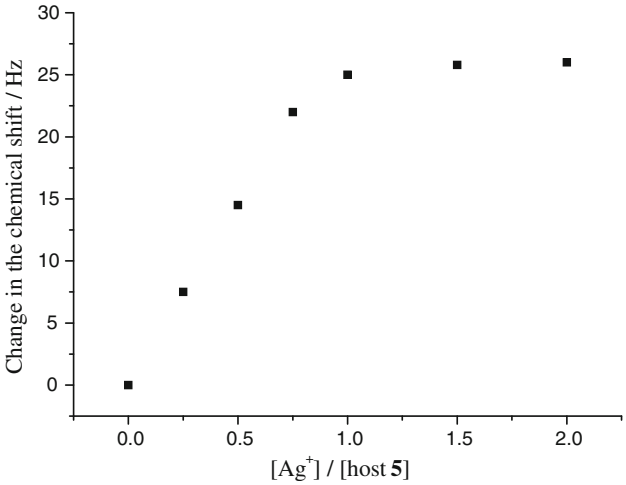


Fig. 3 ^1H NMR shift of NH in compound **5** and compound **5** with Ag^+

proportion to the amount of Ag^+ (ClO_4^-) and became almost constant after the addition of 1.0 mol equiv. of Ag^+ (ClO_4^-), which indicated the 1:1 stoichiometry of the complex in the solution.

Conclusion

Reacting thiacalix[4]arene with *N*,*N*′-bis(2-chloracetamide)ethylene in Na_2CO_3/toluene or $_2CO_3$/toluene system, selectively afforded novel thiacalix[4]-1,3-aza-crown **3** and mono-bridged bisthiacalix[4]-aza-crown **4** in "1 + 1" cyclocondensation or "1 + 2" condensation. Moreover, the novel *bis*-bridged bisthiacalix[4]-1,3-aza-crown **5** was obtained by further condensating compound **4** with *N*,*N*′-bis(2-chloracetamide)ethylene in Na_2CO_3/toluene. All reacting productions were sensitive to the reaction system and greatly influenced by cations template effects. Compounds **3**, **4** and **5** possessed good extraction capabilities and extraction selectivities for soft cations. The Ag^+ and Ni^{2+} extraction percentage of hosts **5** and **3** was as high as 68.8% and 60.6%, respectively. The ^1H NMR titration experiment showed 1:1 stoichiometry of the complex between host **5** and Ag^+.

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