

# Aminopyridyl derivative of thiacalix[4]arene-carboxylic acid as ionizable highly selective Ag<sup>+</sup> ionophore

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**Abstract** A novel mono-ionizable receptor **2** possessing three aminopyridyl and one carboxylic group in 1,3-alternate conformation based on thiacalix[4]arene, confirmed by single crystal X-ray analysis, was prepared. For competitive solvent extraction of alkali metal (Na<sup>+</sup>, K<sup>+</sup> and Cs<sup>+</sup>) and some transition metal (Cu<sup>2+</sup>, Zn<sup>2+</sup>, TI<sup>+</sup>, Ag<sup>+</sup>) cations from aqueous solutions into chloroform, it was found that the introduction of proton-ionizable group (carboxylic acid moiety) into the aminopyridyl-thiacalix[4]arene derivative could further improve its Ag<sup>+</sup> extractability with high selectivity.

**Keywords** Thiacalix[4]arene · Ionizable ligand · Silver ionophore · Solvent extraction

## Introduction

The noble metal element, silver, plays an important role in high technology and the national economy. For example, it has been widely used in the fields of catalysis, optoelectronics, microelectronics, medicine, bio-active materials,

and so on [1, 2]. Therefore, the design of receptors able to extract silver from waters and soils is an area of great interest. The main challenge is the development of reusable ionophores, which have a sufficiently high Ag<sup>+</sup> selectivity to extract Ag<sup>+</sup> from, for example, a millionfold excess of alkali cations and are effective in low concentrations compared to the bulk of the waste. Calixarenes are one of the most important platforms for the preparation of new macrocyclic hosts for complexation of neutral and ionic guest species [3–8]. Moreover, it is now well established that the nature of the substituents both at the upper and lower rims can play an important role in determining the complexation properties by thiacalixarene ligands. For instance, some thiacalix[4]arene podands, prepared by incorporating pyridyl or amide chelating groups at the lower rim of the *p*-*tert*-butylthiacalix[4]arene platform, show significant complexation ability towards all cations examined with maximal levels for Ag<sup>+</sup> [9–12].

Especially, much recent attention has also been devoted to the study of ionizable calixarene. It could be prepared by introduction of proton-ionizable groups into the calixarene ligands, such as carboxylic acid, urea, thiourea, etc. Compared with their non-ionizable analogues, attachment of proton-ionizable groups to neutral calixarene derivatives could further improve their metal ion extraction properties because the ionized group not only participates in metal ion coordination, but also eliminates the need to transfer one or more aqueous phase anions into the organic phase during extraction [13–19]. For example, Bartsch et al. used the carboxylic acid group and the acidity tunable *N*-(X)sulfonyl oxyacetamide functions [OCH<sub>2</sub>C(O)NHSO<sub>2</sub>X] with X group variation from methyl to phenyl to *p*-nitrophenyl to trifluomethyl as the proton-ionizable groups, and anchored them to calixcrowns, it was found that they showed much higher extraction towards alkali and alkaline earth metal

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cations than the unmodified calixcrowns possessing no ionizable groups [15].

Recently, we have undertaken the synthesis and evaluation of 1,3-alternate tetraaminopyridyl-thiacalix[4]arene ligands as  $\text{Ag}^+$  ionophore and found that introduction of the *ortho*-aminopyridine groups onto the lower rim of the thiacalixarene skeleton fixed in the 1,3-alternate conformation could enhance its selectivity and affinity for  $\text{Ag}^+$  to some extent [20]. In order to investigate whether introduction of proton-ionizable groups into the aminopyridyl-thiacalix[4]arene ligands could further enhance its extraction ability towards  $\text{Ag}^+$ , and also in continuation of the research for the  $\text{Ag}^+$  ionophore based on thiacalixarene derivative, herein, we wish to report the synthesis of a novel mono-ionizable ionophore based on triaminopyridyl-thiacalix[4]arene derivative **2** in 1,3-alternate and its selective and efficient extraction ability towards  $\text{Ag}^+$ .

## Experimental

### General

Melting points are uncorrected. The  $^1\text{H}$  NMR spectra were recorded at 298 K in  $\text{CDCl}_3$  at 300 MHz, respectively, on a Varian Mercury-VX300 spectrometer. The chemical shifts were recorded in parts per million (ppm) with TMS as the internal reference. ESI mass spectra were determined using a Finnigan LCQ Advantage mass spectrometer. Elemental analyses were performed with a Thermo Quest Flash EA1112 apparatus. The pH of the aqueous phase from the initial extraction step was determined with a Sartorius Basic PB-10 pH Meter with a supplied with a combined electrode. Cation concentration was measured with a Thermo Intrepid XSP Radial ICP-OES. X-ray data was recorded using a Bruker SMART CCD single crystal diffractometer. The compounds *p*-*tert*-butylthiacalixarene was synthesized by the method described by Kumagai [21]. 1,3-Alternate *p*-*tert*-butylthiacalixarene tetraacetate were synthesized according to the literature procedure [22], the corresponding carboxylic acid **1b** was synthesized as described in the literature [23].

### Synthesis of 1,3-alternate triaminopyridyl-monocarboxylate-thiacalix[4]arene (**2**)

A mixture of acid **1b** (0.23 g, 0.24 mmol) and thionyl chloride (0.8 mL, 11.2 mmol) in dichloromethane (10 mL) was reflux for 4 h. Removal of the solvent and residual thionyl chloride under reduce pressure furnished the acid chloride **1c** as an off-white solid. The crude product **1c** was cooled to room temperature and dissolved in benzene (15 mL), and then aminopyridine (0.09 g, 1.44 mmol) was

added. The stirred mixture was refluxed for 6 hours under  $\text{N}_2$  atmosphere and then the solvent was distilled off, the residue was treated with 10 mL of distilled water, after filtration the precipitation was washed with distilled water ( $3 \times 10$  mL) to give a yellow to dark red precipitate, the mixture of products was then separated by column chromatography (silica gel) to give the triaminopyridyl-monocarboxylate-thiacalix[4]arene product (0.09 g, 33%) as a white solid. mp > 270 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 0.74 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 0.94 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 4.50 (s, 2H,  $\text{ArOCH}_2$ ), 4.77 (s, 2H,  $\text{ArOCH}_2$ ), 5.05 (dd,  $J_1 = 16.2$  Hz,  $J_2 = 12.0$  Hz, 4H,  $\text{ArOCH}_2$ ), 6.96 (t,  $J = 6$  Hz, 2H, PyH), 7.19 (t,  $J = 5.7$  Hz, 1H, PyH), 7.31 (d,  $J = 2.1$  Hz, 2H, ArH), 7.37–7.40 (m, 4H, ArH + PyH), 7.62 (t,  $J = 6.6$  Hz, 2H, PyH), 7.77 (s, 2H, ArH), 7.62 (t,  $J = 6.6$  Hz, 1H, PyH), 8.22 (d,  $J = 8.1$  Hz, 2H, PyH), 8.24 (s, 2H, ArH), 8.34 (d,  $J = 3.6$  Hz, 1H, PyH), 8.48 (d,  $J = 6.6$  Hz, 1H, PyH), 9.00 (br, s, 3H, NH); MS ESI $^+$   $m/z$ : 1257.4 [ $\text{M}^+$ ] (100%). Anal. calcd. for  $\text{C}_{63}\text{H}_{68}\text{N}_6\text{O}_9\text{S}_4$ : C, 64.04; H, 5.80; N, 7.11; S, 10.86. Found: C, 64.35; H, 5.96; N, 7.02; S, 10.20.

### Competitive solvent extraction experiments

An aqueous solution of an equimolar mixture of nitrate salts ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{TI}^+$  and  $\text{Ag}^+$ , approximately 1 mM each) was adjusted to appropriate pH with 0.01 mol  $\text{L}^{-1}$   $\text{HNO}_3$  and  $\text{NH}_4\text{OH}$ . Competitive extraction experiments were performed with equal volumes (10 mL) of the aqueous solution and a  $\text{CHCl}_3$  solution (10 mL) of the required ionophore (1 mM), the two phases were mixed in a stoppered flask and vigorously shaken in a vortex mixer for 15 min. The solution was then allowed to stand for 3 h. This was repeated 3 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 using a standard solution containing a mixture of nitrate salts ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{TI}^+$  and  $\text{Ag}^+$ ). A blank experiment without added ionophore was carried out under similar experimental conditions.

The extraction percentage ( $P_M\%$ ) is defined as 100% times the ratio of the cation amount extracted by the the  $\text{CHCl}_3$  solution of the required ionophore and the added cation amount in the aqueous phase, and it is calculated as:

$$P_M\% = ([\text{M}_0] - [\text{M}]) / [\text{M}_0] \times 100\%$$

where  $[\text{M}_0]$  and  $[\text{M}]$  are initial and final concentrations of metal salt in the aqueous phase before and after the extraction, respectively [24]. Experiments were performed in duplicate, average values are reported, with errors of 5–10% (relative standard deviations, RSDs).

Procedure for single species extraction of  $\text{Ag}^+$ 

The procedure followed that for the competitive solvent extraction experiments with the following changes. All the aqueous solution was adjusted to pH 8 with  $0.01 \text{ mol L}^{-1}$   $\text{HNO}_3$  and  $\text{NH}_4\text{OH}$ , the  $\text{AgNO}_3$  concentration was varied slightly compared to the ionophore concentration (1 mM), with a consecutively varied concentrations (0.25–2 mM) of  $\text{Ag}^+$ .

Crystallographic data for **2**

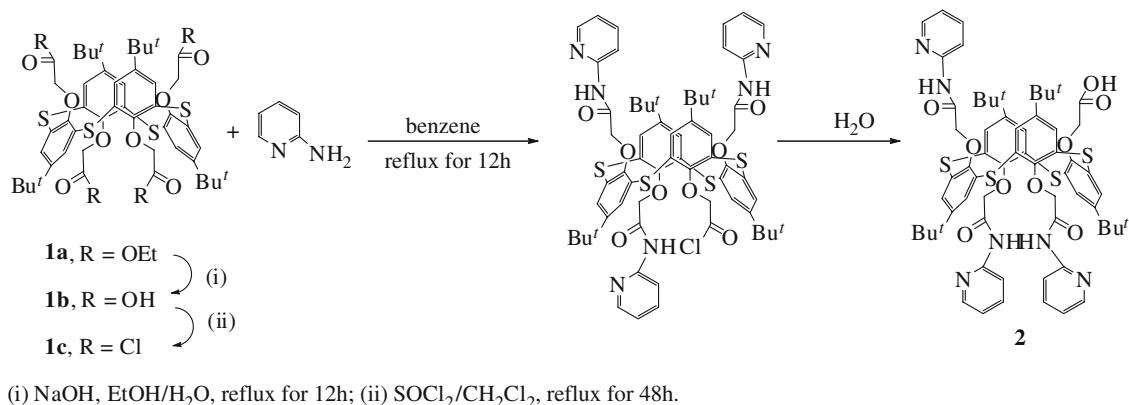
$\text{C}_{63}\text{H}_{68}\text{N}_6\text{O}_9\text{S}_4$ ,  $M = 1181.47$ , monoclinic,  $a = 13.9579(6) \text{ \AA}$ ,  $b = 34.2622(14) \text{ \AA}$ ,  $c = 15.0300(6) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 109.8420(10)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 6761.0(5) \text{ \AA}^3$ , space group =  $\text{C}2/c$ ,  $Z = 8$ ,  $D_c = 1.161 \text{ mg/m}^3$ ,  $\mu = 0.196 \text{ mm}^{-1}$ . Intensity data were collected up to  $\theta = 25.50^\circ$  by using  $2\theta$  scanning mode with graphite filtered Mo K $\alpha$  radiation ( $\lambda = 0.71073$ ) on a  $0.30 \times 0.20 \times 0.20 \text{ mm}^3$  crystal at 294(2) K. A total of 67987 reflections were measured, 11903 were independent and of which 7042 [ $I > 2(I)$ ] were considered observed. The structure was solved by direct methods using SHELXS-97 [25] and refined by Full-matrix least-squares on F2 using SHELXS-97 [26]. All non-hydrogen atoms were located directly by successive Fourier calculations and were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions by using a riding model. No absorption correction was applied. Final R indices [ $I > 2\sigma(I)$ ]  $R1 = 0.0690$ ,  $wR2 = 0.1614$ , and R indices (all data)  $R1 = 0.1133$ ,  $wR2 = 0.1799$  was found for 11903 independent reflections, 1 restraints, and 782 parameters. The GOF value is 0.944. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 674705. Copies of the data can be obtained, free of charge, on application to CCDC,

12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

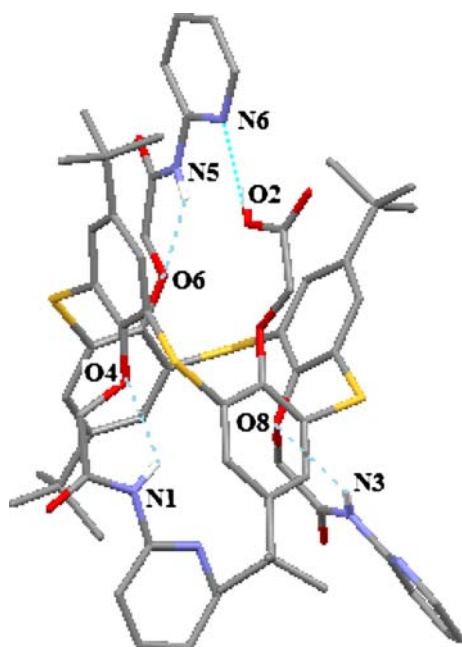
## Results and discussion

As illustrated in Scheme 1, the synthesis started from parent thiacalix[4]arene tetraacetate in 1,3-alternate conformation [22]. The corresponding acid chloride was prepared by hydrolysis of ester with  $\text{NaOH}$  aq. in a mixture of ethanol and water [23], followed by treatment with thionyl chloride in refluxing  $\text{CH}_2\text{Cl}_2$  in good yield. The crude chloride was used without purification for subsequent condensation with the  $\alpha$ -aminopyridine isomer, then treated with water, and the corresponding triaminopyridyl-monocarboxylate-thiacalix[4]arene **2** was obtained in good yields.

Structures of the thiacalix[4]arene derivatives **2** was proved by the combination of  $^1\text{H}$  NMR spectroscopy and mass spectroscopy (ESI-MS). The ESI-MS spectra of **2** shows the only one most intense signals corresponding to the molecular peak [ $\text{M}^+$ ] (100% int.), which suggests that it is triaminopyridyl-monocarboxylate products. The  $^1\text{H}$  NMR spectrum shows two singlets for the *tert*-butyl protons at  $\delta$  0.73 and 0.93 ppm, which is at much higher field than the chemical shift of the *tert*-butyl protons of some reported 1,3-alternate *p*-*tert*-butylthiacalix[4]arene derivatives (approximately  $\delta$  1.25 ppm) [10, 23, 27, 28], the large highfield shift indicates that the *tert*-butyl protons are exposed to the pyridyl current shielding effect operating in the proximal pyridine ring. The protons of  $-\text{O}-\text{CH}_2-\text{C}(\text{O})-$  bonded to a pair of benzene rings form an AB spin system, represent by a doublet with a typical geminal coupling constant ( $J = 15.3 \text{ Hz}$ ) in the region between 4.9 and 5.2 ppm; whereas the protons of  $-\text{O}-\text{CH}_2-\text{C}(\text{O})-$  bonded to the other pair of benzene rings appear as singlet at  $\delta$  4.77 and 4.50 ppm, respectively.



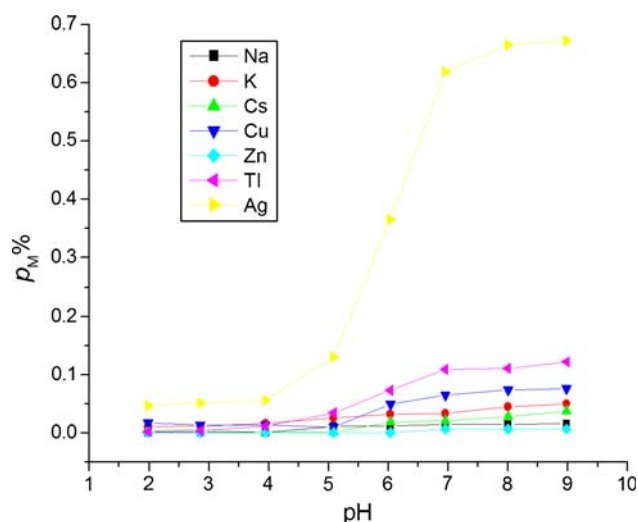
**Scheme 1** Synthesis route of compound **2**



**Fig. 1** Capped sticks drawing of 1,3-alternate-**2**. Dotted lines indicate hydrogen bonds, hydrogen atoms not included in hydrogen bond are omitted for clarity

Recrystallization from EtOH and  $\text{CHCl}_3$  produces X-ray quality colorless crystals of **2**. The ORTEP drawing of **2** analyzed by single crystal X-ray is shown in Fig. 1. In the solid state, it is clear that compound **2** adopts a “1,3-alternate conformation” and the orientations of the carbonyl oxygens of the acetates are outwardly orientated with respect to the cavity because of the electron repulsion between oxygens. There is very strong intramolecular hydrogen bonding between the hydroxy proton of carboxylic acid and the facing pyridyl nitrogen ( $\text{O2-H2}\cdots\text{N6}$ , 1.835 Å). Moreover, all the amide N atoms N1/N3/N5 form intra-molecular H-bonds with neighbor ethereal O atoms O4/O8/O6, respectively. All in all, potential H-bonded donor atoms (phenolic O atoms O4/O6/O8 and the pyridyl N atom N6) form strong intramolecular hydrogen bonds, which make all the potential H-bonded protons (amide N1H1/N3H3A/N5H5A and hydroxyl O2H2 protons) of **2** orientate inwardly with respect to the framework and buried in the cavity of thiacalixarene, thus they could not form strong intermolecular hydrogen bond with adjacent ligands.

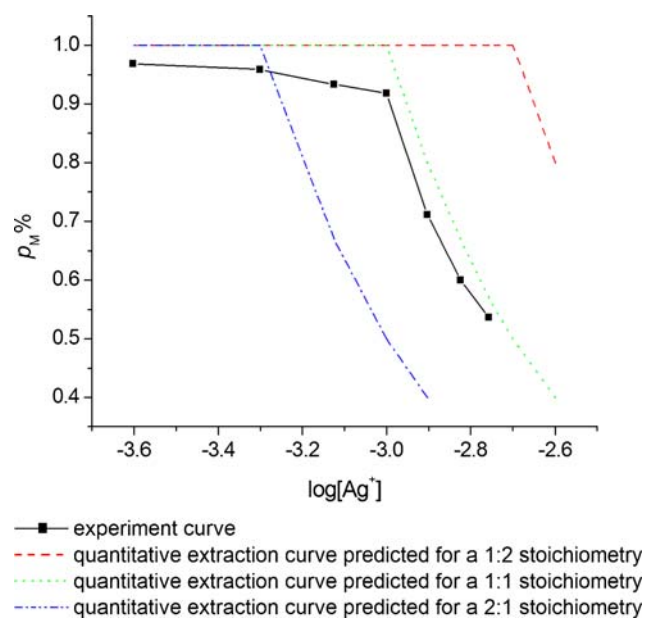
To assess the extraction behavior of ligand **2** for  $\text{Ag}^+$  in competition with alkali metals ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ) and transition metals ( $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Tl}^+$ ), competitive solvent extractions of  $\text{Ag}^+$  in competition with alkali and transition metal cations from aqueous solutions into chloroform were performed. Plots of metal ion extraction percentage of the ligand **2** versus the equilibrium pH of the aqueous phase for competitive solvent extractions are presented in Fig. 2 [13, 19].



**Fig. 2** pH-dependent cation ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Tl}^+$ ,  $\text{Ag}^+$ ) extraction curve of triaminopyridyl-thiacalix[4]arene mono-carboxylic acids **2** in the competitive solvent extraction experiments

Competition experiments revealed that the triaminopyridyl-thiacalix[4]arene mono-carboxylic acids **2** could only extract a small quantity of  $\text{Ag}^+$  and nearly none of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Tl}^+$  and  $\text{Zn}^{2+}$  was extracted by ligand **2** when the aqueous phases were highly acidic, which means that the ligand **2** is not an effective extractant but an selective  $\text{Ag}^+$  ionophore in their neutral, non-ionized form. With the increase of pH, the amount of  $\text{Ag}^+$  extracted dramatically increased, while the extraction percentage of the other cations just show a little increasing trend. At pH higher than 8, it was found that ligand **2** was a reasonably good phase transfer agent for silver cation (about 70%), displaying a slight preference for  $\text{Tl}^+$  (>10%) and  $\text{Cu}^{2+}$  (>7%). Within the other four cations, compound **2** was a poor extractant indicating that ligand **2** could not only efficiently but also selectively extract silver ion from the aqueous phase into organic one under the competing conditions. Therefore, it can be inferred that, at higher pH values, the carboxylic acid groups are deprotonated, and consequently, one ionizable groups neutralize the charge of the complex and act as lariat arms to prevent  $\text{Ag}^+$  from escaping from the cavity of ligand **2**. The data obtained by competitive solvent extraction experiments revealed that attachment of proton-ionizable groups onto the aminopyridyl-thiacalix[4]arene derivative could dramatically improve its extraction ability towards  $\text{Ag}^+$ .

In order to investigate the stoichiometry of ligand **2** with  $\text{Ag}^+$  in the extraction complex, single species extraction of  $\text{Ag}^+$  experiments was carried out between equal volumes of the organic phase with a constant ionophore concentration of (1 mM) ligand **2** and aqueous phase (at pH 8) with a consecutively varied concentrations (0.25–2 mM) of  $\text{Ag}^+$ , reported by van Leeuwen et al. [19]. As shown in



**Fig. 3**  $\text{Ag}^+$  extraction percentages ( $P_M\%$ ) for ionophore **2** (1 mM) as a function of the  $\text{AgNO}_3$  concentration. The experiments were performed with equal volumes of the organic and aqueous phases (10 mL). The markers (■) indicate experimental points. The lines indicate extraction percentages calculated for a 1:2, 1:1, and 2:1 H (Host):M (Metal) stoichiometry

Fig. 3, up to a ratio of 1:1, the  $\text{Ag}^+$  cations were extracted quantitatively, that is to say, the  $K_{ex}$  (extraction constant) is very high. In this case, the  $P_M\%$  will decrease apparently from the stoichiometry point of the complex (at  $[\text{M}_0]_{\text{aqueous}}/[\text{H}_0]_{\text{organic}} > a/b$ ,  $[\text{M}_0]_{\text{aqueous}}$  is initial concentration of metal salt in the  $\text{H}_2\text{O}$  solution before the extraction,  $[\text{H}_0]_{\text{organic}}$  is the initial concentration of host in the  $\text{CHCl}_3$  solution before the extraction,  $a/b$  is the stoichiometry of complex  $[\text{H}_a\text{M}_b]$ ). From the ratio of 1:1, the  $\text{Ag}^+$  extraction percentage apparently decreased as the concentration increased, which closely followed the quantitative extraction curve predicted for a 1:1 stoichiometry (Fig. 3). Therefore, we assume that  $\text{Ag}^+$  forms a 1:1 complex with ligand **2** in the liquid–liquid extraction conditions.

## Conclusion

A novel mon-ionizable receptor **2** possessing three aminopyridyl and one carboxylate group in 1,3-alternate conformation based on thiacalix[4]arene has been prepared. Its structure was confirmed by single crystal X-ray analysis. In the solid state, all the potential H-bonded donor atoms (phenolic O atoms O4/O6/O8 and the pyridyl N atom N6) form strong intramolecular hydrogen bonds, which make all the potential H-bonded protons (amide NH and hydroxyl OH protons) of **2** orientate inwardly with respect to the framework and buried in the cavity of thiacalixarene. The

extraction experiments revealed that attachment of protonizable groups onto the aminopyridyl-thiacalix[4]arene derivative could dramatically improve its affinity and selectivity towards  $\text{Ag}^+$  extraction, and  $\text{Ag}^+$  forms a 1:1 (H:M) complex with ligand **2** in the liquid–liquid extraction conditions.

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