

# Synthesis and binding studies of a novel highly selective Ag(I) ligand

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## Abstract

Ligands bearing *S*- and *N*- donors are an important class of extractants with demonstrated efficiency and selectivity for Ag<sup>+</sup> extraction over metals with similar chemistries. However, the synthesis of some of these ligands can be complicated and low yielding. Here, we report the synthesis of a novel ligand - *N*-(2-((4-vinylbenzyl)thio)ethyl)acetamide, over two simple steps and in a good yield. The extractant was observed to demonstrate excellent selectivity for Ag<sup>+</sup>, extracting only Ag<sup>+</sup> from an aqueous solution also containing Cu<sup>2+</sup> and Pb<sup>2+</sup>. Moderate extraction efficiencies of 36 % for Ag<sup>+</sup> and 0% each for Cu<sup>2+</sup> and Pb<sup>2+</sup> were observed. From mass spectrometry and proton NMR titration data, the extractant was found to form both the 1:1 and 1:2 (Ag<sup>+</sup>:ligand) complexes with Ag<sup>+</sup> indicating that ligand forms bent linear and tetrahedral coordination complexes with Ag<sup>+</sup>. Overall, the results indicate that the novel amide-based ligand is highly selective for Ag<sup>+</sup> removal from aqueous solutions containing Cu<sup>2+</sup> and Pb<sup>2+</sup>. These results indicate the ligand could be easily synthesized and applied for selective silver recovery from low grade ores.

Keywords: Amide-based ligand, selective Ag(I) ligand, soft donor, Job's and mole ratio plots

## Introduction

Silver (Ag) has found important applications in medicine, electronics, synthetic chemistry and water treatment.<sup>1,2</sup> As the world population increases, the industrial demand for silver is expected to increase as well. Unfortunately, silver supply from mining, the primary source of the metal,<sup>3</sup> is threatened due to declining ore grades,<sup>4</sup> leading to the search for alternative sources including urban mining of end-of-life products.<sup>5</sup> However, silver is usually present in a complex mixture with other metals and compounds, which has caused significant challenge with the profitability of urban mining. Hence, highly selective and efficient technologies are required for consistent silver recovery to meet growing global demands.

Common techniques employed for silver extraction include chemical precipitation,<sup>6,7</sup> membrane filtration,<sup>8</sup> ion exchange,<sup>9</sup> electrochemical treatment,<sup>10,11</sup> solid phase extraction/adsorption,<sup>12,13</sup> and liquid-liquid extraction.<sup>14-17</sup> Liquid-liquid extraction has found wide application due to the ability of the extractants to form stable complexes with the silver ion,<sup>18</sup> resulting in efficient extraction and ease of operation.<sup>18,19</sup> Extractants containing at least one of *P*-, *N*-, or *S*- donors have been reported to be selective for the extraction of Ag<sup>+</sup> from aqueous solutions.<sup>16,20-22</sup> The selectivity of these donors towards Ag<sup>+</sup> is consistent with the hard soft acid base (HSAB) principle.<sup>23</sup> Similar selectivity has been reported by other authors, for example, Bray and coworkers<sup>14</sup> observed that the ligand - 1,3,5-tris((pyridin-4-ylthio)methyl)benzene bearing *S*- and *N*- donors was the most efficient and selective for Ag<sup>+</sup> of all three tripodal ligands prepared. The metals Ag<sup>+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup> and Co<sup>2+</sup> were extracted with efficiencies of 73, 16, 8 and 12 %

respectively. In a different study, an oxime-based extractant (LIX63) containing *N*- and *O*- donors was also found to selectively extract  $\text{Ag}^+$  over  $\text{Zn}^{2+}$ , achieving a 60 %  $\text{Ag}^+$  extraction and 0 %  $\text{Zn}^{2+}$  from aqueous solutions. The extracted  $\text{Ag}^+$  was later stripped from the LIX63 extractant using ammonia water containing a *N*- donor.<sup>24</sup> Furthermore, the disulphide extractant - bis(2,4,4-trimethylpentyl)dithiophosphinic acid containing *S*- and *P*- donors was reported to demonstrate remarkable selectivity for  $\text{Ag}^+$  from a chloride solution containing more than 1000-fold excess of other transition metals. Extraction efficiencies of 98.6, 0.2, 0.6, 0.6 0.5 and 0.7% were observed for  $\text{Ag}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$  respectively. The loaded extractant was completely stripped of  $\text{Ag}^+$  using a 0.5 M thiourea solution containing a *S*- donor.<sup>19</sup>

While several ligands with appropriate functionalities for the extraction of silver have been reported<sup>1,25-27</sup>, shortcomings like complex synthesis protocols<sup>14,28,29</sup> and low selectivity for  $\text{Ag}^+$  removal<sup>27</sup> may limit industrial scale applications. In this work, we attempted to address these problems through the design of a novel ligand containing donor groups (*S*- and *N*-) known to preferentially bind  $\text{Ag}^+$  and that could be accessed in simple steps with reasonable yield. Also, the  $\text{Ag}^+$  binding studies towards elucidation of the  $\text{Ag}^+$ -amide ligand complex stoichiometry was undertaken.

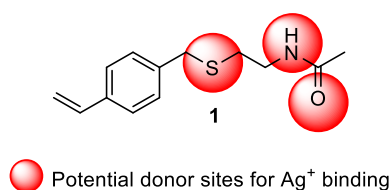


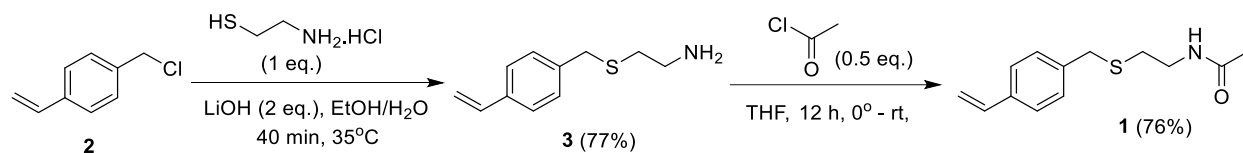
Figure 1. Structural features of the novel *N*-(2-((4-vinylbenzyl)thio)ethyl)acetamide ligand (**1**)

## Experimental Section

**Chemicals.** Acetyl chloride, 4-vinylbenzyl chloride (90 %), and silver perchlorate (97%), tetrahydrofuran (THF) and dichloromethane (DCM) were purchased from Sigma Aldrich. Silver triflate ( $\text{AgOTf}$ ) was purchased from Strem Chemicals. Lithium hydroxide was purchased from Alfa Aesar. 2-Aminoethanethiol hydrochloride was purchased from Acros Organics. Absolute ethanol (99.8%) and ethylacetate were purchased from VWR. All reagents were used without further purification.

**Instrumentation.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR were recorded at room temperature on Bruker<sup>®</sup> Advance spectrometers. Fourier transform infrared (FTIR) spectra were recorded on Bruker<sup>®</sup> Alpha Platinum-Attenuated Total Reflectance IR spectrometer. All accurate mass spectra were run on a Bruker<sup>®</sup> MaXis mass spectrometer. Metal concentrations were measured by means of a PerkinElmer 5300DV Inductively Coupled Plasma Optical Emission spectrophotometer (ICP-OES).

### Synthesis of *N*-(2-((4-vinylbenzyl)thio)ethyl)acetamide



Scheme 1. Synthesis route to *N*-(2-((4-vinylbenzyl)thio)ethyl)acetamide (**1**)

The novel amide ligand was accessed in two steps (Scheme 1). In the first step, the precursor 4-vinylbenzyl cysteamine **3** was synthesized following the method reported by Ghosh and Tochtrop<sup>30</sup>. Briefly, 4-vinylbenzyl chloride (12.7 mL, 0.09 mol) was added in drops for 5 mins to a stirred solution of LiOH (4.3 g, 0.18 mol) and 2-aminoethanethiolhydrochloride (10.2 g, 0.09 mol) dissolved in solvent mixture of water (60 mL) and ethanol (180 mL) and the crude mixture was left to stir at 35 °C for 40 min, after which the solvent was removed *in vacuo*. The crude product was extracted with DCM after it had been solubilized with water. The DCM extract was then dried with anhydrous MgSO<sub>4</sub>, filtered and concentrated *in vacuo* to give 4-vinylbenzyl cysteamine **3** as a viscous yellow oil. Yield: 13.7 g (77 %),  $\nu(\text{cm}^{-1})$  3365, (N-H stretch), 1627, 1567 (N-H bend), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 (d,  $J = 8.0$  Hz, 2H, ArH), 7.27 (d,  $J = 8.0$  Hz, 2H, ArH), 6.70 (dd,  $J = 17.5, 11.0$  Hz, 1H, CH<sub>2</sub>CHPh), 5.73 (d,  $J = 17.5$  Hz, 1H, CH<sub>a</sub>H<sub>b</sub>CHPh), 5.23 (d,  $J = 11.0$  Hz, 1H, CH<sub>a</sub>H<sub>b</sub>CHPh), 3.69 (s, 2H, PhCH<sub>2</sub>S), 2.82 (t,  $J = 6.0$  Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>), 2.51 (t,  $J = 6.0$  Hz, 2H, SCH<sub>2</sub>CH<sub>2</sub>), 1.29 (s, 2H, CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>), <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  138.1 and 136.5 (ArC), 136.4 (CH<sub>2</sub>CHPh), 129.1 and 126.5 (ArC), 113.9 (CH<sub>2</sub>CHPh), 41.0 (CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>), 35.8 (PhCH<sub>2</sub>S), 35.7 (SCH<sub>2</sub>CH<sub>2</sub>),  $m/z$  (ESI) for [C<sub>11</sub>H<sub>16</sub>NS]<sup>+</sup> calculated; 194.1003, found 194.0998. In the second step, the amine **3** (13.7 g, 0.071 mol) was dissolved in dry diethyl ether (150 mL) in a one necked flask. Acetyl chloride (2.53 mL, 0.035 mol) was dissolved in dry diethyl ether (50 mL) and added dropwise into the amine solution using a syringe pump for 90 min at 0° C. The reaction was left to stir and warm up to room temperature overnight. At the end of the reaction time, it was quenched with 2 M HCl (75 mL x 2) and extracted with ether (50 mL). The organic layer was then washed with saturated NaHCO<sub>3</sub> (75 mL x 2), water (150 mL x 2) and finally brine (150 mL). The organic layer was then dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated *in vacuo* to give *N*-(2-((4-vinylbenzyl)thio)ethyl)acetamide **1** as a white solid. Yield: 6.28 (76 %), m.p. = 73 – 75 °C,  $\nu(\text{cm}^{-1})$ : 3292 (N-H stretch), 1632 (C=O bend), <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN) 7.40 (d,  $J = 7.5$  Hz, 2H, ArH), 7.29 (d,  $J = 7.5$  Hz, 2H, ArH), 6.73 (dd,  $J = 17.5, 11.0$  Hz, 1H, CH<sub>a</sub>H<sub>b</sub>CH<sub>c</sub>), 6.53 (s, 1H, CH<sub>2</sub>NHCO), 5.78 (d,  $J = 17.5$  Hz, 1H, CH<sub>a</sub>H<sub>b</sub>CH<sub>c</sub>), 5.23 (d,  $J = 11.0$  Hz, 1H, CH<sub>a</sub>H<sub>b</sub>CH<sub>c</sub>), 3.72 (s, 2H, PhCH<sub>2</sub>S), 3.27 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>NH), 2.48 (t,  $J = 7.0$  Hz, 2H, SCH<sub>2</sub>CH<sub>2</sub>), 1.83 (s, 3H, NHCOCH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>CN) 170.7 (NHCOCH<sub>3</sub>), 139.7 (ArC), 137.4 (ArC), 137.3 (CH<sub>2</sub>=CHArC), 130.2 (ArC), 127.2 (ArC), 114.4 (CH<sub>2</sub>=CHArC), 39.3 (CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>), 35.8 (ArCCH<sub>2</sub>S), 31.5 (SCH<sub>2</sub>CH<sub>2</sub>), 23.0 (NHCOCH<sub>3</sub>).  $m/z$  (ESI) for [C<sub>13</sub>H<sub>14</sub>NNaOS]<sup>+</sup> calculated, 258.0929, found, 258.0923.

### Ag<sup>+</sup> uptake studies

Competitive Ag<sup>+</sup> extractions studies were undertaken following the solvent extraction technique reported by Sole and Hiskey<sup>31</sup>. Briefly, an aqueous solution of equal concentration of Cu<sup>2+</sup>, Ag<sup>+</sup> and Pb<sup>2+</sup> (4 mgL<sup>-1</sup> each) in 0.023 M Na<sub>2</sub>SO<sub>4</sub>

and in 0.476 M HNO<sub>3</sub> was prepared from a 500 mgL<sup>-1</sup> stock solution. The chloroform solvent was pre-saturated with twice its volume of 0.5 M H<sub>2</sub>SO<sub>4</sub> by constant shaking in a separatory funnel for 5 min prior to being used to prepare the ligand solution with molarity equal to 250 times that of Ag<sup>+</sup>. A control experiment involving contacting the ternary metal aqueous solution with the neat chloroform was also undertaken. For each metal extraction experiment, equal volumes (10 ml) of the metal solution and the ligand solution or neat chloroform were contacted by rapid and vigorous stirring (using a stir bar) for 15 min in capped plastic vials partially immersed in an oil bath set at 25 °C. Each experiment was undertaken in duplicate. After stirring, the immiscible solutions were transferred to a separatory funnel, allowed to separate and collected separately. The aqueous layer was collected into a beaker and the residual chloroform was removed over a steam bath in about 15 min. Then the aqueous layer was made back up to 10 ml and prepared for ICP-OES analysis. The metal removal efficiencies were determined as follows;

$$\% RE = \frac{C_i - C_f}{C_i} \times 100$$

Where % *RE* is the percentage removal efficiency, *C<sub>i</sub>* and *C<sub>f</sub>* are the initial and final metal ion concentrations respectively.

The selectivity of the ligands for Ag<sup>+</sup> relative to Cu<sup>2+</sup> and Pb<sup>2+</sup> was determined as follows<sup>32</sup>:

$$K_{Ag^+/M^{n+}} = \frac{D_{Ag^+}}{D_{M^{n+}}}$$

Where  $K_{Ag^+/M^{n+}}$  represents the selectivity coefficient of Ag<sup>+</sup> relative to M<sup>n+</sup> (M<sup>n+</sup> = Cu<sup>2+</sup> or Pb<sup>2+</sup>), *D* is the distribution coefficient of the metal ions between the aqueous and the organic phases defined as:

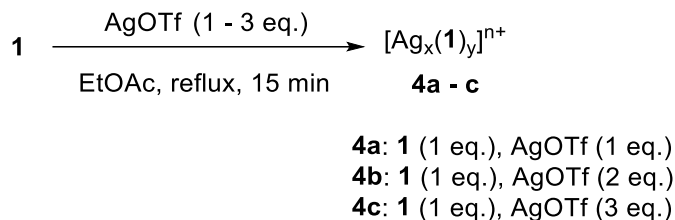
$$D_{M^{n+}} = \frac{C_i - C_f}{C_f} \times \frac{V_{aq}}{V_{org}}$$

$D_{M^{n+}}$  represents the distribution coefficient for the metal ion M<sup>n+</sup>, *C<sub>i</sub>* and *C<sub>f</sub>* are initial and the final metal ion concentrations, *V<sub>aq</sub>* and *V<sub>org</sub>* are the volumes of the aqueous and the organic solutions respectively.

Since equal volumes of the aqueous and the organic solutions were used, the distribution factor formula was simplified to:

$$D_{M^{n+}} = \frac{C_i - C_f}{C_f}$$

## Mass spectrometry studies of Ag<sup>+</sup>-**1** complexes



Scheme 2. Syntheses of Ag<sup>+</sup> complexes of **1** using Ag triflate

The Ag<sup>+</sup> complexes of ligand **1** were synthesized following the procedure reported by Daubinet<sup>33</sup>. Briefly, the ligand **1** (1 eq.) was dissolved in EtOAc (5 mL) and added to AgOTf (1 – 3 eq.) also in EtOAc (5 mL) (Scheme 2). The mixture was refluxed for 15 min after which the product was concentrated *in vacuo*. Finally, the products were characterized by electrospray ionization-mass spectrometry (ESI-MS).

[Ag<sub>x</sub>(**1**)<sub>y</sub>]OSO<sub>2</sub>CF<sub>3</sub> (**4a – c**)

**4a:** Colourless paste. Yield: 60 mg (94 %), **4b:** Colourless paste. Yield: 50 mg (75 %), **4c:** Colourless paste. Yield: 50 mg (85 %). *m/z* (ESI) calculated for [C<sub>13</sub>H<sub>17</sub><sup>107</sup>AgNOS]<sup>+</sup>; 342.0082, found 342.0076 and calculated for [C<sub>26</sub>H<sub>34</sub><sup>107</sup>AgN<sub>2</sub>O<sub>2</sub>S<sub>2</sub>]<sup>+</sup>; 577.1113, found; 577.1107.

### Job's plot for the <sup>1</sup>H NMR titration of AgClO<sub>4</sub> against ligand **1**.

Standard solutions of the ligand **1** (5 mM) in CD<sub>3</sub>OD and AgClO<sub>4</sub> (5 mM) were prepared. Ten separate solution mixtures containing varying ratios of ligand **1** and AgClO<sub>4</sub> were prepared to get different Ag<sup>+</sup> mole fractions (χ<sub>Ag<sup>+</sup></sub>). For example, to prepare a solution mixture with χ<sub>Ag<sup>+</sup></sub> = 0.0, 0.5 mL ligand **1** solution only was measured into an NMR tube. To prepare a solution mixture with χ<sub>Ag<sup>+</sup></sub> = 0.1, 0.45 mL ligand **1** solution was mixed with 0.05 mL AgClO<sub>4</sub> solution inside an NMR tube. Also, to prepare a solution mixture of χ<sub>Ag<sup>+</sup></sub> = 0.2, 0.40 mL ligand **1** solution was mixed with 0.10 mL AgClO<sub>4</sub> solution and so on until a solution mixture of χ<sub>Ag<sup>+</sup></sub> = 0.9 was prepared by mixing 0.05 mL ligand **1** solution with 0.45 mL AgClO<sub>4</sub> solution. The <sup>1</sup>H NMR experiments of all solution mixtures and the free ligand **1** were recorded. The plot of χ<sub>L</sub>·Δδ (where χ<sub>L</sub> = mole fraction of ligand **1** and Δδ = chemical shift of Ag<sup>+</sup>-**1** complex minus chemical shift of free ligand **1**) against χ<sub>Ag<sup>+</sup></sub> was constructed from the data generated.

### Mole ratio plot for the <sup>1</sup>H NMR titration of AgClO<sub>4</sub> against ligand **1**.

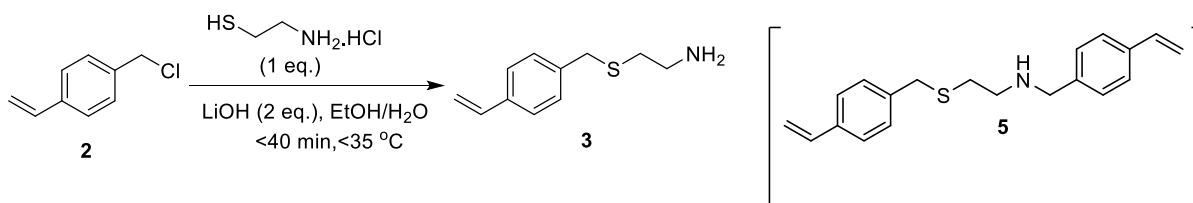
The ligand **1** (13.8 mg, 0.059 mmol) was dissolved in 0.5 mL CD<sub>3</sub>OD and transferred to into amber NMR tube. Standard solution of AgClO<sub>4</sub> (419 mM) in CD<sub>3</sub>OD was also prepared. A constant volume of AgClO<sub>4</sub> solution (25 μL) was added to **1** in the NMR tube to obtain varying Ag<sup>+</sup>/**1** mole ratios (*n*<sub>Ag<sup>+</sup></sub>/*n*<sub>3</sub>). For example, to target a *n*<sub>Ag<sup>+</sup></sub>/*n*<sub>3</sub> = 0.5, 25 μL of AgClO<sub>4</sub> was added using a glass syringe to the neat ligand **1** solution and the <sup>1</sup>H NMR spectrum was recorded. Also, to target a *n*<sub>Ag<sup>+</sup></sub>/*n*<sub>3</sub> = 1.0, 25 μL of AgClO<sub>4</sub> was added using a glass syringe to the solution mixture with *n*<sub>Ag<sup>+</sup></sub>/*n*<sub>3</sub> = 0.5 and the <sup>1</sup>H NMR spectrum was recorded. The constant addition of the AgClO<sub>4</sub> solution was continued until a

$n_{\text{Ag}^+}/n_3 = 4.0$  was achieved. The plot of  $\Delta\delta$  (where  $\Delta\delta$  = chemical shift of  $\text{Ag}^+$ -**1** complex minus chemical shift of free ligand **1**) against  $n_{\text{Ag}^+}/n_3$  was constructed using the data generated.

## Results and discussion

### Synthesis of *N*-(2-((4-vinylbenzyl)thio)ethyl)acetamide (**1**)

The amine **3** was obtained in a 76 % yield and as a pure compound (evidenced by the  $^1\text{H}$  NMR spectrum). Access to pure amine **3** was afforded after findings from a previous study revealed that the reaction conditions (40 min and 35 °C) could help minimize the formation of the debenzylated product **5** (Scheme 3).<sup>34</sup> Though the amine **3** on its own may have been utilized as  $\text{Ag}^+$  scavenger since it contains the donor atoms *S*- and *N*- known for binding  $\text{Ag}^+$ , yet the basicity of the nitrogen group suggested that this amine will be unstable at low pH due to protonation which may limit the amine's  $\text{Ag}^+$  binding potential. Therefore, the amine **3** was treated with acetyl chloride following a nucleophilic addition-elimination mechanism to give the amide **1** also as a pure compound (evidenced by  $^1\text{H}$  NMR) in a 76 % yield.



Scheme 3. Synthesis of 4-vinylbenzyl cysteamine **3** showing the debenzylated side product **5**

### Efficiency and selectivity of $\text{Ag}^+$ extraction from aqueous solutions

The previously published solvent extraction method was employed to investigate the efficiency of the ligands for  $\text{Ag}^+$  extraction.<sup>15,31</sup> The choice of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  as competing ions is borne out of the knowledge that these metals usually coexist with  $\text{Ag}^+$  in ores and mine tailings.<sup>35</sup> Aqueous solutions of the metals containing low concentrations (4 mgL<sup>-1</sup>) of  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  were prepared since  $\text{Ag}^+$  is often present in within this concentration range in repositories where the ligands might find application.<sup>35</sup>

It was observed that neat chloroform itself (the control) was able to extract some metals with a slight preference for  $\text{Ag}^+$  (Figure 2). This is likely due to the differential partial solubility of these metals in chloroform. As expected, the extraction efficiency observed for ligand **1** was higher than of the control (Ligand **1**: 36.1±1.9 vs Control: 13.4±3.8%, Table 1) and this was attributed to the presence of the *S*-, *N*- and *O*- donors in **1**. Notwithstanding the low extraction efficiency observed, the simplicity in preparation of **1** suggests that it should be targeted as a ligand for the industrial scale  $\text{Ag}^+$  extraction. The selectivity of the ligand **1** was also observed to be higher than that for the control and this was attributed to the preferential coordination of the soft donors *S*- and *N*- to  $\text{Ag}^+$  according to the Hard Soft Acid Base (HSAB) rule.<sup>23</sup> Furthermore, ligand **1** was observed to demonstrate excellent selectivity for  $\text{Ag}^+$  over  $\text{Cu}^{2+}$  and

Pb<sup>2+</sup> since based on the ICP-OES data obtained, neither Cu<sup>2+</sup> nor Pb<sup>2+</sup> were extracted by the ligand **1** during the solvent extraction experiment (Figure 2).

Table 1. Efficiency and selectivity of neat chloroform (control) and ligand **1** for Ag<sup>+</sup> relative to Cu<sup>2+</sup> and Pb<sup>2+</sup>

Extractant	Ag <sup>+</sup> Removal Efficiency (%)	$K_{Ag^+/Cu^{2+}}$	$K_{Ag^+/Pb^{2+}}$
Control	13.4±3.8	4.3	7.1
Ligand <b>1</b>	36.1±1.9	36.0	36.1

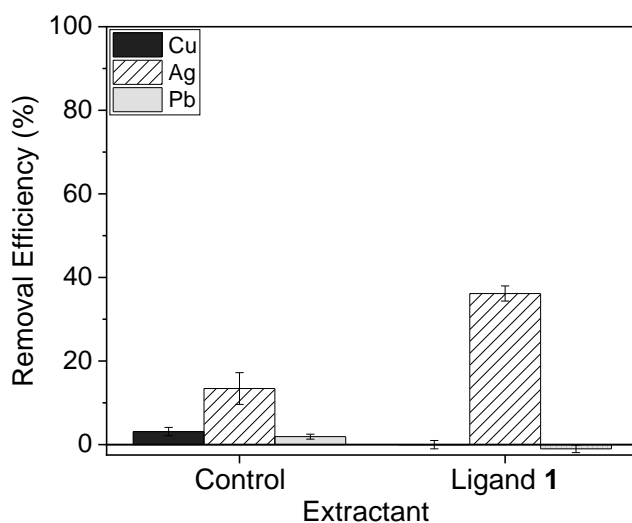
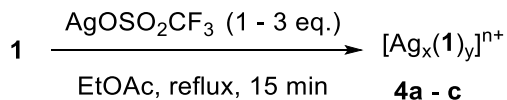


Figure 2. ICP-OES data showing metal extraction efficiencies by neat chloroform (control) and ligand **1**.

### Mass spectrometry studies of Ag<sup>+</sup>-**1** complex

To gain insight into the nature of the binding of Ag<sup>+</sup> by the ligand **1**, Ag<sup>+</sup> complexes of **1** were prepared by varying the equivalents of the silver triflate (1-3 eq) relative to the ligand (Scheme 4). Consequently, the Ag<sup>+</sup>-**1** complexes (**4a-c**) were obtained in moderate to high yields (Table 2) and characterized by means of low- and high- resolution mass spectrometry.



Scheme 4. Syntheses of Ag<sup>+</sup> complexes of **1** using Ag triflate

The low-resolution mass spectrometry (LRMS) data of the complexes **4a – c** (Figure 3) indicated that both the 1:1 and 1:2 (Ag<sup>+</sup>:**1**) complexes are formed and this was confirmed by high resolution mass spectrometry (HRMS) analyses.

Table 2. Effect of Ag<sup>+</sup> equivalent on the stoichiometry of Ag<sup>+</sup>-ligand **1** complex

<b>Entry</b>	<b>AgOSO<sub>2</sub>CF<sub>3</sub></b> <b>eq.</b>	<b>Product</b>	<b>x:y</b>	<b>Yield</b>
1	1	<b>4a</b>	1:1 and 1:2	94%
2	2	<b>4b</b>	1:1 and 1:2	75%
3	3	<b>4c</b>	1:1 and 1:2	85%



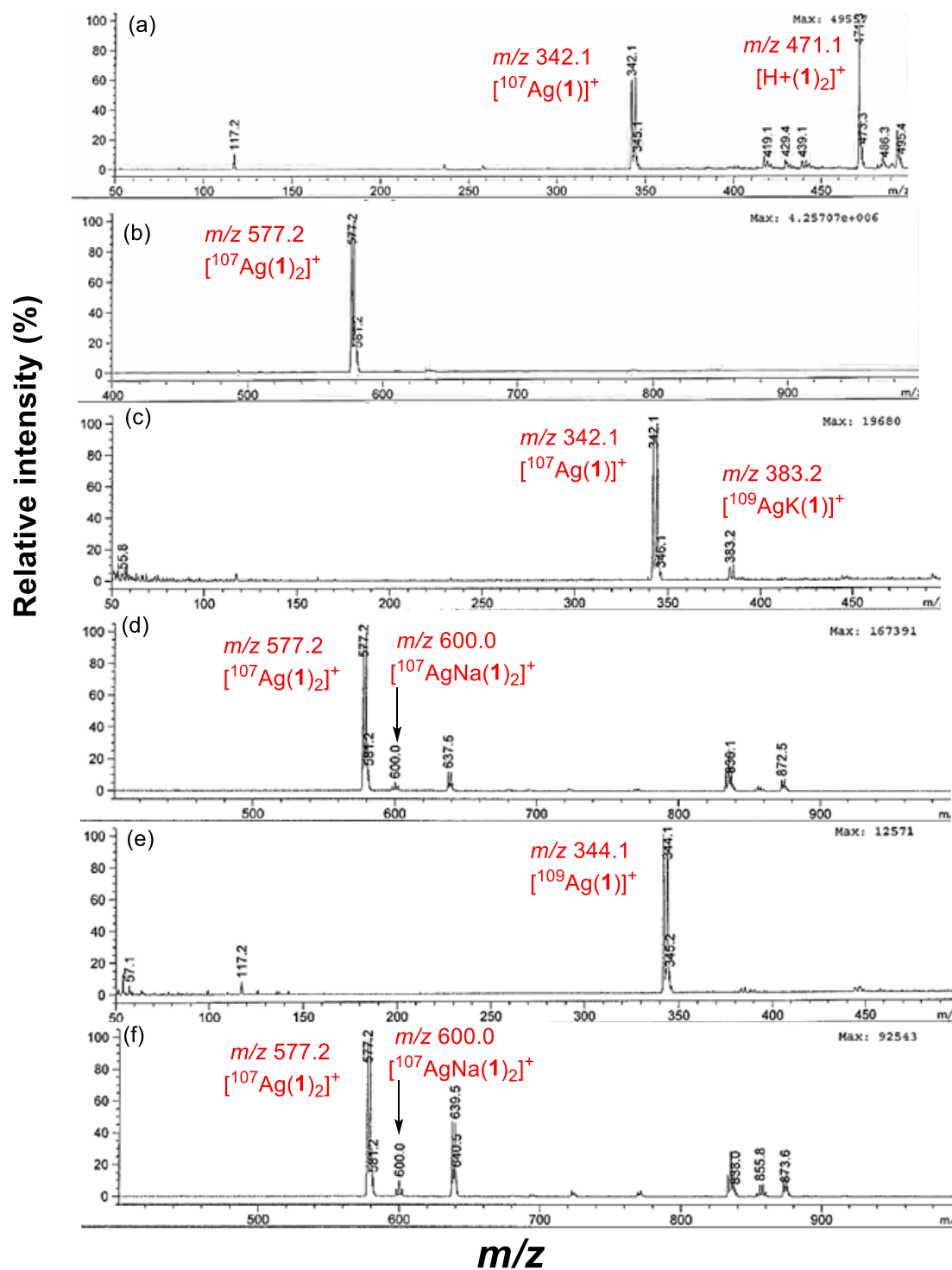


Figure 3. Partial low-resolution ESI mass spectra of  $\text{Ag}^+\cdot\mathbf{1}$  complexes from treatment of ligand **1** with (a) one equivalent (0-500  $m/z$ ), (b) one equivalent (500-1000  $m/z$ ), (c) two equivalents (0-500  $m/z$ ), (d) two equivalents (500-1000  $m/z$ ), (e) three equivalents (0-500  $m/z$ ), (f) three equivalents (500-1000  $m/z$ ) of  $\text{AgOSO}_2\text{CF}_3$

### Job's and mole ratio plots for Ag<sup>+</sup>-**1** complex

The Job's plot for the Ag<sup>+</sup>-**1** complex was constructed from <sup>1</sup>H NMR titration of equal concentrations of ligand **1** and Ag<sup>+</sup> (Figures 4a and b). The gentle curvature of the curve in the Job's plot (Figures 4b) indicates the binding between the ligand **1** and Ag<sup>+</sup> is perhaps weak.<sup>36</sup> Furthermore, it can be observed that the coefficient on the x-axis of the maxima in the curve in the Job's plot (Figures 4b) is at  $\chi_{Ag^+} = 0.5$ , indicating that the ligand **1** may bind Ag<sup>+</sup> in any of the 1:1, 2:2 or any other *n:n* fashion. To confirm the actual stoichiometry, mole ratio plots of the interaction of **1** with Ag<sup>+</sup> was constructed.

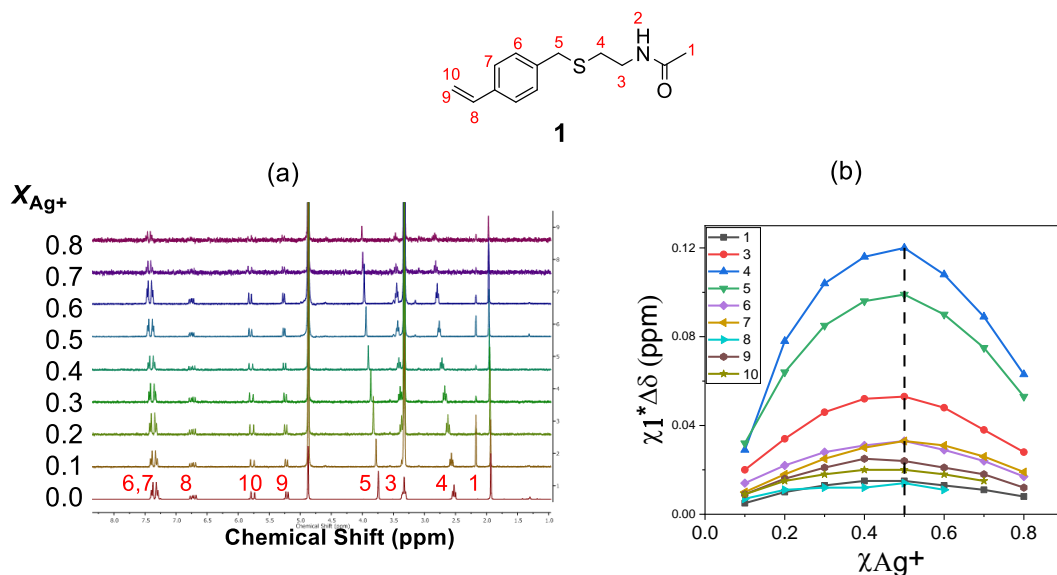


Figure 4. (a) <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) spectra of the interaction of Ag<sup>+</sup> with **1** (b) Job's plots of the interaction of 5 mM Ag<sup>+</sup> with 5 mM ligand **1** at room temperature

The mole ratio plot Ag<sup>+</sup>-**1** was constructed from <sup>1</sup>H NMR titration different from that employed for the Job's plot. Proton NMR spectra after successive addition of the Ag<sup>+</sup> solution to ligand **1** was recorded (Figure 5a), and the mole ratio plots are constructed from the change in chemical shift values obtained from these spectra (Figure 5b). In a typical mole ratio plot, the stoichiometry of a complex is the coefficient on the x-axis where the curve changes shape for example from concave to convex or vice versa. In the Ag<sup>+</sup>-**1** mole ratio plot (Figure 5b), a tentative point of inflection could be identified (for example using the curve representing proton '4') and it corresponds to a  $n_{Ag^+}/n_1 = 1.0$ , indicating that the **1** binds to Ag<sup>+</sup> in a 1:1 fashion and confirms mass spectrometry and Job's plot results. The observation of a distinct point of inflection only at  $n_{Ag^+}/n_1 = 1.0$  may be due to that fact that the 1:1 (Ag<sup>+</sup>:**1**) complex is more stable in solution than the 1:2 (Ag<sup>+</sup>:**1**) complex observed from mass spectrometry analyses. This claim is backed by the observation of a continuous increase in the Δδ (Figure 5b) indicating that other types of stoichiometries (perhaps including the observed 1:2 – Ag<sup>+</sup>:**1** from the LRMS-ESI spectra) may exist for the Ag<sup>+</sup>-**1** complex.

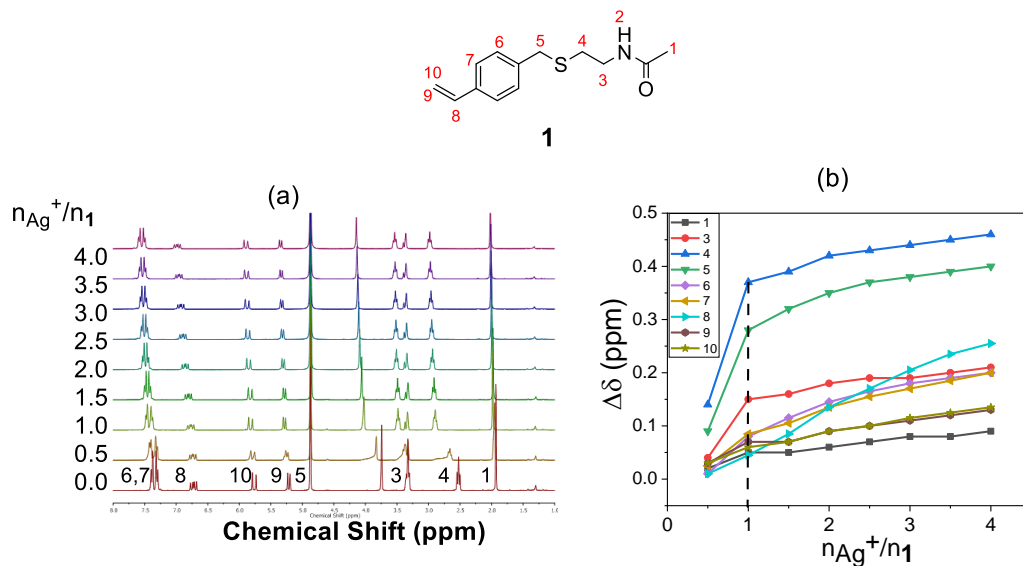


Figure 5. (a) <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) spectra of the interaction of Ag<sup>+</sup> with ligand **1** and (b) mole ratio plot of the interaction of Ag<sup>+</sup> with ligand **1**.

The highest  $\Delta\delta$  values were observed for protons '4' and '5' (the protons on carbons alpha to the S- donor atoms). The next highest  $\Delta\delta$  values were observed for proton '3' (the protons on the carbons alpha to the amide N- donor (Figures 5a and b). The observed high  $\Delta\delta$ 's may be due to deshielding effects experienced by these protons as the S- and N- donors participate in binding Ag<sup>+</sup>. Unsurprisingly, lower  $\Delta\delta$  values were observed for phenyl protons ('6' and '7') since they are not in the neighbourhood of the S- and N- donors. The continuous increase in  $\Delta\delta$  for vinyl proton '8' (Figure 5b) may be attributed to the participation of the  $\pi$  electrons in binding Ag<sup>+</sup> after the S- and N- donor sites are saturated. Based on these observations, it was hypothesized that ligand **1** may bind Ag<sup>+</sup> using its S- and N- donors to form linear and tetrahedral complexes (Figures 6a and b).

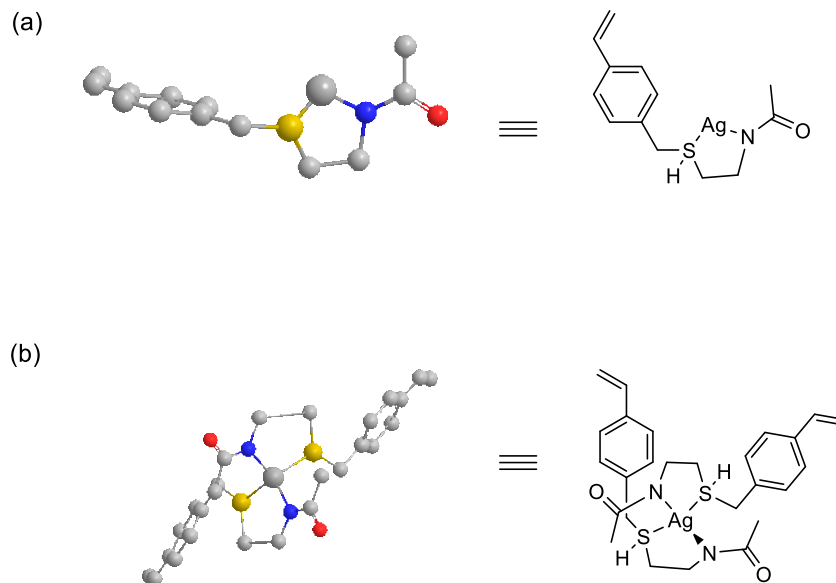


Figure 6. Proposed structures for (a)  $[\text{Ag}(\mathbf{1})]^+$  and (b)  $[\text{Ag}(\mathbf{1})_2]^+$  based on stoichiometry results observed from mass spectrometry and  $^1\text{H}$  NMR titrations (leading to Job's and mole ratio plots).

## Conclusion

A novel amide-based ligand possessing *S*-, *N*- and *O*- donors has been synthesized and tested for  $\text{Ag}^+$  removal from aqueous solutions also containing the base metals –  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ . The ligands were accessed in two simple steps with 76% yield. The ligand was observed to demonstrate excellent selectivity and moderate efficiency for  $\text{Ag}^+$  removal. Detailed binding studies revealed that the ligand forms two different types of complexes with  $\text{Ag}^+$  - the 1:1 and 1:2 ( $\text{Ag}^+:\text{ligand } \mathbf{1}$ ) complexes indicating bent linear and tetrahedral geometries respectively. The simplicity and yield in preparation of the novel ligand suggests that it could be considered for industrial scale  $\text{Ag}^+$  removal purposes. The presence of the vinyl tether offers the ligand as a candidate for linkage *via* polymerization to a nanoparticle with appropriate surface functionalities for  $\text{Ag}^+$  extraction.

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## Declaration of interest statement

The authors declare no conflict of interest.

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