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**Co-ordination polymers and isomerism; a study using  
silver(I) and a  $\pi$ -stacked ligand.**

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## Graphical Abstract

### Abstract

The ligand 2,5-bis(2-pyridylmethylsulfanylmethyl)pyrazine (**L**) was prepared by the base coupling of 2-(sulfanylmethyl)pyridine and 2,5-bis(chloromethyl)pyrazine. This new ligand was treated with  $\text{AgClO}_4$  in a 1:1 metal-to-ligand ratio and with  $\text{AgNO}_3$  in a 1:2 metal-to-ligand ratio to give coordination polymers. The crystal structures of  $\{[\text{Ag}(\text{L})]\text{ClO}_4\}_\infty$  (**1**) and  $\{[\text{Ag}_2(\text{L})](\text{NO}_3)_2\}_\infty$  (**2**) were determined. The Ag(I) ions in the one-dimensional polymeric chains **1** adopted square-pyramidal geometries with the pyridine and pyrazine N donors coordinated in an extremely bent fashion. The structure of **2** revealed two isomeric polymer chains in the one crystal forming a single supramolecular array. The isomeric polymers differed in the donor atoms about the Ag(I) ions and in the arrangement of adjacent ligands along the chain. A feature of both structures was that **L** adopted a "three-layer"  $\pi$ -stacked arrangement.

### Introduction

The use of flexible ligands to form supramolecular arrays has been circumspect, due to the less predictable nature of such systems. However such flexible ligands when reacted with Ag(I) have been shown to generate

some unusual and interesting supramolecular arrays,<sup>1</sup> including helices,<sup>2</sup> helicates,<sup>3</sup> boxes,<sup>4</sup> brick-walls<sup>5</sup> and two-dimensional grids.<sup>6</sup> We are investigating the Ag(I) complexes of a series of flexible ligands based on a heterocyclic spacer linked by two thioether-pyridine arms. We have shown these ligands, which incorporate three heterocyclic rings, can adopt a "three-layer"  $\pi$ -stacked structural motif when complexed with Ag(I).<sup>7</sup> This columnar motif has proved to be a useful building block for the construction of supramolecular systems. Herein we report two polymeric arrays formed by the 1:1 reaction of **L** with AgClO<sub>4</sub> and the 1:2 reaction of **L** with AgNO<sub>3</sub>. Despite the different metal-to-ligand ratios, both arrays are dominated by the "three-layer"  $\pi$ -stacked arrangement of the ligand.

Supramolecular arrays encompassing polymers are typically formed through the standard types of weak interactions e.g.  $\pi$ - $\pi$  stacking,<sup>1,8</sup> M-X...H<sup>9</sup> and H-bonding.<sup>10</sup> The polymers themselves are usually held together by metal-ligand bonds and the metal centres have properties in common with classical coordination complexes. In particular, classical metal complexes may exhibit various types of isomerism including structural, linkage, conformational and optical isomerism. These types of isomerism in a supramolecular array may lead to polymorphism<sup>11</sup> and/or supramolecular isomerism.<sup>12</sup> In addition, there exists the rare phenomenon of two isomers of a classical coordination complex, which have the same donor set but different stereochemistries, being present in the same crystal.<sup>13</sup> Given that

the types of isomerism found in classical coordination chemistry are now being identified in coordination polymer systems, it should not be too surprising to find two different polymeric isomers in one crystal. In addition to the related  $\text{AgClO}_4$  complex with **L**, we now report the  $\text{AgNO}_3$  complex of **L** as the first example of two different coordination polymer chains crystallising in the same crystal.

## Results and Discussion

### Ligand synthesis

The ligand 2,5-bis(2-pyridylmethylsulfanylmethyl)pyrazine (**L**) was prepared by the thioether base coupling of 2,5-bis(chloromethyl)pyrazine and 2-(sulfanylmethyl)pyridine using a 1:2 molar ratio (Scheme 1). The chlorination of the nitrogen containing aromatic precursors was achieved by a variety of different methods with mixed results and deserves some comment. The first method involved using the standard chlorinating agent *N*-chlorosuccinimide, which has not always proved successful for the halogenation of pyridyl arms with low yields being obtained.<sup>14</sup> In our hands using benzene as a solvent, 2-methylpyridine was chlorinated to give 2-(chloromethyl)pyridine, and 2,5-dimethylpyrazine was chlorinated to give 2,5-bis(chloromethyl)pyrazine with yields of 10 and 21%, respectively. In each case, the product required purification by column chromatography. The second method, involved using  $\text{SOCl}_2$  and 2-(hydroxymethyl)pyridine

to give 2-(chloromethyl)pyridine in a moderate yield of 63% without further purification.<sup>15</sup> This method was perfectly adequate for the preparation of 2-(chloromethyl)pyridine although it suffers from the need to use the unpleasant and corrosive  $\text{SOCl}_2$  reagent. However the final method was found to be high yielding and more cost effective. This method involved using the less common but often effective chlorinating agent trichloroisocyanuric acid.<sup>16</sup> We obtained 2-(chloromethyl)pyridine in 90% yield, with no further purification required, from 2-methylpyridine using  $\text{CHCl}_3$  as the solvent. Unfortunately, no reaction occurred between 2,5-dimethylpyrazine and trichloroisocyanuric acid and so the first method, although inefficient, was used to chlorinate the heterocycle.

As isolated ligand **L** was not analytically pure. Attempts to obtain analytically pure material using column chromatography over silica gel were ineffective. However, high-resolution electrospray mass spectrometry in conjunction with the two-dimensional HMBC and HSQC NMR experiments confirmed the successful synthesis of **L**. Subsequently, the ligand was reacted with  $\text{AgClO}_4$  and  $\text{AgNO}_3$  and formed microanalytically pure complexes.

#### **Synthesis and structure of $\{[\text{Ag}(\text{L})]\text{ClO}_4\}_\infty$ **1****

A 1:1 molar ratio of  $\text{AgClO}_4$  and **L** in degassed MeCN gave a cream solid upon concentration of the clear solution and subsequent addition of diethyl

ether. Microanalytical data were consistent with the solid having a 1:1 metal-to-ligand ratio.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were consistent with a symmetrical species in solution and contained peaks similar to those of the free ligand. Variable temperature  $^1\text{H}$  NMR spectra measured in  $\text{CD}_3\text{CN}$  showed no significant changes other than broadening of peaks down to the temperature limit of the solvent. The symmetrical nature of the  $^1\text{H}$  NMR spectra implied that the solution species was either, symmetric and static, or more likely asymmetric and undergoing rapid dynamic processes which may include equilibria between species of differing nuclearities. Electrospray mass spectrometry under normal operating conditions in MeCN showed four major peaks which had the correct isotopic patterns for  $\text{LH}^+$  at 355,  $[\text{Ag}(\text{L})]^+$  at 463,  $[\text{Ag}(\text{L})_2]^+$  at 815 and  $[\text{Ag}_2(\text{L})_2\text{ClO}_4]^+$  at 1023  $m/z$ . The existence of the peak at 1023  $m/z$  indicated that **1** may exist as a dimeric species in solution as has been found in related systems.<sup>7b</sup> However this peak could be from an oligomeric fragment since Ag(I) complexes of similar ligands have a tendency to form polymers in the solid state.<sup>2a,17</sup> Single crystals suitable for X-ray diffraction were grown from the slow evaporation of a MeCN solution of the complex.

The X-ray crystal structure showed that the complex was polymeric and consisted of repeating  $[\text{Ag}_2(\text{L})_2(\text{ClO}_4)_2]$  units. The asymmetric unit contained one ligand (in two halves), one Ag(I) ion and one  $\text{ClO}_4^-$

counterion (Fig. 1). The  $\text{ClO}_4^-$  anion was disordered about a three-fold axis over two sites, with site occupancy factors of 0.84 and 0.16, respectively. Each ligand was joined to an adjacent ligand by a distorted five-coordinate Ag(I) ion. The bridging nature of the Ag(I) ion led to the formation of the coordination polymer, which ran parallel to the  $c$  axis. Five-coordinate Ag(I) ions in extended networks are rare, with only four such crystal structures reported in the literature.<sup>18</sup> Each Ag(I) ion was bound in a square-pyramidal fashion ( $\tau = 0.15$ )<sup>19</sup> by  $\text{N}_{\text{pz}}\text{S}$  coordination from one ligand and  $\text{N}'_{\text{py}}\text{N}'_{\text{pz}}\text{S}'$  coordination from an adjacent ligand. The basal plane was occupied by  $\text{N}_{\text{pz}}\text{SN}'_{\text{py}}\text{S}'$  while the apical site was occupied by an  $\text{N}'_{\text{pz}}$  donor. The nitrogen donor atoms were all coordinated to the Ag(I) ion in a bent manner, which was determined from an analysis of the angle between the Ag(I) ion, the nitrogen atom and the centroid of the associated heterocyclic ring ( $\text{Ag(I)-N}'_{\text{py}}\text{-cent}_{\text{py}}$   $141.5^\circ$ ,  $\text{Ag(I)-N}'_{\text{pz}}\text{-cent}_{\text{pz}}$   $158.5^\circ$  and  $\text{Ag(I)-N}_{\text{pz}}\text{-cent}_{\text{pz}}$   $162.4^\circ$ ). A search of 546 Ag(I)-pyridine bond lengths and  $\text{Ag(I)-N}_{\text{py}}\text{-cent}_{\text{py}}$  bond angles using the Cambridge Structural Database (CSD)<sup>20</sup> revealed that the  $\text{Ag(I)-N}_{\text{py}}$  bond length was in the upper quartile of observed distances and the  $\text{Ag(I)-N}_{\text{py}}\text{-cent}_{\text{py}}$  angle was just outside all the observed values. A similar search of 33  $\text{Ag(I)-N}_{\text{pz}}$  bond lengths and  $\text{Ag(I)-N}_{\text{pz}}\text{-cent}_{\text{pz}}$  bond angles showed that the  $\text{Ag(I)-N}_{\text{pz}}$  bond lengths were just below the upper quartile and the  $\text{Ag(I)-N}_{\text{pz}}\text{-cent}_{\text{pz}}$  angles were at the limit of the observed values. The remaining  $\text{N}_{\text{py}}$  donor was considered to

interact only weakly, if at all, with the Ag(I) ion because not only was the Ag(I)-N<sub>py</sub> distance of 2.710(2) Å at the boundary of reported values, but more importantly the Ag(I)-N<sub>py</sub>-cent<sub>py</sub> angle at 131.8° was 10° smaller than the most extreme value observed in the CSD search. Successful complexation despite the relatively long bond lengths and very unusual bond angles can be attributed to the accommodating nature of the Ag(I) coordination sphere particularly when placed in complicated polymeric arrays.

Each ligand adopted a *syn-syn* arrangement in which the sulfur donors were coordinated to the Ag(I) ion in an endodentate fashion with Ag(I)-S distances around the mean value of 413 observed silver-thioether distances in a CSD search.<sup>20</sup> As the chain progressed alternating ligands were turned around with respect to each other such that the sulfur donors were diametrically opposite each other across the coordinated Ag(I) centre (Fig. 2). One of the centrosymmetric ligands was considered to be coordinated to two Ag(I) ions through all six donor atoms (N<sub>4</sub>S<sub>2</sub>) while the other centrosymmetric ligand was considered to be coordinated to two Ag(I) ions through only two pyrazine and two sulfur donors (N<sub>2</sub>S<sub>2</sub>). Each N<sub>4</sub>S<sub>2</sub> donor ligand was also slightly twisted with respect to the adjacent N<sub>2</sub>S<sub>2</sub> donor ligands. The N<sub>4</sub>S<sub>2</sub> donor ligand adopted a ‘three-layer’  $\pi$ -stacked conformation (centroid-centroid  $\pi$ -stacking distance = 3.49 Å)<sup>8</sup> in which the pyridine rings were tilted at 16.3 ° with respect to the pyrazine ring. The



$N_2S_2$  donor ligand also adopted a ‘three-layer’  $\pi$ -stacked conformation despite the fact that the pyridine rings were uncoordinated. The aromatic rings were also strongly  $\pi$ -stacked (centroid-centroid  $\pi$ -stacking distance = 3.49 Å) with the pyridine rings tilted to a lesser degree with respect to the pyrazine ring (12.2 °) than the  $N_4S_2$  donor ligand. The reduction in the angle at which the rings were tilted with respect to each other in the  $N_2S_2$  donor ligand was thought to be due to the fact that the pyridine rings remained uncoordinated. The coordination of the pyridine rings in the  $N_4S_2$  donor ligand induced a larger tilt of the aromatic rings.

The polymeric chains formed two-dimensional sheets in the *ac* plane through intermolecular interactions between  $ClO_4^-$  ions and hydrogen atoms (O...H 2.16 – 2.51 Å). Each  $ClO_4^-$  ion was situated next to a gap between adjacent ligands in the polymer thread and was involved in a large number of O...H interactions. No intermolecular  $\pi$ -stacking or  $ClO_4^-$  interactions were observed between the two-dimensional sheets. There was no solvent accessible volume available within the crystal structure.<sup>21</sup>

### **Synthesis and structure of $\{[Ag_2(L)](NO_3)_2\}_\infty 2$**

A 2:1 molar reaction of  $AgNO_3$  and **L** in degassed MeCN was allowed to stir for three days. The cream solid, which precipitated, was isolated and gave microanalysis consistent with a 2:1 metal-to-ligand ratio.

The  $^1H$  NMR spectrum in  $CD_3CN$  was consistent with a symmetrical species in solution and contained peaks similar to those of the free ligand.

The  $^{13}\text{C}$  NMR spectrum was not collected due to the low solubility of the complex in all common organic solvents. The variable temperature  $^1\text{H}$  NMR spectra in  $\text{CD}_3\text{CN}$  showed little change, apart from slight broadening of the peaks, down to the temperature limit of the solvent. As with **1**, the symmetrical nature of the  $^1\text{H}$  NMR spectra implied that the solution species was either, symmetric and static, or asymmetric and undergoing rapid dynamic processes, which may include equilibria between species of differing nuclearities. Electrospray mass spectrometry of the complex under normal operating conditions in MeCN showed ions at 189  $[\text{Ag}(\text{MeCN})_2]^+$ , 356  $\text{LH}^+$ , 463  $[\text{Ag}(\text{L})]^+$ , 632  $[\text{Ag}_2(\text{L})\text{NO}_3]^+$ , 818  $[\text{Ag}(\text{L})_2]^+$ , 986  $[\text{Ag}_2(\text{L})_2\text{NO}_3]^+$  and 1157  $[\text{Ag}_3(\text{L})_2(\text{NO}_3)_2]^+$   $m/z$  which were assigned on the basis of their appropriate isotope patterns (Fig. 3). The peaks at 818 and 1157  $m/z$  were clearly visible above the baseline despite their small abundances. The presence of the oligomeric fragments at 632, 986 and 1157  $m/z$  suggested that the complex may be polymeric. The infrared spectrum of  $\{[\text{Ag}_2(\text{L})(\text{NO}_3)_2]\}_\infty$  exhibited one strong very broad band which ranged from 1276 to 1383  $\text{cm}^{-1}$  indicating that bound nitrate ions were probably present.<sup>22</sup> X-ray quality crystals were grown from the slow diffusion of a  $\text{CHCl}_3$  solution of **L** layered with neat  $\text{CH}_2\text{Cl}_2$  and a MeCN solution of  $\text{AgNO}_3$ .

The X-ray analysis revealed that the complex was present as two structurally isomeric polymer chains within the one crystal. The

asymmetric unit contained three separate residues: a water molecule and two isomeric polymer fragments **2a** and **2b**. With respect to the asymmetric unit, isomers **2a** and **2b** both contained two Ag(I) ions, two bound  $\text{NO}_3^-$  ions and one ligand (in two halves).

**Polymeric isomer 2a.** The two Ag(I) ions in **2a** both adopted severely distorted tetrahedral arrangements, however the donor atoms surrounding each metal centre were different (Fig. 4). The Ag(4) ion was coordinated by a  $\text{N}_{\text{py}}\text{N}_{\text{py}}'\text{O}_2$  donor set, while Ag(3) was bound by a  $\text{N}_{\text{pz}}\text{SN}_{\text{pz}}'\text{S}'$  donor set. Thus, all six donor atoms on each ligand present in **2a** were coordinated to Ag(I) ions. Both  $\text{NO}_3^-$  ions were coordinated in a monodentate fashion through oxygen atoms to Ag(4). The Ag-O bond distances were in the middle of the range for similar systems.<sup>20</sup> The O(23)-Ag(4)-O(13) bond angle [76.9(1)°] was particularly distorted away from the tetrahedral value. The thioether donors were bound in an endodentate fashion with Ag(3)-S distances within the normal range. The Ag(I) ions were separated by a relatively short Ag...Ag distance of 2.9477(9) Å.<sup>7b,23</sup> Each ligand in **2a** was joined to an adjacent ligand by the two Ag(I) ions. The bridging nature of the Ag(I) ions led to the formation a one-dimensional polymer, which ran along the (110) diagonal axis (Fig. 5).

Each ligand adopted a 'three-layer'  $\pi$ -stacked arrangement which was similar to that observed in **1**. The 'three-layer' stacks differ slightly for adjacent ligands in the polymeric chain (centroid-centroid  $\pi$ -stacking

distances = 3.59 and 3.61 Å) with the pyridine rings tilted at 11.7° from the pyrazine ring of one ligand and at 13.2° in the neighbouring ligand, respectively. As observed for **1**, the ligands alternated along the polymeric thread such that the sulfur donors were arranged diametrically opposite each other.

**Polymeric isomer 2b.** The two Ag(I) ions in **2b** were both surrounded by the same type of donor atoms and adopted distorted-tetrahedral arrangements (Fig. 6). The coordination sphere surrounding each Ag(I) ion was provided by an N<sub>py</sub>SN<sub>pz</sub>O donor set, with the oxygen donor being supplied by a NO<sub>3</sub><sup>-</sup> anion coordinated in a monodentate fashion. Thus all of the donor atoms on each ligand were coordinated to Ag(I) ions. The NO<sub>3</sub><sup>-</sup> anions in **2b** were badly disordered and were modelled by allowing each NO<sub>3</sub><sup>-</sup> anion to occupy two sites. The site occupancy factors for the NO<sub>3</sub><sup>-</sup> anion attached to Ag(1) and Ag(2) were 0.52 and 0.65, respectively. The sulfur donors were bound in an endodentate fashion with Ag-S bond lengths [2.579(1) and 2.580(2) Å] slightly shorter than those observed in **2a** [2.694(2) and 2.604(3) Å]. The Ag...Ag distance of 3.067(1) Å was in the middle of the range for similar systems and was slightly longer than that observed for **2a** [2.9477(9) Å].<sup>7b,23</sup> Adjacent ligands were joined together by two Ag(I) ions to form a one-dimensional polymer which also ran parallel to the (110) diagonal axis (Fig. 7). The ligands in **2b** were again folded into a 'three-layer' π-stacked

arrangement (centroid-centroid  $\pi$ -stacking distances = 3.81 and 3.51 Å). The strength of the  $\pi$ -stacking was slightly different due to the difference in the tilt of the pyridine rings to the pyrazine rings in adjacent ligands (18.1 ° and 12.3 °, respectively). The ligands alternated along the polymeric chain such that the sulfur donors were arranged adjacent to each other. This was in contrast to **1** and **2a**, which had the sulfur donors arranged diametrically opposite each other. The folding of the ligands in **2b** led to the generation of the same structural motif observed previously for a related dimer,  $[\text{Ag}_2(\text{L}')_2](\text{PF}_6)_2$ .<sup>7b</sup> An orthogonal fit of a portion of **2b** to all the non-hydrogen atoms of the  $[\text{Ag}_2(\text{L}')_2]^{2+}$  cation had a weighted root mean square deviation of 0.320 Å (Fig. 8). In the  $[\text{Ag}_2(\text{L}')_2](\text{PF}_6)_2$  dimer the three coordinate Ag(I) ions diverged by 0.159 Å from the NN'S trigonal planes. In **2b** the four coordinate Ag(I) ions diverged from the NN'S trigonal planes by 0.354 and 0.296 Å for Ag(1) and Ag(2), respectively. Thus, the presence of a coordinated  $\text{NO}_3^-$  ion at each Ag(I) centre made little impact on the position of the Ag(I) ion with respect to the trigonal planes. This highlights the role that simpler discrete complex species have in probing the coordination environments of metal ions in larger more complex arrays.

The polymeric isomers **2a** and **2b** adopted very different arrangements. An end-on view, down the (110) diagonal axis, of the two isomeric chains highlights the difference between the two structures (Fig. 9). Furthermore, chains of **2a** were linked together via weak

C-H...ONO<sub>2</sub> intermolecular interactions to form two-dimensional sheets, as were chains of **2b**. Weak C-H...ONO<sub>2</sub> intermolecular interactions also joined alternating two-dimensional sheets of **2a** and **2b** into a three-dimensional network (Fig. 9). Thus all of the NO<sub>3</sub><sup>-</sup> anions were involved in weak C-H...ONO<sub>2</sub> intermolecular interactions within the two- and three-dimensional arrays. The intermolecular interactions ranged in length from 2.37 – 2.51 Å. In addition to these interactions, the NO<sub>3</sub><sup>-</sup> ions of both **2a** and **2b** interacted with water molecules present in the crystal structure. No intermolecular  $\pi$ -stacking interactions were observed in the three-dimensional network.

The presence of two isomers within one crystal structure was probably the result of very small energy differences between the alternative polymeric arrangements and the influence of crystal packing forces to give the most favourable packing arrangement. Similar arguments have been proposed to explain the presence of two isomeric forms of discrete coordination complexes in the same crystal.<sup>13</sup> In the past the observation of two isomers within one crystal appear to have mainly involved stereoisomers which differed due to the different coordination geometries adopted by the metal centre.<sup>13</sup> The structure of **2** appeared to be remarkable in that both the arrangement in space of the ligand and the donor atoms surrounding the Ag(I) ions differed between the two isomers.

## Conclusion

A feature of the polymers **1**, **2a** and **2b** was the intramolecular ‘three-layer’  $\pi$ -stacking arrangement of the ligands. The arrangement of neighbouring ligands with respect to each other varied between the three polymers. When viewed along the polymer chain **1** and **2a** gave a figure-of-eight arrangement while **2b** gave an S-shaped arrangement (Figure 10). In addition, it appears that the presence of pyrazine spacers, which can coordinate to two metal centres, may promote the ability of the ligand to undergo intramolecular  $\pi$ -stacking due to the removal of electron density from the central spacer. This is particularly evident in **1** where the three-layer  $\pi$ -stack forms, despite the fact some of the pyridine rings remain uncoordinated to Ag(I). In contrast, related ligands containing benzene spacers tend to adopt stretched out ligand arrangements.<sup>17</sup>

Finally, there seems to be no report in the literature of two isomeric coordination polymers occurring in one crystal. However, there is a report of two isomeric hydrogen bonded polymers in the same crystal.<sup>24</sup> Supramolecular isomerism has been defined as "the existence of more than one network structure for the same building blocks."<sup>12</sup> Under this criterion our structure, which contains only one network comprised of two different isomeric polymers, does not constitute an example of supramolecular isomerism.

## Experimental

### General

The precursors 2-(chloromethyl)pyridine<sup>16</sup>, 2-(sulfanylmethyl)pyridine<sup>25</sup> and 2,5-bis(chloromethyl)pyrazine<sup>14</sup> were prepared by literature methods. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on either a Varian <sup>unity</sup>INOVA 300 or 500 MHz spectrometer. All variable temperature and two-dimensional NMR spectra were recorded on a Varian <sup>unity</sup>INOVA 500 MHz spectrometer. Infrared spectra were measured on a Perkin-Elmer Win-IR Spectrum BX FT-IR System (samples in KBr disks). Elemental analyses were performed by the Campbell Microanalytical laboratory at the University of Otago. Electrospray mass spectra (ES MS) were collected at the University of Waikato in positive-ion mode with a VG platform II mass spectrometer, using MeCN–H<sub>2</sub>O (1:1 vol./vol.) as the mobile phase.

**CAUTION:** Although no problems were encountered in this work, transition metal perchlorates are potentially explosive. They should be prepared in small amounts and handled with care.

### **Ligand preparation: 2,5-(2-pyridylmethylsulfanylmethyl)pyrazine (L)**

2-(Sulfanylmethyl)pyridine (9.31 g, 0.0738 mol) was added to degassed MeOH (250 mL) containing 1.72 g (0.0738 mol) of Na metal and was stirred for 1 h. 2,5-bis(chloromethyl)pyrazine (6.53 g, 0.0369 mol) was dissolved in degassed CH<sub>2</sub>Cl<sub>2</sub> and added to the above solution, refluxed for



4 h and stirred overnight. The resulting solution was reduced in volume to give a brown residue, which was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (100 mL), washed with H<sub>2</sub>O (2 x 100 mL), dried (MgSO<sub>4</sub>) and reduced again to give a crude oil. Purification on a silica gel column eluted with CHCl<sub>3</sub>/ethyl acetate (6:4 v/v) gave **L** as a golden oil (yield 4.5 g, 34%). (Found:  $M^+$ , 354.0971, <sup>12</sup>C<sub>18</sub><sup>1</sup>H<sub>18</sub><sup>14</sup>N<sub>4</sub><sup>32</sup>S<sub>2</sub> requires  $M$ , 354.0973); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.54 [2H, d, <sup>3</sup>*J*(HH) 4.0, H12], 8.51 (2H, s, H1), 7.64 (2H, dt, <sup>3</sup>*J*(HH) 7.5, <sup>4</sup>*J*(HH) 2.0, H10], 7.36 [2H, d, <sup>3</sup>*J*(HH) 7.5, H9], 7.17 [2H, ddd, <sup>3</sup>*J*(HH) 7.5, 4.0, <sup>4</sup>*J*(HH) 2.0 Hz, H11], 3.85 (4H, s, H7) and 3.82 (4H, s, H6); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 158.1 (C8), 152.2 (C2), 149.5 (C12), 143.8 (C1), 136.8 (C10), 123.3 (C9), 122.1 (C11) 37.7 (C6) and 34.5 (C7).

### Complexes

**{[Ag(L)]ClO<sub>4</sub>}<sub>∞</sub> 1.** AgClO<sub>4</sub> (29 mg, 0.14 mmol) dissolved in degassed MeCN (20 mL) was added via cannula to **L** (50 mg, 0.14 mmol) dissolved in degassed MeCN (20 mL) and allowed to stir for 1 h. The resulting solution was concentrated to 2 mL and diethyl ether was added (10 mL). The cream solid, which immediately precipitated, was filtered and dried *in vacuo* (yield 30 mg, 38%). Colourless crystals were grown from the slow evaporation of a MeCN solution. (Found: C, 38.4; H, 3.2; N, 10.0; S, 11.4. Calc for C<sub>18</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>ClAg: C, 38.5; H, 3.2; N, 10.0; S, 11.4%); <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 8.46 [2H, d, <sup>3</sup>*J*(HH) 4.0, py-H], 8.31 (2H, s, py-H), 7.82 [2H, t, <sup>3</sup>*J*(HH) 7.5, <sup>4</sup>*J*(HH) 2.0, py-H], 7.45 [2H, d, <sup>3</sup>*J*(HH) 7.5 Hz, py-

H], 7.31-7.34 (2H, m, py-H), 4.04 (4H, s, CH<sub>2</sub>) and 3.89 (4H, s, CH<sub>2</sub>); <sup>13</sup>C NMR (CD<sub>3</sub>CN):  $\delta$  156.5, 152.4, 150.9, 145.2, 139.9, 126.3, 124.4, 38.8 and 35.8; ES MS:  $m/z$  355 LH<sup>+</sup>, 463 [Ag(L)]<sup>+</sup>, 815 [Ag(L)<sub>2</sub>]<sup>+</sup> and 1023 [Ag<sub>2</sub>(L)<sub>2</sub>ClO<sub>4</sub>]<sup>+</sup>; Selected IR (KBr)/cm<sup>-1</sup>: 1087m (ClO<sub>4</sub><sup>-</sup>).

**{[Ag<sub>2</sub>(L)](NO<sub>3</sub>)<sub>2</sub>}<sub>∞</sub> 2.** AgNO<sub>3</sub> (48 mg, 0.28 mmol) dissolved in degassed MeCN (20 mL) was added via cannula to **L** (50 mg, 0.14 mmol) dissolved in degassed MeCN (20 mL) and allowed to stir for 3 days. The cream solid, which precipitated, was filtered and dried *in vacuo* (yield 35 mg, 36%). Colourless crystals were grown from the slow diffusion of a CHCl<sub>3</sub> solution (2 mL) of **L** (20 mg, 0.056 mmol) layered with CH<sub>2</sub>Cl<sub>2</sub> (1 mL) and a MeCN solution (5 mL) of AgNO<sub>3</sub> (19 mg, 0.11 mmol). (Found: C, 31.3; H, 2.6; N, 11.7; S, 9.7. Calc for C<sub>18</sub>H<sub>18</sub>N<sub>6</sub>O<sub>6</sub>S<sub>2</sub>Ag<sub>2</sub>: C, 31.2; H, 2.6; N, 12.1; S, 9.2%); <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  8.49 (2H, d, <sup>3</sup>J(HH) 6.0, py-H), 8.36 (2H, s, py-H), 7.83 [2H, td, <sup>3</sup>J(HH) 7.8, <sup>4</sup>J(HH) 2.1, py-H), 7.46 [2H, d, <sup>3</sup>J(HH) 7.8 Hz, py-H], 7.36 - 7.31 (2H, m, py-H), 4.03 (4H, s, CH<sub>2</sub>) and 3.89 (4H, s, CH<sub>2</sub>); ES MS:  $m/z$  189 [Ag(MeCN)<sub>2</sub>]<sup>+</sup>, 356 LH<sup>+</sup>, 463 [Ag(L)]<sup>+</sup>, 632 [Ag<sub>2</sub>(L)NO<sub>3</sub>]<sup>+</sup>, 818 [Ag(L)<sub>2</sub>]<sup>+</sup>, 986 [Ag<sub>2</sub>(L)<sub>2</sub>NO<sub>3</sub>]<sup>+</sup> and 1157 [Ag<sub>3</sub>(L)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>]<sup>+</sup>; Selected IR (KBr)/cm<sup>-1</sup>: 1276 – 1383w (NO<sub>3</sub><sup>-</sup>).

### X-Ray Crystallography

Diffraction data were collected on a Bruker SMART CCD diffractometer with graphite monochromated Mo-K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation. Intensities were corrected for Lorentz-polarisation effects<sup>26</sup> and a multiscan

absorption correction<sup>27</sup> was applied. The structures were solved by direct methods (SHELXS)<sup>28</sup> and refined on  $F^2$  using all data by full-matrix least-squares procedures (SHELXL 97).<sup>29</sup> The  $\text{ClO}_4^-$  anion in **1** was disordered about a three-fold axis over two sites. The O atoms had large thermal parameters and O(22) was refined isotropically. Both the  $\text{NO}_3^-$  anions in isomer **2b** were disordered over two sites. Many attempts were made to model the disorder, however the best model still gave a number of peaks of around  $1 \text{ e } \text{\AA}^{-3}$  about the disordered  $\text{NO}_3^-$  anion attached to Ag(3). This disorder was not investigated further. In addition N(44) was refined isotropically. Crystallographic data for the three structures are listed in Table 1.

CCDC reference number

See <http://www.rsc.org/suppdata/dt/> for crystallographic files in .cif format.

**[Table 1 about here]**

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**Table 1** Crystallographic data for complexes **1** and **2**

	<b>1</b>	<b>2</b>
Empirical formula	C <sub>18</sub> H <sub>18</sub> AgClN <sub>4</sub> O <sub>4</sub> S <sub>2</sub>	C <sub>36</sub> H <sub>36</sub> Ag <sub>4</sub> N <sub>12</sub> O <sub>13</sub> S <sub>4</sub>
<i>M</i>	561.80	1404.49
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	8.371(5)	11.445(5)
<i>b</i> /Å	10.844(5)	13.146(5)
<i>c</i> /Å	13.407(5)	17.529(5)
$\alpha$ /°	66.954(5)	100.182(5)
$\beta$ /°	80.260(5)	92.571(5)
$\gamma$ /°	73.600(5)	115.658(5)
<i>U</i> /Å <sup>3</sup>	1072.0(9)	2318(1)
<i>Z</i>	2	2
<i>T</i> /K	163(2)	163(2)
$\mu$ /mm <sup>-1</sup>	1.293	1.921
Reflections collected	13364	30447
Unique reflections ( <i>R</i> <sub>int</sub> )	4302 (0.0274)	9379 (0.0366)
<i>R</i> <sub>1</sub> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0310	0.0390
<i>wR</i> <sub>2</sub> (all data)	0.0865	0.1061

### Figure captions and scheme captions

Scheme 1. Schematic diagram of the preparation of the precursors for the thioether base coupling of 2-(sulfanylmethyl)pyridine and 2,5-bis(chloromethyl)pyrazine to form **L**.

Figure 1. Perspective view (crystallographic numbering) of the coordination environment of **1**. Thermal ellipsoids are drawn at the 50% probability level. Bonds drawn in black belong to the asymmetric unit.  $\text{ClO}_4^-$  anion omitted for clarity. Selected bond lengths (Å) and angles (°): Ag(1)-N(2) 2.509(2), Ag(1)-N(3) 2.596(2), Ag(1)-N(4) 2.523(2), Ag(1)-S(1) 2.648(1), Ag(1)-S(2) 2.644(1); N(2)-Ag(1)-N(4) 106.47(7), N(2)-Ag(1)-N(3) 167.51(7), N(4)-Ag(1)-N(3) 75.20(7), N(2)-Ag(1)-S(2) 116.73(5), N(4)-Ag(1)-S(2) 75.80(5), N(3)-Ag(1)-S(2) 75.75(5), N(2)-Ag(1)-S(1) 75.13(5), N(4)-Ag(1)-S(1) 119.92(6), N(3)-Ag(1)-S(1) 93.21(5), S(2)-Ag(1)-S(1) 158.33(3).

Figure 2. A view of the polymeric chain of **1**, illustrating the intramolecular  $\pi$ -stacking, the alternating ligand arrangements and the geometry about the metal centres.  $\text{ClO}_4^-$  anion and hydrogens omitted for clarity.

Figure 3. Electrospray Mass Spectrum of **2** in MeCN. Inset shows expansion of the experimental (**a**) and calculated (**b**) peak at 1157 *m/z*.

Figure 4. Perspective view (crystallographic numbering) of the coordination environment of **2a**. Thermal ellipsoids are drawn at the 50% probability level. Bonds drawn in black belong to the asymmetric unit. Selected bond length (Å) and angles (°): Ag(4)-N(5) 2.287(4), Ag(4)-N(8) 2.266(4), Ag(4)-O(13) 2.583(4), Ag(4)-O(23) 2.548(4), Ag(3)-N(6) 2.337(4), Ag(3)-N(7) 2.352(4), Ag(3)-S(3) 2.694(2), Ag(3)-S(4) 2.604(2); N(6)-Ag(3)-N(7) 119.0(1), N(7)-Ag(3)-S(4) 78.3(1), N(6)-Ag(3)-S(3) 76.5(1), S(4)-Ag(3)-S(3) 152.00(5), N(6)-Ag(3)-S(4) 123.1(1), N(7)-Ag(3)-S(3) 111.3(1), N(8)-Ag(4)-N(5) 143.4(1), N(8)-Ag(4)-O(23) 121.2(1), N(5)-Ag(4)-O(13) 124.5(1), O(23)-Ag(4)-O(13) 76.9(1), N(5)-Ag(4)-O(23) 89.6(1), N(8)-Ag(4)-O(13) 84.6(1).

Figure 5. A view of the polymeric chain of **2a**, illustrating the intramolecular  $\pi$ -stacking, the alternating ligand arrangements and the geometry about the metal centres. Hydrogens omitted for clarity.

Figure 6. Perspective view (crystallographic numbering) of the coordination environment of **2b**. Thermal ellipsoids are drawn at the 50% probability level. Bonds drawn in black belong to the asymmetric unit. The NO<sub>3</sub><sup>-</sup> anions with the lowest site occupancy factors were omitted for clarity. Selected bond length (Å) and angles (°): Ag(1)-N(1) 2.405(4), Ag(1)-N(4) 2.248(4), Ag(1)-S(1) 2.579(1), Ag(1)-O(33) 2.49(2), Ag(2)-N(2) 2.242(4), Ag(2)-N(3) 2.359(4), Ag(2)-S(2) 2.580(2), Ag(2)-O(41) 2.601(7); N(4)-Ag(1)-O(33) 118.9(4), N(1)-Ag(1)-O(33) 77.7(4), N(4)-Ag(1)-S(1) 150.6(1), N(1)-Ag(1)-S(1) 77.7(1), N(4)-Ag(1)-N(1) 123.0(1), O(33)-Ag(1)-S(1) 83.8(1), N(2)-Ag(2)-S(2) 152.6(1), N(3)-Ag(2)-S(2) 78.5(4), N(2)-Ag(2)-O(41) 96.0(1), N(3)-Ag(2)-O(41) 112.9(1), N(2)-Ag(2)-N(3) 122.6(2), O(41)-Ag(2)-S(2) 90.1(2).

Figure 7. A view of the polymeric chain of **2b**, illustrating the intramolecular  $\pi$ -stacking, and the geometry about the metal centres. Hydrogens omitted for clarity.

Figure 8. View of the orthogonal fit between a fragment of the polymeric isomer **2b** (in black) and the [Ag<sub>2</sub>(L')<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>

dimer (in white).  $\text{NO}_3^-$  and  $\text{PF}_6^-$  anions were omitted from the fit.

Figure 9. View down the (110) axis showing the packing of the two different polymeric chains of **2a** (figure-of-eight arrangement) and of **2b** (S-shaped arrangement).

Figure 10. End-on views of the three polymeric chains **1** (left), **2a** (middle) and **2b** (right) illustrating their figure-of-eight and S-shaped arrangements, respectively. Hydrogen atoms and anions were omitted for clarity.



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