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Structural Diversity in One-dimensional Coordination Polymers of a Flexible Multimodal Ligand

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Four one-dimensional coordination polymers were prepared by the reaction of a flexible multimodal ligand, bis(2-pyrazylmethyl)sulfide (L), with AgX salts ($X = ClO_4^-$ or NO_3^-) and CuI in a 2: 1 M-to-L ratio and with $AgCF_3SO_3$ in a 1: 1 M-to-L ratio. The one-dimensional polymers showed considerable structural diversity and the influence of ligand conformation and anion on the formation of these coordination polymers was explored. A ladder-like polymer, 1, was formed with $AgClO_4$ while a U-shaped chain, 2, was formed with $AgNO_3$. An X-shaped chain, 3, was formed with $AgCF_3SO_3$ in which the Ag(I) ion adopted a square-planar geometry. A fused-loop chain, 4, was formed with CuI and these chains were stacked on top of each other to give large channels. Three different conformations and four different coordination modes of L were identified in these structures.

Keywords: Flexible ligands; Multimodal; Coordination polymers; One-dimensional chains; Anion effects

INTRODUCTION

The formation of supramolecular coordination networks has often focussed upon the use of rigid bidentate spacers to connect together metal cations [1,2]. In particular, there are numerous examples of rigid bipyridine spacers being used to produce a variety of generally predictable supramolecular arrays [3,4]. More recently, the use of flexible ligands in the formation of supramolecular arrays has greatly increased [5,6]. This is because flexible ligands offer two major advantages over more conventional rigid ligands. Firstly, the flexibility of the ligand allows it to be present in a greater variety of conformations, thereby increasing the range of structural motifs that can be generated [5,7]. Secondly, greater flexibility increases the ability of the ligand to utilise all of its potential donor sites, either through direct coordination to a metal cation or involvement in other weaker supramolecular interactions such as H-bonding or π-stacking [8]. However, one disadvantage of using flexible ligands is the difficulty of predicting the nature of the resulting supramolecular arrays [9]. In part this disadvantage is offset by the diversity of the arrays which can be formed. Even simple one-dimensional polymers can show variety of form when ligand conformation is an important factor in their formation.

In our system, incorporation of flexibility into **L** was achieved by including a flexible thioether moiety into the ligand (Scheme 1). The presence of thioether donors in ligands, used in coordination to the appropriate metal cation, has been shown to produce structural motifs that were not replicated in similar non-thioether containing ligands [10–12]. With greater flexibility of the ligand allowing for more effective use of its donor atoms, a greater variety of donor atom environments in the ligand should then allow more diversity in the supramolecular arrays formed (Scheme 2). The use of these multimodal ligands has been investigated on a number of occasions particularly in respect to their ability to bind to metal cations, such as Ag(I), through chelating and monodentate donors simultaneously [13–16].

With these factors in mind the flexible multimodal ligand **L** was used with a range of Ag(I) salts including $AgClO_4$, $AgNO_3$ and $AgCF_3SO_3$ as well the Cu(I) salt, CuI. These salts were used as these

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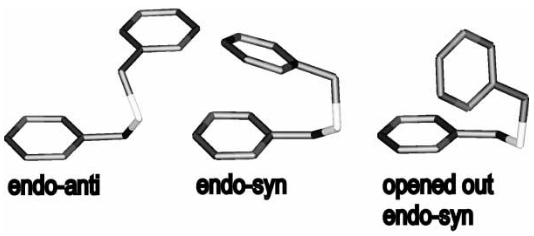


SCHEME 1 Conformations of ligand **L** found in the structures of the one-dimensional coordination polymers **1**–**4**.

metal cations can display a wide variety of coordination geometries [1,2]. Also, in other Ag(I) complexes the differences in the anions have been shown significantly to affect the supramolecular arrays incorporating them [17–19]. Thus the use of these coordinatively-accommodating metal ions would allow other factors, such as the ligand conformation and the effect of the anions, to have a greater influence in the formation of any supramolecular structures. The use of Ag(I) and Cu(I) salts with a flexible bipyridyl ligand previously has led to the formation of supramolecular arrays with considerable structural diversity [20].

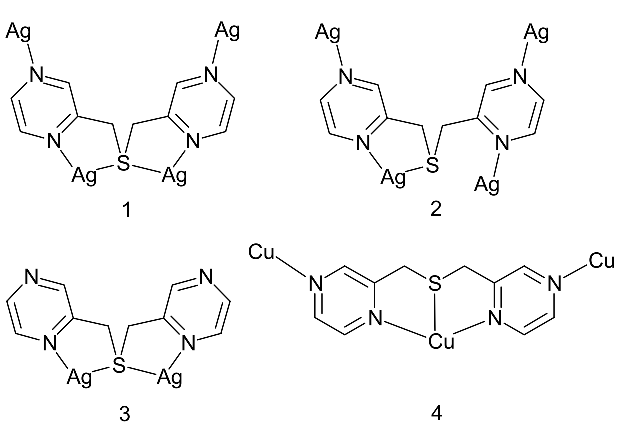
EXPERIMENTAL

The ligand **L** was prepared via literature methods [21]. The ^{1}H, ^{13}C NMR spectra were recorded on a Varian $^{\text{unity}}$INOVA 300 MHz spectrometer. Elemental analyses were performed by the Campbell Microanalytical Laboratory at the University of Otago. Samples were predried under vacuum to remove any volatile solvent residues.

Complexes

Preparation of [Ag(L)ClO$_4$]

$AgClO_4$ (51.5 mg, 0.248 mmol) dissolved in degassed MeCN (25 mL) was added *via* cannula to **L** (53.7 mg, 0.246 mmol) dissolved in degassed MeCN (25 mL) and stirred for 2 h. The resulting solution was concentrated to 5 mL, 1-butanol (10 mL) added and the solution again concentrated *in vacuo* to 10 mL, which caused the formation of a precipitate. The tan solid that precipitated was filtered and dried *in vacuo* (yield 78.8 mg, 75.3%). Found: C, 27.01; H, 2.44; N, 12.71; S, 6.77. Calc. for $C_{10}H_{10}N_4O_4SClAg{\cdot}H_2O$: C, 27.07; H, 2.50; N, 12.63; S, 7.23%.



SCHEME 2 Coordination modes of ligand **L** observed in **1**–**4**.

Preparation of $\{[Ag_2(L)](ClO_4)_2\}_\infty$ **1**

$AgClO_4$ (153 mg, 0.738 mmol) dissolved in degassed MeCN (25 mL) was added *via* cannula to **L** (67.0 mg, 0.307 mmol) dissolved in degassed MeCN (25 mL) and stirred for 26 h. The resulting solution was concentrated to 5 mL, 1-butanol (10 mL) added and the solution again concentrated *in vacuo* to 10 mL, which caused the formation of a precipitate. The fawn solid that precipitated was filtered and dried *in vacuo* (yield 123 mg, 63.3%). Colourless X-ray quality crystals were grown from the slow diffusion of a CH_3NO_2 solution (2 mL) of **L** (19.4 mg, 0.0889 mmol) layered with acetone (10 mL) and an ethyl acetate solution (2 mL) of $AgClO_4$ (34.7 mg, 0.167 mmol). Found for material prepared in bulk as described above: C, 23.82; H, 2.27; N, 9.27; S, 5.86. Calc. for $C_{10}H_{10}N_4O_8SCl_2Ag_2$: C, 18.97; H, 1.59; N, 8.85; S, 5.07%.

Found for material harvested from crystals as described above: C, 19.31; H, 1.87; N, 9.16; S, 5.36. Calc. for $C_{10}H_{10}N_4O_8SCl_2Ag_2$: C, 18.97; H, 1.59; N, 8.85; S, 5.07%.

Preparation of $[Ag_2(L)(NO_3)_2]_\infty$ **2**

$AgNO_3$ (89.8 mg, 0.529 mmol) dissolved in degassed MeCN (25 mL) was added *via* cannula to **L** (54.1 mg, 0.248 mmol) dissolved in degassed MeCN (25 mL) and allowed to stir for 1 h. The resulting solution was concentrated to 5 mL, 1-butanol (10 mL) added and the solution again concentrated *in vacuo* to 10 mL, which caused the formation of a precipitate. This precipitate was then filtered and dried *in vacuo* to give a tan powder (yield 124.7 mg, 90.08%). Yellow crystals of X-ray quality were grown from the slow diffusion of a CH_3NO_2 solution (2 mL) of **L** (18.9 mg, 0.0866 mmol) layered with benzene (2 mL) and a MeCN solution (5 mL) of $AgNO_3$ (32.1 mg, 0.189 mmol). Found: C, 21.92; H, 1.72; N, 14.68; S, 5.78. Calc. for $C_{10}H_{10}N_6O_6SAg_2$: C, 21.52; H 1.81; N, 15.06; S, 5.75. %.

Preparation of $\{[Ag(L)]CF_3SO_3\}_\infty$ **3**

$AgCF_3SO_3$ (124.2 mg, 0.4833 mmol) dissolved in degassed MeCN (25 mL) was added *via* cannula to **L** (105.1 mg, 0.4815 mmol) dissolved in degassed MeCN (25 mL) and stirred for 2 h. The resulting solution was concentrated to 5 mL, 1-butanol (10 mL) added and the solution again concentrated *in vacuo* to 10 mL, which caused the formation of a precipitate. The tan solid that precipitated was filtered and dried *in vacuo* (yield 221.8 mg, 96.93%). Colourless X-ray quality crystals were grown from the slow diffusion of a CH_3NO_2 solution (2 mL) of **L** (19.2 mg, 0.0880 mmol) layered with acetone (5 mL) and an ethyl acetate solution (2 mL) of $AgCF_3SO_3$ (37.9 mg, 0.147 mmol). Found: C, 27.32; H, 1.92; N, 11.64; S, 13.18. Calc. for $C_{11}H_{10}N_4O_3F_3S_2Ag$: C, 27.80; H, 2.12; N, 11.79; S, 13.50%.

Preparation of $[Cu_2(L)I_2]_\infty$ **4**

CuI (107.1 mg, 0.5624 mmol) dissolved in degassed MeCN (25 mL) was added *via* cannula to $\mathbf{L_1}$ (58.2 mg, 0.267 mmol) dissolved in degassed MeCN (25 mL) and stirred for 1 h. The resulting solution was concentrated to 5 mL. The orange solid, which precipitated, was filtered and dried *in vacuo* (yield 60.8 mg, 38.1%). Red X-ray quality crystals were grown from the slow evaporation of a MeCN solution (25 mL) of **5** (29.67 mg, 0.0495 mmol). Found: C, 19.05; H, 1.74; N, 8.45; S, 4.42. Calc. for $C_{10}H_{10}N_4SCu_2I_2H_2O$: C, 18.91; H, 2.22; N, 8.82; S, 5.05%.

X-ray Crystallography

Diffraction data for **1**, **2** and **4** were collected on a Nonius Kappa-CCD diffractometer and data for **3** were collected on a Bruker SMART CCD diffractometer; both had graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. Intensities were corrected for Lorentz-polarisation effects [22] and for **3** a multiscan absorption correction [23] was applied. The structures were solved by direct methods (SHELXS) [24] and refined on F^2 using all data by full-matrix least-squares procedures (SHELXL 97) [25]. All calculations were performed using the WinGX interface [26]. Despite many attempts, crystals of **3** always grew as plates of very poor quality and high mosaicity. Two data sets on separate batches of crystals were collected and gave similar structural solutions. The structure reported herein represented the better result for **3**. The structure of **3** contained a badly disordered $CF_3SO_3^-$ anion and a number of large residual peaks at positions from other atoms and each other which made no chemical sense. Crystallographic data for the four structures are listed in Table I. Crystallographic data for **1–4** have been deposited with the Cambridge Crystallographic Data Centre, as CCDC nos 275383–275386. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Ligand Synthesis

The ligand bis(2-pyrazylmethyl)sulfide **L** may have been synthesized twice before although both times it was not the intended product of the reaction [27,28]. A yield of only 0.15% was reported and this yield was too low for the compound to be identified thoroughly, although it was inferred from the infrared spectrum and microanalytical data that **L** had been formed [28]. Recently we have prepared **L** in satisfactory yield (30%) by the reaction of 2-(chloromethyl)pyrazine with thioacetamide under basic conditions [21].

Synthesis and Structure of $\{[Ag_2(L)](ClO_4)_2\}_\infty$ 1

The 1:1 molar reaction of **L** with $AgClO_4$ in MeCN yielded a tan powder in good yield. Microanalytical

TABLE I Crystallographic data for complexes **1–4**

	1	**2**	**3**	**4**
Empirical formula	$C_{10}H_{10}Ag_2Cl_2N_4O_8S$	$C_{20}H_{20}Ag_4N_{12}O_{12}S_2$	$C_{11}H_{10}AgN_4O_3F_3S_2$	$C_{44}H_{40}Cu_8I_8N_{18}S_4$
M	632.92	1116.08	475.22	2472.82
Crystal system	monoclinic	Triclinic	monoclinic	monoclinic
Space group	$C2/c$	$P{-}1$	$P2_1/n$	$C2/m$
a/Å	17.1898(3)	7.1655(1)	7.133(5)	20.7594(7)
b/Å	7.1704(2)	8.0609(1)	23.112(5)	9.8066(4)
c/Å	16.0922(4)	26.1735(4)	9.697(5)	8.5763(4)
α/°		90.966(1)		
β/°	119.274(1)	92.043(1)	96.217(5)	96.196(2)
γ/°		97.283(1)		
U/Å^3	1730.18(7)	1498.29(4)	1589(1)	1735.8(1)
Z	4	2	4	1
T/K	123(2)	123(3)	168(2)	123(2)
μ/mm^{-1}	2.744	2.799	1.582	6.124
Reflns collected	3635	10553	19239	3862
Unique reflns (R_{int})	1975 (0.0198)	6843 (0.0233)	3158(0.0528)	2098 (0.0227)
R_1 indices [$I > 2\sigma(I)$]	0.0217 (1676)	0.0326 (5407)	0.1367(2503)	0.0248 (1822)
$wR2$ (all data)	0.0484	0.0629	0.4254	0.0560

data were consistent with the solid having a 1:1 ligand-to-metal ratio. Unfortunately, attempts to grow crystals suitable for X-ray structural analysis were totally unsuccessful. Interestingly when the 1:2 molar reaction of **L** with $AgClO_4$ in MeCN was carried out, a tan powder also was isolated. Initially microanalytical data were ambiguous with analyses giving values between those expected for a 1:1 and 1:2 ligand-to-metal ratio for the solid. Despite many repeated attempts satisfactory microanalytical data could not be obtained for material from the bulk reaction. It appeared that a mixture of the two materials was always produced during the bulk reaction. Subsequently, sufficient crystalline material of **1** was harvested and used to provide suitable microanalytical data.

X-ray structure analysis of **1** revealed a ladder-like arrangement of ligands held together by Ag(I) ions (Fig. 1). The ladder was decorated with bound ClO_4^- anions and showed two-fold symmetry about the central S donors which had long bond distances to the Ag(I) ions. This Ag-S distance was just above the upper quartile of reported AgS(thioether) distances and the Ag-O distance just below the upper quartile of reported Ag-O-ClO_3 distances in searches of the Cambridge Crystallographic Database (CSD, version 5.26) [29]. The Ag(I) centre adopted a very distorted cis-divacant octahedral arrangement with trans $N_{pz}N'_{pz}$ (N_{pz} = pyrazine N donor) coordination from one chelated ligand and one monodentate ligand and cis O″S coordination from the chelated ligand and the ClO_4^- anion. The ligand used all available lone pairs on each donor atom, including both on the S donor, and coordinated to four Ag(I) cations. Thus, the Ag(I) ion was surrounded by both chelating and monodentate donors from the multimodal ligands giving rise to a "homogeneous" metal coordination environment throughout the one-dimensional polymer [14]. The ligand **L** adopted an endo-anti conformation with the pyridine rings almost parallel to each other with a tilt of 2.8° and the planes of the pyrazine rings 2.81 Å apart with a centroid-to-centroid distance of 5.622(1) Å. When constrained to this conformation by metal binding, **L** can exist as two enantiomers. Ligand **L** was found to adopt the same conformation in the related one-dimensional solvated ladder $\{[Ag_2(\mathbf{L})(C_6H_6)(MeCN)_2](PF_6)_2{\cdot}MeCN\}_\infty$ in which the enantiomeric forms of **L** alternate along the ladder [21]. This conformation was also found in copper(I) iodide complexes of the closely related pyridine-based ligands [30,31]. In **1**, all the ligands of one ladder were of the same enantiomeric form and pointed in the same direction. The other enantiomeric form was present in the adjacent ladders and they pointed in opposite directions (Fig. 2). An interesting feature of the structure was that the ladders were held together in two-dimensional sheets in the (−1 0 1) plane by strong bridging interactions which involved two diametrically opposite ClO_4^- anions bridging two Ag(I) ions on adjacent ladders [Ag···O−ClO_3 2.749(2) Å] (Fig. 2). Such bridging by counterions has been observed as a structural component in a number of supramolecular Ag structures [32–35]. The Ag ions were 5.3356(3) Å apart and in this case the bridging did not seem to assist in bringing the Ag ions closer together. The sheets were stacked parallel to each other and were held together by a variety of weak interactions giving the over all three dimensional structure. These included face-to-face π interactions [centroid to centroid distance 4.066(1) Å] [36], complimentary perpendicular Ag···N(pyrazine) interactions [4] at 3.644(3) Å and further ClO_4^- bridging interactions [C−H···O−Cl distances in the range 2.44 to 2.52 Å].

Synthesis and Structure of $[Ag_2(L)(NO_3)_2]_\infty$ 2

A tan powder was obtained in high yield from the 1:2 molar reaction of **L** with $AgNO_3$ in MeCN.

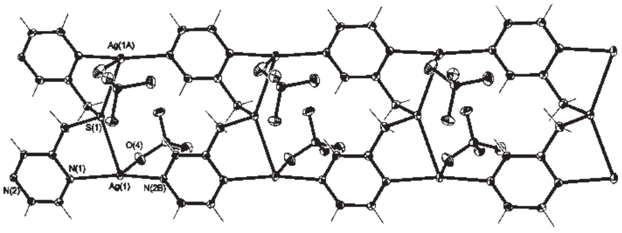


FIGURE 1 Perspective view (crystallographic numbering) of the one-dimensional polymeric ladder **1**, showing the endo-anti ligand conformation. Thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): S(1)–Ag(1) 2.7792(3), Ag(1)–O(4) 2.625(2), Ag(1)–N(2B) 2.213(2), Ag(1)–N(1) 2.266(2); Ag(1)–S(1)–Ag(1A) 140.28(3), O(4)–Ag(1)–S(1) 75.03(4), O(4)–Ag(1)–N(2B) 100.68(7), O(4)–Ag(1)–N(1) 101.71(7), N(2B)–Ag(1)–N(1) 157.48(7), N(2B)–Ag(1)–S(1) 113.30(5), N(1)–Ag(1)–S(1) 75.19(5). (Symmetry codes: A 1 − *x*, *y*, $1\frac{1}{2}$−*z*; B *x*, 1 + *y*, *z*.)

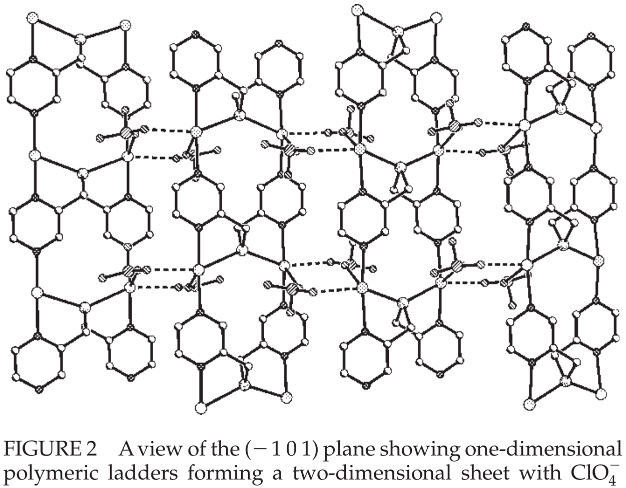


FIGURE 2 A view of the (−1 0 1) plane showing one-dimensional polymeric ladders forming a two-dimensional sheet with ClO_4^- anions bridging between them, hydrogens were omitted for clarity.

The complex had a microanalysis consistent with a 1:2 ligand-to-metal ratio.

X-ray structural analysis showed two parallel one-dimensional U-shaped chains which were linked together by bridging NO_3^- anions (Fig. 3). Other bridging NO_3^- anions held adjacent pairs of chains together to give two dimensional sheets. The chains were twisted at 51.1° with respect to each other. In contrast to **1**, each ligand adopted a folded endo-syn arrangement which gave rise to intramolecular π-stacking interactions with centroid-to-centroid distances of 3.615(2) Å for the ligand in the chain containing S(1) and 3.802(2) Å for the ligand in the chain containing S(2) [36]. The pyrazine rings were tilted by 19.8° and 26.3° for each ligand, respectively. The chains propagated along the *a*-axis and the ligands were oriented in the same way by a simple lattice translation. Bond distances were similar to those in **1** and, just as in the case of **1**, each ligand used all four N donor atoms to bind to four different Ag(I) cations but used the S donor to bind to only one Ag(I) cation. The Ag···S distances to the other Ag(I) ions of 3.4700(10) and 3.6256(10) Å were well outside possible bonding values. Although Ag(1) and Ag(4) were surrounded by both chelating and monodentate donors from the multimodal ligands the remaining two Ag(2) and Ag(3) ions were not and so the environment of the Ag(I) ions was not "homogeneous" throughout the polymer [14]. Although the chains were crystallographically distinct, there were only small differences in bond lengths and angles throughout the chains and the chains were essentially the same as each other. Each chain contained two Ag(I) ions with different geometries separated by 3.2856(5) and 3.1963(5) Å [12,16,37–41]. One of the Ag(I) ions adopted a severely distorted and flattened arrangement which lay between a tetrahedral and a square planar geometry, with $N_{pz}S$ chelation from one **L** ligand, N'_{pz} coordination from another **L** ligand and O″ coordination from a NO_3^- anion. Despite the different conformation of **L**, the Ag-S distances were similar to those of **1**.

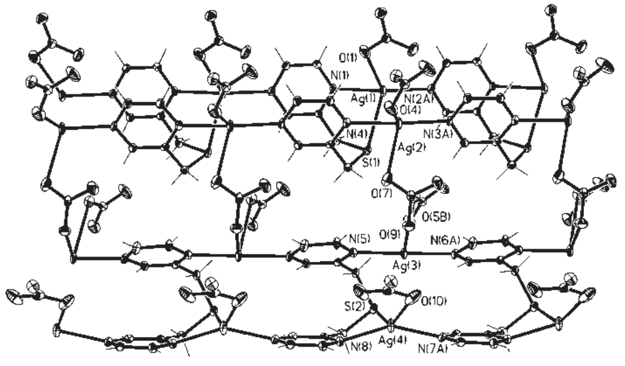


FIGURE 3 Perspective view (crystallographic numbering) of **2** showing the U-shaped chains with NO_3^- anions bridged between them. Thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Ag(1)–N(2A) 2.241(3), Ag(1)–N(1) 2.318(3), Ag(1)–O(1) 2.484(3), Ag(1)–S(1) 2.7700(10), Ag(2)–N(3A) 2.190(3), Ag(2)–N(4) 2.223(3), Ag(2)–O(7) 2.547(3), Ag(3)–N(5) 2.192(3), Ag(3)–N(6A) 2.210(3), Ag(3)–O(9) 2.551(3), Ag(4)–N(7A) 2.263(3), Ag(4)–N(8) 2.291(3), Ag(4)–O(10) 2.580(3), Ag(4)–S(2) 2.7432(10), O(5B)–Ag(3) 2.675(3); N(2A)–Ag(1)–N(1) 148.87(11), N(2A)–Ag(1)–O(1) 117.06(10), N(1)–Ag(1)–O(1) 80.69(10), N(2A)–Ag(1)–S(1) 105.20(8), N(1)–Ag(1)–S(1) 77.28(8), O(1)–Ag(1)–S(1) 128.61(7), N(3A)–Ag(2)–N(4) 165.67(11), N(3A)–Ag(2)–O(7) 106.67(10), N(4)–Ag(2)–O(7) 81.28(10), N(5)–Ag(3)–N(6A) 174.98(11), N(5)–Ag(3)–O(9) 94.33(10), N(6A)–Ag(3)–O(9) 90.81(10), N(7A)–Ag(4)–N(8) 149.34(11), N(7A)–Ag(4)–O(10) 81.04(11), N(8)–Ag(4)–O(10) 119.95(11), N(7A)–Ag(4)–S(2) 103.02(8), N(8)–Ag(4)–S(2) 77.69(8), O(10)–Ag(4)–S(2) 136.46(8). (Symmetry codes: A $1 + x$, y, z; B x, $-1 + y$, z.)

The other Ag(I) ion adopted a distorted cis-divacant octahedral arrangement (Fig. 3) with trans $N_{pz}N'_{pz}$ coordination from two **L** ligands and cis O″O‴ coordination from two different bridging NO_3^- anions. One of the bridging NO_3^- anions was involved in holding the two chains together while the other was involved in holding the pairs of chains together to form two-dimensional sheets in the *ab* plane (Fig. 4). In addition for each chain in a sheet, centrosymmetric pairs of weak N-O···Ag interactions involving the terminal NO_3^- nitrates bound to the NS chelated Ag atoms formed an asymmetric link between adjacent sheets and gave rise to a three-dimensional array (Fig. 4). The interactions were weak with a N–O···Ag distance of 3.015(3) Å for ligands containing S(1) and 2.874(3) Å for ligands containing S(2) [42]. A search of $AgONO_2$ bond distances in the CSD (version 5.26) indicated that the mean value was 2.51 Å with higher quartile values starting at 2.65 Å [29]. The longest bond distance

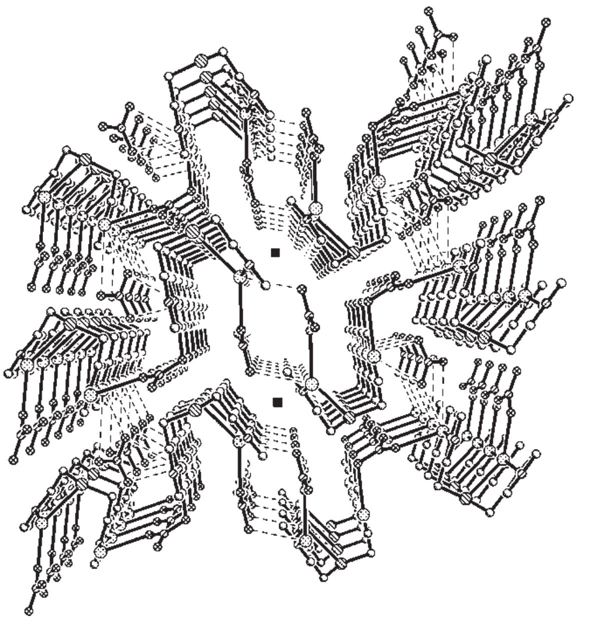


FIGURE 4 View of the *ab* plane showing the one-dimensional U-shaped chains of **2** linked into a three-dimensional structure through $Ag–ONO_2$ bonds and π–π stacking interactions (small black squares). H atoms were omitted for clarity.

reported was 2.861(9) Å [43]. The three dimensional array was further strengthened by π-stacking interactions between the sheets with centroid to centroid distances of 3.585(2) Å for the ligands in the chains containing S(1) and 3.514(2) Å for the ligands in the chains containing S(2) (Fig. 4).

Synthesis and Structure of $\{[Ag(L)]CF_3SO_3\}_\infty$ 3

The 1:2 molar reaction of **L** and $AgCF_3SO_3$ in MeCN on workup produced a tan powder in moderate yield (40%), based on $AgCF_3SO_3$. Microanalysis showed the complex was consistent with a 1:1 metal-to-ligand ratio. Subsequently the same tan powder was obtained in high yield (97%) from the 1:1 molar reaction. Despite careful workup of the reaction solid and filtrate, the 1: 2 product could not be isolated.

The X-ray structure of **3** showed a one-dimensional chain propagating along the [1 0 1] diagonal axis with unbound pyrazine N donors pointing outwards from the chain (Fig. 5). The ligand adopted the same endo-anti arrangement found in **1** with the pyrazine rings almost parallel to each other with a tilt of 5.5° and the planes of the pyrazine rings 2.77 Å apart with a centroid-to-centroid distance of 5.708(7) Å. However, in contrast to **1**, the chain propagated in a different manner because only two out of the four pyrazine N donor atoms were involved in coordination to the Ag(I) ions. The ligands were arranged in two adjacent parallel rows such that each row was shifted by half the distance of a ligand in the direction of the chain, with respect to each other. This arrangement gave the one-dimensional chain an X-shaped cross section (Fig. 6). The S and the two 1-pyrazine N donor atoms of each ligand pointed inwards towards the middle of the two rows of ligands where they chelated to two Ag(I) ions using both lone pairs of the S donor atom (Fig. 5). The Ag(I) ions were $N_{pz}N'_{pz}SS'$ (N_{pz} = pyrazine N donor) coordinated and these five atoms adopted a distorted square planar arrangement (mean deviation from mean plane 0.0015 Å). This stereochemistry is quite rare for Ag(I) ions [44,45]. The Ag-S bond lengths were longer than those found in **1** and **2** and were approaching the upper limit for Ag-S bonding distances in the CSD (version 5.26) but were still <3.16 Å; the distance considered to be non-interacting [12]. The Ag–N distances were within the normal range for such bond lengths [12,37–41,46]. The disordered $CF_3SO_3^-$ showed weak Ag···O interactions, of 2.69(2) Å, above and below the square plane. Such weak axial interactions are a common feature of "square-planar" silver compounds [44,45].

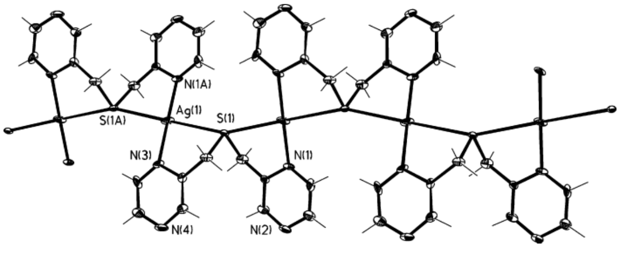


FIGURE 5 View of a one-dimensional chain of **3** with thermal ellipsoids drawn at the 50% probability level. $CF_3SO_3^-$ anions were omitted for clarity. Selected bond lengths (Å) and angles (°): N(1A)–Ag(1) 2.324(8), N(3)–Ag(1) 2.328(8), S(1A)–Ag(1) 2.893(2), S(1)–Ag(1) 2.913(2); N(1A)–Ag(1)–N(3) 179.3(3), N(1A)–Ag(1)–S(1A) 76.7(2), N(3)–Ag(1)–S(1A) 103.9(2), N(1A)–Ag(1)–S(1) 102.5(2), N(3)–Ag(1)–S(1) 76.9(2), S(1)–Ag(1)–S(1A) 179.19(7). (Symmetry codes: A $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$.)

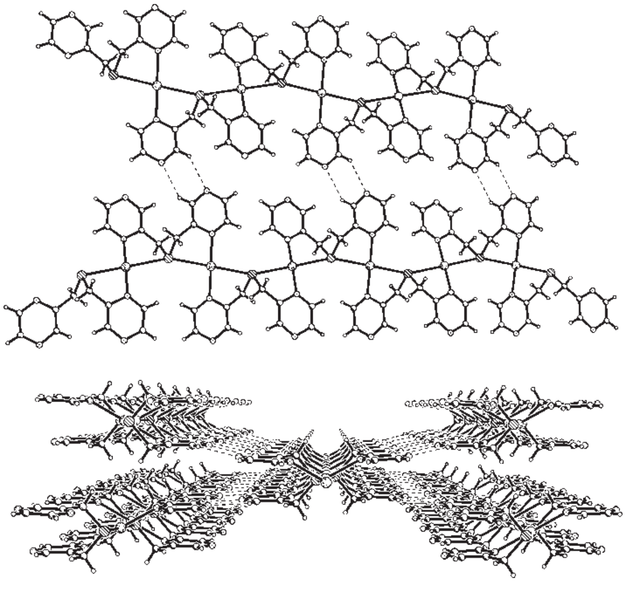
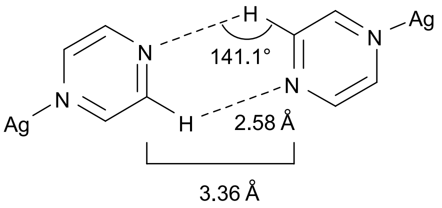


FIGURE 6 View of the N···H–C complementary synthon interactions in **3** (top) which join the X-shaped one-dimensional chains into three-dimensional sheets (bottom). $CF_3SO_3^-$ anions omitted for clarity.

The 4-pyrazine N atoms which all pointed outwards from the chains were involved in dimeric (pyrazine)N···H-C(pyrazine) interactions [47,48] (Scheme 3) with pyrazine rings on adjacent chains (Fig. 6). Recently there has been considerable interest in the N···H–C interaction as a supramolecular synthon [47–52]. Debate has centred around the nature of the interaction, as a consequence of a claim made that many reported N···H–C interactions are merely classical van der Waals contacts [53]. Subsequently, more detailed analyses point to the validity of the N···H–C interaction as a hydrogen bond in a manner analogous to the O···H–C



SCHEME 3 Summary of the metrical parameters for the complementary (pyrazine)N···H–C(pyrazine) interactions in **3**.

hydrogen bond [47,48,54]. The values for the parameters defining the (pyrazine)N···H–C(pyrazine) interactions found in **3** (Scheme 3) were typical of those reported for other related systems [47–52]. Sheets comprising of parallel chains were arranged such that the chains in each sheet were offset with respect to those in adjacent sheets. Thus each chain was involved in N···H–C interactions with two adjacent chains in the sheets directly above and below giving rise to a three dimensional array (Fig. 6). In addition, the chains in each sheet interact with the chains on either side through weak π-stacking interactions involving all pyrazine rings (centroid to centroid distance 3.817(7) Å) (Fig. 6) [36]. The $CF_3SO_3^-$ counterions further strengthen the sheets by occupying cavities between the chains and by interacting with two Ag(I) ions in adjacent chains with Ag···O–S distances in the range 2.78–2.83 Å.

Synthesis and Structure of $\{[Cu_2(L)I_2]\cdot\frac{1}{2}(MeCN)\}_\infty$ 4

The reaction of CuI and **L** in a 2:1 molar metal-to-ligand ratio in degassed MeCN under a N_2 atmosphere was carried out using standard cannula techniques. The resulting solution was reduced in volume causing the formation of an orange precipitate. Microanalysis showed the complex was consistent with a 2:1 metal-to-ligand ratio.

The X-ray crystal structure analysis of **4** revealed pseudo-tetrahedral CuI coordinated ligands linked by CuI-bridged dimers into one-dimensional polymeric fused loop chains (Fig. 7), which were then joined into a three-dimensional array via weak supramolecular interactions. The asymmetric unit was unusual in that it contained half a ligand, two Cu(I) ions with half occupancy, two I^- ions also with half occupancy and a MeCN molecule with quarter occupancy. The Cu(I) and I^- ions were located on mirror planes and the MeCN molecule was disordered over a $2/m$ site. The ligand was folded in an opened out endo-syn conformation where the two pyrazine rings on the ligand were tilted by 79.6° with respect to each other and separated by a centroid-to-centroid distance of 4.926(2) Å (Fig. 7). An endo-syn conformation usually leads to π-stacking between the pyrazine rings of the ligand, but due to the opened out conformation this was not possible.

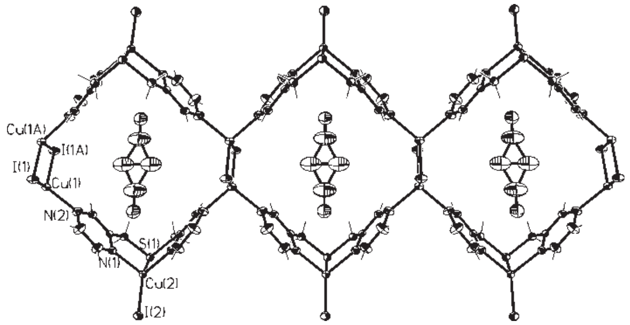


FIGURE 7 A view of the fused loop chains in **4** showing disordered MeCN solvent molecules with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): N(2)–Cu(1) 2.070(3), I(1A)–Cu(1) 2.5710(6), I(1)–Cu(1) 2.6556(6), I(2)–Cu(2) 2.4871(6), Cu(2)–N(1) 2.074(3), Cu(2)–S(1) 2.322(1); Cu(1A)–I(1)–Cu(1) 58.33(2), N(2)–Cu(1)–I(1A) 111.16(7), N(2)–Cu(1)–I(1) 106.10(7), I(1)–Cu(1)–I(1A) 121.67(2), N(1)–Cu(2)–S(1) 86.69(7), N(1)–Cu(2)–I(2) 115.58(7), S(1)–Cu(2)–I(2) 143.20(4). (Symmetry code: A $-x, y, 1-z$.)

The Cu(I) ions were present in two different common structural motifs, an iodide-bridged dimer motif [30,31,55–57] and a distorted tetrahedral motif [58–61]. The iodide-bridged copper dimers linked the ligands together into the fused loop chains, which were then formed into sheets through a variety of weaker supramolecular interactions. The ligands were bound to the iodide-bridged copper dimers through two crystallographically identical Cu–N bonds [2.070(3) Å], where the N donors were in the four-position on the pyrazine rings. Each ligand bridged in an exo-fashion two iodide-bridged copper dimers, with each Cu(I) ion in the dimers being bound to two separate ligands. This created one half of the fused loop chains with the other half being formed by a 180° rotation around a line connecting the centre points between each pair of Cu(I) ions in each dimer (Fig. 7). The iodide-bridged copper dimers had parallelogram geometries, instead of diamonoid geometries, with each Cu(I) ion bound to two I^- ions with two different bond lengths [2.5710(6) Å and 2.6556(6) Å]. This may have been due to weak [62] interactions [3.738(1) Å] between the I^- ions in the dimer and the S donors on the ligand. The Cu(I) ions in the dimers were separated by distances of 2.548(1) Å, which was short for iodide-bridged copper dimers [29,55–57]. The Cu(I) ions with the distorted tetrahedral motifs had N_2SI coordination spheres. They were chelated to the ligands through both of the one-positioned N donors on the pyrazine rings as well as the S donor, thereby utilising all of the available remaining donor atoms on the ligand. These Cu(I) ions were also bound to one I^- anion completing their coordination spheres (Fig. 7).

The fused-loop chains were formed into two-dimensional sheets in the (2 0 −1) plane through complementary weak perpendicular C-H···N(pyrazine) interactions [2.69(4) Å corresponding to C···N distance of 3.462(4) Å]. A variety of weak I···H–C(methylene), Cu···H–C(methylene) and S···I interactions between the sheets formed the overall three-dimensional structure, such that sheets of fused loop chains were stacked on top of each other in the direction of the *c*-axis creating large channels (Fig. 8). In the centre of these channels were weakly bound MeCN solvent molecules. These MeCN solvent molecules were disordered over a high symmetry $2/m$ site. The disorder of the MeCN

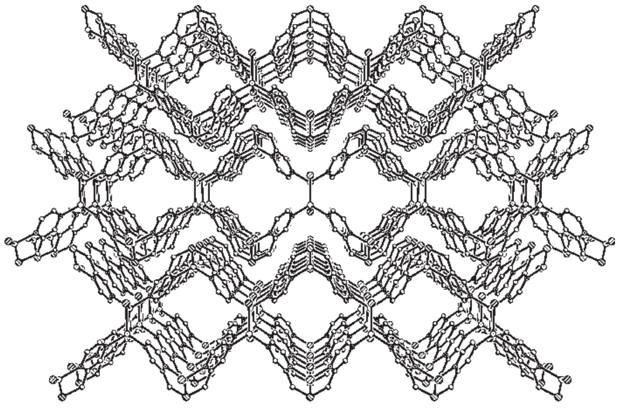


FIGURE 8 A view of the (2 0 −1) plane showing the large channels created by the stacking of the fused loop chains of **4**. MeCN solvent molecules and H atoms omitted for clarity.

molecules was at least partially due to them not being bound in the channels.

COMPARISON

The structures **1**–**4** illustrated a number of important points concerning the use of ligands which were both flexible and multimodal for coordination-polymer synthesis. Firstly the flexibility of the ligand allowed three different conformations (Scheme 1) to be accessed thereby enabling the efficient use of as many donor atoms as possible in forming a stable molecular architecture. This was particularly well illustrated by structures **1** and **2**, where two different conformations gave one-dimensional ladders with similar characteristics and was possibly in response to the different coordination requirements of the counterions. The flexible ligand provided the opportunity to maximise π stacking and other weak supramolecular interactions, such as C–H···N(pyrazine), which then encouraged the formation of tightly packed extended arrays thereby excluding solvent [63].

Secondly, the structures showed that the ligands were capable not only of adopting different conformations but also a wide variety of coordination modes (Scheme 2). One of the most common coordination modes for **L** used the N donor atoms in the 1-positions and the S donor atom to chelate to one Ag(I) or Cu(I) ion, as in **2** and **4,** or two Ag(I) ions, using both S lone pairs, as in **1** and **3**. The N donor atom in the 4-position acted as a monodentate ligand as in **1**, **2** and **4**. This tendency for metal ions to adopt both chelating and monodentate donors with multimodal ligands has been attributed to the drive towards a "homogeneous" metal coordination environment throughout the coordination polymer [14]. Two of our examples, **1** and **3**, were in accord with this notion of a "homogeneous" metal coordination environment. However our two remaining examples, **2** and **4**, showed quite emphatically that other factors, such as counterion and ligand conformation were also involved in influencing metal coordination environment. This was particularly clear in **2** where the Ag(I) ions could easily have adopted a "homogeneous" coordination environment but did not because of the effect of the bridging NO_3^- counterions. Also in **4**, a "homogeneous" coordination environment was not adopted due to the coordination preferences of the CuI moieties. A number of the coordination geometries about the Ag(I) ions were somewhat unusual for example the cis-divacant arrangement in **2** or the square-planar arrangement in **3** and often there were different coordination geometries within the same polymer.

In addition, the metal-to-ligand ratios were an obvious factor affecting the overall structure. Metal ratios can limit the possible binding modes of the ligand thereby affecting the nature of the array. With a 1:1 metal-to-ligand ratio, despite the flexibility of the multimodal ligand **L**, it is impossible for all the donor sites on the ligand, including both on the S donor, to be bound to metal cations without those cations having a coordination number of at least six. Coordination number of 6 are less common for Ag(I) or Cu(I) complexes. Thus in complexes with low metal-to-ligand ratios it would be expected that there were donor atoms not involved in coordination to Ag(I) ions. However our flexible multimodal ligand allows such donors to be utilised in other ways and we find that they form supramolecular synthons as in **3** and **4**.

Finally, comparing coordination polymers with the same metal-to-ligand ratio showed that the counterions have a significant influence on the overall structure. Comparison of **1** and **2** showed the effect of a coordinating counterion like NO_3^-. The structures have features in common, both are one-dimensional ladders in which the ligands are stacked head-to-tail. However, the ligand conformation was different between the structures possibly as a result of the binding or not of the counterion. Further the way in which the ladders pack together was determined to a large extent by the type of counterion with binding anions providing a significant influence.

In conclusion, the various effects influencing these systems were complemented by the versatility of this flexible multimodal ligand in being able to adopt different coordination modes and ligand conformations. In this way a diverse range of one-dimensional polymers was produced.

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