

# Formation of a single-stranded silver(I) helical-coordination polymer containing $\pi$ -stacked planar chiral $N_4S_2$ ligands

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**In-situ planar chirality was induced in an achiral ligand by intramolecular  $\pi$ -stacking interactions upon complexation with silver(I) and crystallisation, to give a single-stranded helix with a nanoscale pitch which assembled into a three-dimensional network.**

The utilisation of chirality in coordination-polymer chemistry is best exemplified by helicity. However, the factors controlling the formation of coordination helices are still not well understood despite the considerable attention this area has received.<sup>1</sup> When achiral ligands are employed to form helices they usually give racemates<sup>2</sup> although there are a few exceptions where spontaneous resolution upon crystallisation (conglomerate crystallisation) occurs.<sup>1b,3</sup> When chiral ligands are employed they can be used as either enantiopure ligands or racemic mixtures. Enantiopure ligands often lead to the stereoselective synthesis of helices<sup>4</sup> whereas racemic mixtures of ligands are less predictable.<sup>5</sup> Typically, helical architectures have been constructed using simple heterocycles<sup>1a,c,2b,6</sup> or flexible oligopyridines.<sup>2c,4a,7</sup> The use of thioether-heterocyclic ligands in this context has been less well studied.<sup>1b</sup> Recently we observed<sup>8</sup> that an acyclic thioether-oligopyridine ligand, 2,6-bis(2'-pyridylmethylsulfanyl)methylpyridine, upon interaction with Ag(I) folded, through strong intraligand  $\pi$ -stacking interactions, in such a way as to exhibit planar chirality. Our strategy was to develop this flexible ligand for polymer formation by retaining most of its features but replacing the central pyridine ring with a 2,3-substituted pyrazine linker. In terms of investigating helix self-assembly, this achiral ligand system has properties in common with chiral ligands derived from racemic mixtures for it may develop planar chirality *in situ* through complexation and conformational folding upon crystallisation. Recently, planar-chiral elements have been incorporated into cyclophanes and used to influence the self-assembly of supramolecular arrays.<sup>9</sup>

The new ditopic ligand **L** (Fig. 1) was prepared in moderate yield (67%) by the base coupling of 2,3-bis(chloromethyl)pyrazine<sup>10</sup> and 6-methyl-2-(sulfanylmethyl)pyridine.<sup>11†</sup> Reaction of **L** with AgClO<sub>4</sub> in a 1:2 molar ratio in MeCN gave a pale-yellow solution which was partially reduced in volume and then treated with diethyl ether to give a white precipitate in 85% yield. Microanalysis of the complex was consistent with a 1:2 ligand:metal ratio.‡ The complex was moderately soluble in MeCN but not appreciably soluble in other common organic solvents. Electrospray mass spectrometry under normal operat-

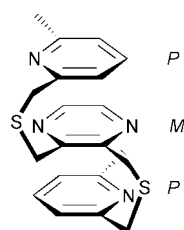


Fig. 1 Ligand **L** folded as the enantiomer found in the crystal structure of  $\{[Ag_2(L)](ClO_4)_2\}_\infty$  showing *P, M, P* planar chirality.

ing conditions in MeCN showed only one peak at  $m/z$  489.0 with an appropriate isotopic pattern for the 1:1  $[Ag(L)]^+$  ion. <sup>1</sup>H and <sup>13</sup>C NMR spectra were consistent with a symmetrical structure for the complex. Variable temperature <sup>1</sup>H NMR spectra measured in CD<sub>3</sub>CN showed no significant changes other than broadening of peaks down to the temperature limit of the solvent. The symmetrical nature of the <sup>1</sup>H NMR spectra implied that the solution species was either symmetric and static, or more likely, asymmetric and undergoing dynamic processes. X-Ray crystal structure analysis§ of the complex revealed a one-dimensional single-stranded helix consisting of repeating  $[Ag_2(L)](ClO_4)_2$  units (Fig. 2). The complex underwent conglomerate crystallisation and the crystal chosen for X-ray analysis belonged to the enantiomorphic space group *P*6<sub>5</sub>22. As is necessary for this space group only the *M* enantiomer of the helix is observed in the crystal. Since **L** was achiral when reacted with Ag(I), the bulk sample should contain equal amounts of both types of enantiomorphic crystals. The helix runs along the 6<sub>5</sub> screw axis with an exceptionally long pitch of 52.48(2) Å, equal to the length of the *c* axis (Fig. 3).<sup>3a,4a</sup> The pitch is long despite the compact nature of the 'three-layer'  $\pi$ -stacked ligand. The intraligand  $\pi$ -stacking distances determined from atom...atom contacts between rings range from

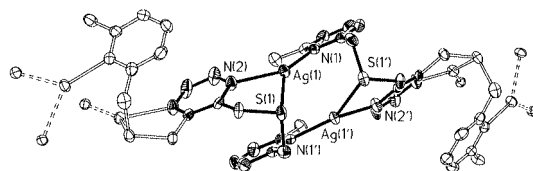


Fig. 2 Fragment of the helix showing the folding of the ligand. The coordination geometry and  $\pi$  stacking about the silver ions are highlighted in black, and dashed bonds indicate the continuation of the polymer (50% probability ellipsoids). Selected bond lengths (Å) and angles (°): Ag(1)–N(1) 2.234(5), Ag(1)–N(2) 2.374(5), Ag(1)–S(1) 2.588(2); N(1)–Ag(1)–N(2) 134.6(2), N(1)–Ag(1)–S(1) 144.9(1), N(2)–Ag(1)–S(1) 77.1(1).

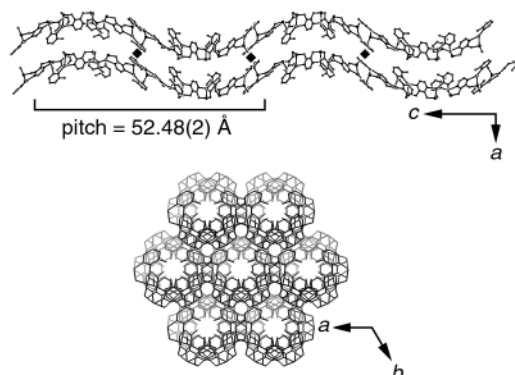


Fig. 3 Views of the helix with H atoms and ClO<sub>4</sub><sup>−</sup> anions omitted. (Top) view of two adjacent strands of the helix. The  $\pi$ -stacking interaction between the helices is indicated by diamonds  $\blacklozenge$ . (Bottom) view down the crystallographic *c*-axis showing the three-dimensional homochiral assembly.

3.30–4.41 Å, with symmetry-related pyridine rings tilted at 22.2° to the central pyrazine ring. The ‘three-layer’ stack causes the two sets of ligand donors,  $N_{\text{pyridine}}$  and  $S_{\text{pyrazine}}$ , to be arranged in opposite directions which is ideal for the linking of metal centres in polymer formation. The ‘three-layer’  $\pi$ -stacking also confers planar chirality on the ligands, with the same  $P,M,P$  enantiomer being observed throughout the helix (Fig. 1).<sup>12</sup> CPK models indicate that it is not possible to build the diastereomerically-related  $P$  helix with this  $P,M,P$  enantiomer of the ligand but that the enantiomerically-related  $P$  helix can be built with the  $M,P,M$  enantiomer. Each Ag(I) atom adopts a distorted trigonal planar arrangement, which links symmetry-related ligands by  $N_{\text{pyrazine}}, S$  chelation from one ligand and  $N'_{\text{pyridine}}$  donation from the other. Thus each ligand binds to four Ag(I) ions. In the repeating units the distance between the Ag(I) ions is 3.116(1) Å, which lies within the range (2.86–3.22 Å) for similar systems.<sup>8,13</sup> The trigonal planes in the repeating unit are tilted at 68.2° with respect to each other. In addition, the trigonal planes across the pyrazine are tilted by a further 16.3°. The combined tilting of these planes across the ‘three-layered’  $\pi$ -stacked ligands generates the shallow helical twist and hence is responsible for the long pitch of the helix. Previously, we found that the related ligand bis(2-pyridylmethyl)sulfide formed a dimeric side-by-side complex with silver(I).<sup>8</sup> That discrete complex was almost identical to the section of the helix highlighted in black in Fig. 2 and indicates that this dimeric arrangement is particularly favourable for ligands of this type in the presence of silver(I).

The helices are close packed (Fig. 3) in such a way that each pyridine ring is involved in an intermolecular  $\pi$ -stacking interaction with a pyridine ring on an adjacent helix (atom...atom contacts between rings range from 3.63 to 3.74 Å). Between any two adjacent helices there are two such interactions per turn of helix. These interactions help to generate a tightly packed three-dimensional network with no solvent accessible volume (Fig. 3). This is further evidenced by the relatively short Ag...Ag distance [8.210(2) Å] between adjacent helices. These intermolecular interactions are probably responsible for the packing together of homochiral helices on crystallisation and the resulting conglomerate crystallisation.

We have shown that an achiral ligand predisposed to intramolecular  $\pi$ -stacking can generate *in-situ* planar chirality on coordination to silver(I) and the formation of a coordination polymer. In addition, this property results in the formation of a single-stranded helix and the packing of homochiral helices. This work points to a complementary approach to that of using racemic mixtures of ligands as a means of investigating the effect of chirality in molecular recognition processes in coordination-polymer chemistry. Currently we are actively pursuing the use of *in-situ* chirality in the formation of supramolecular architectures.

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## Notes and references

† *Synthesis* of 2,3-bis(6'-methyl-2'-pyridylmethylsulfanylmethyl)pyrazine **L**: 6-methyl-2-(sulfanylmethyl)pyridine (4.4 g, 0.031 mol) was added to degassed MeOH (250 ml) containing 0.72 g (0.031 mol) Na metal and was stirred for 1 h. 2,3-Bis(chloromethyl)pyrazine (2.8 g, 0.016 mol) was

dissolved in degassed  $\text{CH}_2\text{Cl}_2$ , added to the above solution, refluxed for 4 h, and stirred overnight. The resulting solution was reduced to give a brown residue which was dissolved in  $\text{CH}_2\text{Cl}_2$  (100 ml), washed with  $\text{H}_2\text{O}$  ( $2 \times 100$  ml), dried ( $\text{MgSO}_4$ ) and reduced to give a golden oil. Yield: 4.0 g (67%). NMR:  $\delta_{\text{H}}$ (500 MHz,  $\text{CDCl}_3$ ) 8.32 (s, 2H), 7.49 (t, 2H,  $^3J$  7.5 Hz), 7.16 (d, 2H,  $^3J$  7.5 Hz), 6.99 (d, 2H,  $^3J$  7.5 Hz), 3.96 (s, 4H), 3.78 (s, 4H), 2.52 (s, 6H). Anal. Calc. for  $\text{C}_{20}\text{H}_{22}\text{N}_4\text{S}_2\text{H}_2\text{O}$ : C, 59.97; H, 6.04; N, 13.99; S, 16.01. Found: C, 59.69; H, 6.03; N, 14.10; S, 16.03%.

‡ *Synthesis* of  $[\text{Ag}_2(\text{L})(\text{ClO}_4)_2] \cdot \text{AgClO}_4$  (54 mg, 0.26 mmol) was dissolved in degassed MeCN and added *via* cannula to **L** (50 mg, 0.14 mmol) dissolved in degassed MeCN and allowed to stir for 1 h. The lemon solution was reduced in volume to 2 ml, diethyl ether was added and the resulting white precipitate was filtered off and dried *in vacuo*. Yield: 89 mg (85%). NMR:  $\delta_{\text{H}}$ (300 MHz;  $\text{CD}_3\text{CN}$ ) 8.03 (s, 2H), 7.82 (t, 2H,  $^3J$  7.5 Hz), 7.39 (d, 2H,  $^3J$  7.5 Hz), 7.29 (d, 2H,  $^3J$  7.5 Hz), 4.30 (s, 4H), 4.13 (s, 4H), 2.51 (s, 6H). Anal. Calc. for  $\text{C}_{20}\text{H}_{22}\text{N}_4\text{S}_2\text{Ag}_2\text{Cl}_2\text{O}_8$ : C, 30.13; H, 2.78; N, 7.03; S, 8.04. Found: C, 30.33; H, 2.76; N, 6.99; S, 7.88%; Colourless crystals were grown from the slow evaporation of an acetonitrile solution of the complex.

§ *Crystal data* for  $[\text{Ag}_2(\text{L})(\text{ClO}_4)_2] \cdot \text{AgClO}_4$ :  $\text{C}_{20}\text{H}_{22}\text{Ag}_2\text{Cl}_2\text{N}_4\text{O}_8\text{S}_2$ ,  $M = 797.18$ , hexagonal,  $P6_322$  (no. 179),  $a = 9.182(2)$ ,  $c = 52.48(2)$  Å,  $U = 3832(2)$  Å<sup>3</sup>,  $T = 163(2)$  K,  $Z = 6$ ,  $\mu(\text{Mo-K}\alpha) = 1.961$  mm<sup>-1</sup>, 49 638 reflections measured, 2623 independent reflections ( $R_{\text{int}} = 0.0455$ ), [2553,  $I \geq 2\sigma(I)$ ],  $R_1 = 0.0420$ , 0.0434 (all data),  $wR_2 = 0.0887$ , 0.0893 (all data).

CCDC 150985. See <http://www.rsc.org/suppdata/cc/b1/b101875m/> for crystallographic data in .cif or other electronic format.

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