

# Helical (Isotactic) and Syndiotactic Silver(I) Metallo-Supramolecular Coordination Polymers Assembled from a Readily Prepared Bis-Pyridylimine Ligand Containing a 1,5-Naphthalene Spacer

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**Abstract:** A ligand in which two pyridylimine binding units are linked by a 1,5-naphthalene spacer is prepared and its silver(I) coordination chemistry investigated. In the solid state, a pair of C–H...N interactions between pyridylimine units link the free ligands into chain structures, with further C–H...N and some  $\pi$ -stacking interactions linking these chains into a three-dimensional structure. The spacer constrains the ligand to dinucleate, and with silver(I)

the metal coordinates to two pyridylimine units from two separate ligands and this leads to the formation of coordination polymers with a range of different anions. Different twisting motifs within the ligand control the tacticity of these coordination polymers and both

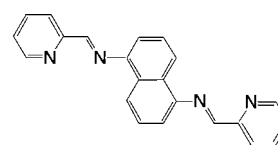
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isotactic, helical polymers and syndiotactic (achiral) polymers result. The core of the isotactic polymer strands contains two metallo-vectors and results in long-range ordering of the metal centres into a  $2 \times n$  grid arrangement. The solution behaviour indicates that exchange between the diastereomeric forms occurs. Since this must involve inversion at the metal centres, atactic species may also form a component of the solution library.

## Introduction

Supramolecular synthesis is a powerful tool for design of complex molecular architectures<sup>[1]</sup> and metal–ligand interactions have played a key role in the development of suitable synthetic routes.<sup>[2]</sup> Control of molecular shape or architecture may potentially be used to encode the molecular function in such systems. Indeed we have recently demonstrated this through design of cylindrical agents that recognise the major groove of DNA.<sup>[3]</sup> We are interested in synthetic routes that will allow sophisticated metallo-supramolecular architectures to be constructed rapidly through simple mixing of commercial reagents. To this end we have employed simple imine systems and have demonstrated that they may be used to assemble discrete cyclophanes, double and triple helicates, dimers, trimers and grids.<sup>[3–8]</sup> We have shown that ligand design can address the challenge not only of defining the supramolecular architecture or superstructure but also of defining the precise topography, conformation or chirality of this superstructure.<sup>[5, 6]</sup> Moreover, the architecture and top-

ography may be used to control the subsequent aggregation of the metallo-supramolecular unit into a larger array.<sup>[7]</sup> To probe such effects further, we have been systematically exploring a range of pyridylimine ligands and herein report the synthesis and coordination chemistry of a bis-pyridylimine ligand based on a 1,5-naphthalene spacer (L, Scheme 1).



Scheme 1. Ligand L.

We were attracted to this spacer unit as it should sterically disfavor the formation of simple dinuclear dimeric structures and consequently might afford (cyclic or linear) arrays of higher nuclearity. The spacer imposes a parallel (but offset) orientation of the two sets of donor atoms in the two binding units and, with a metal ion of tetrahedral coordination geometry, cannot sustain a dinuclear double helix or cyclophane. Ligands in which binding sites are rigidly locked into such a parallel orientation can support grid structures as illustrated by Osborn and Youinou<sup>[9]</sup> with the 3,6-di(2'-pyridyl)pyridazine (DPPN) system (which forms  $2 \times 2$  grid arrays with tetrahedral metal ions) and further elaborated by

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Lehn to create higher order  $N \times N$  grid arrays.<sup>[10]</sup> In the DPPN grid systems the ligand design results in grids in which the ligands lie uniquely above or uniquely below the plane of the metals. Interwoven grids (in which ligands wrap about the metal–metal axis) have also been reported but require the two metal binding sites to be twisted such that they point in opposite directions.<sup>[11]</sup> Such interwoven grids represent tetranuclear circular helicates<sup>[12]</sup> and (with labile metal ions) flexibility introduced between the binding sites can lead to a library of such structures in solution.<sup>[8, 12]</sup> While cyclic arrays of varying nuclearity are often favoured for such systems in solution, in the solid state the formation of an infinite polymer (helical or nonhelical) represents an alternative structural motif in which the metal and ligand requirements may be mutually satisfied and which may compete energetically with cyclic structures even in apparently simple systems.<sup>[13]</sup>

There have been two previous reports of supramolecular arrays generated from ligands containing 1,5-naphthyl spacers. Raymond has employed this spacer to separate catechol binding units.<sup>[14]</sup> The spacer prevents the triple-helix formation (observed with octahedral ions when a phenyl spacer is employed) and instead tetrahedral cluster architectures are accessed when appropriate noncovalent guest templates are present. von Zelewsky has used the spacer to separate chiral pinene–bipyridine units.<sup>[15]</sup> With tetrahedral metal ions an infinite helical polymer is formed (rather than the circular helicate observed for the phenyl spacer). Each polymeric strand intertwines about another creating a higher order double-helical structure.

## Results and Discussion

**Free ligand:** The ligand L was prepared by simply mixing two equivalents of pyridine-2-carboxaldehyde and one of 1,5-diaminonaphthalene in ethanol. Recrystallisation of the product from solution in chloroform afforded yellow crystals, the partial microanalytical data, <sup>1</sup>H NMR spectrum and mass spectrum of which were consistent with the expected ligand formulation ( $C_{22}H_{16}N_4$ ). The structure of the ligand has been confirmed by X-ray crystallography and is shown in Figure 1. In the solid state the pyridylimine units are approximately coplanar (dihedral angle  $6^\circ$ )<sup>[16]</sup> with the pyridyl and imine nitrogen atoms oriented *trans* to each other. Such an orientation is typical for pyridylimine ligands<sup>[17]</sup> and minimises proton–proton interactions while maintaining conjugation. The *trans* configuration creates a donor–acceptor hydrogen-bond motif (analogous to a carboxylic acid, *cis*-amide or pyridone) utilising the weakly acidic imine hydrogen atom and the pyridine nitrogen atom. These motifs form dimeric  $N \cdots H-C$  interactions ( $N \cdots H$  2.83 Å;  $N \cdots H-C$  angle  $168^\circ$ )<sup>[19]</sup> which link the ligands into a chain (Figure 1a). The imine nitrogens point out from the back of these motifs and form short interactions with pyridyl protons on ligands in adjacent chains ( $N \cdots H$  2.76 Å;  $N \cdots H-C$  angle  $161^\circ$ ). These interactions link the chains and give rise to a herringbone-type packing motif (Figure 1b). Some short contacts implying weak  $C-H \cdots \pi$  interactions (face–edge  $\pi$ -stacking interactions) are also observed between the chains. Perpendicular to this hydrogen-bonding plane, the ligands stack together forming

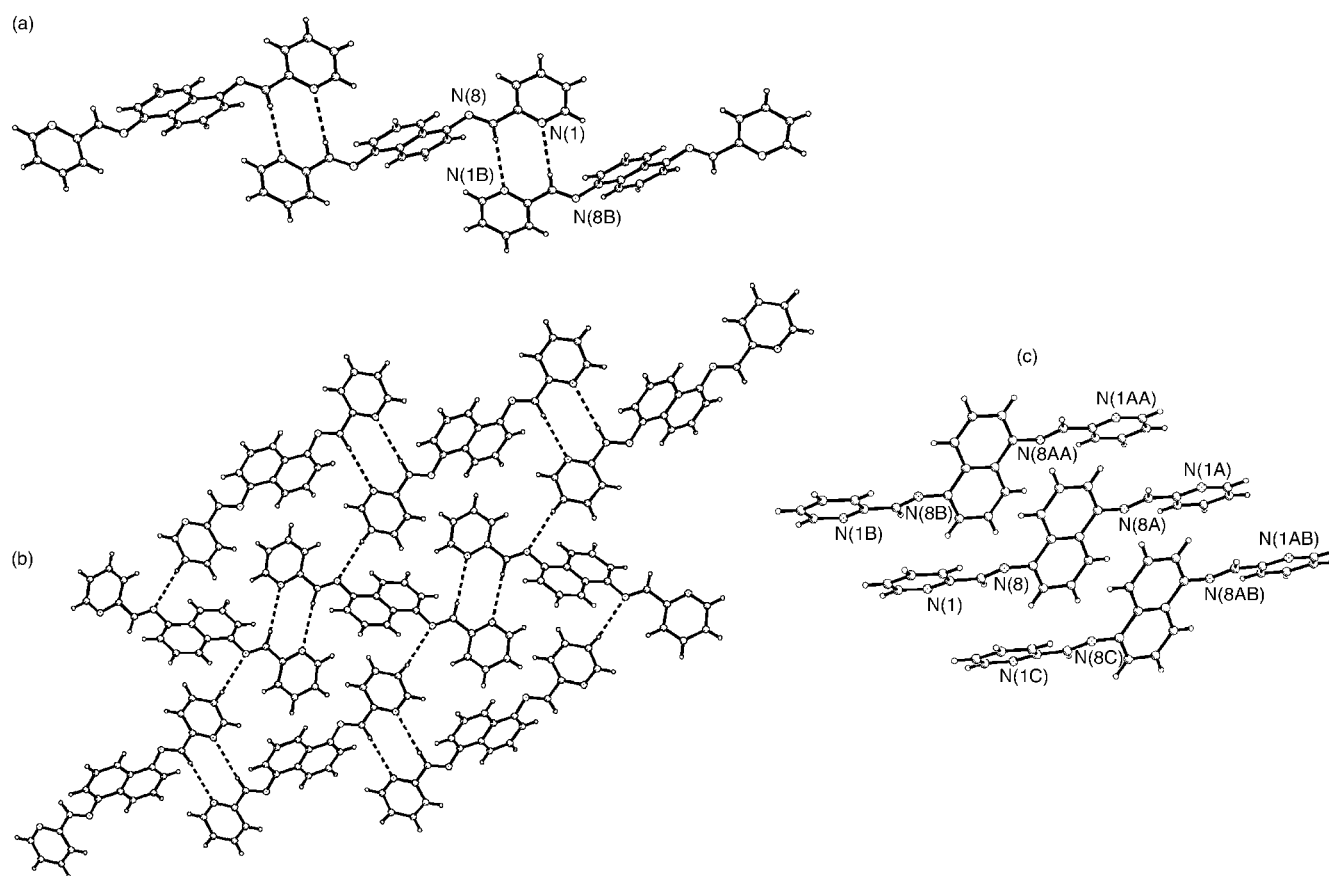


Figure 1. The X-ray crystal structure for L illustrating the H-bonded chains (a), the network of chains (b) and the stacking perpendicular (c) to the plane of b.

columns (Figure 1c; interligand separations  $\approx 3.5$  Å; the imine units are face–face  $\pi$ -stacked with a pyridyl ligand on one side and a naphthyl unit on the other, but there are no naphthyl–naphthyl, pyridyl–naphthyl or pyridyl–pyridyl face–face interactions). The pyridylimine units are twisted with respect to the naphthyl spacers (dihedral angle  $42^\circ$ ).<sup>[16]</sup> This twisting minimises proton–proton interactions and also removes the naphthyl unit from the plane of the hydrogen-bonding motif, facilitating the formation of the hydrogen bonds.

**Silver(I) complex:** Coordination to silver(I) was achieved by stirring one equivalent of L with one equivalent of silver(I) acetate in methanol with the exclusion of light for 30 minutes. Treatment with ammonium hexafluorophosphate afforded a yellow precipitate. Partial microanalytical data for this compound are consistent with a formulation  $[(AgL)_n][PF_6]_n$ .

X-ray quality, pale yellow crystals were obtained by the slow diffusion of diethyl ether into a solution of the complex in acetonitrile. As anticipated each silver(I) centre binds to two pyridylimine units from two separate ligands to give a pseudotetrahedral coordination environment. Rather than giving rise to a cyclic oligomer, an infinite linear polymeric chain is formed (Figure 2). The pyridylimine units are approximately planar (dihedral angle  $11^\circ$ ) while the imine unit is twisted through  $54^\circ$  with respect to the naphthyl spacer.<sup>[16]</sup> In contrast to the free ligand, in which the pyridylimine units are disposed on opposite faces of the naphthyl units, in this complex both metal-binding sites are oriented towards the same face of the naphthyl group (Figure 2a). The twistings of the pyridylimine units with respect to the naphthyl spacer confer a propeller-like twist along the length of the ligand, rendering the ligand chiral. Each ligand in the polymer chain has the same chirality. Similarly, within the chain all the silver(I) centres have the same configuration leading to a chiral, isotactic polymer structure.<sup>[18]</sup> Within the chain, the silver(I) centres are positioned along two parallel vectors (Figure 2b). The silver(I) centres within the chain are separated by 8.44 Å (between the vectors) and 9.68 Å (along the vectors).

The structure contains planes in which all the chains are of the same chirality and these alternate with planes of the opposite chirality leading to an

achiral overall structure. The anions are located within channels between the chains and make a number of short contacts to the chains, most notably to the acidic imine proton ( $F \cdots H-C$  2.47 Å, bond angle  $176^\circ$ ) and to  $H^3$  of the pyridine ring ( $F \cdots H-C$  2.53 Å, bond angle  $168^\circ$ ).<sup>[19]</sup> Remarkably for a system with so many aromatic residues, the structure does not display extensive face–face  $\pi$ -stacking interactions. Within the chains, the naphthyl groups are coplanar with an interplane separation of  $\approx 3.5$  Å, however the overlap is poor and only occurs at the edges of the rings. However, within the chain the naphthyl ring does form a  $C-H \cdots \pi$  interaction with the face of a pyridine from an adjacent ligand ( $C-H \cdots$  centroid 3.08 Å; centroid  $\cdots$  centroid 5.24 Å).

Coordination polymers prepared from bis-monodentate ligands give single-stranded polymers which may have (non-helical) linear or zigzag structures or alternatively may be coiled up to give a helical array.<sup>[20]</sup> Such helicity arises from the coiling, which in turn is controlled by the metal coordination geometry, ligand structure and potential for intrastrand interactions. Coordination polymers prepared from bis-didentate AB-type ligands (such as the one described herein) are different in that the metal centres have intrinsic helicity (just as octahedral metal tris-didentates) which arises from the propeller-type orientation of the didentate binding units about the metal. Thus such coordination polymers are

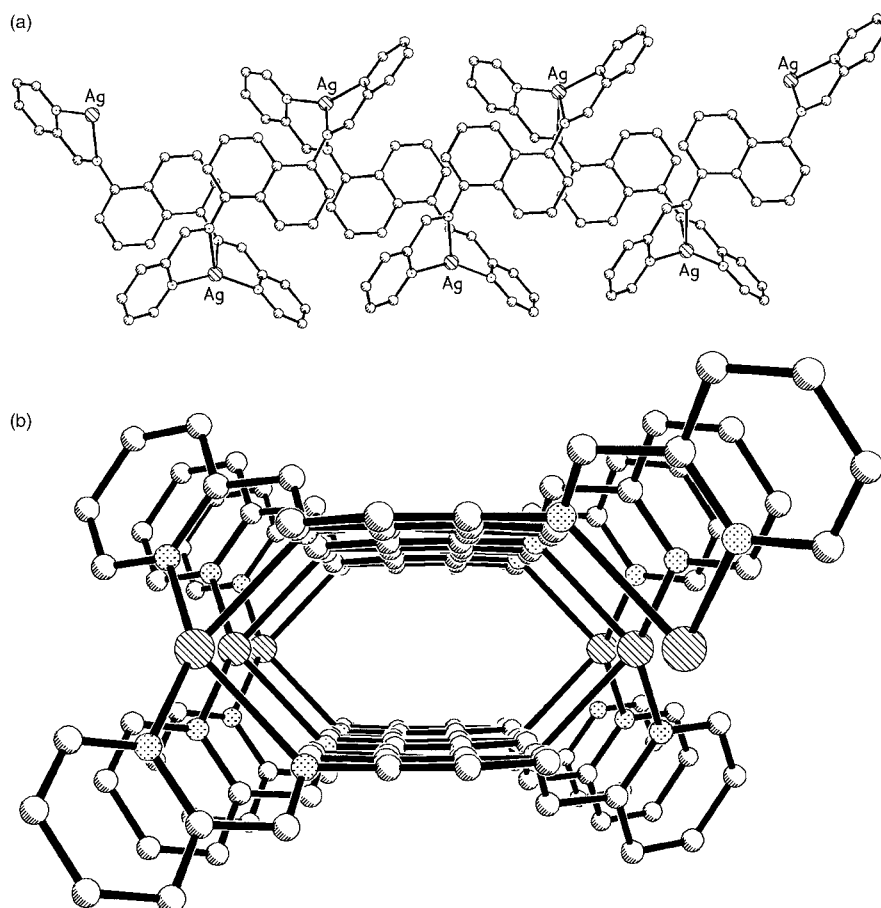


Figure 2. The X-ray crystal structure for the silver(I) hexafluorophosphate chiral isotactic complex of L. The structure of the polymeric strand (a). A view down a strand revealing the two metallo-vectors (b). Hydrogen atoms are omitted for clarity. The structures of the cationic chains in the corresponding perchlorate and trifluoromethanesulfonate salts are almost identical.

afforded an inherent helicity when all the metal centres in the chain are of the same configuration. Indeed, examples have previously been described in which flexible bis-didentate ligands wrap about metal centres (which define a helical axis) and afford infinite helical arrays.<sup>[21]</sup> These are polymeric analogues of discrete double- and triple-helical arrays (in which, similarly, ligands usually wrap around metal centres which define a helical axis). Recently, Lehn et al. have described the structure of a discrete helicate, in which there are two metallo-chains within the core of the helix and which is thus distinct from conventional helical structures.<sup>[22]</sup> This structure arises from coordination of silver(I) to a ligand in which the binding sites are oriented in a colinear fashion. The ligand therefore does not wrap significantly about the helical axis,<sup>[23]</sup> but instead primarily lies across it coordinating to metal centres in both metallo-chains. A propeller-like twist runs along the length of the ligand.

The isotactic helical polymer described herein also contains two metallo-chains at its core which are bridged by ligands with a propeller-like twist which lie across the helical axis. The structure thus represents a polymeric analogue of this alternate type of discrete helicate structure described by Lehn. Lehn comments that his discrete structure represents an "organised pattern of ion dots".<sup>[22]</sup> Such ability to position metals or components within an ordered array is an important feature of supramolecular assembly, yet applications in the field of materials will require control of order and position at nanoscale dimensions and beyond. This may be achieved either through higher level ordering of discrete supramolecular structures<sup>[7, 25]</sup> or through extending the desired structural motif into an oligomeric or polymeric array. The isotactic helical polymer structure described herein leads to an ordered positioning of the metals in a series of  $2 \times n$  rhomboid grid arrangements, with order imposed across the nanoscale and beyond.

We have observed in other silver(I) metallo-supramolecular systems that the anion can play a vital role in determining the solid-state structure adopted<sup>[24]</sup> and so to investigate whether this isotactic helical polymer was a robust, recurring structure or merely one of a library of possible solid-state structures, we have prepared the analogous perchlorate and trifluoromethanesulfonate salts. Pale yellow crystals of the perchlorate salt were obtained from solution in acetonitrile by the slow diffusion of benzene. All crystals examined proved to be severely twinned. However the best data obtained clearly revealed the cation to have an isotactic helical coordination polymer structure identical to that in the hexafluorophosphate salt, although the twinning prevented a complete refinement. Just as in the hexafluorophosphate salt, the anions reside within channels between the chains and make short contacts most notably to the acidic imine proton.

Pale yellow rods of the trifluoromethanesulfonate salt were similarly obtained from solution in acetonitrile by the slow diffusion of diethyl ether. The structure is again an isotactic helical coordination polymer of almost identical structure to that of the hexafluorophosphate and perchlorate salts. The pyridylimine units are again approximately planar (dihedral angles 10 and 12°) and the propeller-like twisting between the

pyridylimine units and the naphthyl spacer (44 and 58°) imparts chirality to the ligand. Within each polymer strand the ligands possess the same chirality and the metal centres all have the same configuration. The silver(I) centres are again located along two parallel vectors with intermetallic distances of 8.53 Å between vectors and 9.48 Å along the vectors. The anions reside between the chains and make short contacts to the acidic imine protons. One imine proton forms H bonds with only the O of an anion (C–H...O 2.53 Å, bond angle 171°) while the other interacts with both O and F in a didentate-type fashion (C–H...O 2.63, bond angle 147°; C–H...F 2.74, bond angle 120°).

While growing crystals, we observed some discrepancies in the colour of the complex. While pale yellow material most frequently crystallised, sometimes a deeper orange coloured material was obtained either exclusively or mixed in with pale yellow crystals. In addition, solutions of the complex in nitromethane appeared to be more orange than those in other solvents and to darken on standing or warming.

We were eventually able to obtain suitable crystals of orange material: while diffusing diethyl ether into a solution in acetonitrile of the trifluoromethanesulfonate salt, orange semicrystalline material was observed to grow towards the top of the vial, while pale yellow crystals grew on the base. These two sets of crystals were separated and each was redissolved in acetonitrile and then subjected to diethyl ether diffusion. From the solution prepared from the pale yellow crystals, only pale yellow blocks were observed to grow. Similarly the solution prepared from the orange material afforded only orange leaflike crystals.<sup>[26]</sup> These orange crystals have also been examined by X-ray diffraction.

The structure is again a coordination polymer (Figure 3). However in this polymer structure, the metal-binding sites are oriented towards opposite faces of the naphthyl rings, as in the free ligand. This mode of twisting does not confer chirality to the ligand. The silver(I) centres alternate in configuration down the chain and an achiral syndiotactic polymer structure results.<sup>[18]</sup> The pyridylimine units are approximately planar (dihedral angles 7 and 4°) and the ligand twisting occurs between the pyridylimine units and the naphthyl spacer (33 and 38°) and is less dramatic than in the isotactic polymers. The syndiotactic polymer has a zigzag structure with intermetallic separations of 9.05 Å. The zigzag chains pack together in planes with multiple C–H... $\pi$  contacts between the chains, primarily from pyridyl protons to the naphthyl rings on adjacent chains. The anions (which are partially disordered) reside between the planes and, as in the isotactic polymers, form short contacts to the imine protons (C–H...O 2.51–2.60 Å; C–H...F 2.70–2.83).

The samples do not fly consistently well in electrospray mass spectrometry and this would be consistent with an oligomer/polymer solution structure. The positive ion electrospray mass spectrum for the silver(I) hexafluorophosphate complex shows weak peaks corresponding to a trimeric array at  $m/z$  1625 ( $[\text{Ag}_3\text{L}_3(\text{PF}_6)_2]^+$ ) and at  $m/z$  738 ( $[\text{Ag}_3\text{L}_3(\text{PF}_6)^2]^+$ ) along with evidence of dimeric species at  $m/z$  1033 ( $[\text{Ag}_2\text{L}_2(\text{PF}_6)^+]$ ) and mononuclear species at  $m/z$  781 ( $[\text{AgL}_2]^+$ ) and  $m/z$  486 ( $[\text{AgL}(\text{CH}_3\text{CN})^+]$ ). While this may indicate the presence of some small linear or cyclic oligomers

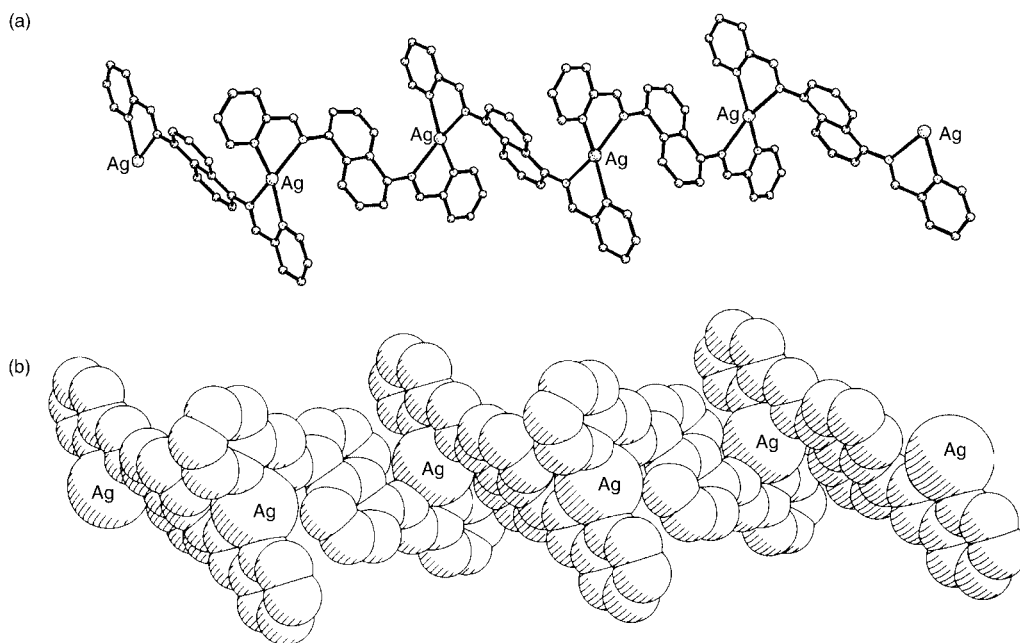


Figure 3. The X-ray crystal structure for the silver(I) trifluoromethanesulfonate achiral syndiotactic complex of L. The structure of the polymeric strand (a). A space-filling representation emphasising the achiral syndiotactic nature of the array (b). Hydrogen atoms are omitted for clarity.

in solution, the peaks may be fragments of a high mass polymeric species.<sup>[15]</sup>

Despite the polymeric solid-state structures, the compounds do exhibit adequate solubility in acetonitrile for investigation by NMR spectroscopy. The  $^1\text{H}$  NMR spectrum of the hexafluorophosphate complex in deuterated acetonitrile (Figure 4a) is sharp at room temperature and shows that in the complex the ligand is symmetrical on the NMR timescale. As the temperature is lowered some of the resonances (particularly those for the naphthyl unit) start to broaden but, within the temperature range of this solvent, no new peaks appear (Figure 4b). This may indicate the presence of multiple rapidly exchanging solution species (e.g. different

length linear or cyclic oligomers) or an intramolecular process, such as rotation between the pyridylimine and naphthyl units, or inversion at the metal centres, which is slowed as the temperature is decreased. No Ag–H<sup>i</sup> coupling is observed, but this is not uncommon for silver pyridylimine complexes in solution in acetonitrile<sup>[5–7]</sup> and again indicates that the fluxional process(es) may involve changes at the metal centres. On dilution, some small shifts in the positions of the peaks are observed, which probably reflects a change in average aggregation number on dilution.  $^1\text{H}$  NMR nuclear overhauser enhancements (NOEs) are observed from the imine proton (H<sup>i</sup>) to H<sup>3</sup> on the pyridine ring (as would be anticipated if the pyridylimine unit is coordinated to a metal

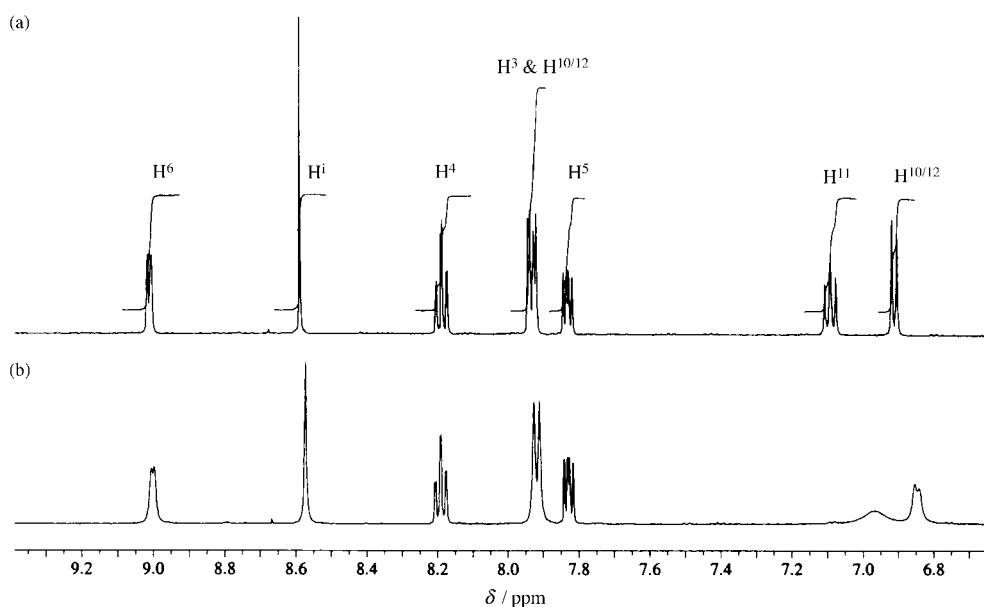


Figure 4. 500 MHz  $^1\text{H}$  NMR spectra for the silver complex in deuterated acetonitrile at 283 K (a) and at 253 K (b).

centre) and also to the naphthyl resonance at  $\delta = 6.9$  ppm which we ascribe to  $H^{12}$ . By contrast, only a weak NOE is observed between  $H^i$  and the peak at  $\delta = 7.9$  ppm, corresponding to  $H^{10}$ . This is consistent with the twisting between the naphthyl group and the pyridylimine unit being such that, on average, the imine proton lies closer to this naphthyl proton; a situation which is observed in both the isotactic and syndiotactic crystal structures.

We have previously observed, in related silver(i) supramolecular systems, that fluxional processes are frequently frozen out more readily in solution in nitromethane than in acetonitrile.<sup>[24]</sup> Moreover the observation of the deeper orange colouration in this solution implies that there might be more of the syndiotactic species present in this solution. Consequently we have also recorded NMR spectra in this solvent. In solution in nitromethane at room temperature, the naphthyl resonances are broadened and the spectrum resembles that in acetonitrile at 253 K. As the temperature is lowered all the peaks broaden and some additional broad peaks appear. However within the temperature range of this solvent, the peaks remain broad, preventing further elaboration of the fluxional process. The spectra of the analogous perchlorate, tetrafluoroborate and trifluoromethanesulfonate salts have also been recorded and are all very similar to that of the hexafluorophosphate salt, implying similar solution species. The spectra of solutions in acetonitrile prepared from both the orange and yellow crystals are identical. It seems probable that the exchange process observed is interconversion between the syndiotactic and isotactic forms, which requires twisting within the ligand (which in solution would be expected to be associated with low energy barriers) and inversion at the metal centres (in a coordinating solvent like acetonitrile this also be expected to be rapid, but, consistent with the data, would be less so in nitromethane). Such exchange, unless concerted in an alternate fashion along the chain, implies the presence of atactic species in solution.<sup>[27]</sup>

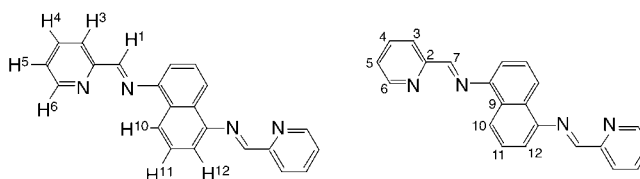
## Conclusion

The work described herein demonstrates how readily prepared pyridylimine ligands can be used to support the formation of polymeric arrays of defined structure. The twisting within the ligand, and the associated metal chirality, control the tacticity of these coordination polymers. Such polymeric arrays have structural analogies with the topologies of discrete supramolecular arrays, yet extend that topology to larger dimensions. Indeed the three isotactic helical polymers described herein contain two metallo-chains at their core and this leads to an ordered positioning of the metals in a series of  $2 \times n$  grid arrangements. The ability to design polymeric structures of defined architecture in which order and position are controlled at the nanoscale range (and indeed beyond) has implications for design of new supramolecular materials with new and controlled functions and we are currently pursuing this further.

## Experimental Section

**General:** All starting materials were purchased from Aldrich and used without further purification. NMR spectra were recorded on Bruker ACF250, DPX300 and 400 instruments by using standard Bruker software. ESI mass spectra were recorded by the EPSRC National Mass Spectrometry Service Centre, Swansea, on a Micromass Quattro(II) (low-resolution triple quadrupole mass spectrometer) at 20 V cone voltage. Microanalyses were conducted on a Leeman Labs CE44 CHN analyser by the University of Warwick Analytical service. Infrared spectra were recorded on a Perkin-Elmer Paragon1000 instrument with the sample compressed in KBr discs.

**Preparation of L:** Pyridine-2-carboxaldehyde (1.2 cm<sup>3</sup>, 12.64 mmol) and 1,5-diaminonaphthalene (1 g, 6.32 mmol) were stirred in ethanol (100 cm<sup>3</sup>) for 24 hours. The mixture was filtered and concentrated in vacuo to a yellow solid. Recrystallisation from chloroform afforded yellow crystals (0.86 g, 41 %; see Scheme 2).



Scheme 2. Numbering scheme used in NMR data assignments.

MS (EI<sup>+</sup>): *m/z* (%): 336 [*M*<sup>+</sup>] (100 %); elemental analysis calcd (%) for C<sub>22</sub>H<sub>16</sub>N<sub>4</sub>: C 78.5, H 4.8, N 16.7; found: C 78.2, H 4.8, N 16.9; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K):  $\delta = 8.75$  (ddd, <sup>3</sup>*J*(H,H) = 4.9, <sup>4</sup>*J*(H,H) = 1.5, 0.9 Hz, 2H; H<sup>6</sup>), 8.71 (s, 2H; H<sup>1</sup>), 8.40 (dt, <sup>3</sup>*J*(H,H) = 7.9, <sup>4</sup>*J*(H,H) = 0.9 Hz, 2H; H<sup>5</sup>), 8.30 (d, <sup>3</sup>*J*(H,H) = 7.3 Hz, 2H; H<sup>10/12</sup>), 7.88 (td, <sup>3</sup>*J*(H,H) = 7.9, <sup>4</sup>*J*(H,H) = 1.5 Hz, 2H; H<sup>4</sup>), 7.52 (t, <sup>3</sup>*J*(H,H) = 7.3 Hz, 2H; H<sup>11</sup>), 7.42 (ddd, <sup>3</sup>*J*(H,H) = 7.6, 4.9, <sup>4</sup>*J*(H,H) = 1.2 Hz, 2H; H<sup>5</sup>), 7.20 (d, <sup>3</sup>*J*(H,H) = 7.3 Hz, 2H; H<sup>10/12</sup>) (assignments confirmed by using COSY. NOE measurements did not allow unambiguous assignment of H<sup>10</sup> and H<sup>12</sup> due to free rotation in solution. However spectral simulation (ACD/HNMR Predictor) indicated H<sup>10</sup> to be the peak at 8.30 ppm and H<sup>12</sup> that at 7.20 ppm); <sup>13</sup>C NMR (75.6 MHz, CDCl<sub>3</sub>, 298 K):  $\delta = 161.3$  (C<sup>7</sup>), 155.2 (C<sup>2/8/9</sup>), 150.1 (C<sup>6</sup>), 148.4 (C<sup>2/8/9</sup>), 137.1 (C<sup>4</sup>), 129.8 (C<sup>2/8/9</sup>), 126.7 (C<sup>11</sup>), 125.7 (C<sup>5</sup>), 123.0 (C<sup>10/12</sup>), 122.4 (C<sup>3</sup>), 114.0 (C<sup>12/10</sup>) (assignments made using <sup>1</sup>H-<sup>13</sup>C correlation expts); IR (KBr):  $\bar{\nu} = 2890$ –3060 (w), 1622 (s), 1583 (m), 1566 (m), 1502 (w), 1466 (m), 1438 (m), 1402 (m), 1352 (w), 1288 (w), 1258 (w), 1224 (w), 1207 (w), 1149 (w), 1043 (w), 993 (m), 927 (m), 913 (w), 864 (w), 798 (s), 780 (s), 743 (m), 666 (w), 622 (m), 544 (w), 493 cm<sup>-1</sup> (m).

**Coordination of L to silver(i):** Care was taken to exclude light during the following procedure. L (0.03 g, 0.09 mmol) and silver(i) acetate (0.015 g, 0.09 mmol) were stirred in methanol for 30 minutes and the solution was then treated with methanolic ammonium hexafluorophosphate. Following stirring at room temperature for 78 hours, the yellow precipitate was collected by vacuum filtration and recrystallised from hot chloroform (0.025 g, 47 %).

MS (ESI<sup>+</sup>): *m/z* (%): 1625 [Ag<sub>3</sub>L<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub><sup>+</sup>], 1033 [Ag<sub>2</sub>L<sub>2</sub>(PF<sub>6</sub>)<sup>+</sup>], 781 [AgL<sub>2</sub><sup>+</sup>], 738 [Ag<sub>3</sub>L<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub><sup>+</sup>], 486 [AgL(CH<sub>3</sub>CN)<sup>+</sup>], 444 [(AgL)<sub>*n*</sub><sup>*n*+</sup>], 337 [LH<sup>+</sup>]; elemental analysis calcd (%) for [Ag<sub>*n*</sub>(C<sub>22</sub>H<sub>16</sub>N<sub>4</sub>)<sub>*n*</sub>][PF<sub>6</sub>]<sub>*n*</sub>·H<sub>2</sub>O: C 43.5, H 3.0, N 9.2; found: C 43.8, H 2.7, N 9.2; <sup>1</sup>H NMR (250 MHz, CD<sub>3</sub>CN, 298 K):  $\delta = 8.95$  (d, <sup>3</sup>*J*(H,H) = 4.6 Hz, 2H; H<sup>6</sup>), 8.60 (s, 2H; H<sup>1</sup>), 8.15 (td, <sup>3</sup>*J*(H,H) = 7.6, <sup>4</sup>*J*(H,H) = 1.5 Hz, 2H; H<sup>4</sup>), 7.90 (m, 4H; H<sup>10/12</sup> and H<sup>5</sup>), 7.78 (ddd, <sup>3</sup>*J*(H,H) = 7.6, 4.6, <sup>4</sup>*J*(H,H) = 1.2 Hz, 2H; H<sup>5</sup>), 7.22 (t, <sup>3</sup>*J*(H,H) = 7.3 Hz, 2H; H<sup>11</sup>), 7.00 (d, <sup>3</sup>*J*(H,H) = 7.3 Hz, 2H; H<sup>12/10</sup>) (assignments confirmed using COSY); <sup>13</sup>C NMR (75.6 MHz, CDCl<sub>3</sub>, 298 K):  $\delta = 161.4$  (C<sup>7</sup>), 151.0 (C<sup>6</sup>), 138.9 (C<sup>4</sup>), 128.5 (C<sup>3</sup>), 127.8 (C<sup>5</sup>), 121.3 (C<sup>11</sup>), 121.3 (C<sup>10/12</sup>), 115.6 (C<sup>10/12</sup>) (assignments made using <sup>1</sup>H-<sup>13</sup>C correlation expts; pendant sequence used and 4<sup>o</sup> carbons not observed); IR (KBr):  $\bar{\nu} = 3000$ –3050 (w), 1622 (s), 1592 (m), 1567 (m), 1504 (m), 1468 (m), 1438 (m), 1402 (m), 1352 (m), 1289 (w), 1265 (m), 1228 (w), 1208 (w), 1161 (w), 1105 (w), 1044 (w), 1014 (w), 994 (m), 928 (m), 840 (s), 779 (s), 782 (s), 741 (m), 666 (w), 623 (m), 559 (s), 493 cm<sup>-1</sup> (m).

The perchlorate, tetrafluoroborate and trifluoromethanesulfonate salts were prepared in an analogous manner by precipitating with appropriate ammonium or sodium salts of the required anion.

**X-ray crystallographic structural characterisations:** For all crystals, data were collected with a Siemens SMART three-circle system with a CCD area detector,<sup>[28]</sup> with crystals held at 180 K or 200 K with the Oxford Cryosystem Cryostream Cooler.<sup>[29]</sup> Refinements used SHELXTL.<sup>[30]</sup> Systematic absences indicated the appropriate space group. The structure was solved by direct methods with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameter of the atom to which the H atom was attached. Specific details of the crystallisations and refinements were as follows (see Table 1 for selected bond lengths and angles for the silver polymers and also Table 2).

Table 1. Selected bond lengths [Å] and bond angles [°] for the silver(I) coordination polymers.

	[(AgL) <sub>n</sub> ][PF <sub>6</sub> ] <sub>n</sub> isotactic	[(AgL) <sub>n</sub> ][CF <sub>3</sub> SO <sub>3</sub> ] <sub>n</sub> isotactic	[(AgL) <sub>n</sub> ][CF <sub>3</sub> SO <sub>3</sub> ] <sub>n</sub> syndiotactic
Ag–N <sub>pyridyl</sub>	2.247(5)	2.258(5) 2.239(4)	2.244(13) 2.263(13)
Ag–N <sub>imine</sub>	2.422(5)	2.418(4) 2.472(5)	2.402(11) 2.416(11)
bite angle	71.93(18)	71.72(17) 71.24(17)	73.1(4) 72.2(4)

*L*: Yellow crystals of the free ligand were obtained from a solution in chloroform. The ligand lay on a crystallographic centre of inversion and the asymmetric unit contained only half a molecule as it had a centre of symmetry.

[(AgL)<sub>n</sub>][PF<sub>6</sub>]<sub>n</sub>: Pale yellow crystals of the hexafluorophosphate anion were obtained from the slow diffusion of diethyl ether into a solution of the complex in acetonitrile. The silver and phosphorus atoms lie on twofold axes (positions 4c, 4d).

[(AgL)<sub>n</sub>][ClO<sub>4</sub>]<sub>n</sub>: Pale yellow crystals of the perchlorate anion were obtained from the slow diffusion of benzene into a solution of the complex in acetonitrile. All crystals examined proved to be severely twinned and this prevented a complete refinement. Space group *P*2<sub>1</sub>/*n*; *a* = 13.452(1) Å, *b* = 9.688(1) Å, *c* = 17.162(2) Å; β = 92.554(5)°.

[(AgL)<sub>n</sub>][CF<sub>3</sub>SO<sub>3</sub>]<sub>n</sub> isotactic polymer: Pale yellow rods of the trifluoromethanesulfonate anion were obtained from the slow diffusion of diethyl ether into a solution of the complex in acetonitrile.

Table 2. Crystallographic data.

	<i>L</i>	[(AgL) <sub>n</sub> ][PF <sub>6</sub> ] <sub>n</sub> isotactic	[(AgL) <sub>n</sub> ][CF <sub>3</sub> SO <sub>3</sub> ] <sub>n</sub> isotactic	[(AgL) <sub>n</sub> ][CF <sub>3</sub> SO <sub>3</sub> ] <sub>n</sub> syndiotactic
formula	C <sub>22</sub> H <sub>16</sub> N <sub>4</sub>	[(AgC <sub>22</sub> H <sub>16</sub> N <sub>4</sub> ) <sub>n</sub> ][PF <sub>6</sub> ] <sub>n</sub>	[(AgC <sub>22</sub> H <sub>16</sub> N <sub>4</sub> ) <sub>n</sub> ][CF <sub>3</sub> SO <sub>3</sub> ] <sub>n</sub>	[(AgC <sub>22</sub> H <sub>16</sub> N <sub>4</sub> ) <sub>n</sub> ][CF <sub>3</sub> SO <sub>3</sub> ] <sub>n</sub>
<i>M</i> <sub>r</sub>	336.40	(589.23) <sub>n</sub>	(593.33) <sub>n</sub>	(593.33) <sub>n</sub>
crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
<i>a</i> [Å]	4.8795(8)	17.4461(22)	14.134(3)	15.203(3)
<i>b</i> [Å]	16.832(3)	9.6788(12)	9.4785(17)	5.6447(12)
<i>c</i> [Å]	10.0879(17)	13.8081(18)	17.633(3)	25.806(5)
α [°]	90.00	90	90.00	90.00
β [°]	90.977(5)	90	94.883(5)	97.267(5)
γ [°]	90.00	90	90.00	90.00
<i>U</i> [Å <sup>3</sup> ]	828.4(2)	2331.6(4)	2353.7(7)	2196.7(8)
<i>T</i> [K]	180(2)	200(2)	180(2)	180(2)
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> <i>n</i> <i>n</i> <i>a</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>Z</i>	2	4	4	4
crystal size [mm]	0.24 × 0.16 × 0.08	0.4 × 0.04 × 0.03	0.16 × 0.02 × 0.01	0.06 × 0.04 × 0.01
data, parameters	2051/119	2053/155	4112/317	3847/277
<i>R</i> ( <i>F</i> ) [ <i>I</i> > 2σ( <i>I</i> )]	0.0529	0.0513	0.0521	0.0579
<i>wR</i> ( <i>F</i> <sup>2</sup> ) (all data)	0.1303	0.1441	0.0971	0.1605
Goof ( <i>F</i> <sup>2</sup> )	1.014	1.038	0.980	0.977

[(AgL)<sub>n</sub>][CF<sub>3</sub>SO<sub>3</sub>]<sub>n</sub> syndiotactic polymer: Orange leaflike crystals of the trifluoromethanesulfonate anion were obtained from the slow diffusion of diethyl ether into a solution of the complex in acetonitrile. The trifluoromethanesulfonate counter ion was very disordered. It was modelled over two positions but in both, the thermal parameters for carbon and sulfur showed that end-for-end disorder was also present. This was modelled by a 1:1 occupation of each site by carbon and sulfur. Although for oxygen and fluorine which also exchange their positions, this aspect of the disorder was not modelled.

CCDC-186143–186146 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ (UK); fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

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