Effect of anion on Ag(i) meso-helical chains formed with 4,4'-dipyridyl ketone: solvent versus anion bridging and anion effects on the strength of ligand binding†

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The synthesis and characterisation by IR spectroscopy and elemental analysis of ten new Ag(i)–L complexes are described. Of these complexes, nine are characterised by single crystal X-ray diffraction: {[Ag(L)][CF$_2$SO$_3$]·1/2H$_2$O}$_n$ (1), {[Ag(L)][ClO$_4$]·1/2H$_2$O}$_n$ (2), {[Ag$_2$(L)$_2$(CH$_3$CN)][ClO$_4$]$_2$·2CH$_3$CN·H$_2$O}$_n$ (3), {[Ag$_2$(L)$_2$(CH$_3$CN)]·(ClO$_4$)}$_n$ (4), {[Ag$_2$(L)$_2$(CH$_3$CN)][PF$_6$]$_2$·2CH$_3$CN}$_n$ (5), {[Ag(L)][CF$_2$SO$_3$]·1/2H$_2$O}$_n$ (6), {[Ag(L)][(BF$_4$)]$_n$ (7), {[Ag(L)]·(PF$_6$)}$_n$ (8) and {[Ag(L)][PF$_6$]·2CH$_3$CN}$_n$ (9). The primary structures of 1–6 were meso-helical one-dimensional (1D) polymers, while 7 was a helical 1D polymer and 8 and 9 were (4,4) networks. Complexes 1–5 possessed 1:1 metal-to-ligand (M:L) ratios, while complexes 6–9 possessed 1:2 M:L ratios. The meso-helical chains of complexes 1 and 2 were di-μ-bridged at the Ag(i) nodes by the counteranions CF$_2$SO$_3$$^-$ and ClO$_4$$^-$, respectively, while the meso-helical chains of complexes 3–5 were di-μ-bridged at the Ag(i) nodes by the CH$_3$CN molecules. The effect of counteranions and solvent molecules on delicate anion–Ag, π–π-stacking and argentophilic interactions was studied through complexes 1–5. The 1D chains of complexes 6 and 7 possessed monodentate L ligand side arms. The uncoordinated N-donors of these side arms were inclined towards the Ag(i) centre of the adjacent chains and demonstrated narrower Ag–N$_{py}$–C$_{pyridyl}$ angles. In the case of complexes 8 and 9, wider Ag–N$_{py}$–C$_{pyridyl}$ angles and stronger N···Ag interactions resulted in (4,4) nets. The effects of the size and nature of the counteranions on the topology were studied through complexes 6–9.

Introduction

1D architectures form an extensively explored area of coordination polymer chemistry. About 40% of the total reported coordination polymers in the last decade are 1D in nature. Yet there have been very few reviews dedicated to 1D coordination polymers between the years 1993 and 2010, because many researchers perhaps consider 1D coordination polymers to be structurally less attractive than their higher dimensional counterparts. However, through weaker interactions these simple and seemingly less attractive structures possess the ability to demonstrate unusual and interesting architectures. In this regard, Ag(i) is particularly useful, and a significant number of 1D coordination polymers contain Ag(i), as its low dimensional and accommodating stereochemistry often allows it to interact with additional donor atoms from solvent or a counteranion.

Rigid linear bridging ligands enable the formation of predictable arrays because of their configuration, coordination activity, and relative orientation of the donor groups. Rigid linear linking ligands such as 4,4’-bipyridine and pyrazine have already been extensively studied for designing linear 1D coordination polymers and higher dimensional networks. Introduction of a bend in these ligands presents a new variable to the study of the coordinating aspects of these linear linkers. The bend provides an opportunity to study lower dimensional structures such as helical, meso-helical, zigzag 9–9 chains and other structures of current interest. One simple bent ligand is 4,4’-dipyridyl ketone (L) (Fig. 1). In the solid state, L contains a chiral axis passing through the carbonyl group of the ligand. NDDO calculations reported for L determined that the two rotational energy maxima for rotation of both pyridine rings through or orthogonal to the molecular plane are approximately 45 and 20 kJ mol$^{-1}$, respectively. In solution, these two enantiomers readily interconvert from one form to another because of the low
energy of conversion, effectively making them appear achiral.\textsuperscript{12,13} However, in the solid state, the conjugating effect between C=O and Py-rings and the hydrogen repulsion in the planar form provide resonance stability to this ligand.\textsuperscript{11} The process of stabilisation “freezes” the racemates making L behave as a two-bladed chiral molecular propeller in the solid state.\textsuperscript{14} An analogous ligand, 4,4′-dipyridyl amine, acts in a similar fashion as a two-bladed molecular propeller.\textsuperscript{15} Surprisingly, there have been a few examples of the use of L in coordination polymer chemistry. LaDuca and co-workers have reported the use of L as a linking ligand with Cu(NO\textsubscript{3})\textsubscript{2}, forming three-fold double helices of [Cu(L)]\textsubscript{n}\textsuperscript{+}\textsuperscript{12} and with AgNO\textsubscript{3} forming zigzag 1D chains of [Ag(L)(NO\textsubscript{3})]\textsubscript{3}\textsuperscript{+}.\textsuperscript{13} The L ligand formed a pair of 1D meso-helical chains di(μ:\textsuperscript{2}O,O')-bridged at the Ag(i) nodes when a CF\textsubscript{3}CO\textsuperscript{-} counteranion was employed. These chains extended their framework by virtue of weak π−π interactions.\textsuperscript{17}

Linear and zigzag polymers are widely encountered in the literature. Helical polymers have gained added interest in the past decade because of their inherent chirality,\textsuperscript{18} while meso-helical polymers remain relatively uncommon. A meso-helix represents an alternative way, compared to a helix, of combining chiral components into an extended structure.\textsuperscript{19} Thus, a lemniscate (κ) or figure of eight can be converted into a meso-helix by transforming it into the third dimension (Fig. 2).\textsuperscript{20} This achiral 1D strand consists of alternate linkages of the M- and P-forms of the ligands to the metal centre (M). The chain is thus represented as −M−(M)−P−(M)−M−(M)−P− and can sometimes be misinterpreted as a zigzag chain.\textsuperscript{21,22}

Herein, we describe the use of the bent bridging ligand L to form two series of related coordination polymers of Ag(i) salts with varying M: L ratios (1 : 1 and 1 : 2). These coordination polymers were structurally characterised by single crystal X-ray diffraction, IR spectroscopy and elemental analysis. The first Ag(i) series comprised six 1 : 1 complexes (1−3, 3a, 4, and 5) generated by employing the counteranions CF\textsubscript{3}SO\textsubscript{3}−, ClO\textsubscript{4}−, BF\textsubscript{4}− and PF\textsubscript{6}−. Since all of the 1 : 1 Ag−L complexes were meso-helical 1D chains, the diversity in counteranions did not play a profound role in determining the primary structure. However, these coordination polymers provided an opportunity to study the delicate anion−Ag versus CH\textsubscript{3}CN−Ag bridging interactions and their consequences for π−π-stacking and argentophilic interactions in this series of related 1D meso-helical chains. The second Ag(i) series comprised four related 1 : 2 complexes (6−9) generated by employing the counteranions CF\textsubscript{3}SO\textsubscript{3}−, ClO\textsubscript{4}− and BF\textsubscript{4}−. In contrast to the first series, the primary structure of these coordination polymers was influenced by the nature of the counteranion, which modulated the extent of interaction between the N-pyridyl (N\textsubscript{py}) donor on the peripheral arms and the Ag(i) ion. The counteranion did not directly interact with the Ag(i) ion.

Results and discussion

Coordination polymers 1−9 were all prepared using the same 1 : 1 v/v CH\textsubscript{3}CN−CH\textsubscript{3}OH solvent system. Reactions were carried out in 1 : 1 and 1 : 2 M : L molar ratios. The products formed showed a considerable degree of sensitivity towards the nature of the counteranion and also the M : L ratio. For AgCF\textsubscript{3}SO\textsubscript{3} and AgBF\textsubscript{4}, two products were isolated and the final products had M : L ratios in agreement with the starting ratios as determined by microanalyses. For AgPF\textsubscript{6}, regardless of the M : L ratio used, a mixture of products was formed and only a 1 : 1 product was isolated. Even when a 2 : 1 M : L ratio was used, only a 1 : 1 product was formed which was found to be a pseudo-polymorph of the other two 1 : 1 AgClO\textsubscript{4} products.

Synthesis and structure of \{[Ag(L)][CF\textsubscript{3}SO\textsubscript{3}]\textsubscript{1/2}H\textsubscript{2}O\}_{\textsubscript{s}}

The 1 : 1 molar reaction between AgCF\textsubscript{3}SO\textsubscript{3} and L resulted in a tan solid. The microanalysis was consistent with the 1 : 1 formulation. Infrared studies of these samples confirmed the
presence of L as the peaks at 1682 (ketonic C=O group), 3124–3053 (aromatic C–H stretching), 1611 and 1555 (C=C bending) and 759–660 cm<sup>−1</sup> (aromatic C–H bending) were observed. The peak corresponding to the C=O moiety of this complex was lower (1682 cm<sup>−1</sup>) than that observed in the free ligand (1731 cm<sup>−1</sup>). The peaks corresponding to the stretching of the S=O, C–F, S–O and C–S bonds of the CF<sub>3</sub>SO<sub>3</sub> counteranion were observed at 1330–1271, 1236–1018, 940–844 and 759–572 cm<sup>−1</sup>, respectively. In infrared studies of AgCF<sub>3</sub>SO<sub>3</sub>, Johnston and Shriver have demonstrated that the peak at 1271 cm<sup>−1</sup> arises from asymmetric SO<sub>3</sub> stretching, at 1236 cm<sup>−1</sup> from symmetric CF<sub>3</sub> stretching and at 760 cm<sup>−1</sup> due to the CF<sub>3</sub> angle deformation and the symmetric C–S stretching.<sup>23</sup>

Complex 1 crystallised in the monoclinic space group C2/c with one Ag(i) cation, one complete L ligand, one CF<sub>3</sub>SO<sub>3</sub> counteranion and half a H<sub>2</sub>O of crystallisation in the asymmetric unit. Complex 1 formed a 1D <i>meso</i>-helical strand running along the [1 0 1] diagonal axis (Fig. 3). The Ag(i) ion was essentially linear with an N–Ag–N angle of 175.72(6)°. The slight bend was a consequence of weak interactions between the Ag(i) cation and the O-atoms of adjacent CF<sub>3</sub>SO<sub>3</sub> anions (Fig. 3).<sup>24</sup> The pyridyl rings of L formed a two-bladed chiral propeller at an angle between the rings of 50.37(9)° and generated 1D strands. From the viewpoint of chirality, these 1D strands consisted of alternate linkages of the <i>M</i>- and <i>P</i>-forms of the ligands with the Ag(i) ions. The chain was thus represented as −<i>M</i>–Ag–<i>P</i>–Ag–<i>M</i>–Ag–<i>P</i>–, resulting in a <i>meso</i>-helical structure.<sup>19</sup>

Adjacent <i>meso</i>-helical chains were formed into antiparallel pairs through a weak π–π interaction [centroid-to-centroid distance 3.803(2) Å; inter-planar dihedral angle 9.80(0)°, minimum interatomic distance 3.615(2) Å; minimum ring slippage between planes 1.664 Å]. The pairs of chains were di[μ:<i>x</i>2O2<sub>3</sub>O′]-bridged by weak Ag⋯SO<sub>3</sub>CF<sub>3</sub> interactions which appeared to pull the Ag(i) ions closer together. The Ag⋯Ag distance was found to be 3.4704(16) Å. The bridging CF<sub>3</sub>SO<sub>3</sub> anions on each side of the pairs of chains were linked together by hydrogen-bonding interactions with H<sub>2</sub>O of solvate [H⋯O distance of 1.94(4) Å corresponding to an O⋯O distance of 2.71(2) Å]. The pairs of chains interact with an adjacent pair of chains through π–π interactions [centroid-to-centroid distance 3.766(2) Å, inter-planar dihedral angle 0°, minimum interatomic distance 3.746(2) Å; ring slippage between planes 1.680 Å] such that the rings involved in the interaction are registered every fifth pyridyl ring along the chains.

**Synthesis and structure of {[Ag(L)][ClO<sub>4</sub>]·1/2H<sub>2</sub>O}·x<sub>2</sub>**

Evaporation of the solvents from a 2:1 molar reaction between AgClO<sub>4</sub> and L resulted in X-ray quality colourless crystals of 2. However, the microanalysis was consistent with a 1:1 formulation. Infrared studies of these samples confirmed the presence of L as the peaks at 1680 (ketonic C=O group), 3095 (aromatic C–H stretching), 1612–1555 (C=C bending) and 759–657 cm<sup>−1</sup> (aromatic C–H bending) were observed. The presence of peaks at 1285, 1055, 952 and 691–619 cm<sup>−1</sup> indicated the presence of ClO<sub>4</sub><sup>−</sup>

Complex 2 crystallised in the monoclinic space group C2/c with one Ag(i) cation, one complete L ligand, one ClO<sub>4</sub> counteranion and half a H<sub>2</sub>O of crystallisation in the asymmetric unit. It formed infinite 1D <i>meso</i>-helical strands running along the [1 0 1] diagonal axis (Fig. 4). The Ag(i) ion was essentially linear with an N–Ag–N angle of 170.12(6)°. The slight bend indicated a relatively weak interaction between an adjacent ClO<sub>4</sub>− anion at 2.727(2) Å and the Ag(i) cation. The Ag⋯OCIO<sub>3</sub> interactions fell in the middle of the range of Ag⋯O contact lengths [2.291–3.238 Å] for similar two-coordinated Ag⋯OCIO<sub>3</sub> complexes as indexed in the CSD database (version 5.33).<sup>25,26</sup> The pyridyl rings of L formed a two-bladed chiral propeller and registered an angle of 53.37(8)° between the planes of the rings. This complex possessed achiral <i>meso</i>-helical 1D chains similar to 1.

The adjacent <i>meso</i>-helical chains were formed into antiparallel pairs through two complementary interactions. One of which was weak π–π interactions involving all of the pyridine rings of the adjacent chain [centroid-to-centroid distance 3.763(2) Å, inter-planar dihedral angle 3.62(8)°, minimum interatomic distance 3.593(2) Å; minimum ring slippage between planes 1.589 Å]. The other involved the Ag ions of the chains being di[μ:<i>x</i>2O2<sub>3</sub>O′]-bridged together by ClO<sub>4</sub>−
vents from a 1 : 1 molar reaction between AgBF4 and formed into two-dimensional (2D) sheets in the ac plane. The distances were 2.727(2) Å and 2.905(2) Å. The bridging ClO4− anions on each side of the pairs of chains were linked together by H-bonding interactions with H2O of solvate anions on each side of the Ag3 complexes of \( \text{[Ag2(L)2(CH3CN)} \cdot \text{ClO4} \cdot 2\text{CH3CN·H2O]} \)∞, 3. Slow evaporation of the solvents from a 1 : 2 molar reaction between AgClO4 and L resulted in X-ray quality colourless crystals of 3. Again, the microanalysis was consistent with a 1 : 1 formulation. Infrared analysis revealed that the peak corresponding to the C–O moiety of this complex was lower (1665 cm−1) than that observed in 2 (1680 cm−1). The peaks corresponding to the stretching and bending of aromatic rings of L and those for ClO4− were similar to 2. Slow evaporation of the solvents from a 1 : 1 molar reaction between AgBF4 and L resulted in colourless crystals of \( \text{[Ag}(L)2\text{CH3CN)]2\text{BF4}·\text{CH3CN·H2O]} \)∞, 3a which were found to be isomorphous with 3 (experimental section).

Complex 3 formed infinite 1D meso-helical strands along the c axis which through bridging interactions were formed into two-dimensional (2D) sheets in the ac plane. It crystallised in the monoclinic space group \( P2_1/c \) with two crystallographically distinct Ag(i) cations, two complete L ligands, two ClO4− counteranions, three CH3CN molecules and a H2O of crystallisation in the asymmetric unit. The crystallographically distinct Ag(i) cations were present in different 1D meso-helical polymeric strands running parallel to each other along the c axis (Fig. 5). One Ag(i) cation possessed a linear geometry by coordinating with two N-donors of the L ligand, while the other Ag(i) cation possessed a T-shaped geometry by exhibiting additional coordination to a CH3CN molecule. The linear Ag(i) cation displayed a slight bend and the Npy−Ag2–Npy angle measured 174.57(14) Å. This bend may have been the consequence of the weak Ag2⋯OCIO3 interactions [O23⋯Ag2 contact was 2.742(4) Å]24 and the weak N⋯Ag interactions with the free CH3CN molecules [the N7⋯Ag2 contact was 2.853(5) Å and the N6⋯Ag2 contact was 3.023(4) Å]. The CH3CN⋯Ag contacts for the two-coordinated Ag(i) cations were in the range of 2.555–3.265 Å.25,26 A CH3CN molecule coordinated to Ag1 at nearly perpendicular angles [the N(1)–Ag(1)–N(5) and N(5)–Ag(1)–N(2A) angles were 95.87(14)° and 94.84(14)°, respectively] and generated T-shaped Ag(i) nodes. The NCH3CN–Ag distance was 2.505(4) Å. The Npy−Ag1–Npy angle of the T-shaped Ag(i) cation was 163.77(14)°. The T-shaped Ag1 displayed a distorted geometry and deviated from the

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**Fig. 4** Left: view of the 1D cationic meso-helical polymeric strand of 2 running along the [1 0 1] direction (crystallographic numbering; ellipsoids 50% probability level). Right: view showing weak bridging in 2 by ClO4− anions on each side of the meso-helical pair (Fig. 4). The Ag⋯Ag distance was 3.369(17) Å and the Ag⋯ClO4− distances were 2.727(2) Å and 2.905(2) Å. The bridging ClO4− anions on each side of the pairs of chains were linked together by H-bonding interactions with H2O of solvate [H⋯O distance of 2.37(4) Å corresponding to an O⋯O distance of 3.039(3) Å]. There were no other noteworthy H-bonding interactions observed in the structure.

**Fig. 5** Left: view of the two distinct 1D cationic meso-helical polymeric strands of 3 running along the c axis (crystallographic numbering; ellipsoids 50% probability level). Right: view showing bridging of two distinct meso-helical strands of 3 with CH3CN molecules and weak bridging of the pair of strands with ClO4− and CH3CN molecule. A non-interacting ClO4− counteranion and the H2O molecules were omitted for clarity.
plane (N5 N1 N2) by 0.2144 Å. The Ag–Npy bond lengths were found to be 2.171(4) Å and 2.177(4) Å, while the Ag–Npy bond lengths of T-shaped Ag(i) were slightly elongated [the Ag1⋯N1 bond length was 2.203(4) Å and the Ag1⋯N2 bond length was 2.198(4) Å]. The bound CH3CN displayed a bend in the C–N–Ag angle [147.0(4)°] by virtue of the weak interaction of CH3CN with Ag2 of a neighbouring chain [the N⋯Ag2 contact was 3.121(4) Å]. The pyridyl rings of L formed a two-bladed chiral propeller and bridged the Ag(i) cores and formed infinite 1D meso-helical strands running along the c axis. The pyridyl rings of L coordinated to linear Ag(i) registered an angle of 40.3(2)° between the planes of the rings, while the pyridine rings of the other L registered an angle of 46.0(2)° between the planes of the rings.

The linear and T-shaped Ag(i) ions were present in separate strands and formed a pair of dissimilar strands. This pair of strands was d(μ3-C≡N)-bridged by the CH3CN molecules (Fig. 5) and displayed weak π–π-stacking interactions [the centroid-to-centroid distances were 3.717(3) Å (inter-planar dihedral angle 5.5(2)°, minimum interatomic distance 3.601(3) Å; minimum ring slippage between planes 1.293 Å) and 3.749(2) Å (inter-planar dihedral angle 1.8(2)°, minimum interatomic distance 3.701(2) Å; minimum ring slippage between planes 1.600 Å)]. These distances were registered every alternate pyridine ring throughout the pair of strands. One ClO4− counteranion bridged this pair of strands by virtue of C–H⋯anion interactions [the O11⋯H13 contact was 2.59 Å and the corresponding O11⋯H⋯C13 contact was 3.222(6) Å; the O14⋯H1 contact was 2.46 Å and the corresponding O14⋯H⋯C1 contact was 3.143(6) Å]. The Ag⋯Ag distance was 3.4858(6) Å. A pair of strands was linked with an adjacent pair of strands by the weak bifurcated bridging (μ2:O) of the ClO4− counteranion on one side [the O3Cl⋯O23⋯Ag1 and the O2Cl⋯O23⋯Ag2 contacts were 3.205(5) Å and 2.742(4) Å, respectively] and the weak bifurcated bridging (μ2:Cl) of a CH3CN molecule on the other side [the N7⋯Ag2 and N7⋯Ag1 contacts were 2.854(5) and 3.329(5) Å, respectively] (Fig. 5). This asymmetric bridging was augmented by virtue of weak π–π-stacking interactions [centroid-to-centroid distance was 3.790(2) Å, inter-planar dihedral angle 1.8(2)°, minimum interatomic distance 3.746(2) Å; minimum ring slippage between planes 1.681 Å] and these interactions were registered every second pyridyl ring. The H2O of crystallisation interacted with three ClO4− counteranions by virtue of H-bonding interactions. One interaction was relatively strong [H⋯O distance of 2.17(4) Å corresponding to an O⋯O distance of 2.966(6) Å], while the other two were weaker and interacted in a bifurcated fashion [H⋯O distances of 2.67(7) and 2.81(5) Å corresponding to O⋯O distances of 3.168(7) and 3.468(6) Å, respectively].

Synthesis and structure of ([Ag(L)3(CH3CN)3][ClO4]2(CH3CN·H2O)n), 4

Slow evaporation of a solvent from a solution of AgClO4 and L in a 1:1 M:L ratio resulted in X-ray quality colourless crystals of 4. The infrared spectrum revealed that the peaks corresponding to the ketonic C==O group, stretching and bending of aromatic rings of L and ClO4− were similar to those of 2.

Complex 4 formed infinite 1D meso-helical strands along the c axis which through bridging interactions were formed into 2D sheets in the ac plane. It crystallised in the monoclinic space group P21/c with two crystallographically distinct Ag(i) cations, two complete L ligands, two ClO4− counteranions and three CH3CN molecules in the asymmetric unit. The crystallographically distinct Ag(i) cations were present in different 1D meso-helical polymeric strands running parallel to each other along the c axis (Fig. 6). One Ag(i) cation possessed a linear geometry by coordinating with two N-donors of the L ligand, while the other Ag(i) cation possessed a four-coordinated geometry by exhibiting additional coordination to two CH3CN molecules. The linear Ag(i) cation displayed a slight bend and the Npy⋯Ag1–Npy angle measured 165.85(18) Å. This bend may have been a consequence of the weak N⋯Ag interactions with the three CH3CN molecules [the N⋯Ag contacts ranged between 2.887(7) and 3.043(6) Å].25,26 The four-coordinated Ag(i) cation adopted a geometry between a seesaw and a trigonal pyramid as evidenced by a τv value of 0.70.23 The N5⋯Ag2 and N7⋯Ag2 distances were 2.414(6) Å and 2.657(6) Å, respectively. The

Fig. 6 Left: view of the two distinct 1D cationic meso-helical polymeric strands of 4 running along the c axis (crystallographic numbering; ellipsoids 50% probability level). Right: view showing bridging of two distinct meso-helical strands of 4 with CH3CN molecules and weak bridging of the pair of strands with ClO4− and CH3CN molecule. Only the major component of the disordered ClO4− counteranion is shown and the other ClO4− counteranion was omitted for clarity.
Synthesis and structure of \(\text{Ag}^{2+}\)–\(\text{Ag}^{2+}\)–\(\text{Npy}\) angle of the four-coordinated \(\text{Ag}^+\) cation was 155.14(17)°. The \(\text{Ag}1\)--\(\text{N}^\text{py}\) bond lengths were found to be equal [2.186(5) Å], while the \(\text{Ag}2\)--\(\text{N}^\text{py}\) bond lengths were slightly elongated [the \(\text{Ag}2\)···\(\text{N}3\) bond length was 2.233(5) Å and the \(\text{Ag}2\)···\(\text{N}4\) bond length was 2.225(5) Å]. The bound \(\text{CH}_3\text{CN}\) displayed a bend in the C–N–Ag angle [the C23–N5–Ag2 angle was 141.5(6)° and the C27–N7–Ag2 angle was 166.1(3)°] by virtue of the weak interaction of \(\text{CH}_3\text{CN}\) with \(\text{Ag}1\) of a neighbouring chain [the N5···\(\text{Ag}1\) and N7···\(\text{Ag}1\) contacts were 2.887(7) and 3.043(6) Å, respectively]. The pyridyl rings of \(L\) formed a two-bladed chiral propeller and bridged the \(\text{Ag}^+\) cores and formed infinite 1D meso-helical strands running along the c axis. The pyridyl rings of \(L\) coordinated to the linear \(\text{Ag}^+\) registered an angle of 45.6(3)° between the planes of the rings, while the pyridine rings of the other \(L\) registered an angle of 50.7(3)° between the planes of the rings.

The linear and four-coordinated \(\text{Ag}^+\) cations were present in separate strands and formed a pair of dissimilar strands. This pair of strands was \(\text{di(μ:κ^2N)}\)-bridged by \(\text{CH}_3\text{CN}\) molecules (Fig. 6) and displayed weak π–π-stacking interactions [the centroid-to-centroid distances were 3.884(4) Å (inter-planar dihedral angle 5.8(3)°), minimum interatomic distance 3.770(4) Å; minimum ring slippage between planes 1.254 Å] and 3.945(4) Å (inter-planar dihedral angle 1.5(3)°), minimum interatomic distance 3.935(4) Å; minimum ring slippage between planes 1.939 Å]. These distances were registered every alternate pyridyl ring throughout the pair of strands. The \(\text{Ag}^+\)····\(\text{Ag}^+\) distance was 3.694(3) Å. A pair of strands was linked to an adjacent pair of strands by the weak \(\text{μ:κ^2O}_\text{O}^\text{′′}\)-bridging of the \(\text{ClO}_4^-\) counteranion on one side [the O1\(\text{Cl}1\)···\(\text{Ag}2\) and the O2\(\text{Cl}2\)···\(\text{Ag}1\) contacts were 3.201(16) Å and 2.953(13) Å, respectively] and the weak \(\text{μ:κ^3N}\)-bridging of a \(\text{CH}_3\text{CN}\) molecule on the other side [the N6···\(\text{Ag}1\) and N6···\(\text{Ag}2\) contacts were 2.886(6) and 3.217(6) Å, respectively] (Fig. 6). This asymmetric bridging was augmented by virtue of weak π–π-stacking interactions [centroid-to-centroid distance was 3.884(4) Å (inter-planar dihedral angle 5.8(3)°), minimum interatomic distance 3.770(3) Å; minimum ring slippage between planes 1.254 Å] and 3.944(4) Å (inter-planar dihedral angle 1.5(3)°), minimum interatomic distance 3.935(4) Å; minimum ring slippage between planes 1.939 Å] and these interactions were registered every alternate pyridyl ring. The \(\text{Ag}^+\)····\(\text{Ag}^+\) distance between the adjacent pair of strands was 4.139(3) Å.

Complex 5 formed infinite 1D meso-helical strands along the \(b\) axis which through bridging interactions were formed into 2D sheets in the \(ab\) plane. It crystallised in the monoclinic space group \(P2_1/c\) and the asymmetric unit consisted of two crystallographically distinct \(\text{Ag}^+\) cations, two complete \(L\) ligands, two \(\text{PF}_6^-\) counteranions and four \(\text{CH}_3\text{CN}\) molecules. The two crystallographically distinct \(\text{Ag}^+\) cations and ligands were alternately present in the same 1D meso-helical strand despite it running along the crystallographic \(b\) axis (Fig. 7). The \(\text{Ag}^+\) cations displayed a pseudo T-shaped three-coordinated geometry by coordinating with two \(\text{N}^\text{py}\)-donors of two distinct \(L\) ligands and a \(\text{CH}_3\text{CN}\) molecule. \(\text{Ag}1\) deviated from the plane of the donor atoms (N3 N1 N5) by 0.120 Å, while \(\text{Ag}2\) deviated from the plane (N2 N4 N7) by 0.160 Å. The \(\text{Ag}^+\) nodes were bridged by two \(L\) ligands and 1D meso-helical strands were generated. The pyridyl rings of \(L\) formed a two-bladed chiral propeller. The pyridyl rings of the two \(L\) ligands registered the angles of 48.43(15)° and 48.05(15)° between the planes of the rings.

Two \(\text{CH}_3\text{CN}\) molecules coordinated to \(\text{Ag}1\) and \(\text{Ag}2\) at distances of 2.632(3) and 2.664(3) Å, respectively. The bound \(\text{CH}_3\text{CN}\) molecules displayed a bend in C–N–Ag angles [the C23–N5–Ag1 angle was 141.7(2) and the C27–N7–Ag2 angle was 143.6(2)°] by virtue of weak interactions with \(\text{Ag}^+\) cations of neighbouring chains. These interactions resulted in the \(\text{di(μ:κ^2N)}\)-bridging of the two antiparallel chains at...
alternate Ag(i) nodes by the bound CH3CN molecules generating a 2D sheet in the ab plane (Fig. 7). The N5⋯Ag1 contact was 2.772(3) Å, while the N7⋯Ag2 contact was 2.751(3) Å. The bridging was augmented by very weak π-π-stacking interactions [the centroid-to-centroid contact was 3.9103(18) Å (inter-planar dihedral angle 8.01(15)°, minimum interatomic distance 3.7430(18) Å; minimum ring slippage between planes 1.175 Å)]. The Ag⋯Ag distances at the bridged nodes [Ag1⋯Ag1 3.5632(4) Å and Ag2⋯Ag2 3.4709(4) Å] were considerably shorter than that at the non-bridged nodes [Ag1⋯Ag1 4.4372(5) Å and Ag2⋯Ag2 4.5448(5) Å]. The uncoordinated CH3CN molecules interacted with the pyridine rings of the anti-parallel chains through weak N⋯H–C interactions that ranged between 2.30 and 2.83 Å. There were no noteworthy H-bonding interactions observed in the structure.

**Synthesis and structure of [[Ag(L)2](CF3SO3) 1/2H2O]$_{n}$, 6**

A 1:2 molar reaction between AgCF3SO3 and L resulted in colourless crystals of 6. The microanalysis was consistent with a 1:2 formulation. Infrared studies of these samples confirmed the presence of L as the peaks at 1675 (ketonic C=O group), 3200–3000 (aromatic C–H stretching), 1640–1554 (C=C bending) and 756–660 cm$^{-1}$ (aromatic C–H bending) were observed. The peaks corresponding to the stretching of the S=O, C–F, S–O and C–S bonds of the SO3CF3$^{–}$ counteranion were observed at 1328–1284, 1222–1145, 949–830 and 660–634 cm$^{-1}$, respectively.

Complex 6 crystallised in the monoclinic space group C2/c to form a 1D meso-helical chain decorated with L arms (Fig. 8). The chains ran along the c axis. The asymmetric unit contained one Ag(i) cation, two L ligands, one CF3SO3$^{–}$ counteranion and half a H2O of crystallisation. The Ag(i) ions formed a distorted trigonal planar arrangement with three nitrogens of the pyridyl rings at angles of 112.8(2)$^\circ$, 116.1(2)$^\circ$ and 127.5(2)$^\circ$ for N3–Ag1–N4, N1–Ag1–N3 and N1–Ag1–N4, respectively, while N2 remained uncoordinated forming the decorating arm of the meso-helix. The Ag(i) ion deviated by 0.251 Å from the plane of three bound N-donors. The weak interaction between O$_{H2O}$⋯Ag1 [2.825(6) Å] distorted the planarity of the AgN$_3$ moiety. In addition, the H$_2$O molecule was H-bonded to the ketone O atom bridging two adjacent chains. The counteranions did not interact significantly with the polymeric stands.

The pyridyl rings of L formed a two-bladed chiral propeller. The L ligands which formed the polymeric backbone registered an angle of 48.8(4)$^\circ$, while the decorated L arms registered an angle of 58.6(4)$^\circ$ between the planes of the pyridine rings. The uncoordinated N2 of the dipyril ketonic arms showed a slight inclination towards Ag1 of an adjacent chain with N2⋯Ag1 contact of 3.153(8) Å$^{29,30}$ and registered an angle of 111.95$^\circ$ between the Ag(i)⋯N2$_{py}$⋯C6$_{py}$. This long contact distance and very narrow angle indicated that there is essentially no interaction between pyridyl N2 and Ag1 (Fig. 9). The arrangement of the decorated arms created a cavity encompassing two CF3SO3$^{–}$ counteranions.

**Synthesis and structure of [[Ag(L)2](BF4)]$_{n}$, 7**

Slow evaporation of solvents from a solution of AgBF4 and L in a 1:2 M:L ratio resulted in X-ray quality colourless crystals of 7. The microanalysis of the bulk reaction with similar molar and solvent ratios was consistent with a 1:2 formulation. Infrared studies of these samples confirmed the presence of L as the peaks at 1677 (ketonic C=O group), 3106–3054 (aromatic C–H stretching), 1608–1535 (C=C bending) and 756–660 cm$^{-1}$ (aromatic C–H bending) were observed. The peaks at 1032, 756 and 520 cm$^{-1}$ confirmed the presence of the BF4$^{–}$ counteranion.

Complex 7 crystallised in the monoclinic space group P21/c to form infinite polymeric chains along the b axis. Each asymmetric unit contained one Ag(i) cation, two L ligands and one BF4$^{–}$ counteranion (Fig. 10). One L ligand bridged the three coordinated Ag(i) nodes and extended the polymer to a 1D chain, while the second L ligand interacted with Ag(i) through monodentate interactions and formed dominant side arms.
The Ag(I) ion deviated by 0.133 Å from the plane of three bound 

–

L

registered an angle of 65.49(10) 

registered an angle of 57.50(10) 

L

ler. The 

11 of these complexes, the Ag(I) 

three Npy at the angle of 109.33(6) 

The Ag1 bond distances to the other Npy-donors of 2.2121 

arms resided in the vicinity of Ag1 of the adjacent chain. 

symmetric structure. The uncoordinated N2 of these side 

formed a two-bladed chiral propel-

L

formed a two-bladed chiral molecu-

L

ligand formed a two-bladed chiral molecu-

L

ligand formed a two-bladed chiral molecu-

L

ligand formed a two-bladed chiral molecu-

L

ligands bridged the four coordi-

A

A

A

Ag(i) cation adopted a slightly distorted trigonal-planar geometry with three Npy at the angle of 109.33(6), 149.54(6) and 99.89(6) for N3–Ag1–N4, N1–Ag1–N3 and N1–Ag1–N4, respectively. The Ag(i) ion deviated by 0.133 Å from the plane of three bound 

N-donors. 

The pyridyl rings of L formed a two-bladed chiral propeller. The L ligands which formed the polymeric backbone reg-

istered an angle of 57.50(10), while the decorated L arms registered an angle of 65.49(10) between the planes of the rings. The two crystallographically distinct L ligands were pseudo enantiomers of each other. The uncoordinated N2 of the L side arm showed a significant inclination towards Ag1 with a N2⋯Ag1 contact of 2.6582(18) Å29,30 and registered an angle of 138.80° between the Ag(i)–Npy–Cgpy.31 A search of the CSD database identified 12 complexes with Ag(i)⋯N(pyridine) contacts in the range of 2.60–2.70 Å. For 11 of these complexes, the Ag(i)–Npy–Cgpy angle ranged from 132 to 141°, while one had a value of 125°. The consistency of the angles within this range suggested the presence of a weak interaction between pyridyl N and Ag(i). By virtue of this close contact and the positioning of the decorated arms on the adjacent chains, cavities existed in what appeared to be a pseudo (4,4) rhombic network (Fig. 10). The four Ag1 ions occupied the corners of the rhombus, and the adjacent sides of the network measured 11.102 Å and 11.471 Å. The four ligands of the rhombus were arranged such that two C–O groups of the opposite ligands, which were pseudo enantio-

mers of each other, pointed above the plane of the rhombus and towards each other, while the remaining two C–O groups of the ligands, which were also pseudo enantiomers, pointed below the plane and splayed away from each other (Fig. 10). This arrangement caused the pseudo (4,4) network to be flat and achiral. The weak CH–π-interactions between C–H25⋯Cg2 (N2 containing pyridine) [the distance between H–centroid was 2.72 Å]32 and the weak π–π-interactions [the Cg2⋯Cg2 contact was 3.7572(16) Å, inter-planar dihedral angle 0°, minimum interatomic distance 3.736(16) Å; ring slippage between planes 1.525 Å]33 may have helped to facil-

tate the positioning of N2 near the Ag ion. 

The BF4− counteranion resided within each cavity of the pseudo network by virtue of two weak attractive forces. A weak anion–π-interaction existed between BF4− and the pyridine ring containing N3 [F3B⋯Cg 3.314(9) Å]34 and also weak CH–anion interactions existed between BF4− and pyridyl H atoms [the F⋯H contact distances ranged from 2.35 to 2.61 Å, and the corresponding F⋯C distances ranged from 3.027(2) to 3.203(3) Å]. The cation–anion interactions stacked the adjacent layers of grids in an offset –A–B–A–B– fashion.

Synthesis and structure of [[Ag(L)2][PF6]]∞, 8, and 

[((AgL)2][PF6]2CH3CN)]∞, 9

Slow evaporation of solvents from a solution of AgPF6 and L in a 1 : 2 M : L ratio resulted in X-ray quality colourless crystals of both 8 and 9. The microanalyses of these samples were consis-
tent with a 1 : 2 formulation. Infrared studies of these samples confirmed the presence of L as the peaks at 1686 and 1674 (ketonic C=O group), 1604 and 1556 (C=C bending) and 690–647 cm−1 (aromatic C–H bending) were observed. The environ-
ment around the ketonic C=O may have caused the C=O peak to split in two separate peaks. The very strong sharp peak at 818 cm−1 and strong sharp peak at 556 cm−1 indicated the presence of PF6− counteranions.28 

Complex 8 crystallised in the monoclinic space group P21/n to form an infinite 2D network in the ac plane. Each asymmetric unit of this complex contained one Ag(i) cation, two L ligands and one PF6− counterion. The Ag(i) cation adopted a four-coordinated geometry between a seesaw and a trigonal pyramid as evidenced by a τ4 value of 0.78.27 The Ag1–Npy bonds were in the normal range from 2.244(3) to 2.383(3) Å. The four Npy donors coordinated to the Ag(i) ion at angles between 94.52(11) and 138.04(12)°. These pyridyl rings demonstrated more regular Ag(i)–Npy–Cgpy angles of between 150.51 and 175.69°. The L ligand formed a two-bladed chiral molecular propeller, and the pyridyl rings of L registered angles of 54.44(16)° and 42.16(17)° between the planes of the rings. The two crystallographically distinct L ligands had the same pseudo enantiomeric form. Both the L ligands bridged the four coordi-

nated Ag nodes, and a corrugated (4,4) rhombic network was
generated (Fig. 11). The adjacent sides of the network measured 11.070(3) Å and 11.651(3) Å. The four ligands of the rhombus were arranged in an irregular way such that the C═O groups of three of the ligands pointed above and one pointed below the plane of the rhombus (Fig. 11). The three ligands with the C═O groups which pointed above were of the same pseudo enantiomeric form, while the one with the C═O group pointing below was of the other pseudo enantiomeric form. This arrangement caused the (4,4) network to be achiral and extremely corrugated and the planes of the adjacent facing rhomboids oriented themselves at angles of 66.3°. The adjacent sheets of the (4,4) network were interdigitated and stacked on top of each other in a -A–B–A- fashion along the b axis. These sheets interacted with each other by weak O=C═O⋯π interactions [O⋯Cg5 contact was 3.282(3) Å] and weak π⋯π interactions [Cg4⋯Cg2 contact was 3.899(3) Å, inter-planar dihedral angle 12.50(17)°, minimum interatomic distance 3.739(3) Å; minimum ring slippage between planes 0.9035 Å].

The two PF$_6^-$ counteranions resided within the cavity being slightly above and below the plane of the rhombus by virtue of several weak anion–CH interactions [H⋯F contact distances between 2.44 and 2.97 Å] and strong anion–carbonyl interactions. The F11⋯C6 contact was 2.874(4) Å and the F14⋯C17 contact was 2.959(4) Å. A search of the CSD database suggested that for complexes containing pyridyl ketone like ligands, there were only two out of 204 observations which displayed a F⋯C=C=O contact below the van der Waals limit of 3.2 Å. In total in the CSD there are 422 observations of general O=C⋯F–PF$_6^-$ interactions which range from 2.53 to 3.17 Å with a mean contact of 3.02 Å. Complex 9 crystallised in the triclinic space group P1 to form an infinite 2D network in the ab plane. Each asymmetric unit comprised one Ag(i) cation, two L ligands, one PF$_6^-$ counteranion and two CH$_3$CN of crystallisation. The Ag(i) cation adopted a distorted tetrahedral geometry as evidenced by a τ$_4$ value of 0.91. The four pyridine N-atoms coordinated to the Ag(i) ion at angles between 93.43(12) and 119.90(12)° and interacted with the Ag(i) ions in the regular range of 2.268(4)–2.352(4) Å. These pyridyl rings demonstrated Ag(i)⋯N$_{py}$–C$_{6py}$ angles between 168.46 and 175.58°. The L ligand formed a two-bladed chiral molecular propeller, and the pyridyl rings of L registered angles of 53.78(14)° and 77.20(9)° between the planes of the rings. The two crystallographically distinct L ligands were of the same pseudo enantiomeric form. Both the L ligands bridged the Ag nodes perpendicular to each other and a regular (4,4) rhombic network was generated (Fig. 12). The adjacent sides of the network measured 10.950(7) Å and 11.108(7) Å. These distances corresponded to the length of crystallographic a and b axes. The four ligands of the rhombus, all of the same pseudo enantiomeric form, were arranged such that the C═O groups of the two ligands pointed above and two pointed below the plane of the rhombus (Fig. 12). This arrangement gave a more regular network which was also chiral. The adjacent sheets of the (4,4) network, which were enantiomers of each other, were interdigitated and stacked on top of each other in a -A–B–A- fashion along the c axis.

The PF$_6^-$ counteranions were embedded in the cavities of the (4,4) network by virtue of weak anion–π and CH–anion interactions. The distance between F15-to-centroid contact was 3.028(4) Å, while the distance between H1⋯F15 was 2.47 Å and the corresponding C9⋯F16 distance was 3.369(5) Å. No other noteworthy π⋯π-stacking and H-bonding interactions were observed.

Comparison of structures
In structures 1–9, the coordination environment of the Ag(i) ions ranged from linear to trigonal pyramidal. The L ligand bridged the Ag(i) cores and generated the primary structure of 1D meso-helical chains in complexes 1–6, a helical 1D chain in complex 7 and 2D networks in complexes 8 and 9.
The influence of the coordinating ability of the anions on the stoichiometry of the resultant Ag(I) complexes was demonstrated by our closely related series of coordination polymers.40–42 The weakly coordinating CF₃SO₃⁻ counteranion did not have an influence on the variation in stoichiometry as the stoichiometries of both complexes 1 and 6 were consistent with the starting M:L ratios of 1:1 or 1:2, respectively. The ClO₄⁻ counteranions demonstrated stronger coordination to Ag(I) in the presence of L as compared to the CF₃SO₃⁻ counteranion. This prevented the formation of coordination polymers with different M:L ratios, as regardless of the starting M:L ratios, 2:1, 1:2 or 1:1, only the 1:1 complexes 2, 3 and 4, respectively, could be isolated. An excess of ClO₄⁻ present in the preparation of 2 resulted in di(μ²-O,O′)-bridging of the 1:1 polymer chain with ClO₄⁻, while a deficiency as in the case of 3 and 4 instead resulted in di(μ²-N)-bridging of the 1:1 chains with CH₃CN molecules. The starting M:L ratio of 1:2 in the reaction of AgPF₆ with L resulted in 5 with 1:1 and 8 and 9 with 1:2 M:L ratios. Owing to the non-coordinating nature of the PF₆⁻ counteranion, the 1:1 1D chains of 5 were di(μ²-N)-bridged by CH₃CN molecules.

In the 1:1 M:L complexes, the AgN₂ moieties with the linear geometry displayed a slight bend in the Nₚp-Ag-Nₚp angles by virtue of weak Ag–anion interactions.24 In the isostructural complexes 1 and 2, the counteranions bridged the Ag(i) nodes of the adjacent meso-helical strands from both sides through di(μ²-O,O′)-bridging of the Ag(i) cores of the adjacent strand. The bulky CF₃SO₃⁻ counteranion of 1 displayed less influence on the bend in the linearity of Ag(i) cation [175.72(7)° vs. 170.12(6)°] and registered higher Ag–O distances when compared with the less bulky ClO₄⁻ anion (Table 2). The tighter bridging of the Ag(i) nodes by the ClO₄⁻ counteranions resulted in a shorter Ag⋯Ag contact distance and stronger π–π-interactions (Table 2). The ClO₄⁻ counteranions of the pseudo-polymorphous complexes 2, 3 and 4 revealed various bridging modes. The adjacent strands of 2 were di(μ²-O,O′)-bridged by ClO₄⁻ counteranions, while the chains of 3 and 4 were weakly di(μ²-N)-bridged by CH₃CN molecules. However in 3 and 4, the ClO₄⁻ counteranions assisted the μ²-N bridging of the CH₃CN molecules by bridging the adjacent pair of strands through μ²-O and μ²-O,O′ interactions, respectively. The bridging of ClO₄⁻ counteranions

Table 1 Table showing angles between planes of pyridyl rings of ligand L in Ag–L complexes

| Structure | Angle (°) |
|----------|-----------|
| 1        | 50.37(9)  |
| 2        | 53.37(8)  |
| 3        | 40.3(2) and 46.0(2) |
| 4        | 45.6(3) and 50.7(3) |
| 5        | 48.05(15) and 48.43(15) |
| 6        | 48.8(4) and 58.6(4) |
| 7        | 57.50(10) and 65.49(10) |
| 8        | 54.44(16) and 42.16(17) |
| 9        | 53.78(14) and 77.2(9) |
along with the bifurcated bridging of a CH$_3$CN molecule from the other side extended the structures of 3 and 4 to 2D grids. In 2 and 3, the *meso*-helical chains bridged by ClO$_4^-$ recorded shorter Ag···Ag contact distances but weaker π···π-interactions than the *meso*-helical strands bridged by CH$_3$CN. Surprisingly, the *meso*-helical strands of 4 demonstrated slightly tighter bridging by CH$_3$CN molecules but higher Ag···Ag contact and weaker π···π-interactions than the pseudo-polymorphous 3. The CH$_3$CN molecules of 5 bridged the pair of *meso*-helical chains more tightly as compared to the bridging observed in 3. This was evidenced by a shorter Ag···Ag contact in the case of 5 as compared to 3. However, the π···π-interactions were found to be weaker in 5. In 5, the Ag···Ag contact at the bridged nodes was considerably shorter than that at the unbridged nodes, thus highlighting the effect of CH$_3$CN bridging.

A search of the CSD database (version 5.33) for Ag-anion interactions shorter than the sum of the van der Waals radii suggested that out of 1182 reported AgClO$_4$ complexes about 22% of the complexes demonstrate μ$_2$O,O'-bridging of the counteranion, while in about 7% of the complexes the ClO$_4^-$ counteranions displayed di[μ$_2$O,O']-bridging of the Ag(i) ions. Similarly, out of 1038 reported AgCF$_3$SO$_3$ complexes about 13% of the complexes demonstrate μ$_2$O,O'-bridging of the counteranion, while in about 5% of the complexes, the CF$_3$SO$_3^-$ counteranions displayed di[μ$_2$O,O']-bridging of the Ag(i) ions. Out of 959 reported AgCH$_3$CN complexes, only 2.2% of the complexes demonstrate μ$_2$N-bridging of CH$_3$CN molecules, while in 1.6% of the complexes, the CH$_3$CN molecules displayed di[μ$_2$κ,N]-bridging of the Ag(i) ions (Fig. 13).

In the 1:2 M:L complexes 6 and 7, the uncoordinated N2 donor of the decorating L side arms of the strands displayed inclination towards the Ag(i) centre on the adjacent polymeric chain and forced an unusual geometry on that metal centre. The counteranions in both these complexes did not coordinate to the Ag(i) ion. However, the size of the counteranion played a critical role in elaborating the dimensionality of the chains. In the former complex, the bulkier CF$_3$SO$_3^-$ counteranion reduced the Ag(i)–N$_2$py–C$_p$py angle [111.95°] and thus restricted the coordination of N2 with the Ag(i) cation [the N2···Ag contact was 3.152(7) Å]. By contrast, the less bulkier BF$_4^-$ counteranion displayed less interference in the N···Ag interactions [the N2···Ag contact was 2.6593(18) Å and the Ag(i)–N$_2$py–C$_p$py angle was 138.80°] and thus facilitated the generation of a pseudo (4,4) network. The pyridyl rings of the decorating L side arms of 7 displayed more flexibility (as evident from Table 1) and thus assisted the formation of the pseudo (4,4) network. The pyridyl rings of 9 displayed wider Ag(i)–N$_2$py–C$_p$py angles [150.51–175.69°] and shorter Ag-N contacts [2.244(3)–2.384(4) Å] and thus facilitated in the formation of a corrugated (4,4) network. The pyridyl rings of 9 displayed further wider Ag(i)–N$_2$py–C$_p$py angles [168.46–175.58°] and shorter Ag-N contacts [2.267(4)–2.353(4) Å] and thus helped form a regular (4,4) network. Out of 2523 examples in the CSD database (version 5.33) for a search of Ag(i)–N$_2$py–C$_p$py angles, 125 complexes were observed to be in the range of 89.8–140.8°. Scrutinizing the Ag(i)–N$_2$py contact distances [ranging between 2.512 and 3.280 Å] in these complexes, it was observed that the distances are within the sum of the van der Waals radii for Ag–N [3.25 Å]. There were 2472 observations with Ag(i)–N$_2$py–C$_p$py angles between 144.6 and 180° and their Ag(i)···N$_2$py distances range within 2.084–2.399 Å. This shows that the wider the Ag(i)–N$_2$py–C$_p$py angle, the stronger the Ag(i)···N$_2$py interaction.

The C=O groups of the four ligands of the rhombus of 6 splayed outwards. In 7, the C=O groups of the four ligands of the rhombus were arranged such that two C=O groups of the opposite ligands, which were pseudo enantiomers, pointed above the plane of the rhombus and towards each other, while the two C=O groups of the remaining ligands, which were also pseudo enantiomers, pointed below the plane and were splayed away from each other. This arrangement produced an achiral sheet. The rhombus of the 2D network of 9 has a regular orientation with two C=O groups pointing up and two pointing down and two CH$_3$CN molecules in each cavity. All four ligands of the rhombus were of

Table 2  Table showing π···π, Ag···Ag and bridging interactions in the 1st series of Ag–L complexes

| Complexes | π···π  | Ag···Ag  | Bridging |
|-----------|-------|-------|----------|
| 1         | 3.803 Å | 3.4704 Å | 2.927(2) Å  |
| 2         | 3.763 Å | 3.369 Å | 2.727(2) Å  |
| 3         | 3.717 Å | 3.4858 Å | 2.742(4) Å  |
| 4         | 3.884 Å | 3.694 Å | 2.414(6) Å  |
| 5         | 3.910 Å | 3.5632 Å | 2.632(3) Å  |
the same pseudo enantiomeric form producing a chiral sheet. By contrast, the rhombus of the 2D network of 8 has an irregular orientation with three C=O groups pointing up and one pointing down and no CH3CN molecules in the structure. Three ligands of the rhombus had the same pseudo enantiomeric form, while the remaining ligand was of the other pseudo enantiomeric form. This gave rise to an achiral sheet. Thus, the irregular orientation of the C=O groups in 8 appeared to make the structure corrugated rather than flat, while the vacillations of the C=O groups prevented the formation of true 2D networks in 6 and 7. These differences may have been the cause of the embedding of the counteranions and the solvent molecules in the network cavities.

Conclusions

In conclusion, we have described two series of related coordination polymers of Ag(i) salts and L ligand with varying M:L ratio (1:1 and 1:2). The primary structure of the first Ag(i) series was not sensitive to the counteranion. However, the delicate anion–Ag and CH3CN–Ag bridging interactions showed a subtle effect on π–π-stacking and argentophilic interactions. Owing to these delicate interactions, a transition from 1D meso-helical chains to 2D grids was observed. The second Ag(i) series displayed a remarkable sensitivity to the counteranion showing a transition from ordered 1D meso-helical chains to 2D (4,4) nets.

Experimental section

Commercially available 4,4’-dipyridyl ketone was acquired from Chem Bridge. All chemicals were used as received without further purification. All solvents were of LR grade or above. The samples for microanalysis studies were dried under vacuum to remove volatile sample residues. Elemental microanalyses were carried out at the Campbell Microanalytical Laboratory, University of Otago. All measured microanalysis results were within an uncertainty of 0.4%. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR system.

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.

Reaction of L with AgCF3SO3 in a 1:1 ratio

Solid AgCF3SO3 (13.94 mg, 0.054 mmol) dissolved in CH3CN (0.8 mL) was added dropwise to a methanolic solution of L (10 mg, 0.054 mmol). The resultant solution was sonicated and allowed to evaporate slowly for a week to yield X-ray quality colourless crystals of [Ag(L)][CF3SO3]2·2CH3CN·H2O (1:3101 (w, br), 1665 (m, sh), 1609 (w, sh), 1556 (w, sh), 1286 (m, br), 1056 (s, br), 950 (m, sh), 758 (m, sh), 688 (m, sh), 659 (s, sh) and 620 (s, sh)).

Reaction of L with AgClO4 · H2O in a 1:2 ratio

Solid AgClO4 · H2O (22.5 mg, 0.108 mmol) dissolved in CH3CN (1.5 mL) was added dropwise to a methanolic solution of L (10 mg, 0.054 mmol). The resultant solution was sonicated and allowed to stand for a week to yield X-ray quality colourless crystals of [Ag(L)][ClO4]2·1/2H2O (complex 2) which on drying in vacuo converted into a tan powder. Yield (based on L): 10 mg, 47%; analysis found: C 33.51, H 2.25 and N 7.61; calculated for the formula C11H8O5N2Ag: C 33.75, H 2.06 and N 7.16; selected IR/cm−1: 3095 (w, br), 1682 (m, sh), 1609 (w, sh), 1554 (w, sh), 1417 (m, sh), 1282 (m, br), 1162 (w, sh), 1034 (s, br), 879 (m, sh), 758 (m, sh), 691 (m, sh), 657 (s, sh) and 619 (s, sh).

Reaction of L with AgClO4 · H2O in a 2:1 ratio

Solid AgClO4 · H2O (11.2 mg, 0.054 mmol) dissolved in CH3CN (1 mL) was added dropwise to a methanolic solution of L (20 mg, 0.108 mmol). The resultant solution was sonicated and allowed to evaporate slowly for a week to yield X-ray quality colourless crystals of [Ag2(L)2(CH3CN)2][ClO4]2·2CH3CN·H2O (complex 3) which on drying in vacuo converted into a tan powder. Yield (based on L): 11 mg, 50%; analysis found: C 34.26, H 2.51 and N 7.06; calculated for the formula C11H8O5N2Ag: C 35.04, H 2.03 and N 7.42; calculated for the formula C11H8O5N2Ag: C 34.87, H 2.13 and N 7.39; selected IR/cm−1: 3108 (w, br), 1682 (m, sh), 1609 (w, sh), 1556 (w, sh), 1286 (m, br), 1056 (s, br), 950 (m, sh), 758 (m, sh), 688 (m, sh), 659 (s, sh) and 620 (s, sh).

Reaction of L with AgBF4 in a 1:1 ratio

Solid AgBF4 (21.2 mg, 0.108 mmol) dissolved in CH3CN (1.5 mL) was added dropwise to a methanolic solution of L (20 mg, 0.108 mmol). The resultant solution was sonicated and allowed to stand for a week to yield colourless crystals of [Ag2(L)2(CH3CN)2][BF4]2·2CH3CN·H2O (complex 3a) which on drying in vacuo converted into a tan powder. The crystals were twinned and of poor quality. However, these crystals were found to be isostructural to complex 3 [a = 7.5055(8) Å, b = 19.063(3) Å and c = 23.000(3) Å; α = 90°, β = 91.312(4)° and γ = 90°; V = 3290(1) Å3]. Yield: 21 mg, 51%; analysis found: C 35.04, H 2.03 and N 7.42; calculated for the formula C11H8O5N2Ag: C 33.87, H 2.13 and N 7.39; selected IR/cm−1: 3108 (w, br), 1682 (m, sh), 1609 (w, sh), 1554 (w, sh), 1417 (m, sh), 1282 (m, br), 1162 (w, sh), 1034 (s, br), 879 (m, sh), 760 (m, sh), 658 (s, sh) and 520 (s, sh).

Reaction of L with AgClO4 · H2O in a 1:1 ratio

Solid AgClO4 · H2O (11.3 mg, 0.054 mmol) dissolved in CH3CN (1.5 mL) was added dropwise to a methanolic solution of L (10 mg, 0.054 mmol). The resultant solution was sonicated and allowed to stand for a week to yield X-ray quality colourless crystals of [Ag2(L)2(CH3CN)2][ClO4]2·2CH3CN (complex 4) which on drying in vacuo converted into a tan powder. Yield (based on L): 10 mg, 47%; analysis found: C 33.51, H 2.25 and N 7.61; calculated for the formula C11H8O5N2Ag: C 33.75, H 2.06 and N 7.16; selected IR/cm−1: 3095 (w, br), 1682 (m, sh), 1609 (w, sh), 1554 (w, sh), 1286 (m, br), 1056 (s, br), 950 (m, sh), 758 (m, sh), 688 (m, sh), 659 (s, sh) and 620 (s, sh).
The reaction of L with AgBF₄ in a 2:1 ratio

Yield (based on Ag(I)): 22 mg, 65%; analysis found: C 44.47, H 2.84, N 9.00, and S 4.91; calculated for the formula C₂₂H₁₆O₂N₄PF₆Ag: C 42.54, H 2.60 and N 7.16; selected IR/cm⁻¹: 3102 (w, br), 1675 (m, sh), 1609 (w, sh), 1554 (w, sh), 1281 (m, br), 1061 (s, br), 951 (m, sh), 758 (m, sh), 688 (m, sh), 656 (s, sh) and 620 (s, sh).

Reactions of L with AgCF₃SO₃ in a 2:1 ratio

Yield: 15 mg, 71%; analysis found: C 33.51, H 2.25 and N 7.61; calculated for the formula C₁₃H₂₀O₃N₂ClAg: C 33.75, H 2.06 and N 7.16; selected IR/cm⁻¹: 3102 (w, br), 1675 (m, sh), 1609 (w, sh), 1554 (w, sh), 1281 (m, br), 1061 (s, br), 951 (m, sh), 758 (m, sh), 688 (m, sh), 656 (s, sh) and 620 (s, sh).

Reactions of L with AgPF₆ in a 2:1 ratio

Reaction 1: solid AgPF₆ (13.2 mg, 0.054 mmol) dissolved in CH₃CN (4 mL) was added dropwise to a 4 mL methanolic solution of L (20 mg, 0.108 mmol). The resultant clear solution was stirred overnight and concentrated in volume to 2 mL. Addition of 0.5 mL of diethyl ether yielded a brown crystalline precipitate which was filtered, washed with diethyl ether and dried in vacuo. Yield (based on Ag(i)): 13 mg, 55%. X-Ray quality colourless crystals of [[Ag(L)₂(CH₃CN)₂](PF₆)₃·CH₃CN]∞ (complex 5) were grown by slow evaporation of solvents (1:1 v/v CH₃CN:CH₃OH) from the solution of AgPF₆ (6.9 mg, 0.027 mmol) and L (10 mg, 0.054 mmol). Analysis found: C 33.43, H 2.34 and N 7.81; calculated for the formula C₁₃H₁₈ON₄PF₆Ag: C 32.96, H 2.96 and N 8.24; selected IR/cm⁻¹: 3629 (w, br), 1675 (m, sh), 1612 (w, sh), 1555 (m, sh), 1284 (m, sh), 1160 (w, sh), 1134 (w, sh), 881 (m, sh), 821 (vs, sh), 757 (m, sh), 690 (m, sh), 651 (s, sh) and 555 (s, sh).

Reaction 2: solid AgPF₆ (13.2 mg, 0.054 mmol) dissolved in CH₃CN (1 mL) was added dropwise to a methanolic solution of L (20 mg, 0.108 mmol). The resultant solution was sonicated and allowed to evaporate slowly for a week to yield X-ray quality colourless crystals of [[Ag(L)₂(CH₃CN)₂](PF₆)₂·CH₃CN]∞ (complex 6) which on drying in vacuo converted into a tan powder. Yield (based on Ag(i)): 20 mg, 60%. Analysis found: C 42.65, H 2.69 and N 9.11; calculated for the formula C₂₂H₂₄O₄N₄PF₆Ag: C 42.54, H 2.60 and N 9.02; selected IR/cm⁻¹: 1686 (m, sh), 1674 (m, sh), 1604 (w, sh), 1556 (w, sh), 1494 (w, sh), 1413 (m, sh), 1281 (m, sh), 1158 (w, sh), 949 (w, sh), 818 (vs, sh), 690 (m, sh), 647 (s, sh) and 556 (s, sh).

Reactions of L with AgCF₃SO₃ in a 2:1 ratio

Solid AgCF₃SO₃ (13.94 mg, 0.054 mmol) dissolved in CH₃CN (1 mL) was added dropwise to a methanolic solution of L (20 mg, 0.108 mmol). The resultant clear solution was sonicated and allowed to evaporate slowly for a week to yield X-ray quality colourless crystals of [[Ag(L)₂(CH₃CN)₂](CF₃SO₃)₂·CH₃CN]∞ (complex 7) which on drying in vacuo converted into a tan powder. X-Ray data indicated that crystals might carry a well-ordered structure. A CH₃CN molecule in the ESI along with a description of how the disordered components of the complexes were treated. X-Ray diffraction data were collected at the University of Otago on a Bruker APEX II CCD diffractometer with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation. Intensities were corrected for Lorentz and polarisation effects and multiscan absorption corrections were applied to all structures. The structures were solved by direct methods such as SHELXS13,44 or SIR-9245 and refined on F² using all data by full-matrix least-squares procedures such as SHELXL 97.43 Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in ideal positions except for the hydrogen atoms of the H₂O molecules in 1, 2, 3, 4 and 6 which were located from the Fourier synthesis maps. In 1, the CF₃SO₃⁻ anion was disordered over two sites with site occupancy of 0.36 and 0.64. This CF₃SO₃⁻ anion and H₂O molecule were modelled using DFIX constraints. In 4, both ClO₄⁻ anions were disordered (50%). A very disordered CH₃CN of solvent was removed from the structure using the SQUEEZE procedure of PLATON 46 as it could not be modelled. Analysis of the X-ray data indicated that crystals might carry a well-defined twin. However, a twin law that superimposed all or half of the reflections could not be found. The twinning was evident in both data collections for 4. As a result, the precision of the data for 4 was not high. The crystals of 5 were of poor quality. Two different data sets for 5 were collected and solved, both of which were of poor quality because of weakly diffracting crystals. The solution reported herein represents the best quality solution. A CH₃CN molecule in 5 was disordered and the C and N atoms of this molecule were refined isotropically and the hydrogen atoms of this molecule were not placed. The disordered CH₃CN molecule was modelled with site occupancy of 0.6 and 0.4 and additional restraints were used to maintain the linearity. A CF₃SO₃⁻ anion was disordered with site occupancy of 0.51 and 0.49. The F and O atoms of this molecule were refined isotropically. In 8, the PF₆⁻ anion was disordered on a four-fold axis over two sites with site occupancy of AgBF₄ (21.2 mg, 0.108 mmol). The resultant solution was allowed to react overnight. Addition of 0.5 mL of diethyl ether to this solution resulted in colourless crystalline solid which was filtered and dried in vacuo. Yield (based on Ag(i)): 28 mg, 43%; analysis found: C 48.17, H 3.07 and N 10.18; calculated for the formula C₁₃H₁₆O₃N₂ClAgBF₄: C 47.72, H 3.17 and N 11.59; selected IR/cm⁻¹: 3106-3054 (w, br), 1677 (m, sh), 1608 (w, sh), 1555 (m, sh), 1409 (m, sh), 1282 (m, sh), 1160 (w, sh), 1032 (s, br), 756 (m, sh), 660 (s, sh), 520 (m, sh).

Solid AgBF₄ (10.6 mg, 0.054 mmol) dissolved in CH₃CN (1 mL) was added dropwise to a methanolic solution of L (20 mg, 0.108 mmol). The resultant solution was sonicated and allowed to evaporate slowly for a week to yield X-ray quality colourless crystals of [[Ag(L)₂(BF₄)₂]∞ (complex 7).
Table 3  Crystal and structure refinement data for complexes –

| Structure | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     | 9     |
|-----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Formula   | C_{24}H_{18}O_{9}N_{4}S_{2}F_{6}Ag_{2} | C_{22}H_{18}Ag_{2}Cl_{2}N_{4}O_{11} | C_{28}H_{27}Ag_{2}Cl_{2}N_{7}O_{11} | C_{28}H_{25}Ag_{2}Cl_{2}N_{7}O_{10} | C_{30}H_{28}Ag_{2}F_{12}N_{8}O_{2}P_{2} | C_{46}H_{34}O_{11}N_{8}S_{2}F_{6}Ag_{2} | C_{22}H_{16}AgBF_{4}N_{4}O_{2} | C_{22}H_{16}AgF_{6}N_{4}O_{2}PC | C_{26}H_{22}AgF_{6}N_{6}O_{2}P |
| Formula weight | 900.28 | 801.04 | 924.21 | 906.19 | 1038.26 | 1268.67 | 563.07 | 621.23 | 703.34 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Triclinic |
| Space group | C2/c | C2/c | P2_1/c | P2_1/c | P2_1/c | P2_1/c | P2_1/c | P2_1/n | P1 |
| a/Å     | 13.7574(9) | 12.4586(5) | 7.5345(3) | 7.8231(5) | 7.9890(5) | 27.5782(15) | 11.020(11) | 11.0709(7) | 10.950(7) |
| b/Å     | 11.2371(8) | 9.8846(4) | 19.1191(10) | 18.8411(11) | 22.9536(15) | 10.6328(5) | 18.3216(17) | 18.5174(12) | 11.1081(7) |
| c/Å     | 19.0368(12) | 21.2874(9) | 23.0434(11) | 22.8612(13) | 20.1547(15) | 18.6286(9) | 17.558(10) | 11.6388(8) | 12.1273(9) |
| α/°    | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 |
| β/°    | 92.046(3) | 90.874(3) | 91.046(3) | 91.046(3) | 90.874(3) | 91.046(3) | 91.046(3) | 91.046(3) | 90.874(3) |
| γ/°    | 93.529(2) | 102.7935(18) | 92.045(1) | 90.874(3) | 91.046(3) | 91.046(3) | 91.046(3) | 91.046(3) | 91.046(3) |
| V/Å³   | 2929.3(5) | 3317.4(3) | 3369.3(5) | 3695.3(6) | 4844.8(6) | 2167.4(5) | 2370.8(3) | 1458.7(2) | 85.248(2) |
| Z      | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 2 |
| T/K    | 90(2) | 90(2) | 70(2) | 90(2) | 90(2) | 90(2) | 90(2) | 90(2) | 90(2) |
| μ/mm⁻¹ | 1.577 | 1.811 | 1.412 | 1.387 | 1.249 | 0.987 | 0.994 | 0.993 | 0.819 |
| Total reflections | 22 092 | 39 118 | 39 984 | 38 976 | 58 540 | 26 131 | 26 132 | 21 026 | 17 617 |
| Unique reflections (Rint) | 8857 (0.0312) | 9878 (0.0325) | 9643 (0.0411) | 9961 (0.0394) | 9915 (0) | 9998 (0.0538) | 9900 (0.0347) | 9898 (0.0210) | 9112 (0.0289) |
| R1 indices | 0.0199 | 0.0285 | 0.0495 | 0.0687 | 0.0694 | 0.0596 | 0.0221 | 0.0340 | 0.0446 |
| wR2 (all data) | 0.0522 | 0.1269 | 0.1158 | 0.1792 | 0.2414 | 0.1368 | 0.0559 | 0.0846 | 0.1247 |
| Goodness-of-fit | 1.088 | 1.209 | 1.069 | 1.066 | 1.149 | 1.150 | 1.083 | 1.145 | 1.082 |
occupancy of 0.35 and 0.65. This PF₆⁻ anion was modelled using DFIX constraints. All calculations were performed using the WinGX²⁵ interface. Detailed analyses of the extended structure were carried out using PLATON⁴⁶ and MERCURY (version 3.0)⁴⁷晶胞lographic data are listed in the appendix.

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