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Control of metallo-supramolecular assemblies via steric, hydrogen bonding and argentophilic interactions; formation of a 3-dimensional polymer of circular helicates

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## Control of metallo-supramolecular assemblies via steric, hydrogen bonding and argentophilic interactions; formation of a 3-dimensional polymer of circular helicates.

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This work shows how multiple non-covalent interactions are employed to control metallosupramolecular architectures and we demonstrate that a ligand, which contains two bidentate domains separated by a ArOH spacer, forms a mesocate when complexed with Ag(I). However, changing this to an ArOCH<sub>2</sub>CH<sub>2</sub>Ph spacer unit results in a 1-dimensional helical polymer upon reaction with the same cation. Reaction of Ag(I) with the ArOMe derivative gives a hexanuclear circular helicate which forms inter-assembly Ag•••Ag interactions resulting in a 3-dimensional honeycomb-like polymer of hexanuclear circular helicates.

### Introduction.

Self-assembly of metallosupramolecular complexes is an area of chemistry which continues to receive an intense level of attention.<sup>1–4</sup> Understanding the forces that govern the formation of these complexes has allowed for the creation of more and more complex structures from helicates and mesocates,<sup>5,6</sup> through to circular helicates,<sup>7</sup> cages<sup>8–10</sup> and beyond.<sup>11–14</sup> Arguably the most studied of these assemblies is the helicate, which consists of two or more ligand strands partitioned into separate binding domains each of which coordinates different metal ions and coordination in this manner results in a helical twist.<sup>14–16</sup> The programming requirements of the ligand strand in order to successfully assemble these polynuclear species are well established.<sup>11,12</sup>

Generally in dinuclear double helical assemblies the metal centres possess the same chirality, resulting in the formation of [M<sub>2</sub>L<sub>2</sub>]<sup>n+</sup> complexes of two configurations (e.g. ΔΔ and ΛΛ) unless the chirality of the assembly is controlled, usually by the inclusion of a chiral centre on the ligand strand.<sup>17</sup> However it is possible for the metal centres to have opposite chiralities (e.g. ΔΛ) and in such situations a mesocate, the achiral analogue, is formed.<sup>18</sup> Even though the first structure of a mesocate was reported some time ago,<sup>19</sup> in comparison to the helicate, the conditions required for their formation are much less understood.<sup>5,20</sup>

Using much the same methodology of helicate assembly larger

species can be produced which contain three or more metal ions in a circular arrangement. These circular helicates contain the same binding arrangement of ligand strands *i.e.* the ligand partitions into two binding domains each of which coordinates a different metal ion, but it does so in a circular arrangement giving species of the formula [M<sub>n</sub>L<sub>n</sub>]<sup>x+</sup> where n = 3 to 10.<sup>7,21</sup> The rules that govern the formation of these species are much less understood compared to the linear helicates however, methods utilising anion templation and steric interactions have been reported which are required to prevent the formation of the entropically favoured linear helicates.<sup>22–24</sup>

The self-assembly of linear helicates are well understood and as a result the self-assembly is no longer limited to just metal-ligand interactions and assemblies that include anions and s-block metal ions are known.<sup>25,26</sup> One such example of higher orders of self-assembly has been demonstrated by Ward *et al.*<sup>6</sup> In this work they demonstrate the formation of triple helix comprised of three infinite chains of double helicates. The basic unit is a bis-bidentate ligand which forms a dinuclear double helicate with Ag(I) (e.g. [Ag<sub>2</sub>L<sub>2</sub>]<sup>2+</sup>). This subunit then interacts with another dinuclear helicate via Ag•••Ag interactions giving a 1-dimensional helicate polymer creating an infinite chain of double helicates. Inter-chain interactions results in three of these chains intertwining giving the final structure of a triple helix of double helicates.<sup>6</sup> Argentophillic, or Ag•••Ag interactions, are well recognised as being able to develop complex subunits into long one dimensional polymeric chains, as well as into multi-dimensional polymeric assemblies.<sup>27–31</sup>

### Experimental and theoretical methods

#### Experimental

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Electronic Supplementary Information (ESI) available: [synthetic details of L<sup>1</sup> – L<sup>3</sup> and crystallographic data]. See DOI: 10.1039/x0xx00000x

**Materials and measurements.** Chemicals were purchased and used without further purification apart from 1,3-di( $\alpha$ -bromoacetyl)cresol which was prepared by a previously reported method.<sup>32</sup>  $^1\text{H}$  NMR spectra were recorded either on a 400 MHz Bruker Advance DP X400 or on a 500 MHz Bruker Advance 500. Mass spectra were obtained on a Bruker MicroTOF-q LC mass spectrometer.

**Synthesis of  $\text{L}^1$ .** To a round bottomed flask charged with pyridine-2-thioamide (87 mg, 0.63 mmol) and 1,3-di( $\alpha$ -bromoacetyl)cresol (100 mg, 0.29 mmol) and equipped with a magnetic follower was added ethanol (30 ml) and the reaction heated to 60°C under nitrogen for 12 hrs. After this time a yellow precipitate formed, which was isolated by filtration and washed with EtOH (3 x 5 ml) and Et<sub>2</sub>O (3 x 5 ml). This solid was then suspended in concentrated aqueous ammonia (sp.G. 0.88, 10 ml) for 12 hrs after which time the yellow solid was isolated by filtration and washing with water (2 x 2 ml), EtOH (2 x 2 ml) and Et<sub>2</sub>O (2 x 2 ml) giving pure ligand  $\text{L}^1$  (47 mg, 75 %).  $^1\text{H}$  NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO)  $\delta$ : 12.4 (s, 1H, -OH); 8.7 (d,  $J$  = 4.52, 2H, py); 8.48 (s, 2H, tz); 8.28 (d,  $J$  = 7.84, 2H, py); 8.05 (td,  $J$  = 7.68, 1.48, 2H, py); 7.98 (s, 2H, Ph); 7.57 (dd,  $J$  = 6.94 Hz, 5.12, 2H, py); 2.42 (s, 3H, -CH<sub>3</sub>).  $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 167.6, 153.3, 151.5, 150.3, 150.2, 138.5, 129.3, 128.5, 126.0, 120.3, 119.9, 119.4, 20.9 (-CH<sub>3</sub>). ESI-MS  $m/z$  428 (M + H<sup>+</sup>). HR ESI-MS found 429.0832 C<sub>23</sub>H<sub>17</sub>N<sub>4</sub>OS<sub>2</sub> requires 429.0838 (error 1.32 ppm).

**Synthesis of  $\text{L}^2$ .** To a two necked round bottom flask containing  $\text{L}^1$  (140 mg, 0.33 mmol) and sodium hydride (60% dispersion in mineral oil, 100 mg, 2.5 mmol) was placed under a dinitrogen atmosphere and left to purge for 30 minutes. To this anhydrous DMF (25 mL) was added and left to stir at 80 °C for 1 h. After this time (2-bromoethyl) benzene (0.5 ml, 3.7 mmol) was added and left for 12 h. The reaction was cooled to room temperature and methanol was added whilst under N<sub>2</sub>. The solvent was removed by rotary evaporation. Purification *via* column chromatography (Al<sub>2</sub>O<sub>3</sub>, DCM) (87 mg, 50 %).  $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.68 (d,  $J$  = 4.8, 2H, py); 8.37 (d,  $J$  = 7.92, 2H, py); 8.00 (s, 2H, tz); 7.85 (td,  $J$  = 7.68, 1.6, 2H, py); 7.71 (s, 2H, Ph); 7.39-7.32 (m, overlapping, 5H, Ph) 7.24 (d,  $J$  = 6.48, 2H, py); 3.85 (t,  $J$  = 6.28, 2H, -OCH<sub>2</sub>CH<sub>2</sub>); 2.96 (t,  $J$  = 6.2 Hz, 2H, -OCH<sub>2</sub>CH<sub>2</sub>); 2.49 (s, 3H, -CH<sub>3</sub>).  $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 167.3, 152.5, 152.2, 151.5, 149.5, 138.5, 137.0, 134.3, 130.7, 129.5, 128.7, 128.5, 126.8, 124.5, 119.9, 119.7, 73.6 (-OCH<sub>2</sub>CH<sub>2</sub>), 37.3 (-OCH<sub>2</sub>CH<sub>2</sub>), 21.1 (-CH<sub>3</sub>). ESI-MS  $m/z$  532 (M + H<sup>+</sup>). HR ESI-MS found 532.1385 C<sub>31</sub>H<sub>24</sub>N<sub>4</sub>OS<sub>2</sub> requires 532.1392 (error 1.22 ppm).

**Synthesis of  $\text{L}^3$ .** To a two-necked round bottom flask charged with  $\text{L}^1$  (120 mg 0.28 mmol) and NaH (60% dispersion in mineral oil, 100 mg, 2.5 mmol) and equipped with a magnetic follower was purged with dinitrogen. After 10 mins anhydrous DMF (20 ml) was added and the reaction heated to 60°C for 1 hr. After this time dimethyl sulphate (0.5 ml, 5 mmol) was added and the reaction stirred at this temperature for at least 24 hrs. Ethanol (5 ml) was added (to quench any unreacted

sodium hydride) and the solvents removed by rotary evaporation. The resultant brown oil was then suspended in water (20 ml) and extracted in DCM (2 x 50 ml) and after removal of the solvent the product was purified by column chromatography (Al<sub>2</sub>O<sub>3</sub>, DCM) giving ligand  $\text{L}^2$  as an off-white solid (55 mg, 45 %).  $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.58 (d,  $J$  = 4.36, 2H, py), 8.30 (d,  $J$  = 7.92, 2H, py), 8.05 (s, 2H), 7.97 (s, 2H), 7.77 (dt,  $J$  = 7.7, 1.7, 2H, py), 7.28 (ddd,  $J$  = 7.4, 4.8, 1.0 Hz, 2H, py), 3.56 (s, 3H, -OCH<sub>3</sub>), 2.43 (s, 3H, -CH<sub>3</sub>).  $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  167.4, 153.7, 152.6, 151.5, 149.5, 137.1, 134.3, 130.8, 128.2, 124.5, 119.9, 119.8, 60.1 (-OCH<sub>3</sub>), 21.1 (-CH<sub>3</sub>). ESI-MS  $m/z$  442 (M + H<sup>+</sup>). HR ESI-MS found 443.0986 C<sub>24</sub>H<sub>19</sub>N<sub>4</sub>OS<sub>2</sub> requires 443.0995 (error 1.71 ppm).

**Synthesis of [Ag<sub>2</sub>( $\text{L}^1$ )<sub>2</sub>]<sup>2+</sup>.** To a suspension of  $\text{L}^1$  (0.01 g 0.023 mmol) in MeCN (2 ml) was added Ag(ClO<sub>4</sub>) (0.005 g, 0.024 mmol) and the reaction briefly heated and sonicated until all the ligand dissolved and gave a yellow solution. Chloroform was then allowed to slow diffuse into the solution giving yellow crystals after a few days (0.009g 66%).  $^1\text{H}$  NMR (400 MHz, CD<sub>3</sub>CN)  $\delta$  (ppm) 12.45 (s, 1H, OH), 8.62 (d,  $J$  = 4.8, 2H, py), 8.09 (d,  $J$  = 8.5, 2H, py), 8.08 (s, 2H, tz), 7.95 (dt,  $J$  = 7.8, 1.5, 2H, py), 7.77 (s, 2H, Ph), 7.51 (ddd,  $J$  = 7.5, 4.8, 0.8 Hz, 2H, py), 2.31 (s, 3H, -CH<sub>3</sub>). ESI-MS  $m/z$  = 1171 corresponding to {[Ag<sub>2</sub>( $\text{L}^1$ )<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>}<sup>+</sup>. Small amounts of a black impurity were present (presumably reduction of Ag(I)) which made a satisfactory elemental analysis unobtainable.

**Synthesis of [Ag<sub>n</sub>( $\text{L}^2$ )<sub>n</sub>]<sup>n+</sup>.** To a suspension of  $\text{L}^2$  (0.01 g 0.019 mmol) in MeNO<sub>2</sub> (2 ml) was added Ag(BF<sub>4</sub>) (0.004 g, 0.024 mmol) and the reaction briefly heated and sonicated until all the ligand dissolved and gave a colourless solution. Diisopropyl ether was then allowed to slow diffuse into the solution giving colourless crystals after a few days (0.01 g 73%).  $^1\text{H}$  NMR (400 MHz, CD<sub>3</sub>NO<sub>2</sub>)  $\delta$  (ppm) 8.63 (brs, 2H), 8.25 (brs, 5H overlapping), 7.85 (brs, 2H), 7.75 (brs, 2H), 7.09 (brs, 3H, overlapping), 6.86 (brs, 2H), 3.81 (brs, 2H), 2.81 (brs, 2H) and 1.81 (brs, 3H). ESI-MS  $m/z$  = 897 corresponding to {[Ag<sub>2</sub>( $\text{L}^2$ )](trif)}<sup>+</sup>, 1173 corresponding to {[Ag( $\text{L}^2$ )<sub>2</sub>]}<sup>+</sup>, 1429 corresponding to {[Ag<sub>2</sub>( $\text{L}^2$ )<sub>2</sub>](trif)}<sup>+</sup> and 1687 corresponding to {[Ag<sub>3</sub>( $\text{L}^2$ )<sub>2</sub>](trif)<sub>2</sub>}<sup>+</sup>. In the same manner as [Ag<sub>2</sub>( $\text{L}^1$ )<sub>2</sub>]<sup>2+</sup> small amounts of silver metal was present negating the use of elemental analysis.

**Synthesis of [Ag<sub>6</sub>( $\text{L}^3$ )<sub>6</sub>]<sup>6+</sup>.** To a suspension of  $\text{L}^3$  (0.01 g 0.23 mmol) in MeNO<sub>2</sub> (2 ml) was added Ag(BF<sub>4</sub>) (0.0045 g, 0.24 mmol) and the reaction briefly heated and sonicated until all the ligand dissolved and gave a colourless solution. Diisopropyl ether was allowed to slow diffuse into the solution giving pale yellow crystals after a few days which were isolated by filtration and dried under vacuum (0.009 g, 62 %). Found: C, 44.7; H, 2.8; N, 8.7%; C<sub>24</sub>H<sub>18</sub>N<sub>4</sub>OS<sub>2</sub>AgBF<sub>4</sub> requires C, 45.2; H, 2.8; N, 8.8%.  $^1\text{H}$  NMR (400 MHz, CD<sub>3</sub>CN)  $\delta$  (ppm) 8.62 (d,  $J$  = 4.8, 2H, py), 8.22 (d,  $J$  = 7.9, 2H, py), 8.04 (s, 2H, tz), 7.99 (dt,  $J$  = 7.7, 1.6, 2H, py), 7.89 (s, 2H, Ph), 7.51 (ddd,  $J$  = 7.5, 5.0, 0.7 Hz, 2H), 3.48 (s, 3H, -OCH<sub>3</sub>), 2.24 (s, 3H, -CH<sub>3</sub>). ESI-MS  $m/z$  = 3735 corresponding to {[Ag<sub>6</sub>( $\text{L}^3$ )<sub>6</sub>](BF<sub>4</sub>)<sub>5</sub>}<sup>+</sup> along with lower

molecular weight species e.g.  $[\text{Ag}_n(\text{L}^3)_n](\text{BF}_4)_{n-1}^+$  where  $n = 1$  to 5.

### Crystallography.

Single crystal X-ray diffraction data was collected at 150(2) K on either a Bruker Apex Duo diffractometer equipped with a graphite monochromated  $\text{Mo}(\text{K}\alpha)$  radiation source or a Bruker Venture diffractometer equipped with a  $\text{Mo}-\mu\text{S}$  source and a cold stream of  $\text{N}_2$  gas. Solutions were generated by conventional heavy atom Patterson or direct methods and refined by full-matrix least squares on all  $F^2$  data, using SHELXS-97 and SHELXL software respectively. Absorption corrections were applied based on multiple and symmetry-equivalent measurements using SADABS. For  $[\text{Ag}_n(\text{L}^2)_n]^{n+}$  the tetrafluoroborate counter anions were disordered and these were modelled in two positions using the *PART* instruction. In all cases of disordered atoms/molecules *DELU*, *SIMU*, *SADI*, and in some cases *ISOR*, constraints were used in the least-squares refinement. Furthermore, the structure contained disorder that could not be satisfactorily modelled and as a result the diffuse electron density was removed using the solvent mask facility in Olex2, resulting in voids in the crystal structure.<sup>33</sup> The solvent mask removed a total of 208.9 electrons in the unit cell which corresponds to five molecules of nitromethane and a molecule of diisopropylether in the unit cell. For  $[\text{Ag}_6(\text{L}^3)_6]^{6+}$  one of the tetrafluoroborate counter anions was disordered and refined poorly. It was constrained using *DELU*, *SIMU*, *SADI*, and in some cases *ISOR* and its occupancy was fixed to 10.50 and using this the molecule refined reasonably well. Due to this the occupancy of the counter anions is low (e.g. six silver ions and five tetrafluoroborate anions) however, the valance of the cation is not in any doubt and the structure refined well using this value. Furthermore, the structure contained disorder that could not be satisfactorily modelled and as a result the diffuse electron density was removed using the solvent mask facility in Olex2, resulting in voids in the crystal structure.<sup>33</sup> The solvent mask removed a total of 644.3 electrons in the unit cell (107.4 per asymmetric unit) which corresponds to five molecules of acetonitrile in the asymmetric unit (30 in the unit cell).

Crystal data for  $[\text{Ag}_2(\text{L}^1)_2]^{2+}$ :  $M = 1510.47$ , triclinic *P*-1,  $a = 7.5797(2)$ ,  $b = 10.6965(3)$ ,  $c = 17.3538(5)$  Å,  $\alpha = 103.551(1)$ ,  $\beta = 101.676(1)$ ,  $\gamma = 90.482(1)^\circ$   $V = 1337.20(7)$  Å<sup>3</sup>,  $Z = 1$ ;  $\mu(\text{Mo}_{\text{K}\alpha}) = 1.356 \text{ mm}^{-1}$ ,  $T = 150 \text{ K}$ . A total of 31032 reflections were collected with 8125 independent reflections ( $R_{\text{int}} = 0.0438$ ). The final  $R_1$  values were 0.0492 ( $I > 2\sigma(I)$ ). The final  $wR(F^2)$  values were 0.1297 ( $I > 2\sigma(I)$ ). The final  $R_1$  values were 0.0705 (all data). The final  $wR(F^2)$  were 0.1424 (all data). The goodness of fit on  $F^2$  was 1.068, largest peak and hole 1.735 and -2.228 eÅ<sup>-3</sup>. CCDC 1507028.

Crystal data for  $[\text{Ag}_n(\text{L}^2)_n]^{n+}$ :  $M = 3092.64$ , triclinic *P*-1,  $a = 7.820(4)$ ,  $b = 18.768(9)$ ,  $c = 25.836(12)$  Å,  $\alpha = 80.419(16)$ ,  $\beta = 82.135(19)$ ,  $\gamma = 83.58(3)^\circ$   $V = 3688(3)$  Å<sup>3</sup>,  $Z = 1$ ;  $\mu(\text{Mo}_{\text{K}\alpha}) = 0.715 \text{ mm}^{-1}$ ,  $T = 150 \text{ K}$ . A total of 101583 reflections were collected with 18381 independent reflections ( $R_{\text{int}} = 0.0990$ ). The final  $R_1$  values were 0.0588 ( $I > 2\sigma(I)$ ). The final  $wR(F^2)$  values were 0.1467 ( $I > 2\sigma(I)$ ). The final  $R_1$  values were 0.0961 (all data). The final  $wR(F^2)$  were 0.1640 (all data). The goodness of fit on  $F^2$  was 1.0362, largest peak and hole 1.792 and -1.444 eÅ<sup>-3</sup>. CCDC 1507029.

Crystal data for  $[\text{Ag}_6(\text{L}^3)_6]^{6+}$ :  $M = 3736.71$ , trigonal *R*-3c,  $a = 26.047(11)$ ,  $c = 41.751(2)$  Å,  $\alpha = 90$ ,  $\beta = 90$ ,  $\gamma = 120^\circ$   $V = 24530.9(19)$  Å<sup>3</sup>,  $Z = 6$ ;  $\mu(\text{Mo}_{\text{K}\alpha}) = 0.939 \text{ mm}^{-1}$ ,  $T = 150 \text{ K}$ . A total of 41376 reflections were collected with 8300 independent reflections ( $R_{\text{int}} = 0.0510$ ). The final  $R_1$  values were 0.0547 ( $I > 2\sigma(I)$ ). The final  $wR(F^2)$  values were 0.1432 ( $I > 2\sigma(I)$ ). The final  $R_1$  values were 0.0983 (all data). The final  $wR(F^2)$  were 0.1697 (all data). The goodness of fit on  $F^2$  was 1.0586, largest peak and hole 2.301 and -0.760 eÅ<sup>-3</sup>. CCDC 1507030.

## Results and Discussion.

In this work we describe a ligand, which contains two bidentate pyridyl-thiazole domains partitioned by a ArOH spacer (Fig. 1), which forms a dinuclear mesocate with Ag(I). However, changing the central phenol unit to an ethyl phenyl ether results in a helical polymer upon coordination with the same metal ion, whilst the methyl ether derivative results in a hexanuclear cyclic helicate which forms a 3-dimensional polymer in the solid state via Ag...Ag interactions.

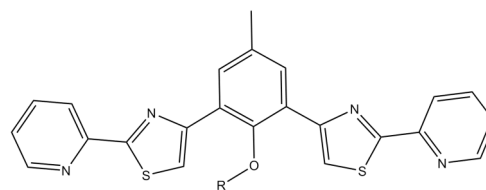


Fig. 1: The simple framework used in ligands  $\text{L}^1\text{-L}^3$  where R in  $\text{L}^1 = \text{H}$ , R in  $\text{L}^2 = \text{CH}_2\text{CH}_2\text{Ph}$  and R in  $\text{L}^3 = \text{CH}_3$ .

The ligand  $\text{L}^1$  was prepared by reaction of pyridine-2-thioamide with 2,6-di(2-bromoethanone)cresol and this can then be functionalised at the oxygen atom by deprotonation and reaction with either 2-bromoethylphenyl giving  $\text{L}^2$  or dimethyl sulfate to give  $\text{L}^3$ .

Reaction of  $\text{L}^1$  in nitromethane with  $\text{Ag}(\text{ClO}_4)$  gave a clear yellow solution which after slow diffusion of  $\text{CHCl}_3$  gave crystals suitable for X-ray analysis. Analysis in the solid state shows that a dinuclear mesocate is formed e.g.  $[\text{Ag}_2(\text{L}^1)_2](\text{ClO}_4)_2$  (Fig. 2).

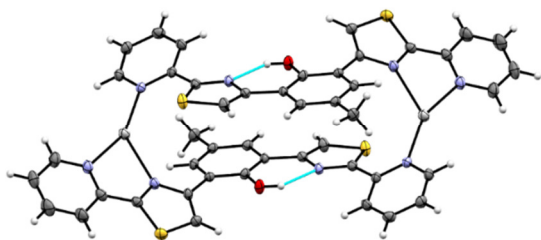


Fig. 2: X-ray crystal structure of the dinuclear mesocate complex  $[Ag_2(L^1)_2]^{2+}$  showing hydrogen bonding between the nitrogen atom of the thiazole group and the hydrogen atom of the hydroxyl group. Thermal ellipsoids shown at 50% probability.

In this structure the ligand partitions into a bidentate pyridyl-thiazole domain and a monodentate pyridyl domain each of which coordinates a different metal ion resulting in a three coordinate Ag(I) centre. The Ag-N bond lengths range from 2.197 (3) Å to 2.360 (3) Å with the longest bonds arising from the thiazole-metal interactions. The remaining uncoordinated thiazole unit acts as a hydrogen bond acceptor to the ArOH proton which prevents the ligand from acting as a bis-bidentate donor. The formation of a mononuclear species is prevented by the geometric constraints of the ligand strand which cannot act as a tetradentate donor to a single metal ion so a mesocate is formed. The formation of a mesocate is relatively unusual as helicates are generally favoured due to  $\pi$ -stacking interactions but in this case this assembly is prevented by the steric constraints of the -OH unit with the hydrogen bonding stabilising the mono- and bidentate partitioning of the ligand. This dinuclear species also occurs in solution as an ion at  $m/z$  1171 corresponding to  $\{[Ag_2(L^1)_2](ClO_4)\}^+$  is observed in the ESI-MS.<sup>34</sup> However in the  $^1H$  NMR ( $CD_3CN$ ) six aromatic signals are observed which indicates that a symmetrical ligand species is present which wouldn't be expected as in the solid state as the ligand partitions into different binding domains. It is likely that the symmetry observed in solution is a result of fluxional behaviour as the bidentate / monodentate domains can easily interchange. Regardless, it is clear the dinuclear nature of the complex is observed in both the solid and solution state. Reaction of  $L^2$  with  $Ag(BF_4)$  in  $MeNO_2$  gave a colourless solution from which colourless crystals were deposited by slow diffusion of diisopropyl ether. In the solid state, in an analogous fashion to  $L^1$ , the ligand partitions into two donor units each of which coordinates a Ag(I) ion and this cation is further coordinated by a bidentate unit of a different ligand. However, the remaining bidentate domain of this ligand, rather than wrap around the  $[Ag_2(L^2)]^{2+}$  unit and coordinate the other metal ion in the same assembly, goes on to coordinate a different Ag(I) ion in a different assembly resulting in a 1-dimensional helical metal-containing polymer. The Ag-N bond lengths range from 2.269 (4) – 2.573 (3) Å and interestingly the phenol ether oxygen atom lies close to the silver cation (ave. 2.731 Å) which although quite long is within the sum of the van der Waals radii. As would be expected ESI-MS analysis shows fragments of the polymeric structure with ions corresponding to  $\{[Ag_2(L^2)]BF_4\}^+$ ,  $\{[Ag(L^2)_2]\}^+$ ,  $\{[Ag_2(L^2)_2]BF_4\}^+$  and  $\{[Ag_3(L^2)_2](BF_4)_2\}^+$  observed. In the  $^1H$  NMR

( $CD_3NO_2$ ) the corresponding signals are observed in the aromatic region but these are significantly broadened which is again as expected for a polymeric species.

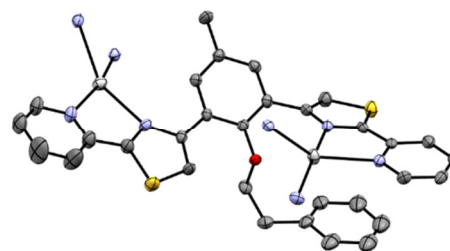


Fig. 3: Crystal structure of the  $[Ag_n(L^2)_n]^{n+}$  polymer with a partial view showing the  $[Ag_2(L^2)_2]^{2+}$  unit (top) and the polymeric complex  $[Ag_n(L^2)_n]^{n+}$  (bottom) with alternating ligand strands coloured blue and green and hydrogen atoms omitted for clarity. Thermal ellipsoids shown at 50% probability.

The formation of this species is the result of two factors; firstly, the removal of the phenol hydrogen atom prevents the formation of the intramolecular hydrogen bond leaving all four nitrogen atoms to act as metal donors. Secondly, the inclusion of the ethyl phenyl unit which forms  $\pi$ -stacking interactions between itself and the planar pyridyl-thiazole domain promotes the formation of the polymeric unit (Fig. 3). The ability to undergo  $\pi$ -stacking is a useful tool in the formation of self-assembled species and can control the self-assembly of helicates.<sup>18,35</sup>

Reaction of  $L^3$  with  $Ag(BF_4)$  in MeCN gave a colourless solution from which crystals were obtained either by slow diffusion of diisopropyl ether or slow evaporation. Analysis by X-ray crystallography shows that the asymmetric unit cell contains one ligand coordinated to one Ag(I) metal ion via a bidentate pyridyl-thiazole domain (Fig. 4 a)). The remaining bidentate pyridyl-thiazole domain coordinates a different silver metal ion with the two sites bridged by the central -OMe spacer and the bidentate domains arrange themselves in an 'over and under' conformation giving rise to a hexanuclear circular helicate e.g.  $[Ag_6(L^3)_6]^{6+}$  (Fig. 4 b)). The formation of this hexanuclear structure is a consequence of several factors; the two bidentate binding domains are separated by a cresol unit which prevents formation of a mononuclear species. Furthermore, the lack of intramolecular hydrogen bonding results in all four nitrogen atoms coordinating the Ag(I) ions (unlike  $[Ag_2(L^1)_2]^{2+}$ ) and the lack of intermolecular  $\pi$ -stacking prevents formation of a polymeric species (unlike  $[Ag_n(L^1)_n]^{n+}$ ).

As a result of this a hexanuclear species is observed with the nuclearity (i.e. six Ag(I) ions) a consequence of the 2,6-substitution pattern of the central cresol spacer.

This coordination motif is further supplemented by Ag...Ag interactions and it is through these argentophilic interactions that a 3-dimensional polymer develops. Each of the Ag(I) metal ions interacts with another Ag(I) ion, of a different  $[\text{Ag}_6\text{L}_6]^{6+}$  unit, connecting them together into a 3-dimensional infinite honeycomb-like structure of hexanuclear circular helicates. The direction of the Ag...Ag interaction from each Ag(I) ion alternates around the circular helicate pointing 'up and down' with respect to one another in a crown-like fashion (Fig. 4 c)). Resulting in one Ag(I) ion connecting to a Ag(I) ion of a  $[[\text{Ag}_6(\text{L}^3)_6]^{6+}]$  unit above its corresponding unit, the next Ag(I) ion in the circular helicate connects to a Ag(I) ion of a  $[[\text{Ag}_6(\text{L}^3)_6]^{6+}]$  unit below it. As a result, the connectivity of each  $[[\text{Ag}_6(\text{L}^3)_6]^{6+}]$  unit comprises of three alternating interactions with three circular helicates above and three below (Fig. 4 d and e)).<sup>36</sup>

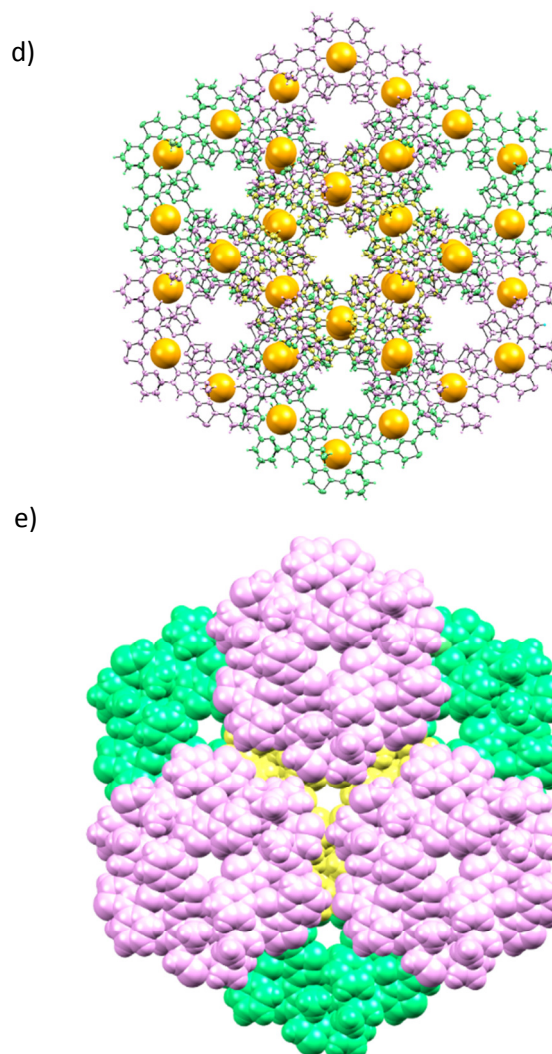
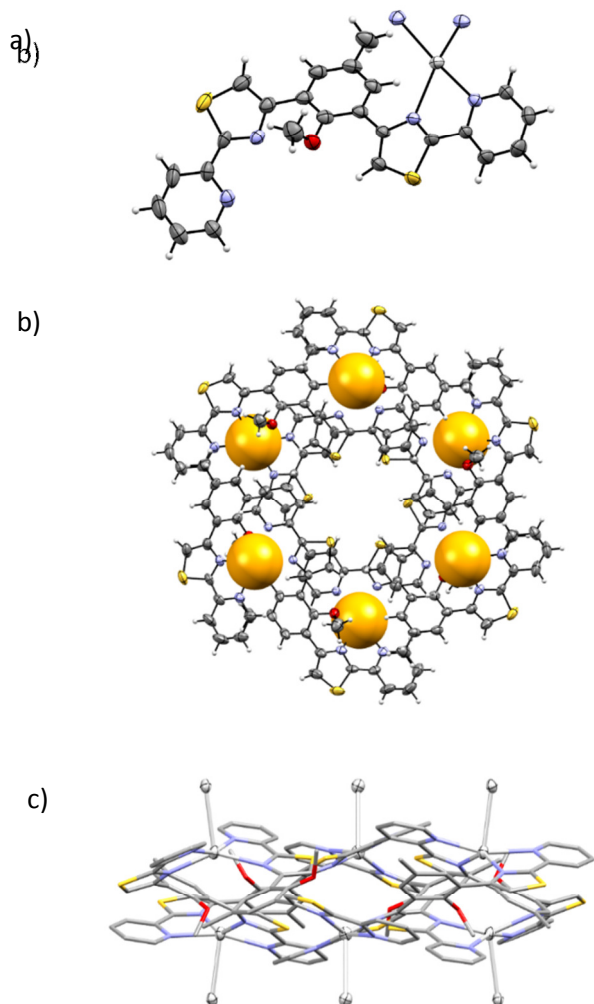


Fig. 4: Crystal structure of the  $[\text{Ag}_6(\text{L}^3)_6]^{6+}$  polymer a) Partial view showing the  $[\text{Ag}(\text{L}^3)]^+$  unit, b) crystal structure of the hexanuclear circular helicate  $[\text{Ag}_6(\text{L}^3)_6]^{6+}$ . Ag(I) atoms have been coloured orange and shown in spacefilling view. c) Side view of the hexanuclear circular helicate  $[\text{Ag}_6(\text{L}^3)_6]^{6+}$  with the Ag...Ag interactions shown as thermal ellipsoids. Hydrogen atoms removed for clarity. d) and e) Crystal structure of the polymeric assembly  $[[\text{Ag}_6(\text{L}^3)_6]^{6+}]_n$  in its polymeric form as a result of Ag...Ag interactions. In d) Ag(I) atoms have been coloured orange and shown in spacefilling view and in e) the assembly is shown entirely in spacefilling view without any highlighting of the Ag(I) ions. Units connected through argentophilic interactions 'above' the central circular helicate (yellow), are coloured pink and those 'below' are coloured green. Thermal ellipsoids in all above figures are shown at 50% probability.

Analysis of  $[\text{Ag}_6(\text{L}^3)_6]^{6+}$  in  $\text{CD}_3\text{CN}$  by  $^1\text{H}$  NMR showed the presence of one major product containing eight different proton environments, indicating a symmetrical ligand as would be expected from the solid-state structure. Analysis by ESI-MS gave an ion at  $m/z$  3735 corresponding to  $\{[\text{Ag}_6(\text{L}^3)_6](\text{BF}_4)_5\}^+$  along with lower molecular weight species e.g.  $\{[\text{Ag}_n(\text{L}^3)_n](\text{BF}_4)_{n-1}\}^+$  where  $n = 1$  to 5. This would suggest that in the solution state a reaction of Ag(I) metal ions with  $\text{L}^3$  forms the circular helicate species  $[\text{Ag}_6(\text{L}^3)_6]^{6+}$  and that the polymeric

effect of the Ag...Ag interactions is only observed as an artefact of the solid state. This would be expected as the Ag...Ag bonds would be easily solvated in solution.

## Conclusions

This work has demonstrated the control and formation of multiple silver-containing metallocsupramolecular complexes based on the same ligand framework (e.g. two bidentate units separated by a 1,3-cresol spacer) via a combination of non-covalent interactions. The formation of the dinuclear double mesocate species  $[\text{Ag}_2(\text{L}^1)_2]^{2+}$  was shown to be a result steric interactions, which prevent the formation of the helicate, and stabilisation of the mesocate via hydrogen bonding interactions. The formation of the helical polymer  $[\text{Ag}_n(\text{L}^2)]_n^{n+}$  was a direct result of replacing the phenol unit with an ethyl phenyl ether. The absence of the phenol hydrogen unit prevents the hydrogen bonding to the thiazole and allows for all four nitrogen donor atoms to coordinate the metal ion, whilst  $\pi$ -stacking interactions between the ethyl phenyl unit and the terminal pyridines of the ligands helps promote the  $\pi$ -stacking of the polymeric structure. The formation of the hexanuclear circular helicate  $[\text{Ag}_6(\text{L}^3)_6]^{6+}$  was a result of the anisole spacer which doesn't undergo hydrogen bonding to the adjacent thiazole (preventing formation of the mesocate) and will not contribute to  $\pi$ -stacking, preventing the linear helicate polymer. Finally, Ag...Ag interactions between the circular helicate units allowed for the 3-dimensional infinite honeycomb-like structure of hexanuclear circular helicates species  $[[\text{Ag}_6(\text{L}^3)_6]^{6+}]_n$  to be formed. It is remarkable that such subtle changes in the ligand framework can give rise to substantially different self-assembled species.

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- Ions are also present in the ESI-MS corresponding to higher oligomers e.g.  $\{[\text{Ag}_n(\text{L}^1)_2](\text{ClO}_4)_{n-1}\}^+$  (where  $n = 3$  and  $4$ ) and we presume that this is due to aggregation in the ESI-MS process.
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- The 3-dimensional polymer could be considered to be a metal organic framework as a dried sample (which still gave a high quality X-ray diffraction pattern) contains voids of approximately  $3500 \text{ \AA}^3$  in the unit cell. However, these voids do not seem readily accessible as a BET isotherm obtained using  $\text{N}_2$  at 77K showed no appreciable surface area.