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Introduction

The synthesis and structural characterisation of coordination polymers has continued to expand as an area of extremely active research in recent years.¹ Interest in applications such as gas sorption and sieving, molecular separation, catalysis and optical properties have brought the study of these materials to the forefront of modern coordination and materials chemistry.² Central to the rational design of such materials is the notion of molecular self-assembly and, more crucially, the inherent reversibility in the formation of metal–ligand bonds.³ Often, the design of supramolecular materials can be governed almost entirely by careful choice of reaction conditions, taking advantage of bond reversibility to favour the formation of one

The influence of anion, ligand geometry and stoichiometry on the structure and dimensionality of a series of Ag^I-bis(cyanobenzyl)piperazine coordination polymers[†]

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Two new bis-(cyanobenzyl)piperazine ligands have been prepared, and have been used to prepare five Ag(i) coordination polymers which have been structurally characterised. Ligand N_N' -bis((4-cyanophenyl)methyl)piperazine L1 gave two structurally related two-dimensional coordination polymers poly-[Ag₂(L1)(CF₃SO₃)₂(C₃H₆O)_{1.5}] **2** when reacted with silver trifluoromethanesulfonate in tetrahydrofuran and acetone, respectively. Compounds **1** and **2** display similar ligand geometries but form different extended networks, as a result of the inclusion of coordinating solvent molecules and the resulting influence on the flexible metal geometry. Reaction of N_N' -bis((3-cyanophenyl)methyl)piperazine L2 with silver ions gave rise to three new structurally characterised species. Complex poly-[Ag₂(L2)(C₃H₆O)₂]₂(PF₆) **3** forms a one-dimensional chain structurally related to **1**. Complex poly-[Ag₂(L2)(C₃H₆O)₂]₂(CF₃SO₃)₂] **4** formed under similar conditions to **3**, except with the inclusion of a coordinating anion which links equivalent chains to those found in **3** into a two-dimensional sheet. Finally, complex poly-[AgL2]CF₃SO₃ **5** was formed simply by altering the reaction stoichiometry, producing a three-dimensional PtS network containing linear, acentric anion channels. Analysis of the structures reveals that the ligand geometries are largely consistent, leading to the extended structures being more influenced by the nature of the anions and solvent molecules.

thermodynamically favoured product amongst many possible kinetic side-products.⁴ For studies investigating the formation of crystalline metal–organic assemblies, Ag(I) is often the metal ion of choice, as its soft Lewis acid character favours reversibility, while a lack of strongly preferred coordination geometries leads to a range of interesting coordination architectures.⁵

A relatively common fragment in organic chemistry, and particularly in pharmaceuticals,⁶ piperazine has seen use as a bridging ligand in coordination polymer synthesis, alongside the related compounds hexamethylenetetramine and DABCO (1,4-diazabicyclo[2.2.2]octane).⁷ Furthermore, the *N*-substituted heterotopic derivatives of piperazine, commonly containing pyridyl, amidopyridyl or phosphonate groups, are becoming increasingly popular.⁸ Interestingly, cyclic alkyl amines such as piperazine possess a low energy barrier to stereochemical inversion, with the result that interconversion between isomers of *N*-substituted cyclic amines can readily take place,⁹ a property which may further lend itself to the self-assembly process. Crucially, the coordinating ability of the piperazine nitrogen atoms is likely to be dependent on the method of functionalisation; conjugation between the nitrogen atom

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[†] Electronic supplementary information (ESI) available: Powder X-ray diffraction plots for L1, L2 and compounds 1–5, additional structural diagrams. CCDC 997441–997447. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ce00816b



and adjacent amido or aryl functionality would be expected to prevent metal coordination from taking place through these centres.

To date, the majority of functionalised piperazine ligands reported have featured pyridyl functional groups, with fewer studies reporting the use of other functionalities.¹⁰ As well as amines and nitrogen heterocycles, nitrile functional groups are also an excellent soft Lewis basic platform for coordinating to Ag(1) in non-coordinating solvents, and heterotopic nitrile-containing ligands are known to form intricate metallosupramolecular architectures on reaction with Ag(I).¹¹ Herein we report the synthesis of two new cyanobenzyl piperazine ligands (Fig. 1), containing both amine and nitrile nitrogen donors. These ligands represent particularly interesting and uncommon examples of divergent heterotopic ligands, being derived from a combination of very long and very short potential bridging distances by virtue of the closely separated piperazine nitrogen atoms and substantial distance between the nitrile groups. We have employed these new ditopic ligands to prepare a series of Ag(1) coordination polymers, whose structures are heavily influenced by the nature and geometry of the donor ligands.

Experimental

Materials and methods

All reagents, solvents and starting materials were purchased from Sigma Aldrich, Alfa Aesar or Merck and were used as received. NMR spectra were recorded on a Bruker AVANCE spectrometer operating at 400 MHz for ¹H and 100 MHz for ¹³C nuclei, with all samples dissolved in CDCl₃ and peaks referenced to the residual solvent peak. Melting points were recorded in air on an Electrothermal melting point apparatus, and are uncorrected. Mass spectrometry was carried out using a Micromass Platform II ESI-MS instrument, with samples dissolved in dichloromethane. Microanalysis was performed by Campbell Microanalytical Laboratory, University of Otago, New Zealand. Infrared spectra were obtained using an Agilent Cary 630 spectrometer equipped with an Attenuated Total Reflectance (ATR) sampler. Bulk phase purity of all crystalline materials was confirmed with X-ray powder diffraction patterns recorded with a Bruker X8 Focus powder diffractometer operating at Cu K α wavelength (1.5418 Å), with samples mounted on a zero-background silicon single crystal stage. Scans were performed at room temperature in the 2θ range 5–55° and compared with predicted patterns based on single crystal data (ESI†).

X-ray crystallography

Refinement and structural information is presented in Table 1. Data collections for all compounds except for 1 and 4 were performed on a Bruker APEX-II diffractometer, using graphitemonochromated Mo K α (λ = 0.71073 Å) radiation, while the diffraction data for 1 and 4 were collected at the Australian Synchrotron on the MX1 beamline, operating at 17.4 keV $(\lambda = 0.7108 \text{ Å})$ with data collections conducted using BluIce control software.¹² Data for compounds 1 and 4 were collected with a 360° scan in Φ , and the crystals were then reoriented and a second 360° scan in Φ was conducted, and the data from both collections merged in order to provide sufficient completeness. Corrected anomalous dispersion values were calculated where necessary using Brennan and Cowan data.13 Diffraction data for L1, L2, 2, 3 and 5 were processed using the Bruker SAINT suite of programs,¹⁴ with multi-scan absorption correction carried out with SADABS,¹⁵ while the remaining diffraction data were processed, reduced and corrected with the XDS software suite.¹⁶ All structures were solved using direct methods with SHELXS and refined on F^2 using all data by full matrix least-squares procedures with SHELXL-97 within OLEX-2.17-19 Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.2 times the isotropic equivalent of their carrier atoms. The functions minimized were $\Sigma w (F_0^2 - F_c^2)$, with $w = [\sigma^2 (F_0^2) +$ $aP_2 + bP]^{-1}$, where $P = [max(F_0)^2 + 2F_c^2]/3$.

Synthesis of N,N'-bis((4-cyanophenyl)methyl)piperazine L1

Piperazine (1.0 g, 11.6 mmol) was added to potassium carbonate (6.4 g, 46.5 mmol), potassium iodide (20 mg, 0.1 mmol) and 4-(chloromethyl)benzonitrile (3.7 g, 24.7 mmol) in 50 mL acetonitrile and the mixture was heated to reflux overnight under a nitrogen atmosphere. On cooling, the mixture was filtered, and the filtrate was concentrated to approximately 10 mL volume in vacuo to give a small batch of colourless crystals (150 mg). The precipitate, comprising a mixture of the product and inorganic salts, was added to 20 mL water, stirred for 10 minutes, and filtered to yield 3.14 g of white powder, which gave identical analysis to the crystalline material. Combined yield 3.29 g (10.4 mmol; 90%); m.p. 210-214 °C; found C, 76.10; H, 6.35; N, 17.80; C₂₀H₂₀N₄ requires C, 75.91; H, 6.38; N, 17.71%; $\delta_{\rm H}$ (400 MHz, CDCl₃) 2.49 (s, 8H), 3.57 (s, 4H), 7.46 (d, 4H, ${}^{3}J_{1} = 8.3$ Hz), 7.62 (d, 4H, ${}^{3}J_{1}$ = 8.2 Hz); δ_{C} (100 MHz, CDCl₃) 53.10, 62.38, 110.91, 118.92, 129.49, 132.11, 144.10; m/z (ES+) 317.1 ([M + H⁺],

Table 1 Crystallographic and refinement information for L1, L2 and complexes 1-5

| | | | | 0 | | | |
|---|--|--|--|--|----------------------------------|--|------------------------------------|
| Compound reference | L1 | L2 | 1 | 2 | 3 | 4 | 5 |
| Chemical formula | $\mathrm{C}_{20}\mathrm{H}_{20}\mathrm{N}_4$ | $\mathrm{C}_{20}\mathrm{H}_{20}\mathrm{N}_4$ | $C_{22}H_{20}Ag_{2}F_{6}N_{4}O_{6}S_{2}$ | $C_{48}H_{52}Ag_{4}F_{6}N_{8}O_{8}S_{2}\cdot 2(CF_{3}O_{3}S)\cdot C_{3}H_{6}O$ | $C_{16}H_{22}AgN_2O_2\cdot F_6P$ | $C_{22}H_{20}Ag_2F_6N_4O_6S_2\cdot 2(C_3H_6O)$ | $C_{20}H_{20}AgN_4 \cdot CF_3O_3S$ |
| Formula mass | 316.40 | 316.40 | 830.28 | 1834.79 | 527.20 | 946.44 | 573.34 |
| Crystal system | Triclinic | Triclinic | Triclinic | Monoclinic | Triclinic | Triclinic | Monoclinic |
| a/ằ | 6.5627(5) | 6.1328(5) | 7.9580(16) | 25.839(6) | 8.2084(4) | 8.2890(17) | 13.6310(8) |
| $b/ m \AA$ | 8.2007(7) | 7.1872(6) | 9.1570(18) | 11.480(3) | 10.3939(4) | 9.838(2) | 16.7804(8) |
| $c/ m \AA$ | 8.5966(7) | 10.0545(9) | 10.069(2) | 24.597(8) | 12.6354(6) | 11.203(2) | 10.9261(6) |
| $\alpha / ^{\circ}$ | 83.164(4) | 78.816(5) | 76.71(3) | 90.00 | 71.597(2) | 102.51(3) | 90.00 |
| <i>B</i> /° | 71.318(3) | 74.898(5) | 84.84(3) | 113.623(13) | 77.611(3) | 102.92(3) | 115.623(2) |
|)//o | 71.589(3) | 79.084(6) | 67.98(3) | 90.00 | 86.597(2) | 93.06(3) | 90.00 |
| $V/Å^3$ | 415.77(6) | 415.21(6) | 662.0(2) | 6685(3) | 999.03(8) | 864.3(3) | 2253.4(2) |
| Temperature/K | 123(2) | 123(2) | 100(2) | 123(2) | 123(2) | 100(2) | 123(2) |
| Radiation source | Mo K α | Μο Κα | Synchrotron | Mo Ka | Μο Κα | Synchrotron | Μο Κα |
| Space group | $P\bar{1}$ | $P\bar{1}$ | Pī | C2/c | $P\bar{1}$ | $P\bar{1}$ | Cc |
| Ζ | 1 | 1 | 1 | 4 | 2 | 1 | 4 |
| No. of reflections measured | 4352 | 4445 | 22 772 | 29608 | 24422 | 29855 | 15 087 |
| No. of independent reflections | 2071 | 1982 | 3324 | 8054 | 5805 | 4279 | 8532 |
| Observed reflections $(I > 2\sigma(I))$ | 1540 | 1406 | 3277 | 4635 | 4520 | 3960 | 7553 |
| $R_{ m int}$ | 0.0249 | 0.0261 | 0.0192 | 0.1157 | 0.0601 | 0.0389 | 0.0312 |
| Final R_1 values (obs. data) | 0.0517 | 0.0500 | 0.0208 | 0.0589 | 0.0397 | 0.0352 | 0.0396 |
| Final w $R(F^2)$ values (obs. data) | 0.1247 | 0.1049 | 0.0494 | 0.1224 | 0.0679 | 0.0895 | 0.0833 |
| Final R_1 values (all data) | 0.0704 | 0.0741 | 0.0211 | 0.1189 | 0.0604 | 0.0385 | 0.0468 |
| Final $wR(F^2)$ values (all data) | 0.1372 | 0.1158 | 0.0496 | 0.1506 | 0.0755 | 0.0916 | 0.0875 |
| | | | | | | | |

calculated for $C_{20}H_{21}N_4^+$ 317.2); $v_{max}(ATR)/cm^{-1}$ 2954w, 2807m, 2219m, 1604m, 1453m, 1343m, 1290m, 1258m, 1156m, 1008s, 841s sh, 806s sh.

Synthesis of N,N'-bis((3-cyanophenyl)methyl)piperazine L2

Piperazine (210 mg, 2.4 mmol) was added to potassium carbonate (2.7 g, 19.5 mmol) and 3-(bromomethyl)benzonitrile (1.0 g, 5.1 mmol) in 40 mL acetonitrile and the mixture was heated to reflux overnight under a nitrogen atmosphere. On cooling, the mixture was filtered and concentrated to approximately 5 mL volume on a rotary evaporator, yielding pale yellow crystals, which were filtered and dried in air. Yield 550 mg (1.7 mmol; 73%). m.p. 120-122 °C; found C, 75.92; H, 6.41; N, 17.69; C₂₀H₂₀N₄ requires C, 75.91; H, 6.38; N, 17.71%; $\delta_{\rm H}$ (400 MHz, CDCl₃) 2.48 (s, 8H), 3.54 (s, 4H), 7.42 (t, 2H, ${}^{3}J_{1} = 7.8$ Hz), 7.53–7.57 (m, 4H, overlapping), 7.66 (s, 2H); $\delta_{\rm C}$ (100 MHz, CDCl₃) 53.01, 61.98, 112.42, 118.94, 129.04, 130.81, 132.41, 133.33, 140.02; m/z (ES+) 339.1 ([M + Na⁺], calculated for $C_{20}H_{20}N_4Na^+$ 339.2), 317.1 ([M + H⁺], calculated for $C_{20}H_{21}N_4^+$ 317.2); $v_{max}(ATR)/cm^{-1}$ 2957w, 2834w, 2774m, 2615m, 2222w, 1457m sh, 1340m sh, 1282m sh, 1126m, 1003m, 828m, 792s sh, 684s sh.

Synthesis of poly-[Ag₂(L1)(CF₃SO₃)₂] 1

To a solution of L1 (10 mg, 32 µmol) in 5 mL tetrahydrofuran was added silver trifluoromethanesulfonate (15 mg, 59 µmol) dissolved in 5 mL tetrahydrofuran. The solution was filtered and the filtrate allowed to stand in a sealed vial for one week. The colourless crystals formed were filtered and dried in air. Yield 15.5 mg (19 µmol; 58%); m.p. 218–221 °C (decomp.); found C, 31.94; H, 2.51; N, 6.50; $C_{22}H_{20}N_4O_6F_6S_2Ag_2$ requires C, 31.83; H, 2.43, N, 6.75%; $v_{max}(ATR)/cm^{-1}$ 2250m, 1608w, 1466m, 1297s, 1226s, 1165m, 1020s, 858s, 807s.

Synthesis of poly- $[Ag_2(L1)(CF_3SO_3)_2(C_3H_6O)_{1.5}]$ 2

To a solution of L1 (10 mg, 32 µmol) in 5 mL acetone was added silver trifluoromethanesulfonate (15 mg, 59 µmol) in 5 mL acetone. The resulting colourless solution was enclosed in darkness and left to stand at room temperature. The resulting colourless crystals were filtered and dried after one week. Yield 9.7 mg (11 µmol; 33%); m.p. 216–220 °C (decomp); found C, 31.07; H, 2.68; N, 6.43; $C_{22}H_{20}N_4O_6F_6S_2Ag_2\cdot H_2O$ requires C, 31.15; H, 2.61; N, 6.60%, consistent with loss of lattice acetone molecules and uptake of water on standing in air; $v_{max}(ATR)/cm^{-1}$ 3443w br, 2237w, 1460w, 1287s, 1163s, 1036s, 983w, 860m, 815m, 759w.

Synthesis of poly-[Ag₂(L2)(C₃H₆O)₂]₂(PF₆) 3

To a solution of L2 (20 mg, 63 μ mol) in 10 mL of acetone was added 64 mg (250 μ mol) of silver hexafluorophosphate dissolved in 10 mL of acetone, and the mixture was filtered and sealed. The colourless crystals which formed within several hours were filtered and dried after 2 days. Yield 24.1 mg (46 μ mol; 36%); m.p. 276–292 °C; found C, 29.46; H, 2.59;

N, 6.70; $C_{20}H_{20}N_4F_{12}P_2Ag_2$ requires C, 29.22; H, 2.45; N, 6.82%, consistent with loss of lattice acetone molecules; v_{max} (ATR)/cm⁻¹ 3067w br, 2236m, 1581m, 1445m sh, 1341m, 1297s sh, 1141m, 1033s, 858s, 807s, 692s.

Synthesis of poly-[Ag₂(L2)(C₃H₈O)₂(CF₃SO₃)₂] 4

To L2 (20 mg, 63 µmol) in 5 mL acetone was added silver trifluoromethanesulfonate (64 mg, 250 µmol) in 5 mL acetone. The mixture was quickly filtered and allowed to stand, giving a fine white precipitate within several minutes. The mixture was sealed and allowed to stand for one week, giving colourless crystals which rapidly lost crystallinity when removed from the solution. Yield 48.4 mg (51 µmol; 81%); m.p. 188–193 °C (decomp.); found C, 30.38; H, 2.78; N, 6.36; $C_{22}H_{20}N_4O_6F_6S_2Ag_2\cdot 2H_2O$ requires C, 30.50; H, 2.79; N, 6.47%, consistent with loss of lattice acetone and uptake of water on standing in air; $v_{max}(ATR)/cm^{-1}$ 3435m br, 2256s, 1638m, 1462w, 1246s, 1158s, 1023s, 898w, 979m.

Synthesis of poly-[AgL2]CF₃SO₃ 5

To L2 (20 mg, 63 µmol) in 5 mL acetone was added silver trifluoromethanesulfonate (16 mg, 63 µmol) in 5 mL acetone. The resulting solution was enclosed in darkness and left at room temperature to crystallise. Colourless crystals were filtered after 48 hours and dried in air. Yield 10.7 mg (19 µmol; 29%); m.p. 185–188 °C; found C, 43.94; H, 3.57; N, 9.65; $C_{42}H_{40}N_8O_6F_6S_2Ag_2$ requires C, 43.99; H, 3.52; N, 9.77%; $\nu_{max}(ATR)/cm^{-1}$ 2834w, 2236w, 1441w, 1264s, 1145s, 1028m sh, 803m, 742m, 662m.

Results and discussion

Structures of L1 and L2

Compounds L1 and L2 were formed by reaction of piperazine with 4-chloromethyl- or 3-bromomethylbenzonitrile, respectively. Each compound was crystallised from hot acetonitrile, and the structures were determined crystallographically, where the diffraction data were solved and refined in the triclinic space group $P\overline{1}$ in both cases. L1 and L2 were observed to display very similar structures in the solid state (Fig. 2); both adopt the expected chair conformation for the central piperazine ring with *trans*-diequatorial orientation of the pendant cyanobenzyl groups. Both structures contain half of one molecule within the asymmetric unit, with inversion centres located at the centre of the piperazine rings.

Similarities are also observed in the extended structures of L1 and L2. For both compounds, the primary intermolecular contacts are offset face-to-face π - π interactions between adjacent cyanophenyl groups, with mean interplanar distances of 3.451(2) and 3.635(2) Å, respectively (ESI,† Fig. S2). In the structure of L1, an additional intermolecular interaction is observed, in the form of a reciprocating pair of C-H…N interactions between the nitrile groups and *ortho* hydrogen atoms of two adjacent cyanophenyl groups, with C…N distance 3.572(2) Å and C-H…N angle 167.68(9)°.²⁰ No other significant intermolecular



Fig. 2 Structures of L1 (left) and L2 (right) with labelling scheme for the unique heteroatoms. Hydrogen atoms omitted for clarity.

interactions were obvious in the structures of L1 or L2, with both forming densely packed molecular arrangements.

Synthesis of Ag(1) complexes of L1 and L2

The syntheses of complexes 1–5 were each achieved by combining solutions of the appropriate ligand and metal salts in acetone or tetrahydrofuran solutions. Each of the crystalline phases were recovered from the sealed solutions within several days. It must be noted that, while the lability of the coordination bonds is beneficial to the self-assembly process, such a property can also promote the formation of mixed crystalline phases, and can lead to instability of the solid materials on extended drying. As such, the identities of the bulk phase materials were primarily confirmed by X-ray powder diffraction (ESI†), as well as infrared spectroscopy and elemental analysis. The conditions for each synthesis were subsequently optimised to avoid the formation of mixed phases. All silver-containing species were prepared and stored in the dark, however no strong light sensitivity was observed.

Structure of *poly*-[Ag₂(L1)(CF₃SO₃)₂] 1

Ligand L1 was combined with two equivalents of silver trifluoromethanesulfonate in tetrahydrofuran, and the resulting mixture was allowed to stand for several days, yielding colourless single crystals which were isolated by filtration. Analysis of the material by single crystal X-ray diffraction yielded data which were solved and refined in the triclinic space group $P\bar{1}$, revealing a compound of the formula poly- $[Ag_2(L1)(CF_3SO_3)_2]$ 1. The asymmetric unit of 1 contains one Ag(1) ion, a trifluoromethanesulfonate anion and half of an L1 molecule, with the remaining symmetry equivalent atom sites generated by an inversion centre within the piperazine ring. Each silver ion displays a highly distorted sawhorse-type four-coordinate geometry, and is coordinated by two equivalent triflate oxygen atoms, one piperazine nitrogen atom and one nitrogen atom from a nitrile group (Fig. 3). The coordinating triflate oxygen atoms bridge between two symmetry-related silver ions to generate a four-membered ring. The Ag-O bonds, at 2.5978(13) and 2.5306(14) Å, are considerably longer than the Ag-N bonds (2.243(2) and 2.285(2) Å for nitrile and amine coordination, respectively), consistent with both



Fig. 3 Structure of **1** with partial heteroatom labelling scheme. Hydrogen atoms omitted for clarity. Symmetry codes used to generate equivalent atoms: i) 1 - x, y, 1 - z; ii) 1 - x, 1 - y, -z; iii) -x, 1 - y, -z.

the weak nature of triflate as a ligand and the bridging coordination mode.

As would be expected by steric considerations, the piperazine rings in 1 display a chair conformation, with silver ions occupying the axial positions of the two crystallographically equivalent amine sites. Emanating from the equatorial positions, the benzonitrile arms adopt a similar geometry to that observed in the structure of the free ligand, with both nitriles coordinating to silver ions, with the result that each molecule of L1 connects four silver ions. The extended structure of 1 is a two-dimensional sheet, in which chains of L1-linked silver ions are extended into a second dimension by bridging through triflate oxygen atoms (Fig. 4). Adjacent layers associate by slight overlap of parallel phenyl ring π -systems, with a mean interplanar distance of 3.420(3) Å, and are further supported by interdigitation of triflate CF₃ groups (ESI,† Fig. S3).

Structure of *poly*-[Ag₂(L1)(CF₃SO₃)₂(C₃H₆O)_{1.5}] 2

When ligand L1 was reacted with silver trifluoromethanesulfonate in acetone rather than tetrahydrofuran, a different crystalline material, *poly*-[Ag₂(L1)(CF₃SO₃)₂(C₃H₆O)_{1.5}] 2 was isolated after standing for several days, and the X-ray diffraction data were solved and refined in the monoclinic space group C2/c. The asymmetric unit was found to contain two non-equivalent



Fig. 4 Extended structure of 1 viewed perpendicular to the twodimensional network. Hydrogen atoms omitted for clarity.

silver ions, one complete molecule of L1, two triflate anions and acetone molecules disordered over three unique sites with a total occupancy of 1.5 molecules per asymmetric unit. As was the case in complex 1, L1 coordinates to four silver ions through amine and nitrile donors. Ag1 is best described as having a 3 coordinate, T-shaped geometry, with strong bonds to nitrile, amine and triflate oxygen donors, giving bond lengths of 2.216(5), 2.281(5) and 2.491(5) Å, respectively (Fig. 5). In addition, a weak interaction to an oxygen atom of a second triflate anion is observed, with a Ag–O distance of 2.728(6) Å.

The Ag1 coordination sphere is capped by an interaction with a phenyl ring C9–H9 group engaged in a possible agostic interaction,²¹ defined by a relatively long Ag–H distance of 2.85 Å and a C–H···Ag angle 98.7°. The more strongly bound triflate anion of the two involved in bonding to Ag1 bridges to Ag2 in a μ^2 - κ O: κ O' fashion, where the bond to Ag2 is somewhat longer, at 2.636(4) Å. The coordination sphere of Ag2 is completed by one nitrile and one piperazine amine group (Ag–N bond lengths 2.220(5) and 2.284(5) Å, respectively), and one oxygen atom from a coordinating acetone molecule disordered over two positions. Further interaction is provided by a second disordered acetone molecule, which provides a weak interaction to either of two symmetry-related Ag2 sites (Ag2–O50 distance 2.744(11) Å).

Although the geometry and coordination pattern of the L1 ligand is similar to that observed in the structure of 1, the extended structure of 2 displays several key differences. Firstly, the linear chains of L1-linked silver ions present in 1 are prohibited from forming in 2, due to a mismatch in geometry of the two silver sites caused by the presence of coordinating acetone molecules. This results in an inclined orientation of the two L1 units connected to each silver ion, rather than the parallel orientation required for chain formation (Fig. 6). The divergence of adjacent L1 molecules gives rise to a two-dimensional sheet when extended through L1 links only. These networks are further linked by the bridging triflate ions, which join parallel pairs of sheets, giving the bilayer



Fig. 5 Structure of **2** with partial labelling scheme. Solvent disorder and hydrogen atoms omitted for clarity. Symmetry codes used to generate equivalent atoms: i) +x, 1 - y, -1/2 + z; ii) +x, 2 - y, 1/2 + z; iii) 1/2 - x, -1/2 + y, 1/2 - z.



Fig. 6 (top) Extended structure of compound 2. Hydrogen atoms, solvent disorder and acetone carbon atoms omitted for clarity. (bottom) Topological representation of the bilayer sheet structure of 2. L1 nodes coloured blue, silver nodes coloured grey, with green linkages representing triflate bridges.

structure shown in Fig. 6. Surprisingly, no strong π - π interactions were observed in the structure, either within the networks or between adjacent layers, which associate with interdigitation of both terminal triflate groups and acetone ligands. Both elemental analysis and infrared spectroscopy showed the loss of lattice acetone molecules and association of atmospheric water on standing in air.

Structure of poly-[Ag₂(L2)(C₃H₆O)₂]₂(PF₆) 3

Single crystals of poly-[Ag₂(L2)(C₃H₆O)₂]₂(PF₆) 3 were formed by reaction of ligand L2 with silver hexafluorophosphate in acetone. Analysis of the structure by single crystal X-ray diffraction provided a structure model in the triclinic space group $P\bar{1}$, in which the asymmetric unit contains half of an L2 molecule, one silver ion, two coordinating acetone molecules and a non-coordinating hexafluorophosphate anion. The silver ion displays an approximately tetrahedral geometry, with coordination to piperazine amine and nitrile groups at Ag-N distances 2.254(2) and 2.231(3) Å, respectively. As expected, the coordinating acetone molecules are comparatively weakly bound, with Ag-O bond lengths of 2.464(2) and 2.452(2) Å. As was the case with the previous structures, the piperazine ligand itself exists in a chair conformation, with an inversion centre located within the six-membered ring. The pendant alkyl arms occupy equatorial positions of the piperazine nitrogen sites, while coordination to the four equivalent silver ions takes place

with axial geometry from the amines, as well as through both nitrile groups (Fig. 7).

When extended through the bridging L2 molecules, compound 3 forms a one-dimensional chain in which each unique half of an L2 molecule forms a loop with an adjacent fragment via two silver ions, as shown in Fig. 7. Despite the silver ion geometry in 3 being comparable to the acetonecoordinated fragment in 2, the divergent orientation of the ligand axes around each silver ion, which gave rise to higher dimensionality in 2, is offset by the bent geometry of the coordination sites of ligand L2, which allows the formation of a lower dimensional assembly. Although the geometry of the phenyl groups within each chain prohibits any intramolecular π - π interaction, adjacent chains associate by way of parallel offset face-to-face interactions, with mean interplanar distance 3.575(3) Å. The combination of these interactions with the chain propagation direction gives a series of layers parallel to the crystallographic ac plane, with adjacent sheets separated by interstitial layers of hexafluorophosphate anions (ESI⁺).

Structure of poly-[Ag₂(L2)(C₃H₈O)₂(CF₃SO₃)₂] 4

Following the elucidation of the structure of 3, containing a non-coordinating anion, ligand L2 was reacted with silver trifluoromethanesulfonate in acetone, with the expectation of additional dimensionality provided by a potential bridging functionality, as seen in the structures of 1 and 2. The diffraction data for 4 were solved and refined in the triclinic space group $P\bar{1}$, and revealed a structure of the formula *poly*-[Ag₂(L2)(C₃H₈O)₂(CF₃SO₃)₂]. The asymmetric unit of 4 contains one silver ion in a sawhorse geometry, where the *trans* positions are occupied by a piperazine amine and a nitrile group, with bond distances 2.288(2) and 2.208(3) Å, respectively. The equatorial sites are filled by two triflate oxygen atoms, at Ag–O distances 2.594(3) and 2.536(2) Å, and a weakly associated acetone molecule, with Ag–O distance 2.983(2) Å. As was observed in the structure of 2, the triflate ions bridge between two silver ions in a μ^2 - κ O: κ O' fashion, forming an 8-membered metallocycle, shown in Fig. 8.

Consistent with the structures observed for compounds 1–3, each of the four nitrogen donor sites in L2 is occupied by equivalent silver ions. Inspection of the extended structure of 4 reveals several other similarities to the previous structures. When extended through L2 linkages alone, a one-dimensional chain equivalent to that observed in 3 results. However, where the coordination sphere of 3 was completed by acetone molecules, the presence of bridging triflate anions in 4 provides links into a second dimension. The resulting two-dimensional sheet structure is reminiscent of the structure of 1, with slight variation in both ligand geometry and anion bridging mode (Fig. 9). However,



Fig. 7 (top) Structure of **3** with partial atom labelling scheme. Hydrogen atoms omitted for clarity. Symmetry codes used to generate equivalent atoms: i) 2 - x, -y, -z. (bottom) Extended structure of **3** showing two adjacent 1-dimensional chains. Hydrogen atoms omitted for clarity.



Fig. 8 Structure of **4** with partial atom labelling scheme. Hydrogen atoms omitted for clarity. Symmetry codes used to generate equivalent atoms: i) -x, 1 - y, 1 - z; ii) -x, 2 - y, 1 - z.



Fig. 9 Extended structure of 4 viewed perpendicular to the twodimensional sheet. Hydrogen atoms omitted for clarity.

whereas the sheets in 1 closely associated with one another through multiple π - π interactions, no particular attractive interactions are observed between the layers of 4, where acetone molecules and anion trifluoromethyl groups protrude towards the inter-layer regions. On removal from the mother liquor, the crystals of 4 were observed to rapidly lose single crystallinity, most likely by displacement of these interstitial acetone molecules. Powder X-ray diffraction showed loss of bulk crystallinity immediately on drying in air, with only broad and low-intensity peaks observed corresponding to a poorly crystalline desolvated phase, which we were unable to further characterise crystallographically. Similar to the case in 2, elemental analysis on the amorphous air-dried sample of 4 showed loss of lattice acetone molecules and uptake of atmospheric water.

Structure of poly-[Ag(L2)]CF₃SO₃ 5

In an attempt to increase the dimensionality of the polymeric Ag-L2 adducts, ligand L2 was reacted with silver trifluoromethanesulfonate in a 1:1 ratio. Colourless crystals deposited overnight, which were analysed by single crystal X-ray diffraction. The diffraction data, solved in the monoclinic space group Cc, revealed an asymmetric unit containing one complete molecule of L2 coordinating through each nitrogen atom to a single silver ion, with a non-coordinating triflate counterion. The geometry of the silver ion is best described as highly distorted tetrahedral, where the four coordination sites are filled by the four unique nitrogen donors from L2 (Fig. 10). Each of the Ag-N bond lengths falls in the range 2.315(3)-2.421(4) Å, with slightly shorter bonds being provided by the amine donors compared to the nitriles. The geometry of the L2 molecule is comparable to the aforementioned examples, where the chair conformation is adopted with axially coordinated silver ions, however each cyanobenzyl group in 5 is twisted about the N-CH₂ bonds in a trans orientation to the silver ions. This arrangement, in contrast to the approximately cis oriented species displayed previously, imparts a greater divergence on the overall assembly, and prevents the formation of complementary loops leading to one-dimensional features as observed in the previous structures.



Fig. 10 Structure of 5 with partial labelling scheme. Hydrogen atoms omitted for clarity. Symmetry codes used to generate equivalent atoms: i) +x, 1 - y, -1/2 + z; ii) 1/2 - x, -1/2 + y, +z; iii) -1/2 + x, 1/2 - y, +z.

When extended through the divergent Ag-L2 linkages, the structure of 5 takes the form of a three-dimensional polymer. Considering both the ligand and metal ion as four-connected nodes, the network is described by the PtS topology (Fig. 11). The nodal geometries involved are well matched to the PtS network, as the L2 nodes, visualised at the centroid of the piperazine ring, adopt a distorted square planar connectivity, while the silver ion nodes connect in a distorted tetrahedral fashion. The network is somewhat distorted by the large variations in internodal distance, caused by the substantially different bridging distances imparted by L2.

Interestingly, the presence of the non-coordinating triflate counterions in 5 gives rise to a series of anion channels within the structure, oriented parallel to the crystallographic [1,0,1] vector. Although the cationic network itself displays additional symmetry in the form of a twofold axis and corresponding inversion centre located within the piperazine ring, the extra symmetry is broken by the ordering of the anions, whose directionality within the channels enforces an overall noncentric structure. When the synthesis was repeated using the higher symmetry anion hexafluorophosphate, an equivalent network was formed, however a high quality structure



Fig. 11 (top) Topological representation of the PtS network within 5 viewed slightly offset from the [1,1,0] vector, where blue nodes represent L2 units and grey nodes represent Ag ions. (bottom) Extended structure of 5 viewed along the [1,0,1] vector, parallel to the anion channels.

model was unable to be elucidated from the single crystal data. We ascribe this difficulty to incommensurate ordering of the anion channels, which align with the primitive c axis, preventing cell indexing. Instead, the identity of the structure was confirmed using X-ray powder diffraction, which showed the material to be identical in the bulk phase to compound 5 (ESI†).

Discussion

Close inspection of the structures of compounds 1–5 reveals several interesting trends. The presence of the recurring looped chain structural motif in 1, 3 and 4 suggests a clear preference for the entropically favoured low-dimensionality assembly in the first instance. Despite the differing ligand geometries, the structures of 1 and 4 are very closely related, and effectively differ only by the trifluoromethanesulfonate bridging mode and the presence of a weakly bound acetone molecule in 4. Using tetrahydrofuran as the solvent for the synthesis of 1 prevented the addition of coordinating acetone, observed in 2–4, the presence of which altered the steric environment in 2 sufficiently to force the formation of a different extended structure.

A structural dependence on reaction stoichiometry was not observed for L1, despite numerous attempts to generate an analogous network to 5, instead only giving phases 1 and 2 at metal:ligand ratios from 2:1 to 1:2. However, as described above, altering the stoichiometry for silver triflate and hexafluorophosphate adducts of L2 had the effect of forming a higher dimensional assembly, where the silver coordination sphere was saturated entirely by L2 binding sites.

The similarities in ligand geometry and binding mode within all five structures can be highlighted by examination of the Ag-Ag distances resulting from bridging through piperazine and through the two nitrile arms. In all cases, L1 and L2 display the same coordination habit, linking two silver ions in a trans-diaxial mode through the piperazine ring and two additional silver ions through the nitrile arms. The Ag-Ag distances across the piperazine bridges are approximately constant throughout all structures, falling in the range 5.79-5.99 Å. The Ag-Ag distances for silver ions linked by benzonitrile arms display some variation between L1 and L2, as expected, with Ag-Ag distances in the range 21.24-21.48 Å for 1 and 2 and 19.28-19.76 Å for 3-5. Allowing for the discrepancy caused by the different phenyl substitution patterns between L1 and L2, these values show remarkable consistency, given the variability in the extended structures.

The divergence of the L2 geometry in 5 compared to the other structures is revealed by examining the orientation of the flexibly linked cyanobenzyl groups. In structures 1–4, a convergent-type geometry conducive to the formation of dinuclear loops is adopted by the L1 and L2 ligands, which can be rationalised by the small Ag–N–CH₂–C torsion angles, all of which fall in the range 40–60° (ESI,† Fig. S1). The opposite case is observed in 5, where the cyanobenzyl groups are oriented in the opposite direction to the nearby piperazine-bound silver ions (θ = 176.9–177.9°), effectively preventing the formation of

a simple low-dimensional structure. One possible origin of this conformational change is an increase in steric crowding around the coordination sphere by incorporation of a second coordinating piperazine, forcing a ligand rearrangement. Such a coordination mode was not observed in structures 1–4, which instead featured anion or solvent coordination to complete the silver coordination spheres.

Conclusions

We have prepared and characterised two new bis-cyanophenyl piperazine ligands L1 and L2, and investigated their coordination behaviour in the presence of Ag(I) ions. Ligand L1 produced two related two-dimensional polymers, *poly*- $[Ag_2(L1)(CF_3SO_3)_2]$ 1 and *poly*- $[Ag_2(L1)(CF_3SO_3)_2(C_3H_6O)_{1.5}]$ 2, when reacted with silver trifluoromethanesulfonate in tetrahydrofuran or acetone, respectively. The two structures displayed very similar ligand geometries, however they differed in the coordination of solvent molecules to the Ag(I) ion in compound 2, forcing a reorientation of the L1 donor atoms around the coordination sphere. This small change caused a significant difference to the nature of the extended network between 1 and 2.

Three coordination polymers were prepared from L2, by reaction with silver trifluoromethanesulfonate or hexafluorophosphate in acetone. The complexes poly-[Ag₂(L2)(C₃H₆O)₂]₂(PF₆) 3 and *poly*-[Ag₂(L2)(C₃H₈O)₂(CF₃SO₃)₂] 4 were structurally related materials, where the one-dimensional chains present in 3 were linked into a two-dimensional layer by incorporation of the bridging trifluoromethanesulfonate anion in 4. Finally, complex *poly*- $[Ag(L2)]CF_3SO_3$ 5 was prepared by altering the stoichiometry of the reaction between L2 and silver trifluoromethanesulfonate. Complex 5 displays a three-dimensional PtS topology and contains one-dimensional anion channels in which the noncentric ordering of the trifluoromethanesulfonate species imposes lower crystallographic symmetry on the overall assembly. The structural features present in complexes 1 to 5 were rationalised by examination of the key structural feature of the ligand geometry, especially the torsion angle describing the twist of the pendant aromatic arms relative to the conserved Ag-N(piperazine) bonding arrangement. The variations in coordination tendency between the anions and solvents employed in the study were also explored.

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