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Engineering silver(I) coordination networks through hydrogen bonding

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The silver(I) coordination networks [Ag_2(μ-O_2CCF_3)$_2$(μ-NN)$_2$]$_\infty$ exist as a polymer of macrocycles or a double-stranded polymer when NN = 1,2-C_6H_4{NHC(O)-4-C_5H_4N}$_2$ or 1,2-C_6H_4{NHC(O)-3-C_5H_4N}$_2$, respectively. Crystal engineering of the polymers is achieved through interchain hydrogen bonds.

The combination of dynamic coordination chemistry with non-covalent interactions, such as hydrogen bonding, provides a powerful method for creating complex structures from simple building blocks.[1–6] By incorporating hydrogen bonding amide groups into bis(pyridyl) ligands, which are known to form networks with silver(I) salts through dynamic coordinate bonds,[7,8] it should be possible to use the known patterns of self-assembly through hydrogen bonding between amide units to further engineer the solid-state structures.[4] Several beautiful examples have been reported recently[6] and this article further demonstrates the potential of the approach by reporting two remarkable network structures from the U-shaped bis(amido-4-pyridyl) and bis(amido-3-pyridyl) ligands 1,2-C_6H_4{NHC(O)-4-C_5H_4N}$_2$ (**1a**) and 1,2-C_6H_4{NHC(O)-3-C_5H_4N}$_2$ (**1b**), shown in Chart 1.

The ligand **1a** exists in a chiral conformation in the solid state (**A** and **B**; Chart 1) and intermolecular hydrogen bonding leads to a ribbon structure with alternating conformers, ···**A**···**B**···**A**···**B**···, in the solid state (Chart 1). Similar head-to-tail association is found in the new network structures reported below and allows an element of crystal engineering.

Reaction of ligands **1a** and **1b** with AgO_2CCF_3 gave the polymeric complexes [Ag_2(μ-O_2CCF_3)$_2$(μ-**1a**)$_2$]$_\infty$ (**2a**) and [Ag_2(μ-O_2CCF_3)$_2$(μ-**1b**)$_2$]$_\infty$ (**2b**), which were isolated as very sparingly soluble white solids. Since the isolated complexes were so sparingly soluble, crystals of **2a** and **2b** were grown by diffusion of a tetrahydrofuran–methanol solution of AgO_2CCF_3 into dichloromethane–methanol solutions of **1a** and **1b**.† It is useful in discussing the complex structures of these compounds to consider them to self-assemble in a hierarchical fashion,[9] first through the dipyridyl silver(I) bonds, then through the trifluoroacetate silver(I) bonds and, finally, through the hydrogen bonding, but this does not presume that the associated bond energies necessarily follow this sequence.

In complex **2a**, the dipyridyl ligands and silver(I) ions form macrocycles, [Ag_2(μ-**1a**)$_2$]$^{2+}$, that are connected by pairs of μ_2-η^1-trifluoroacetate ligands to form the one-dimensional polymer [Ag_2(μ-O_2CCF_3)$_2$(μ-**1a**)$_2$]$_\infty$, which has tetrahedral silver(I) centres, as shown in Fig. 1(a). Each [Ag_2(μ-**1a**)$_2$]$^{2+}$ macrocycle contains one ligand in conformation **A** and one in conformation **B** (colour coded red and blue), and they further associate through amide–amide hydrogen bonds [N(2)···O(1B) = 2.788(4) Å] to give a three-dimensional network [Fig. 1(b)]. The hydrogen bonding occurs between amide groups of ligands on adjacent chains in a manner analogous to the head-to-tail ···**A**···**B**···**A**···**B**··· pattern of the free ligand **1a**. Thus, **A** ligands of one polymer chain are sandwiched between **B** ligands from two adjacent polymer chains, and *vice versa*, so that propagation occurs along the *c* axis in an ···**A**···**B**···**A**···**B**··· fashion. Since each polymer is overlapped by polymers at the top (**A** ligands) and bottom (**B** ligands) of the chain, propagation of the network also occurs along the *b* axis and a beautiful three-dimensional network is formed [Fig. 1(b)].

In complex **2b**, the dipyridyl ligands and silver(I) ions form polymeric chains [Ag_2(μ-**1b**)$_2$]$_n^{2n+}$ in which all ligands **1b** have the same conformation, **A** or **B** [red or blue in Fig. 2(a)]. Pairs of polymer chains are then connected by pairs of μ_2-η^1-trifluor-

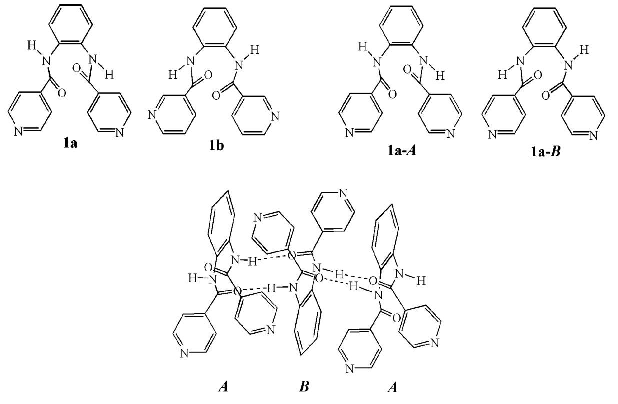

Chart 1 (Top left) Ligands **1a** and **1b**. (Top right) C_2 conformations **A** and **B** of ligand **1a**. (Bottom) Head-to-tail ···**A**···**B**···**A**···**B**··· hydrogen bonding pattern found for **1a**.

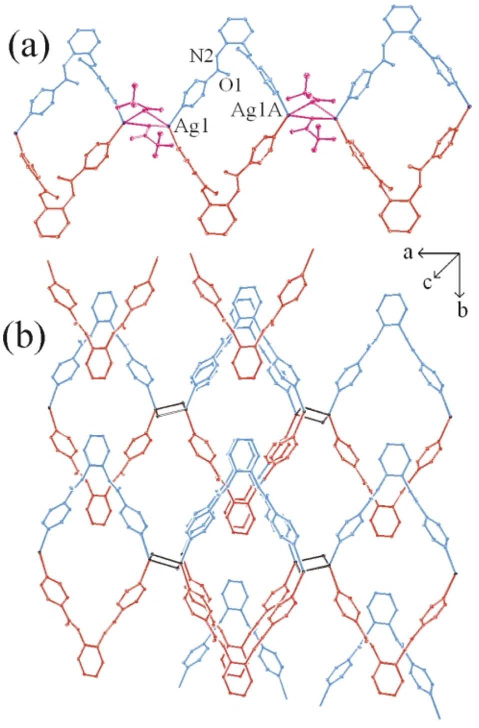

Fig. 1 Structure of **2a**: (a) polymer of disilver rings with conformers **A** and **B** of ligand **1a** colour coded red and blue; (b) three-dimensional network formed through amide–amide hydrogen bonds [N(2)···O(1B) = 2.788(4) Å; symmetry code: $x - 1/2, -y + 3/2, z$]. Only the bridging oxygen atom of the trifluoroacetate groups is shown.

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oacetate ligands to form the double-stranded polymer $[Ag_2(\mu\text{-}O_2CCF_3)_2(\mu\text{-}\mathbf{1b})_2]_\infty$, as shown in Fig. 2(a). Since each double-stranded polymer contains one strand composed of **A** ligands and one composed of **B** ligands, the overall structure is racemic. The bridging anions in **2b** also close 32-membered macrocycles, $Ag_4O_2(\mathbf{1b})_2$, compared to the 30-membered macrocycles, $Ag_2(\mathbf{1a})_2$, in **2a** (Fig. 1 and 2). Finally, the double-stranded polymer chains associate through amide–amide hydrogen bonds [N(2)···O(2A) = 2.785(5) Å, N(3)···O(1A) = 2.762(5) Å] to form a three-dimensional network [Fig. 2(b)]. This hydrogen bonding gives a very similar head-to-tail ···**A**···**B**···**A**···**B**··· pattern to that found in complex **2a** [compare Fig. 1(b) and 2(b)] and so a related network structure is formed.

Complexes **2a** and **2b** were also characterised by elemental analysis and ESI-MS. The elemental analyses show that the stoichiometry of the bulk reaction products is the same as that of the single crystals, with loss of the loosely bound solvate molecules.‡ The ESI-MS of a dilute CH_2Cl_2–methanol solution of complex **2a** (reported for the ^{107}Ag isotope) showed peaks at *m*/*z* 425, 645, 743 and 963, corresponding to $[Ag\mathbf{1a}]^+$, $[Ag_2(O_2CCF_3)\mathbf{1a}]^+$, $[Ag(\mathbf{1a})_2]^+$ and $[Ag_2(O_2CCF_3)(\mathbf{1a})_2]^+$, respectively. Similarly, the ESI-MS of a solution of **2b** showed peaks at *m*/*z* 425, 645, 743, 849, 955 and 963, corresponding to $[Ag\mathbf{1b}]^+$, $[Ag_2(O_2CCF_3)\mathbf{1b}]^+$, $[Ag(\mathbf{1b})_2]^+$, $[Ag_2(\mathbf{1b})_2 - H]^+$, $[Ag_3(\mathbf{1b})_2 - 2H]^+$ and $[Ag_2(O_2CCF_3)(\mathbf{1a})_2]^+$, respectively. The ESI-MS data therefore suggest that similar low molecular mass chains or macrocycles are present in solution and that the elegant three-dimensional coordination networks self-assemble on crystallisation. We note that the polymer chains found in **2b** can be considered to be formed by ring-opening polymerisation of the macrocycles found in **2a** and that the energy difference between rings and chains, arising from substitution of 3- and 4-pyridyl substituents in the ligands, is probably small. These are the first examples of silver(I) networks formed by complementary self-assembly using bipyridine ligands, anions and hydrogen-bonding amide groups. This work supports the view that the strategy of combining dynamic coordination chemistry with hydrogen bonding to assemble novel networks has great potential in the design of molecular materials.[6]

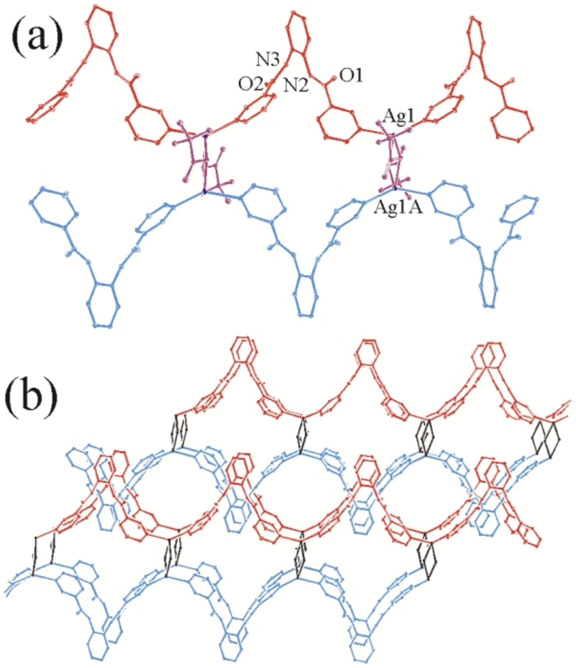

Fig. 2 Structure of **2b**: (a) double-stranded polymer with conformers **A** and **B** of ligand **1b** colour coded red and blue; (b) three-dimensional network formed through amide–amide hydrogen bonds [N(2)···O(2A) = 2.785(5) Å, N(3)···O(1A) = 2.762(5) Å; symmetry codes: (i) $-x + 2, -y + 1, -z$, (ii) $-x + 3, -y + 1, -z$,). Only the bridging oxygen atom of the trifluoroacetate groups is shown. There are also weak CH···O (trifluoroacetate) interactions that will be discussed elsewhere.

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Notes and references

† *Crystal data* for $\mathbf{2a}\cdot 2.5(ClCH_2CH_2Cl)$: $C_{45}H_{36}Ag_2Cl_5F_6N_8O_8$, M = 1323.813, monoclinic, $C2/m$, a = 9.4067(19), b = 24.330(5), c = 11.965(2) Å, β = 98.8(3)°, V = 2704.8(9) Å^3, Z = 2, $R1$ = 0.0552, $wR2$ = 0.1576 for data with $I > 2\sigma(I)$ at 150 K. For $\mathbf{2b}\cdot 1.5(CH_2Cl_2)\cdot(MeOH)$: $C_{42.50}H_{35}Ag_2Cl_3F_6N_8O_9$, M = 1237.88, triclinic, $P\bar{1}$, a = 9.3701(19), b = 12.076(2), c = 12.400(3) Å, α = 88.01(3), β = 85.14(3), γ = 73.19(3)°, V = 1338.4(5) Å^3, Z = 1, $R1$ = 0.0612, $wR2$ = 0.1700 for data with $I > 2\sigma(I)$ at 150 K In each case, the solvate molecules occupy the channels in the lattice. CCDC 229152 and 229153. See http://www.rsc.org/suppdata/cc/b4/b400523f/ for crystallographic data in CIF or other electronic format.

‡ *Elemental analysis data* for **2a**: anal. calcd (%) for $C_{20}H_{14}N_4AgF_3O_4$: C 44.55, H 2.62, N 10.39; found: C 44.10, H 2.41, N 10.23. For **2b**: anal. calcd (%) for $C_{20}H_{14}N_4AgF_3O_4$: C 44.55, H 2.62, N 10.39; found: C 43.98, H 2.39, N 9.95.

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