Supramolecular assembly of low-dimensional silver(I) architectures *via* amide–amide hydrogen bonds

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The ligand nicotinamide (L) is used to propagate the linear coordination geometry of AgL_2 into 1-D and 2-D assemblies *via* a combination of coordinate covalent bonds and specific intermolecular hydrogen-bond interactions; the precise nature of the resulting lamellar structures are also influenced by the nature of the counterion.

Some recent efforts in the field of crystal engineering have focused on the predictable assembly of organic molecular solids *via* intermolecular interactions,[1] and it has become clear that certain functional groups *e.g.* carboxylic acids and amides, are reliable, robust connectors for the formation of hydrogen-bonded organic networks.[2] However, relatively little work has been done in constructing predictable assemblies of coordination compounds *via* directional intermolecular interactions.[3] Ordered assemblies of transition metal complexes (*e.g.* 'coordination polymers'[4]) are being studied for their potential as useful conductive, porous and magnetic materials.[5] From a crystal engineering standpoint, the advantage of using transition metals is that the shape of the main building unit can be controlled by using a metal–ligand system that is known to exhibit a desired coordination geometry. A specific geometry can then be propagated throughout the crystal structure by attaching substituents (intermolecular connectors) to the ligands. In order to probe the strength and reliability of various intermolecular connectors, a low-dimensional metal–ligand system is a convenient starting point, as this may allow us to drive the assembly of linear coordination complexes into one or two dimensions in the crystal lattice *via* specific intermolecular interactions. Silver(I) is one of the few metal ions that commonly displays linear coordination, thus AgL_2 complexes of silver(I) with pyridine derivatives provide the required low-dimensional building blocks.[6] The amide functionality is an appropriate intermolecular connector for this study,[7] in part due to its well known ability to form hydrogen-bonding networks in organic molecular solids,[8] and also because it is unlikely that silver(I) ions will coordinate to either the amide carbonyl oxygen or amine nitrogen atoms in the presence of a pyridine nitrogen. In order to also investigate the influence of the steric requirements and hydrogen-bonding ability of the counter ion on the supramolecular assembly, we have initiated a systematic structural study of a family of silver complexes. We now report the X-ray single crystal structures of three new compounds,[9] $[Ag(C_5H_4NCONH_2)_2][O_3SCF_3]$ **1**, $[Ag(C_5H_4NCONH_2)_2][BF_4]$ **2** and $[Ag(C_5H_4NCONH_2)_2][PF_6]$ **3**, which contain infinite low-dimensional architectures, assembled through intermolecular hydrogen bonds.‡

The reaction of silver(I) triflate with nicotinamide leads to the formation of dinicotinamidesilver(I) triflate **1** (mp 183–185 °C), where the cationic complex contains a silver ion coordination to two nicotinamide ligands in a near-linear fashion, L–Ag–L 174.29(8)°. As expected, the coordination to the silver ion is through the ring nitrogen atoms. The 1-D geometry of the complex cation is propagated in the solid state through amide–amide hydrogen bonds [N···O 2.920(3) Å], leading to infinite $C_1^1(12)$ chains.[10] Neighbouring chains are linked through symmetry related hydrogen bonds, r(N···O) = 2.898(3) Å, forming a 'head-to-head' $R_2^2(8)$ motif. These two intermolecular interactions create an infinite ladder-like arrangement (Fig. 1). There are no further hydrogen-bond interactions between adjacent cationic ladders. The anion acts as a cross-link between two cationic ladders *via* weak hydrogen bonds to the two remaining amide hydrogen atoms, r(N···O) = 3.094(3) and 3.179(3) Å. Thus the presence of a triflate ion, which has oxygen atoms readily available as hydrogen-bond acceptors, does not disrupt the formation of the intended ligand–ligand hydrogen bonds, and the amide functionalities propagate a linear assembly of the silver complexes.

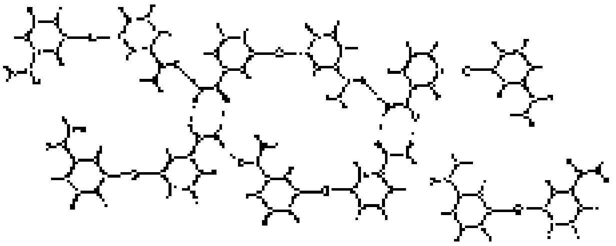

Fig. 1 Infinite 1D ladder motif in **1**, constructed *via* $C_1^1(12)$ and $R_2^2(8)$ hydrogen bonds between linear cationic moieties

Reaction of silver(I) tetrafluoroborate with nicotinamide yields the linear complex, dinicotinamidesilver(I) tetrafluoroborate **2** (mp 217–220 °C), where again the silver ion is coordinated to two ligands in a linear fashion, N–Ag–N [177.3(2)°]. However, in this structure, two unique amide–amide hydrogen bonds, r(N···O) = 2.966(7) and 2.863(7) Å, form two $C_1^1(4)$ chains, which generate infinite two-dimensional sheets (Fig. 2). The anions are sandwiched between cationic sheets, held there by two N–H···F; r(N···F) = 2.979(7) and 3.082(8) Å, and one C–H···F; r(C···F) = 3.138(7) Å, hydrogen bonds. The overall crystal packing displays an ...ABAABA...

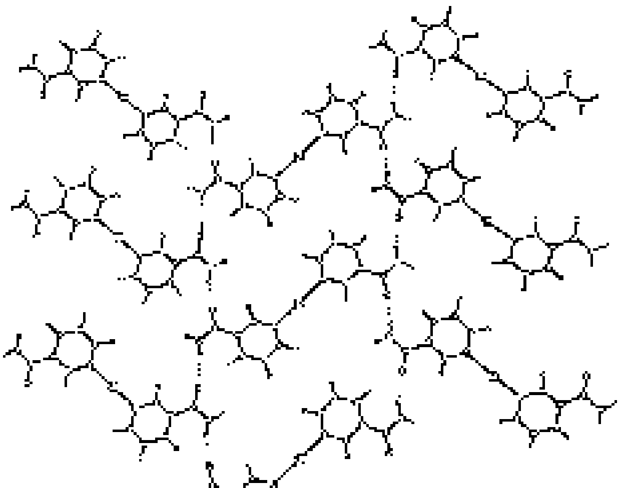

Fig. 2 2D cationic network in **2**, formed by $C_1^1(4)$ hydrogen bonds (the same 2D motif is found in the crystal structure of **3**

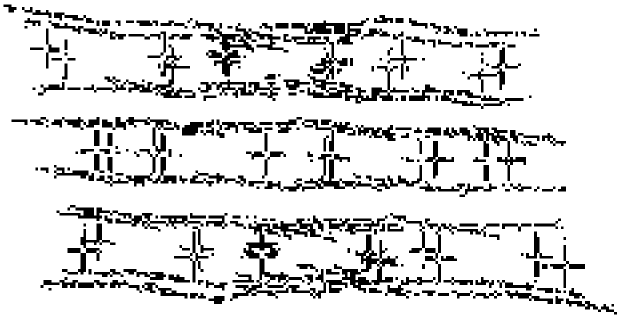

Fig. 3 Edge-on view of the lamellar crystal packing in **3**; hexafluorophosphate counter ions are positioned between silver-containing cationic sheets

arrangement, where A is a cationic sheet and B is an anionic layer (Fig. 3). Within ABA units the distance between cationic sheets is *ca.* 3.6 Å, while the separation between ABA units is *ca.* 3.2 Å, with no hydrogen bonds between cationic layers.

The reaction of silver(I) hexafluorophosphate with nicotinamide yields dinicotinamidesilver(I) hexafluorophosphate **3** (mp 234–238 °C), which again contains the expected linear cationic complex, N–Ag–N 173.4(1)°. Neighboring cations are linked *via* two unique amide–amide hydrogen bonds, $r(\mathrm{N}\cdots\mathrm{O})$ = 2.943(4) and 2.870(4) Å, leading to a 2D network that is virtually identical to the cationic sheet observed in **2** (Fig. 2). The anions are positioned between sheets through two N–H$\cdots$F hydrogen bonding interactions, $r(\mathrm{N}\cdots\mathrm{F})$ = 3.033(4) and 3.058(4) Å. The crystal structure displays an ...ABAABA... packing (Fig. 3), with cationic sheets separated by *ca.* 3.8 Å within ABA units and *ca.* 3.4 Å between ABA units.

The structures of **1**, **2** and **3** demonstrate that the silver ion provides the desired linear $\mathrm{AgL_2}$ building unit, and neighboring amide functionalities assemble these complexes into either 1-D or 2-D supramolecular architectures *via* intermolecular hydrogen bonds. Although the precise geometries of the hydrogen-bond networks change in this series, amide–amide interactions persist in the presence of anions with widely differing geometries and coordinating abilities. Consequently, we have gained a level of control over the way in which adjacent linear silver(I) complexes are arranged within the 3-D lattice. However, a detailed comparison of the crystal structures of **1** *vs.* **2** and **3** indicates that the counter ion does play an important role in the assembly of these complexes, resulting in the formation of either 1-D or 2-D cationic motifs based on prevailing amide–amide interactions. For example, 2-D cationic sheets are observed in structures where the anion is approximately spherical and with relatively low-coordinating ability ($[\mathrm{BF_4}]^-$ and $[\mathrm{PF_6}]^-$), whereas cationic ladders arise in the presence of a more anisotropic counter ion with stronger hydrogen-bond acceptors. In the case of the lamellar 2-D assemblies displayed by **2** and **3**, we hope to specifically control inter-layer separations by altering the characteristics of the counterion. Moreover, we are also examining how changes to the position of the amide functionality (*e.g.* 4-carboxamidepyridine *vs.* 3-carboxamidepyridine) and the presence of other substituents on the ligand, influence the nature of the hydrogen-bond networks and the resulting 3-D packing.

The work presented here illustrates that directional hydrogen bonds can be used in assembly of transition-metal complexes even in competition with potentially disruptive counterion interactions. Consequently, we can expect that many principles of crystal engineering that have been developed and tested in organic solid-state chemistry will assume further relevance in supramolecular aspects of coordination chemistry.

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Notes and References

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‡ *Crystal data*: **1**: $\mathrm{C_{13}H_{12}AgF_3N_4O_5S}$, triclinic, space group $P1$, a = 7.4761(5), b = 108812(7), c = 11.1832(9) Å, α = 98.898(6), β = 106.639(6), γ = 99.406(5)°, U = 845.2(1) Å^3, Z = 2, D_c = 1.969 g cm^{-3}, μ = 1.383 mm^{-1}, R_1 (all data) = 0.0191, R^2 (all data) = 0.0460.

2: $\mathrm{C_{12}H_{12}AgBF_4N_4O_2}$, monoclinic, space group $P2_1/c$, a = 9.9693(7), b = 9.7488(6), c = 15.5105(10) Å, β = 97.971(4)°, U = 1492.9(2) Å^3, Z = 4, D_c = 1.953 g cm^{-3}, μ = 1.410 mm^{-1}, R_1 (all data) = 0.0591, R_2 (all data) = 0.1185.

3: $\mathrm{C_{12}H_{12}AgF_6N_4O_2P}$ monoclinic, space group $P2_1/c$, a = 8.1458(7), b = 9.9241(10), c = 20.000(2) Å, β = 98.387(7)°, U = 1559.5(3) Å^3, Z = 4, D_c = 2.064 g cm^{-3}, μ = 1.442 mm^{-1}, R_1 (all data) = 0.0346, R_2 (all data) = 0.0566. CCDC 182/831.

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