Synthesis of a chiral adamantoid network— the role of solvent in the construction of new coordination networks with silver(I)

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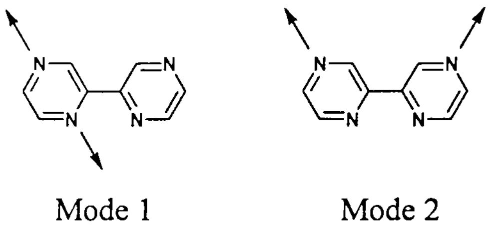
Depending on the crystallisation solvent used, reaction of 2,2′-bipyrazine with $AgBF_4$ results in the formation of either a chiral three-dimensional adamantoid coordination network or a two-dimensional sheet incorporating five coordinate Ag(I) ions.

Inorganic supramolecular chemistry and in particular the construction of polymeric coordination networks is an extremely topical area of research.[1] Chiral coordination polymers are particularly intriguing as such systems have potential future applications as stereoselective hosts for the separation of racemic mixtures. One of the most obvious methods of introducing chirality into coordination polymers is to use polymeric helicates and this method has been exploited to generate one-dimensional polymers.[2–4] Some of these polymeric helices spontaneously resolve through weak π–π[3] or H-bonding[4] interactions to give chiral three-dimensional structures within a given crystal. Structures formed through stronger metal–ligand bonds are rare[5] and resolution often relies upon weaker interactions[6] to induce the chirality within the system. We are interested in developing a strategy for preparing three-dimensional coordination polymers in which the chirality of the system is introduced *via* these more robust metal–ligand interactions, an integral feature of the network itself. We have targeted one of the most commonly studied structural motifs in coordination polymer chemistry, namely the adamantoid or super-diamondoid structure.[7,8] Such compounds, formed by the reaction of tetrahedral metal ions [*e.g.* Cu(I) or Ag(I)] with linear connecting units (*e.g.* 4,4′-bipyridyl), may not, at first, be an obvious choice. However, although conventionally considered to be built from edge-sharing adamantane units, such networks may also be thought of in terms of fused 4_1 and 4_3 helices.[8] These helices display opposing hands so that the conventional adamantoid structure does not exhibit chirality.

Our strategy was to see whether we could perturb the balance of these helices in order to remove the racemic nature of their orientation. In an attempt to achieve this, we have targeted a ligand system [2,2′-bipyrazine (bpyz)] which provides two different modes by which it can bridge adjacent metal centres. This ligand provides not only two independent types of binding sites, the chelating bidentate site and the two monodentate N-donor sites, but also two possible modes for bridging metal centres (Scheme 1). These two bridging modes provide a possible mechanism for generating two independent helices when reacted with a suitable metal centre and thus, potentially, an asymmetric adamantoid network. Two ligands which have a similar combination of one bidentate and two monodentate donor sites, 2,2′-bi-1,6-napthyridine and 5,5′-dicyano-2,2′-bipyridine, have previously been shown to generate one-dimensional helical structures with Cu(I)[9] and Ag(I)[10] in the elegant work of Janiak and coworkers but no examples of three-dimensional helical structures were prepared.



Scheme 1 Two possible bridging modes demonstrated by 2,2′-bipyrazine.

Single crystals of $\{[Ag(bpyz)](BF_4)\}_\infty$ were prepared by slow mixing of solutions of $AgBF_4$ and the ligand in $MeNO_2$, followed by diffusion of diethyl ether vapour into the homogeneous reaction solution.† Single crystal X-ray diffraction experiments‡ revealed that $\{[Ag(bpyz)](BF_4)\}_\infty$ crystallises in the chiral tetragonal space group $P4_32_12$ and that the Ag(I) centre is coordinated by one chelating ligand and by two monodentate N-donors from two further bpyz ligands in a distorted tetrahedral geometry. Each Ag(I) centre is linked to four nearest-neighbour Ag(I) centres, two *via* the chelating ligand and two more through the two monodentate pyrazine-like donors forming a distorted adamantoid array. Inspection of the extended lattice viewed down the *c*-axis confirms that the structure forms two distinct channels (A and B) which represent different helices running through the network (Fig. 1). The square-shaped channel, A (*ca.* 4.9 Å cross-section), runs through a 4_3 helix in which each Ag(I) centre is linked to the next Ag(I) centre along the helix through a pyrazine unit (bridging mode 1, Scheme 1) [Fig. 2(a)]. In contrast, the rhomboid-shaped channel, B (*ca.* 3.5 Å cross-section), runs through a 2_1 helix in which adjacent Ag(I) centres are linked through bridging mode 2 (Scheme 1) *via* two monodentate N-donor ligands [Fig. 2(b)]. Whereas in a conventional adamantoid lattice, adjacent helices which have opposing hands are chemically identical, in $\{[Ag(bpyz)](BF_4)\}_\infty$ adjacent anti-parallel helices are chemically distinct, displaying different bridging modes and different pitches. Therefore the structure of $\{[Ag(bpyz)](BF_4)\}_\infty$ has an overall chirality and represents the

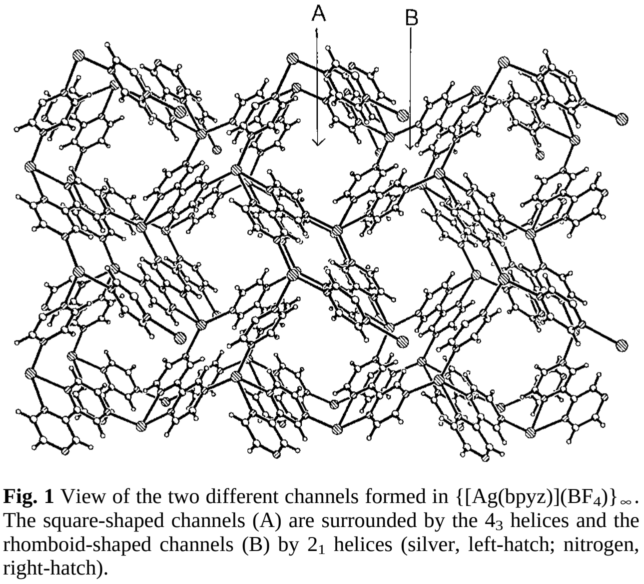


Fig. 1 View of the two different channels formed in $\{[Ag(bpyz)](BF_4)\}_\infty$. The square-shaped channels (A) are surrounded by the 4_3 helices and the rhomboid-shaped channels (B) by 2_1 helices (silver, left-hatch; nitrogen, right-hatch).

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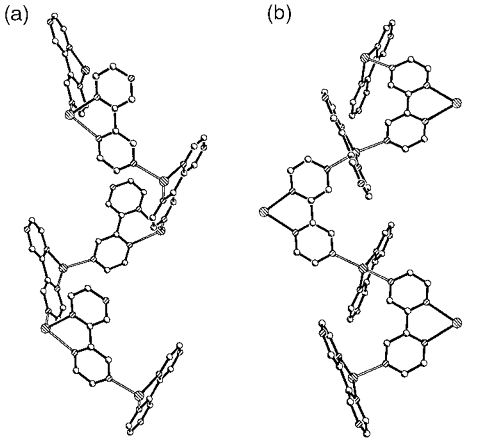

Fig. 2 (a) View, perpendicular to channel A, showing the 4_3 helix and illustrating the propagation of the channel periphery through bridging mode 1; (b) view, perpendicular to channel B, showing the 2_1 helix and illustrating propagation through bridging mode 2 (silver, left-hatch; nitrogen, right-hatch).

first example of a chiral adamantoid network. The channels are filled by BF_4^- counter-anions and $MeNO_2$ solvent molecules. Interestingly the BF_4^- anions sit exclusively in the channel generated by the 2_1 helix (channel B) leaving the more open channels generated by the 4_3 helix (channel A) open for solvent inclusion. This channel represents some 45.2%[11] of the total crystal volume and therefore this system appears promising for potential use as a chiral host material.

When single crystals were grown in an analogous manner but replacing non-coordinating $MeNO_2$ with the co-ordinating solvent MeCN, a different product, $\{[Ag(bpyz)(MeCN)](BF_4)\}_\infty$, was isolated. Single crystal X-ray diffraction experiments‡ show that this network adopts an entirely different structure. In this case, each Ag(I) centre coordinates a MeCN ligand leading to a distorted trigonal-bipyramidal Ag(I) environment. As with $\{[Ag(bpyz)](BF_4)\}_\infty$ each Ag(I) centre is coordinated by one chelating and two monodentate bpyz ligands resulting in each Ag(I) being linked to four nearest-neighbour Ag(I) junctions. However, in this case, the coordination of the MeCN ligand flattens the extended lattice to give a two-dimensional (4,4) sheet (Fig. 3). Each of these sheets undulates, with the MeCN ligands protruding from its surface resulting in interdigitation of adjacent $\{[Ag(bpyz)(MeCN)](BF_4)\}_\infty$ layers. The five-coordinate geometry observed here is rare for Ag(I), which prefers linear or tetrahedral coordination, and has only been observed three times before within coordination networks.[12]

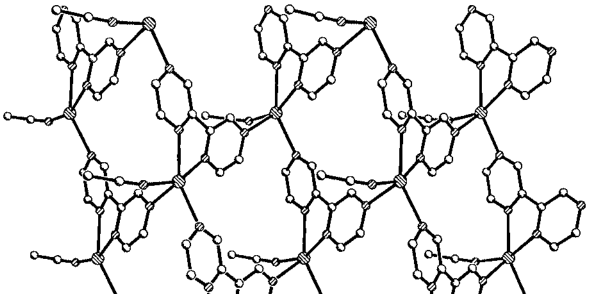

Fig. 3 View of the (4,4) two-dimensional sheet formed by $\{[Ag(bpyz)(MeCN)](BF_4)\}_\infty$ (silver, left-hatch; nitrogen, right-hatch).

In conclusion, we have shown that by using a ligand that can exhibit different bridging modes we can induce the formation of a chiral adamantoid network. The effect of solvent of crystallisation upon network structure has also been demonstrated by the formation of an extended two-dimensional lattice which incorporates five-coordinate Ag(I) centres. We are currently investigating whether the chirality of the adamantoid lattice can be controlled by the use of chiral anions.

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Notes and references

† *Experimental*: $\{[Ag(bpyz)](BF_4)\}_\infty$: a solution of $AgBF_4$ (10 mg, 0.05 mmol) in $MeNO_2$ (10 cm^3) was slowly diffused into a solution of 2,2′-bipyrazine {bpyz} (8 mg, 0.05 mmol) in $MeNO_2$ (10 cm^3) to give a homogeneous reaction solution. Diethyl ether was then diffused into the reaction solution affording colourless block crystals. Yield (8 mg, 44%). $\{[Ag(bpyz)(MeCN)](BF_4)\}_\infty$ was prepared analogously but replacing $MeNO_2$ with MeCN. Yield (54%). Satisfactory spectroscopic and analytical data were obtained.

‡ *X-Ray experimental, general procedures*: data for both compounds were collected on a Stoe Stadi-4 four-circle diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Hydrogen atoms were placed in geometrically calculated positions and allowed to ride on their parent atoms.

Crystal data: $\{[Ag(bpyz)](BF_4)\cdot 2MeNO_2\}_\infty$: $C_{10}H_{12}AgBF_4N_6O_4$, M = 474.94, tetragonal, space group $P4_32_12$ (no. 96), a = 11.396(7), c = 13.913(9) Å, U = 1807(2) Å^3, Z = 4, D_c = 1.746 g cm^{-3}, μ(Mo-Kα) = 1.183 mm^{-1}, T = 150(2) K. 1595 unique reflections (R_{int} = 0.0852) [1391 with $I > 2\sigma(I)$]. Final R = 0.0549, wR_2(all data) = 0.1262. Flack parameter = −0.12(12).

$\{[Ag(bpyz)(MeCN)](BF_4)\}_\infty$: $C_{10}H_9AgBF_4N_5$, M = 393.90, monoclinic, space group $P2_1/n$ (no. 14), a = 7.326(3), b = 18.423(6), c = 10.218(4) Å, U = 1356.7(9) Å^3, Z = 4, D_c = 1.531 g cm^{-3}, μ(Mo-Kα) = 1.531 mm^{-1}, T = 150(2) K. 2384 unique reflections, [1794 with $I > 2\sigma(I)$]. Final R = 0.0531, wR_2(all data) = 0.0913.

CCDC 182/1569. See http://www.rsc.org/suppdata/cc/a9/a909868b/for crystallographic files in .cif format.

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