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A new type of supramolecular entanglement in the silver(I) coordination polymer $[Ag_2(bpethy)_5](BF_4)_2$ [bpethy = 1,2-bis(4-pyridyl)ethyne]

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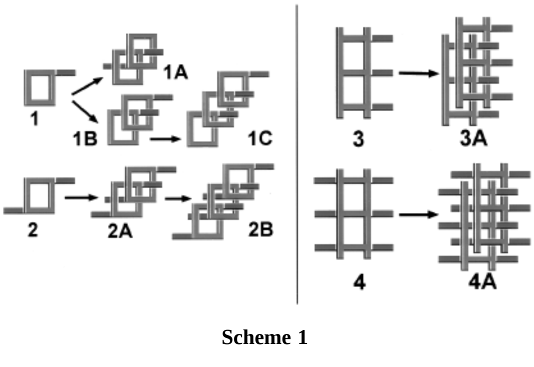
The polymeric compound $[Ag_2(bpethy)_5](BF_4)_2$, obtained from $AgBF_4$ and 1,2-bis(4-pyridyl)ethyne (bpethy) in molar ratio 1:3, contains infinite molecular ladder motifs with monodentate ligands as sidearms on both sides, that are threaded through the squares of adjacent polymeric units in a mutual relationship, to give infinite 'polythreaded' bidimensional layers.

Two topical areas in metal-directed supramolecular chemistry,[1] that have attracted much interest in recent times, deal, respectively, with (*i*) the construction of fascinating interwoven/intertwined molecular arrays, such as catenanes, rotaxanes, knots and helicates,[2] and (*ii*) the crystal engineering of polymeric networks,[3] which are often interpenetrated.[4] Though these two fields are characterized by different objectives, the self-assembly of extended coordination frames has recently produced noteworthy examples of structural motifs typical of the former area involved in polymeric systems, such as polyrotaxanes,[5] polypseudo-rotaxanes,[6] and polycatenated molecular ladders[7] and multiple layers.[8] The stimulating current developments in the supramolecular chemistry of intertwined organic systems have revealed a variety of novel structural motifs that might have a parallel relevance also in coordination chemistry. New possible molecular modules are, for example, self-complementary units, represented by rings (or polygons) bearing one sidearm (see **1** in Scheme 1), which can self-assemble *via* non-covalent bonds to give supramolecular oligomeric or polymeric species, with the sidearm of each unit threaded through the ring of the lateral unit (see **1A**, **1B** and **1C**). Systems like these, called 'supramolecular daisy chains', have been recently discussed in the presentation of a plerotopic organic monomer that gives an array of the **1A** type.[9] A variation of the previous motif **1** can be the addition of a second sidearm, as in **2**, that can oligomerize or polymerize *via* a mutual threading involving adjacent units, as in **2A** and **2B**. On passing from finite to infinite molecular modules one can imagine the extension of rings **1** and **2** into polymeric ladder species (such as **3** and **4**, respectively). Indeed, different examples of molecular ladders have been described within coordination polymers,[7,10] including a species like **4** (called a molecular 'railroad').[11] Supramolecular assembling of **3** and **4** with identical adjacent motifs can produce, *inter alia*, two-dimensional entanglements characterized by 'polythreading' (as in **3A**) or 'mutual polythreading' (as in **4A**). We report here the characterization of an example of a type **4A** supramolecular entanglement in a coordination polymer obtained from the self-assembly of $AgBF_4$ and 1,2-bis(4-pyridyl)ethyne (bpethy). Many reactions with different silver salts in varied conditions have been carried out, but only linear $[Ag(bpethy)]^+$ polymers were isolated using metal-to-ligand molar ratios up to 1:2. We have therefore attempted reactions with a higher excess of the ligand, and from $AgBF_4$ and bpethy in molar ratio 1:3 in MeCN–Et_2O we have obtained a derivative characterized by single crystal X-ray analysis as the novel species $[Ag_2(bpethy)_5](BF_4)_2$.†



Scheme 1

The structure is comprised of ladder-like polymeric units, shown in Fig. 1, bearing, as extensions of each rung (C), two additional monodentate dangling bpethy molecules (A), that are folded in opposite directions on the two sides of the ladder. The Ag···Ag distances are 13.93 Å along the siderails and 14.48 Å within the rungs.

The coordination geometry at the silver centres (see Fig. 1, top) is flattened tetrahedral. The two rows of lateral arms form dihedral angles with the ladder plane of *ca.* 137°, resulting in a stretched zigzag shaped section (see Fig. 1, bottom). In contrast, the related 'railroad' polymer of $[Ni_2(4,4'\text{-bpy})_5(H_2O)_4]$-$(ClO_4)_4\cdot 3(4,4'\text{-bpy})\cdot 4H_2O$ is flat,[11] because the Ni^{2+} centres are octahedral and all the 4,4′-bipyridyl groups lie almost coplanar. The square grids, in this species, are smaller (11.39 × 11.34 Å).

All the ladders of $[Ag_2(bpethy)_5](BF_4)_2$ run in the same direction, [−1 0 1], and are closely disposed on layers. The ladder planes are stacked parallel at a distance of 3.51 Å and display an inclination of *ca.* 22° with respect to the average plane of the layer (see Fig. 2, top). The most interesting

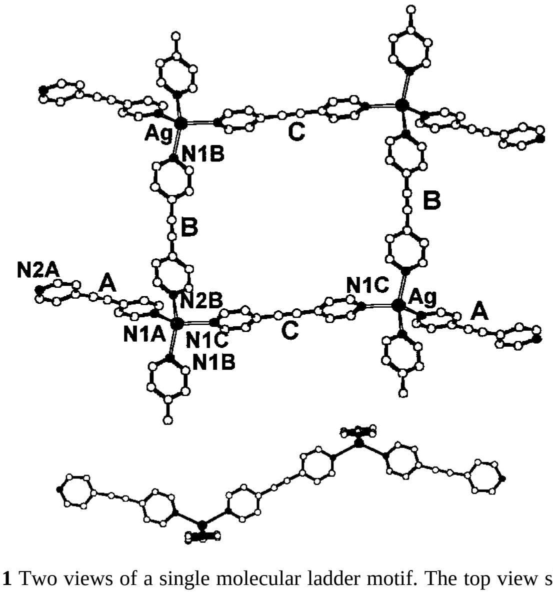


Fig. 1 Two views of a single molecular ladder motif. The top view shows the three types of bpethy ligands (A, B and C, the latter lying on inversion centres). The Ag–N bond lengths are in the range 2.300(2)–2.424(2) Å; two of the N–Ag–N angles are significantly larger [N1B–Ag–N2B 139.92(8), N1A–Ag–N1C 125.00(9)°] than the other four [in the range 95.52(8)–103.01(8)°].

structural feature, however, consists of the fact that the terminal bpethy ligands of each ladder are threaded into the squares of the adjacent ladders, in a mutual relationship. The length of the ligands is such that the threading involves not only the first but also the second nearest neighbouring ladders. Each square is therefore penetrated by four bpethy molecules, two entering by one side and two by the opposite one, as shown in Fig. 2 and 3, thus resulting in a supramolecular entanglement originated by five polymeric units. The aromatic rings of all the threaded molecules are parallel to those of the ligands of the ladder rungs. An extended system of stacked rings is thus formed, with π–π interactions [plane separation 3.5–3.6(1) Å, lateral offset 1.9–3.0(1) Å] that stabilize the whole entanglement.[12] An additional stabilization can be attributed to weak attractive CH–π interactions,[13] involving H atoms of the terminal (A) and of the rung ligands (C), that point toward the centres of the rings and of the C≡C moieties of the siderail ligands (B) (H···bar distances and C–H···bar angles: 2.66–2.79 Å, 144–168°, with bar = the baricentre of the π system). The schematic representation of the 'mutual polythreading' in this species given in Fig. 2 (bottom) shows that two adjacent ladders are displaced by *ca.* 1/4 of the polymer period along the direction of extension. The sequence of the ladders in a layer is therefore of the *ABCDABCD* type. The entangled layers stack along the crystallographic ***b*** axis, leaving interlayer voids that are occupied by the BF_4^- anions.

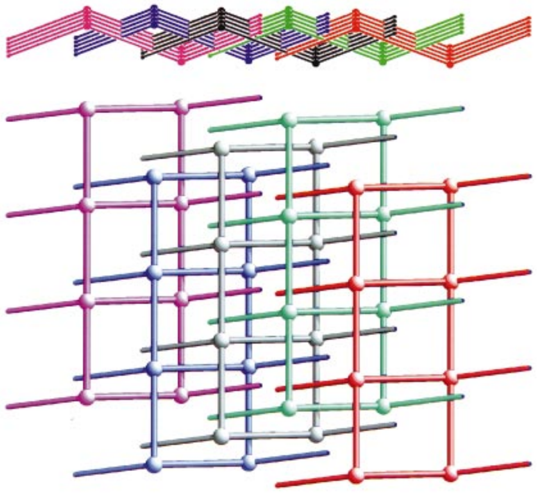


Fig. 2 Two schematic views of the entangled ladders: approximately down the direction of propagation (top), and down the perpendicular to the polythreaded layer, showing the relative displacement of the adjacent ladders (bottom).

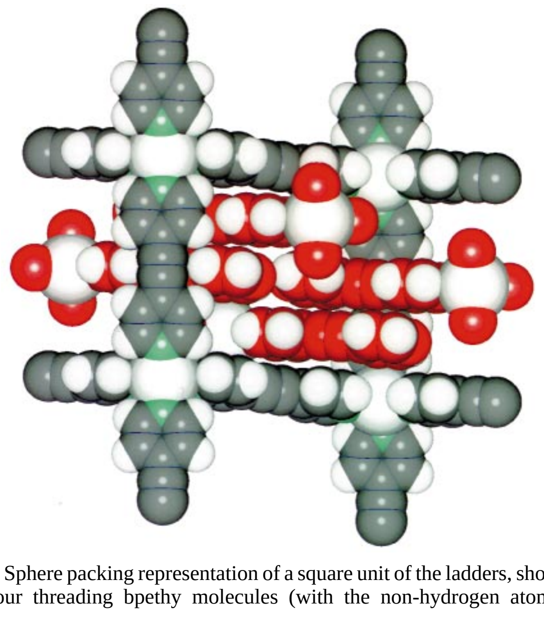


Fig. 3 Sphere packing representation of a square unit of the ladders, showing the four threading bpethy molecules (with the non-hydrogen atoms in red).

A variety of appealing interpenetrated frameworks has been recently described in coordination polymer chemistry.[4] While interpenetration requires breaking of links to separate the individual nets, other types of polymeric supramolecular architectures can be, in principle, disentangled by simply unthreading the components. These species are much less known, at present, and include examples such as infinite double-helices,[6] a clothlike warp-and-weft sheet structure,[14] and bilayer species interdigitated in a gear-like (or tongue and groove) fashion.[15] The fascinating 'polythreaded' structure here described belongs to this class of polymers and can be considered a model of a new type of infinite entanglement, that can be extended to other systems.

Notes and references

† *Crystal data*: $C_{60}H_{40}Ag_2B_2F_8N_{10}$, $M = 1290.38$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.397(1)$, $b = 11.109(1)$, $c = 13.696(2)$ Å, $\alpha = 80.65(1)°$, $\beta = 69.11(1)°$, $\gamma = 69.66(1)°$, $U = 1384.4(3)$ Å^3, $Z = 1$, μ(Mo-Kα) = 0.784 mm^{-1}, 21682 reflections measured, 8249 unique ($R_{\mathrm{int}} = 0.0251$), final $R1$ and $wR2$ values 0.0373 and 0.0978 for 5299 independent reflections [$I > 2\sigma(I)$]. The data collection was performed at 293 K on a Siemens SMART CCD area-detector by the ω-scan method, within the limits $2 < \theta < 31°$. The structure was solved by direct methods (SIR97) and refined by full-matrix least-squares (SHELX97). Anisotropic thermal parameters were assigned to all the non-hydrogen atoms but to the minor component (28%) of the disordered anion. CCDC 182/1163. See http://www.rsc.org/suppdata/cc/1999/449/ for crystallographic files in .cif format.

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