Coordination polymers with macrocyclic cages and pockets within their backbones†

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The reaction between the flexible ligand 1 (1,4-bis(pyridine-2-yl-methanethio)benzene) and Ag+ produces two novel coordination polymers with macrocyclic cages or pockets contained within their backbones, depending upon the ratio of starting materials.

Reactions developed for assembling modular building blocks into supramolecular nanostructures is one of the most active areas of chemical research, not only because of the interesting structural diversity associated with this class of complexes, but also because of the potential applications of such structures in optics, catalysis, sensing, and host–guest chemistry. Most structures investigated thus far have been molecular systems or networks of molecular systems contained within a crystalline lattice. In addition, several examples of polymeric versions of macrocycles and coordination polymers with Ag+ and pyridyl-type ligands have been reported. Herein, we report a novel reaction that allows one to generate polymers with three-dimensional supramolecular cages contained within the backbone through the use of flexible ligand 1 and Ag+. Two types of polymers can be generated, depending upon the ratio of starting materials used, where one ligand 1 adopts a folded conformation (2) and another where it adopts both linear and folded conformations within the structure (3) (Scheme 1).

Colorless single crystals of one-dimensional polymer 2, \([\{\text{Ag}(L)\} \text{CF}_3\text{SO}_3\}]_n \quad (L = 1)\), were obtained by the reaction of 1 and AgCF3SO3 in a 1 : 1 ratio in acetone at room temperature.† Coordination polymer 2 exhibits a repeat unit where 1 adopts a folded conformation with the pyridine moieties pointed away from the central arene linker and towards one another (Fig. 1a). Ligand 1 acts as a bis-bidentate ligand to link two Ag+ ions. This repeat unit generates one-dimensional zig-zag networks, in which the silver metal ions are coordinated in distorted square planar geometries to two nitrogen and two sulfur atoms (Fig. 1b). The Ag–N distance is 2.21 Å, indicative of a bonding interaction. In contrast, there are comparatively weak bonding interactions between the silver and sulfur atoms as evidenced by an average bond distance of 2.93 Å. An interesting feature of the structure is the presence of pockets (7 × 6 × 5 Å), a result of the folded geometry of ligand 1 within the polymer structure (Fig. 1c, encapsulated triflate ion is shown in dark blue).

In contrast, if the amount of ligand 1 is increased to 1.5 equivalents, the reaction with AgCF3SO3 yields a novel polymeric structure \([\{\text{Ag}(L)\}_1 \text{CF}_3\text{SO}_3\}]_n \quad (L = 1)\) containing macrocyclic cages along the backbone (Scheme 1). The ligand in polymer 3 adopts two different conformations (Fig. 2). In the first conformational type, ligand 1 coordinates to Ag+ through nitrogen and sulfur atoms, adopting a folded geometry similar to that seen in polymer 2 (Fig. 2a). The second conformational type involves coordination to Ag+ only through nitrogen atoms, resulting in a more linear geometry (Fig. 2b). The distance between the two nitrogen atoms in the type 1 conformation is 6.94 Å and much shorter than 12.06 Å observed for the type 2 conformation.

Each Ag+ ion in 3 is coordinated to three nitrogen atoms, two from the ligand in the type 1 conformation and one from the ligand in the type 2 conformation. In addition, both sulfur atoms from the ligand in the type 1 conformation coordinate to Ag+ ions. This results in the formation of macrocyclic cages along the polymer backbone (Fig. 3). This unusual structure is a result of the folded


Fig. 1 Structure of 2 showing (a) a folded conformation of 1, (b) ball and stick, and (c) space filling representation of one-dimensional polymer. Note that triflate anion is encapsulated, as shown. (Ag, orange; N, light blue; S, yellow; C, gray; CF3SO3, dark blue.)

Fig. 2 (a) Type 1 folded conformation and (b) type 2 linear conformation in polymer 3.
The average Ag–S distance of 2.79 Å indicates a weak bonding coordination polymers based on the flexible ligand formed from the ligand in the type 1 conformation (average 2.43 Å), slightly shorter than that the Ag–N distances for the complex approximately 9.

Fig. 3 ORTEP and space filling representations of the macrocyclic cage in 3 (a) with top view and (b) with side view. (Ag, orange; N, light blue; S, yellow; C, gray.)

conformation of the ligand, where the pyridine groups act as the walls of each cage. The dimensions of the macrocyclic cage are approximately 9 × 8 × 5 Å. The ligand in the type 2 conformation within polymer 3 connects adjacent macrocyclic cages generating the repeat structure (Fig. 4). One silver center and three nitrogen atoms coordinated to silver metal are almost all in one plane with a torsion angle of 168.5°. The Ag–N bond distance for the complex formed with the ligand in the type 2 conformation (2.37 Å) is slightly shorter than that the Ag–N distances for the complex formed from the ligand in the type 1 conformation (average 2.43 Å). The average Ag–S distance of 2.79 Å indicates a weak bonding interaction. The π–π stacking interactions between the central arene rings for the type 2 ligands and the pyridine groups in the type 1 ligands are significant as evidenced by the very short ring–ring distance of 3.3 Å and likely contribute to the assembly process and stabilization of the supramolecular polymeric structure (Fig. 4).

In conclusion, this work describes the formation of novel Ag(i) coordination polymers based on the flexible ligand 1 which acts as a spacer with two different conformations. The resulting polymers contain unique macrocyclic pockets or cages in their backbones. These polymers may exhibit unusual molecular sieving and separation properties as a result of their unusual structures much like the non-covalent crystalline lattices formed by molecular squares.12 Efforts to explore such properties are underway.

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Notes and references


