

## Polymeric silver(I) coordination tubes†

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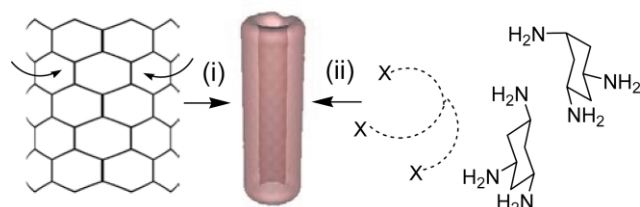
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Isolated polymeric Ag(I) coordination tubes are self-assembled from the rigid triamino ligands *cis,cis*-1,3,5-triaminocyclohexane (*cis*-tach) and *cis,trans*-1,3,5-triaminocyclohexane (*trans*-tach), forming two topologically equivalent framework motifs.

Coordination polymers are popular components in the construction of polynuclear coordination networks as functional materials.<sup>1</sup> Their flexibility and ease of assembly makes them attractive architectures to emulate systems which are often hard to construct and derivatise using a covalent approach. Archetypal targets include molecular tubes (*i.e.* discrete tubes that exist outside of an array), as the unique physical properties associated with tubular architectures such as mechanical strength, gas absorption, electrochemical, and photophysical properties are highly desirable;<sup>2–3</sup> furthermore some of these properties are realised by carbon-based nanotubes which have great potential for application in molecular electronics and nanolithography.<sup>2</sup> However, the construction of tubular 1-D materials is extremely challenging.<sup>3</sup> One route *via* the self-assembly of nanotube-like architectures, using coordinative or weaker interactions,<sup>4</sup> may be a viable approach. For example, research in this area has been successful in creating a large number of porous materials in which the channels are encapsulated within networks of high dimensionality (and thus exist only within such networks),<sup>5</sup> or exist as coordinatively bound arrays of tubes<sup>6</sup> and just one example of isolated columnar polymers constructed using coordinate bonds.<sup>7</sup> The synthesis of isolated 1-D polymeric tubes constructed using coordinate bonds may be addressed in one of two ways: (i) by constructing a curved honeycomb 6<sup>3</sup> network analogous to carbon-nanotubes, which may be problematic due to steric interactions that prevent the curvature process or (ii) to utilise metal–ligand systems that possess a degree of preorganisation and a number of arms that can ‘wrap’ round to form the tubular network, see Scheme 1.

In this work we have adopted the second approach by reaction of our pre-organised ligand systems with soft metal ions such as silver(I). Silver was chosen because of the great number of 1-D silver(I) coordination polymers reported in the form of chains<sup>8</sup> and helicates<sup>9</sup> that use rigid ligands. By engineering certain degrees of flexibility into the ligand system, we have synthesised two examples of isolated, infinite tubes based on two novel silver(I) coordination polymers. These are assembled using the ligand *cis,trans*-1,3,5-triaminocyclohexane (*trans*-tach) or its isomer *cis,cis*-1,3,5-triaminocyclohexane (*cis*-tach). Both ligands are based

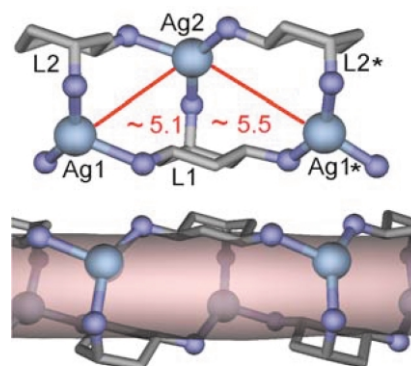


**Scheme 1** A depiction of two possible methods for assembling a nanotube along with the ligands utilised in this work.

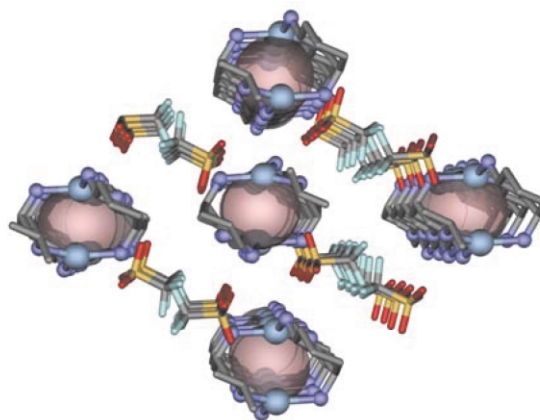
† Electronic supplementary information (ESI) available: experimental details. See <http://www.rsc.org/suppdata/cc/b3/b312876h/>

upon a rigid cyclohexane backbone but have inherent flexibility due to the primary aliphatic amino groups. Interestingly, each ligand forms the tubular structure by virtue of the nitrogen donor geometry, and as such comprise a novel synthetic route to the construction of the isolated tubes: {[Ag(*trans*-tach)]CF<sub>3</sub>SO<sub>3</sub>}<sub>∞</sub> (**1**) and {[Ag(*cis*-tach)](CF<sub>3</sub>SO<sub>3</sub>) CH<sub>3</sub>OH}<sub>∞</sub> (**2**).<sup>‡</sup> Complexation of these ligands with silver(I) triflate<sup>10</sup> results in 1-D coordination polymers of 4<sup>2.6</sup> topology (each ligand is regarded as a three-connected node). The asymmetric unit of **1** consists of two crystallographically independent *trans*-tach ligands (L1, L2), two silver(I) ions (Ag1, Ag2) as well as two triflate counterions, see Fig. 1.

The overall tubular structure (Figs. 1 & 2) is formed by two chains coordinating Ag1 and Ag2 ions through the equatorial amino groups of the L1 and L2 (Ag⋯Ag distances along the chains are 8.1038(6) Å).



**Fig. 1** Top: macrocycle formation of **1**. Bottom: 1-D coordination polymer of **1**. Ag atoms are shown as large blue circles, carbon in grey and nitrogen as small blue circles. Symmetry code \*:  $x, 1+y, z$ . Each Ag(I) adopts a trigonal planar coordination sphere (N–Ag1–N angles: 147.92(17), 114.35(17), 97.47(17)°  $\Sigma = 359.74(17)^\circ$  and N–Ag2–N: 148.32(16), 108.14(16), 103.08(16)°  $\Sigma = 359.54(16)^\circ$ ) by coordinating two equatorial and one axial amino group of three different ligands.



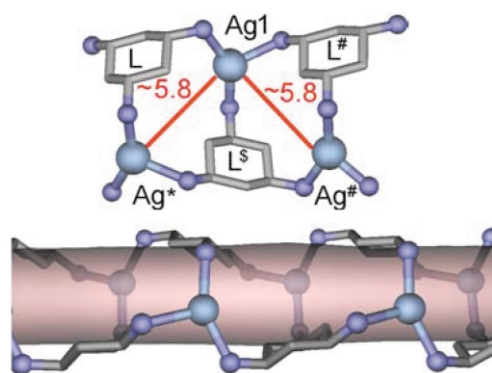
**Fig. 2** Packing arrays of **1** along the crystallographic *b* axis. Ag(I) atoms are shown as large blue circles, carbon in grey, sulfur in yellow, oxygen in red, fluoride in light blue and nitrogen as small blue circles.

Both chains are linked together *via* coordination of the remaining axial amino groups, and this arrangement leads to a staggered chain conformation of the overall tubular structure and to the formation of two independent macrocyclic subunits (Fig. 1). These 2:2 subunits are formed *via* coordination of one axial and one equatorial amino group of each ligand to two silver(I) ions, and each cycle consists of 12 ring atoms with inter-macrocycle Ag...Ag distances of 5.1075(6) and 5.5221(6). Finally, the 1-D coordination polymers are packed in isolated arrays with inter-tubular distances of 7.3, 10.9 and 12.4 Å, and these arrays are connected by hydrogen-bonded interactions involving the triflate counterions (Fig. 2).

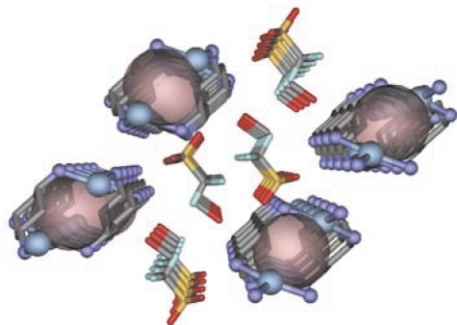
The asymmetric unit of **2** consists of one *cis*-tach ligand and one silver(I) ion as well as one triflate counterion and a methanol solvent molecule. As with **1**, the metal coordination occurs exclusively in one dimension, forming tubes connected by hydrogen-bonded interactions to triflate counterions (hydrogen-bonded methanol molecules are also included in the structure). The 4<sup>2</sup>.6 topology (Fig. 3) is formed by macrocycles of two silver(I) atoms and two *cis*-tach units coordinated *via* two of their constituent nitrogen atoms. Furthermore, the macrocycle dimensions are larger than those formed in **1** (inter-macrocycle Ag...Ag distances 5.7591(4) Å).

Similar to the tubes found in **1**, the tubes found in **2** are packed in ordered arrays (Fig. 4) and are separated by a distance of between 8.6 and 12.4 Å. Rather than the staggered chain framework formed in **1**, the 1-D coordination polymer is facilitated by the *cis*-orientation of the third amino group, which results in the appearance of the ligand 'wrapping around' the channel walls.

Tubular structures are desired by chemists as modes for ion transport, electron transfer in biological or material systems, and for the construction of functional materials. To date there are few reported examples of tubular coordination structures. One important example is the formation of a one-dimensional silver(I)



**Fig. 3** Top: macrocycle formation of **2**. Bottom: one-dimensional coordination polymer of **2**. Ag atoms are shown as large blue circles, carbon in grey and nitrogen as small blue circles. Symmetry codes \*:  $3/2-x$ ,  $-1/2+y$ ,  $3/2-z$ , #:  $3/2-x$ ,  $1/2+y$ ,  $3/2-z$  and \$:  $x$ ,  $-1+y$ ,  $z$ . Each Ag(I) ion has a trigonal planar coordination sphere (N–Ag–N angles: 102.42(10), 106.94(10), 150.33(11)°  $\Sigma$  = 359.69(11)°) with three *cis*-amines of different ligands forming the channel (Ag–N1, N2, N3 distances: 2.232(3), 2.230(3), 2.393(3) Å, respectively).



**Fig. 4** Packing arrays of **2** along the crystallographic *b* axis. Ag(I) atoms are shown as large blue circles, carbon in grey, sulfur in yellow, oxygen in red, fluoride in light blue and nitrogen as small blue circles.

polymer by an aromatic bidentate ligand,<sup>7</sup> which represents a synthetic route using silver(I) triflate. The most significant tubular structure of a silver(I) coordination compound is reported by Hong *et al.*<sup>6a</sup> with a diameter of 13.4 Å. However, the coordination bonds between tubes in this structure means that these polymers are not isolated, representing tubes within a higher dimensionality coordination network. By employing this rational design strategy, involving rigid and wrapping ligands, the self-assembly of two truly isolated tubular silver(I) coordination polymers is realised. In future, this design approach will be extended by investigation into the coordination of other soft metals and also *via* derivatisation of the amino residues in order to enlarge the pore size and increase the functionality of the materials, and to examine the structure of these networks deposited on surfaces using techniques like SEM.

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## Notes and references

† Full synthetic and analytical details are given in the ESI.†

Crystal data for **1** – C<sub>7</sub>H<sub>15</sub>AgF<sub>3</sub>N<sub>3</sub>O<sub>3</sub>S, *M* = 386.15, monoclinic, space group *P*2<sub>1</sub>, *a* = 12.4287(5), *b* = 8.1038(4), *c* = 13.0208(6) Å,  $\beta$  = 106.313(2)°, *V* = 1258.65(10) Å<sup>3</sup>, *Z* = 4,  $\mu$ (Mo–K $\alpha$ ) = 1.809 mm<sup>-1</sup>, 8335 reflections measured, 5440 unique which were used in all calculations.

Final *R*1 = 0.036 and *wR*2 = 0.075 (all data). Data were measured at 150(2) K on a Nonius KappaCCD diffractometer [ $\lambda$ (Mo–K $\alpha$ ) = 0.71073 Å], graphite monochromator, 224 frames were recorded in 2.0° steps, each for 60 s, crystal-detector distance 40 mm. Crystal data for **2** – C<sub>8</sub>H<sub>19</sub>AgF<sub>3</sub>N<sub>3</sub>O<sub>4</sub>S, *M* = 418.19, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 8.5527(2), *b* = 7.8253(2), *c* = 21.9735(6) Å,  $\beta$  = 98.4620(10)°, *V* = 1454.62(6) Å<sup>3</sup>, *Z* = 4,  $\mu$ (Mo–K $\alpha$ ) = 1.578 mm<sup>-1</sup>, 20446 reflections measured, 3314 unique which were used in all calculations. Final *R*1 = 0.035 and *wR*2 = 0.084 (all data). Data were measured at 150(2) K, 363 frames were recorded in 1.4° steps at a rate of 30 seconds/degree, crystal-detector distance 40 mm. In both cases, structure solution was done with SHELXS-97 and refinement with SHELXL-97 *via* WinGX.<sup>11</sup> Hydrogen atom positions calculated and subsequently riding. CCDC 222115 and 222116. See <http://www.rsc.org/suppdata/cc/b3/b312876h/> for crystallographic data in .cif or other electronic format.

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