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Metallatubulane: synthesis and structural analysis of an infinite tubular coordination network formed by the self-assembly of a tetracyanocyclophane and silver cations

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Reaction of a tetracyano[1,1,1,1]metacyclophane blocked in the 1,3-alternate conformation and silver cations under self-assembly conditions leads to a tubular coordination network formed by double bridging of consecutive rings by linearly coordinated metal centres.

Tubular structures are interesting architectures, in particular with respect to their ability to transport ions and molecules. In principle, such structures may be obtained either using non reversible covalent bond formation processes or under self-assembly conditions using reversible interactions. It has been shown that tubular systems may be formed by 1-D chains adopting a helical structure, as observed for polypeptides in natural systems.[1,2] On the abiotic side, helical coordination polymers composed of synthetic organic ligands and metal centres,[3,4] which may be considered as tubular systems, have also been reported. Using self-assembly of silver ions and polydentate ligands, tubular systems formed by the interconnection of metallamacrocycles have been reported.[5,6] Other strategies based on the organisation of cyclic units into tubular arrangements using liquid crystalline phases[7] or polymeric backbones[8] have been shown to be successful as well. Finally, the formation of carbon nanotubes by rolling 2-D graphite sheets has also been demonstrated.[9]

Following the above-mentioned strategy based on the use of H-bonds between cyclic peptides, we reasoned that, by making the appropriate choice of ligands and metal centres, tubular coordination networks may be formed using the self-assembly strategy based on the formation of reversible coordination bonds. The formation of such a structure requires a complementary pair of ligand and metal cation that affords their reversible and mutual interconnection (Fig. 1).

Here, we report the synthesis of the exo-ligand **1** as well as the structural analysis of its tubular coordination network obtained in the presence of silver cations.

We believed that the exo-ligand **1** (Scheme 1) would be promising for the formation of infinite metallatubulanes. Ligand **1** is based on a [1,1,1,1]metacyclophane backbone that is blocked in the 1,3-alternate conformation and bears four nitrile groups as coordination sites, which are located below and above the main plane of the macrocycle in an alternate fashion and thus occupy the apexes of a pseudo-tetrahedron. The choice of **1** was based on the structural study of its hydroxy analogue **3**, which was demonstrated to be in the 1,3-alternate conformation,[10] the mercapto analogue **4**,[11] and on our previous observation dealing with the formation of 1-D coordination networks using ligand **6**.[12] Indeed, it was found that when using the calix **6**, owing to its inherent flexibility, two nitrile groups located on the same face of the ligand could act as a chelate for Ag^+ cations (Fig. 1). Thus, for the linear coordination network formed by bridging consecutive calix units by Ag^+ cations, the coordination geometry adopted by the latter was tetrahedral. In terms of topology, the above mentioned network is in principle of the tubular type; however, the presence of metal centres aligned along the tube axis obstructs the channel. In order to circumvent this, the ligand **1** was designed, which incorporates methyl groups that induce considerable rigidity and thus prevent the chelation process.

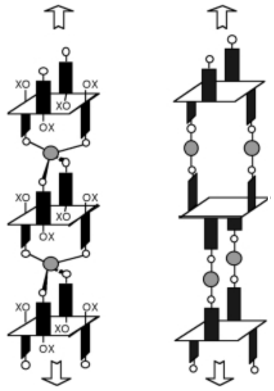
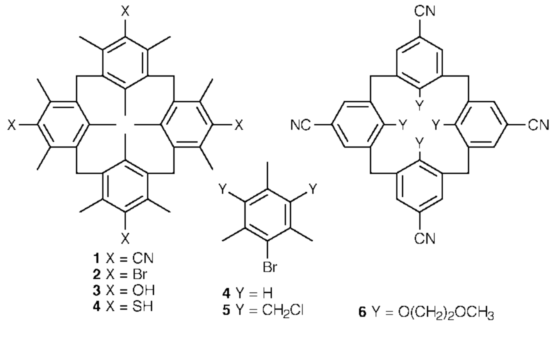


Fig. 1 Schematic representation of two types of tubular coordination networks which can be formed by the self-assembly of ligand **6** with Ag^+ cations adopting a tetrahedral coordination geometry (left) or ligand **1** and Ag^+ cations adopting a linear coordination geometry (right).

The synthesis of **1** (Scheme 1) was based on the strategy used for the preparation of **3**.[10] Starting with **4**, compound **5** was obtained in 84% yield upon treatment with $ClCH_2OMe$ in CH_2Cl_2 in the presence of $SnCl_4$ at −15 °C. Upon heating an equimolar mixture of **4** and **5** in $EtNO_2$ and in the presence of $SnCl_4$ for 6 h at 60 °C , the cyclic cyclophane **2** was obtained in 74% yield. The desired **1** was obtained in 54% yield upon treatment of **2** with CuCN in refluxing DMF for 15 h.[13] The 1,3-alternate conformation was established in the solid state by X-ray diffraction for both **1** and **2** (structures not reported here).

The metal cation used for the self-assembly of **1** into a tubular network was Ag(I), which forms kinetically labile complexes and can adopt a linear coordination geometry.[14] Furthermore, Ag^+ has been extensively used for the formation of coordination networks,[15] in particular using nitrile containing ligands.[16]



Scheme 1

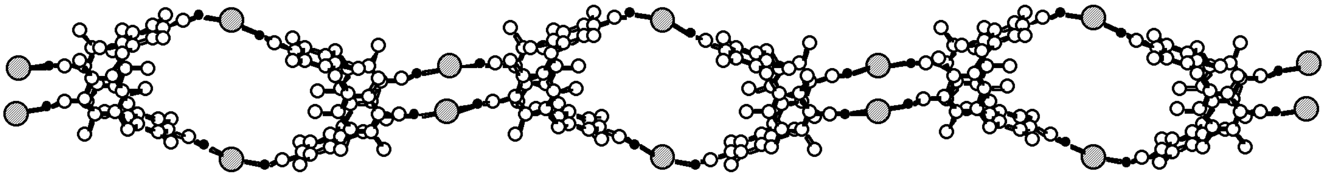


Fig. 2 A portion of the X-ray structure showing the formation of a cationic tubular coordination networks obtained by mutual bridging of Ag+ cations and ligands **1** (view perpendicular to the tube axis). For clarity, H atoms, solvent molecules and anions are not shown.

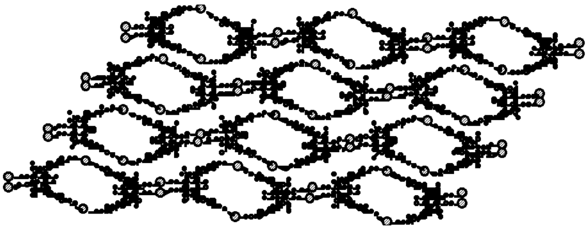


Fig. 3 A portion of the structure showing the packing of the cationic tubular coordination networks (projection normal to the tube axis). For clarity, H atoms and solvent molecules (CH_2Cl_2 and MeOH) are not shown.

Upon slow diffusion of a CH_2Cl_2 (0.75 ml) solution of the ligand **1** (2 mg, 3.18×10^{-6} mol) into a MeOH (1 ml) solution of $AgPF_6$ (8 mg, 3.18×10^{-5} mol) in large excess, colourless crystalline material was obtained. The analysis of single-crystals by X-ray crystallography† revealed the presence of disordered CH_2Cl_2 and MeOH solvent molecules in the lattice in addition to **1**, Ag^+ and PF_6^- anions. As predicted (Fig. 1), in addition to the anions and solvent molecules, the crystal was composed of cationic tubular coordination networks formed by the bridging of consecutive cyclic units by Ag^+ cations (Fig. 2). The ligand **1** adopts the imposed 1,3-alternate conformation. The nitrile groups are almost linear with an average C–C–N angle of *ca*. 177.5° and an average C–N distance of 1.142 Å. In the unit cell, two different Ag^+ cations are present. The coordination sphere around both crystallographically non-equivalent Ag^+ cations is composed of two nitrogen atoms (N–Ag–N 153.8 and 162.3°, C–N–Ag 171.5 and 150.3, 178.3°, N–Ag 2.155 and 2.126, 2.138 Å) and PF_6^- anions with Ag–F distances varying from 2.811 to 2.983 Å. Two Ag^+ cations located on the same face of the molecule are separated by 9.891 and 9.593 Å. The packing of the cationic component (Fig. 3) shows parallel disposition of tubular networks. Interestingly, the 1-D tubular networks are interconnected in a dihapto mode by strong metal–π interactions between Ag^+ cations and the aromatic moiety belonging to the next tubular strand (Ag^+–centroid distance of 3.087 Å). The same observation has been made with metallamacrocyles formed by connecting two cyclic *para*-dimethylaminopyridine derivatives with two Ag^+ cations.[14] Thus, taking into account the above interactions, the arrangement obtained may be described as a 2-D network with translations into two directions of space of two distinct assembling cores based on N–Ag^+–N and Ag^+–π interactions. Thus, the overall structure may be described as stacks of 2-D networks separated by PF_6^- anions. The tubular arrangement is not empty and occupied by solvent molecules. However, none of the solvent molecules (disordered CH_2Cl_2 and MeOH) present are included within the cavity of the cyclophanes but are rather located within cavities formed by interconnection of the cyclic units by silver cations.

In conclusion, employing the self-assembly strategy, the formation of a silver tubular coordination network using a [1,1,1,1]metacyclophane backbone that is blocked in the 1,3-alternate conformation and bears four nitrile groups was achieved and structurally characterised in the solid state by single-crystal X-ray analysis. The exchange of included solvent molecules, as well the enhancement of the size of the tubulane are currently under investigation.

Notes and references

† *Crystal data* for $C_{22}H_{22}N_2AgPF_6 \cdot MeOH \cdot 0.75CH_2Cl_2$: $M = 663.01$, monoclinic, space group $C2/m$, $a = 24.2853(5)$, $b = 19.1082(7)$, $c = 11.9631(4)$ Å, $\beta = 108.051(2)°$, $V = 5278.2(5)$ Å^3, $Z = 8$, $D_c = 1.67$ g cm^{-3}, μ(Mo-Kα) = 1.039 mm^{-1}. Data were collected on a Nonius KappaCCD diffractometer using Mo-Kα graphite monochromated radiation ($\lambda = 0.71073$ Å) at 173 K. A colourless crystal of dimensions $0.20 \times 0.16 \times 0.14$ mm was used and a total of 28 326 reflections were collected, $2.5 < \theta < 27.5°$. 3937 unique reflections having $I > 3\sigma(I)$ were used for structure determination and refinement. Absorption corrections were partially integrated in the data reduction procedure. The structure was solved using direct methods and refined against $|F|$. Hydrogen atoms were introduced as fixed contributors when a residual electronic was observed near their expected positions. The MeOH and one of the CH_2Cl_2 molecules are disordered over two positions lying near symmetry elements of the space group. Site C28 was refined as containing a mixture of 50% of Cl and 50% of C and site C29 was refined as containing a mixture of 50% of C and 50% of O. Three solvent atoms were kept with isotropic temperature factors, all other atoms were refined with anisotropic temperature factors. Final results: $R(F) = 0.063$, $Rw(F) = 0.083$, GOF = 1.521, maximum residual electronic density = 0.98 e Å^{-3}. For all computations the Nonius OpenMoleN package17 was used. CCDC 182/1514. See http://www.rsc.org/suppdata/cc/a909029k/ for crystallographic data in .cif format.

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