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Molecular tectonics: infinite cationic double stranded helical coordination networks

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Upon crystallisation of two bismonodentate tectons based on two pyridine units, interconnected at the *meta* position by a tetra- or hexa-ethylene glycol fragment and Ag$^+$ cation, double stranded helical infinite coordination networks were formed and structurally characterised. The cationic double helical architectures obtained may be regarded as analogues of DNA in terms of topology.

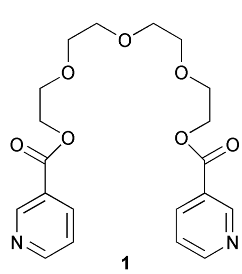
Among the purely organic helical systems, DNA is certainly the most commonly known example. The DNA double helix is formed upon self-assembly of two complementary helical strands. The driving force for the formation of the double helical arrangement is the establishment of H-bonds between complementary nucleic acid bases. However, in principle, any type of attractive interaction may be used to generate double helical architectures. In particular, one may generate such structures using coordination bonds.[1] The design of helical coordination networks is a subject of current interest.[2] Although some examples of single stranded helical coordination networks have been reported, double helical metalloorganic architectures are rather rare.[2,3] Helical assemblies may be of the finite type such as helicates[4] or infinite assemblies generated upon self-assembly of molecular organic and metallic tectons in the crystalline phase. The most well known example of the use of coordination bonds to generate double helical structures was reported by Lehn *at al.*[1] We have also demonstrated this point through the formation of a single strand helical infinite coordination network using silver cation and a macrocyclic framework bearing two 2,2′-bipyridine units.[5]

Based on our previous work on the formation of doubly interwoven coordination networks,[6] we have generated double helical arrangements, analogous to the DNA structure, through the use of coordination bonds.

Here we report on the design of two pyridine based tectons **1** and **2** and their self-assembly in the crystalline phase into infinite double helices using silver cation.

The design of the organic tectons **1** and **2** was based on the interconnection of two pyridine units as monodentate coordination sites by a polyethylene glycol fragment of different length. The junction between the two pyridines and the spacer was ensured by an ester group and the connection was achieved at the *meta* position of the aromatic ring. The polyethylene glycol was chosen because it would adopt an helical conformation and furthermore would interact with metal cations through its oxygen atoms by charge–dipole interactions. The difference between tectons **1** and **2** is related to the length of the polyethylene glycol unit. Whereas for compound **1** the pyridines were connected by a tetraethyleneglycol unit, for compound **2** the spacer was hexaethylene glycol. The two spacers were chosen in order to study the effect of the length and the conformation of the spacer on the formation and the pitch of the helical architecture. The synthesis[7] of **1** and **2** was easily achieved by treating tetra- (87% yield) and hexa- (90% yield) ethyleneglycol with nicotinoyl chloride in dry THF and in the presence of Et_3N at rt for 48 h.

Dealing with the metallic partner required to assemble the organic tectons **1** and **2** into coordination networks, Ag$^+$ cation was chosen because of its rather loose stereochemical demands.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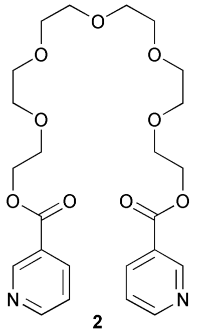
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Upon slow diffusion at rt of a EtOH solution containing $AgBF_4$ (5 mg) into a $CHCl_3$ solution of **1** (4 mg) and further evaporation of the mixture, colourless crystals were obtained after several days. An X-ray diffraction study on a single crystal† revealed, the following feature. The crystal (orthorhombic, space group *Pnna*,) is composed of **1**, Ag$^+$ cation and BF_4^- anion. The cationic part of the structure is composed of double helical networks with opposite chirality. The BF_4^- anions are disordered and located within empty spaces without any specific interactions with cationic components. The double helical network generated upon self-assembly between **1** and Ag$^+$ cation may be described as follows. The bis monodentate tecton **1** adopts an helical conformation (OCCO dihedral angles of 50.0° and 63.8°) for which the two pyridine units, which are parallel to the plane of the ester groups ($d_{C=O}$ = 1.20 Å, d_{C-O} = 1.32 Å), are outwardly oriented (Fig. 1a) and coordinated each to a silver cation (d_{Ag-N} = 2.17 Å). The iteration of the binding process, *i.e.* bridging of consecutive Ag$^+$ cations by **1** (NAgN angles of 160.9–174.0°) leads to a single stranded infinite helical coordination polymer (Fig. 1b). Two adjacent helical strands form infinite double helices (Fig. 1c) through the interactions of oxygen atoms of the tetraethyleneglycol units of one strand with Ag$^+$ cations belonging to the other strand (d_{O-Ag} of *ca.* 2.72 Å and 2.86 Å). For the double helix, the two strands are of the same chirality. The consecutive double helices are of opposite chirality and packed in a parallel fashion leading to a racemate (Fig. 1d).

In order to establish the robustness of the approach and the role played by the spacer on the formation and metrics of the double helical assembly, the tecton **2** was studied under the same conditions.

Upon slow diffusion at rt of a *i*-PrOH solution containing $AgPF_6$ (5 mg) into a PhCl solution of **2** (4 mg), colourless crystals were obtained after several days and studied by X-ray crystallography on a single crystal. The crystal (triclinic, space group $P\bar{1}$) was composed of **2**, Ag$^+$ cation, PF_6^- anion and a chlorobenzene molecule. The latter is disordered. The PF_6^- anions and the solvent molecules occupy the empty space generated upon packing of the cationic networks with no specific interactions. The cationic component of the crystal is an infinite double helical arrangement which may be described in

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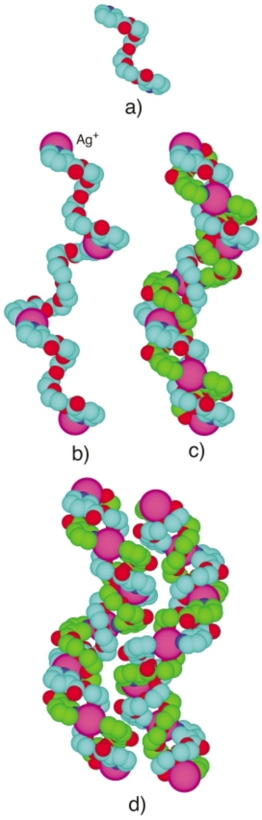

Fig. 1 Description of the conformation adopted by **1** in the crystalline phase (a), a portion of a single strand infinite helical coordination network through the bridging of consecutive tectons **1** by Ag$^+$ cations (b), a portion of the double helix formed between two single stranded helices (the chirality is arbitrary) (c) and the parallel packing of consecutive double helices with opposite chirality (d). H atoms and anions are omitted and the C atoms belonging to different strands composing the double helices are differentiated by colour for clarity.

a similar way as in the case of **1**. The tecton **2** adopts again an helical conformation (OCCO dihedral angles of 50.0° and 63.8°), however, due to the longer size of the hexaethylene glycol spacer, the latter forms a more circular array of O atoms of the pseudo crown ether type (the central COOC fragment is disordered). Again, the two pyridine units, outwardly oriented, are almost parallel to each other and coplanar. The ester groups ($d_{C=O}$ = 1.18 Å, $d_{C–O}$ = 1.35 Å) are again in the same plane as the pyridine rings. Both pyridines located at each extremity of **2** are coordinated to a silver cation ($d_{Ag–N}$ of *ca.* 2.17 Å). The translation of the coordination process (NAgN angles of *ca.* 170°) leads again to a single stranded infinite helical network (Fig. 2a). As in the case of **1**, the interactions between the oxygen atoms of the hexaethylene glycol units of one strand, adopting a pseudo crown type arrangement, with Ag$^+$ cations belonging to the other strand, with two short (2.61 Å and 2.81 Å) and two long (3.13 Å and 3.52 Å) O–Ag$^+$ distances, lead again to a double helical arrangement with the same chirality for both strands. The packing of consecutive double helices bearing opposite chirality is again parallel and leads to a racemate (Fig. 2b).

In conclusion, based on the self-assembly approach, the formation of two topologically equivalent double helical architectures in the crystalline phase was demonstrated using two tectons bearing two pyridines as monodentate coordination sites and a polyethylene glycol spacer capable of interaction with Ag$^+$ cation. The effect of the length of the spacer on the metrics of the double helix formed was also established.

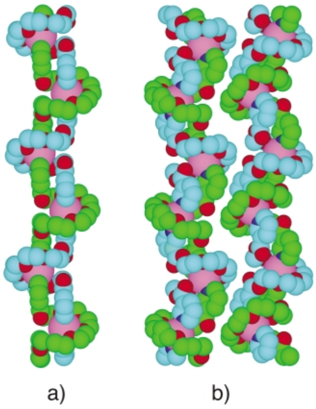

Fig. 2 A portion of the double helix formed between two single stranded helices generated upon self assembly between **2** and AgPF$_6$ (the chirality is arbitrary) (a) and the parallel packing of consecutive double helices with opposite chirality. (b) H atoms and anions and solvent molecules are omitted, the C atoms belonging to two different strands composing the double helices are differentiated by colour for clarity.

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Notes and references

† (**1**, AgBF$_4$): (Colourless, 173 K), $C_{20}H_{24}AgBF_4N_2O_7$, M = 599.10, orthorhombic, a = 20.0363(1), b = 24.8375(3), c = 10.0921(4) Å, U = 5022.3(2) Å^3, Z = 8, space group *Pnna*, D_c = 1.58 g cm^{-3}, Mo-Kα, μ = 0.874 mm^{-1}, 3612 data with $I > 3\sigma(I)$, R = 0.067, Rw = 0.079; (**2**, AgPF$_6$): (Colourless, 173 K), $C_{48}H_{64}Ag_2N_4O_{18}\cdot 2PF_6\cdot C_6H_5Cl$, M = 1603.29, triclinic, a = 9. 7761(2), b = 16.3455(3), c = 21.3158(4) Å, α = 93.081(5), β = 95.122(5), γ = 91.951(5), U = 3385.0(1) Å^3, Z = 2, space group $P\bar{1}$, D_c = 1.57 g cm^{-3}, Mo-Kα, μ = 0.766 mm^{-1}, 9409 data with $I > 3\sigma(I)$, R = 0.077, Rw = 0.103, Data were collected on a Nonius Kappa CCD and structural determination was achieved using the Nonius OpenMoleN package.[8] CCDC 197617 and 197618. See http://www.rsc.org/suppdata/cc/b2/b211226b/ for crystallographic data in CIF format.

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