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Double stranded interwound infinite linear silver coordination network[†]

Bruno Schmaltz, Abdelaziz Jouaiti, Mir Wais Hosseini* and André De Cian

Laboratoire de Chimie de Coordination Organique, Université Louis Pasteur, F-67000 Strasbourg, France. E-mail: hosseini@chimie:u-strasbg.fr

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Upon self-assembly of a bismonodentate ligand based on two pyridine units interconnected at the *para* position by a hexaethylene glycol fragment using ester junctions and Ag^+ cation, a double stranded interwound infinite linear network was obtained in the crystalline phase; the formation of this unprecedented architecture is a result of the loop type conformation of the connector segment which forms a pseudo-crown ether. The loop surounds the metal cation which is linearly coordinated to two pyridines belonging to consecutive units, thus forming the 1-D network.

The design of molecular networks, in particular in the crystalline phase, can be based on concepts developed in the context of molecular tectonics.[1a] The latter concerns the self-assembly of molecular tectons[1b] or building blocks with programmed information into their structure about the energy of inter- and intra-molecular interactions. For metallo-organic coordination networks[2,3] which are generated upon self-assembly[4] of metal cations with organic ligands and in some cases the anion[5] as tectons, the design principle lies in the match between the requirements of different partners. Under self-assembly conditions, discrete metallo-organic complexes are generated from endo-ligands in the presence of cations. In contrast, the formation of coordination networks, based on translational symmetry of assembling cores, requires the use of exo-ligands *i.e.* organic ligands for which the coordination sites are oriented in a divergent fashion.

When using flexible fragments connecting two coordination poles (composed of one or several coordination sites), depending on the conformation of the spacer, in the presence of metal cations one may expect the formation of either discrete complexes (metallamacrocycle) by an obturation process or infinite coordination networks by iteration (Fig. 1).

Pursuing our efforts to understand the basic principles governing the formation of coordination networks,[6] the above mentioned competition between the formation of discrete and infinite coordination networks was investigated by designing the bis-monodentate ligand **1**. The design of the latter was based on two coordinating pyridine units interconnected by the hexaethyleneglycol moiety using ester junctions. The two coordination sites were connected at the 4 position of the pyridine ring. The latter was chosen as a monodentate coordination site because of its frequent use in the design of coordination networks.[7] Concerning the flexible spacer, this may either be an innocent segment such as a polymethylene chain or a functionalised fragment. Owing to its well known ability to interact with cations, the hexaethylene glycol unit appeared to be the most attractive fragment since it may play both structural and recognition roles.

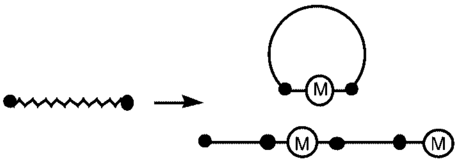


Fig. 1 Schematic representation of the competition between the formation of a metallamacrocycle and an infinite coordination polymer when a bismonodentate ligand is used in conjunction with a metal cation adopting a linear coordination geometry.

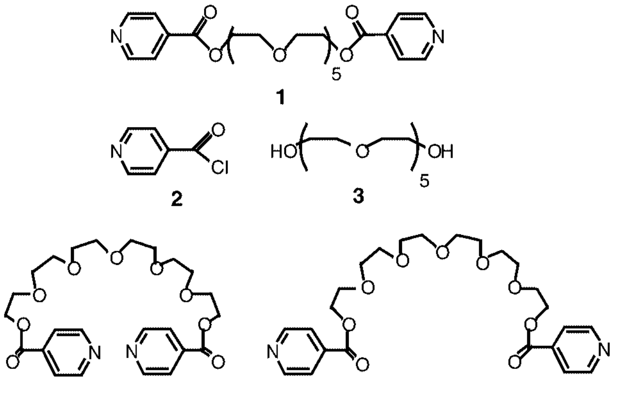
Here we report the first example in the crystalline phase of an intertwound double stranded linear coordination network based on the self assembly of ligand **1** and Ag^+ cations.

The rather straightforward synthesis of **1** (slightly yellowish oil) was achieved in THF under argon by condensing, in the presence of Et_3N, the commercially available isonicotinoyl chloride **2** with hexaethyleneglycol **3** in 86% yield (Scheme 1).

Depending on the conformation of the polyethylene glycol chain and rotations around the C(O)O bond, compound **1** (Scheme 1) may either behave as an endo-ligand with a convergent orientation of both pyridines or as an exo-ligand for which the two monodentate coordination sites are oriented in a divergent fashion. Thus, in the presence of metal cations adopting a linear coordination geometry, whereas for the first case a metallamacrocycle would be expected, for the divergent orientation an infinite coordination network should be obtained (Fig. 1).

The best suited cation appeared to be Ag^+ due to its extended coordination flexibility, in particular its ability to adopt a linear coordination geometry.

Upon slow diffusion at room temp. of a EtOH solution containing $AgClO_4$ into a PhCl solution of **1**, stable colourless crystals were obtained overnight. X-Ray diffraction[‡] on a single-crystal revealed the following relevant features: the crystal (monoclinic system, space group *C*2/*c*) was only composed of **1**, Ag^+ cations and ClO_4^- anions. No solvent molecules were present in the crystal. The combination of **1** and Ag^+ leads to the formation of an infinite polycationic linear coordination network. The latter is obtained by translation of an assembling core composed of a silver cation bridging two consecutive organic tectons. No specific interactions between the polycationic network and the ClO_4^- anions are observed. In a first approximation, the metal cation adopts a linear



Scheme 1

[†] Dedicated to G. Ourisson on the occasion of his 75 birthday.

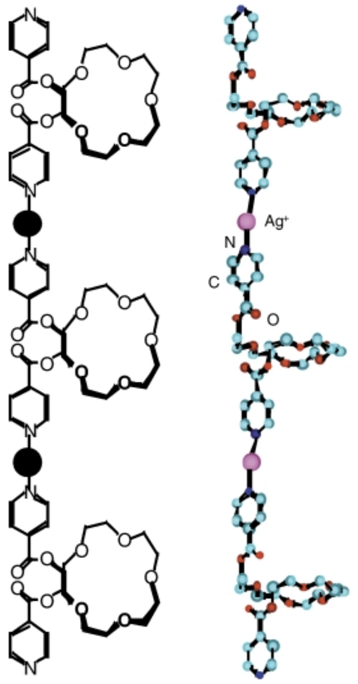


Fig. 2 Schematic (left) and a portion of the X-ray structure (right) of the cationic 1-D network obtained upon self-assembly of ligand **1** and Ag+. H atoms and anion molecules are omitted for clarity.

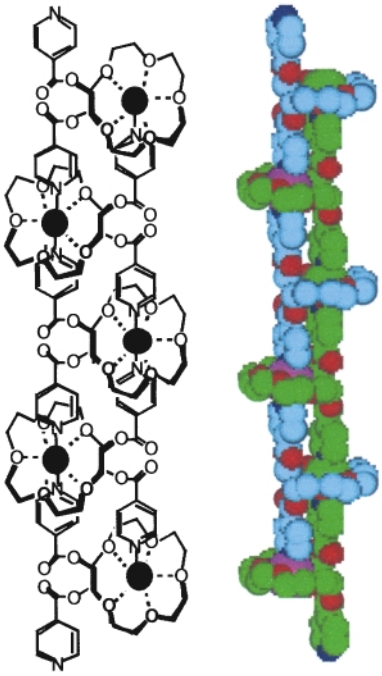


Fig. 3 Schematic (left) and a portion of the X-ray structure (right) of the double stranded cationic interwound 1-D network obtained due to interactions between Ag+ cations and hexaethylenglycol units adopting a pseudo crown ether type conformation. H atoms and anions molecules are omitted for clarity.

coordination geometry with an N–Ag–N angle of 173.6°. Due to the unsymmetrical environment of the Ag+ cation, the two N–Ag distances of 2.154 and 2.169 Å are slightly different. The ligand **1** adopts an interesting and particular conformation. The two pyridine units are almost parallel and co-planar but are oriented in opposite directions, thus allowing the formation of the network. Because of the *gauche* conformation of all six OCH_2CH_2O units, the hexaethylene glycol fragment adopts an almost circular conformation which closely resembles crown ether type units (Fig. 2). Furthermore, all pseudo-crown ether moieties adopt the same orientation and are located on the same side of the 1-D network. Of the six OCH_2CH_2O units, only one is disordered.

What was not predicted but is particularly interesting is that two adjacent linear networks are interwoven, leading thus to a double stranded interwound infinite linear network (Fig. 3). The driving force for the formation of such an architecture seems to be the loop type disposition of the polyethylene glycol units leading to interactions between silver cations belonging to one strand and selected ether oxygen atoms of the other strand. Taking into account these interactions, the coordination sphere around the cation may be described as comprising two nitrogen and five oxygen atoms. Among the five O atoms interacting with the cation, there are two rather short Ag–O distances of *ca*. 2.70 and 2.74 Å, one Ag–O distance in the medium range (3.05 Å) and two rather long Ag–O distances of *ca*. 3.26 and 3.44 Å. From this perspective, the assembling core may be regarded as a Ag+ cation interacting strongly with two pyridine units belonging to one strand and weakly with five O atoms belonging to the other strand. Another curious feature is the orientation of loops within the double stranded interwound network: whereas for one strand all the loops adopt the same type of turn, for example left, for the other strand the opposite turn (right) is observed.

In conclusion, using the neutral acyclic tecton **1** based on two pyridines interconnected by the hexaethylene glycol through two ester junctions and Ag+ cation, an unusual architecture consisting of a double stranded interwound infinite linear network was obtained unexpectedly in the crystalline phase. This observation opens the way to the design of other systems for which the nature of the coordination site, the connecting segment as well as the metal cation may be varied. Work along these lines is in progress.

Notes and references

‡ *Crystal data* for **1**·$AgClO_4$: $C_{24}H_{32}AgN_2O_9{\cdot}ClO_4$, colourless, M = 699.85, monoclinic, space group $C2/c$, a = 34.290(4), b = 10.902(2), c = 19.323(4) Å, β = 114.855(5)°, U = 6554(1) Å^3, Z = 8, D_c = 1.42 g cm^{-3}, λ(Mo-Kα) = 0.71073 Å, μ (Mo-Kα) = 0.756 mm^{-1}, 2352 data with $I > 3\sigma(I)$, R = 0.077, R_w = 0.115; Data were collected on a Nonius Kappa CCD and structural determination was achieved using the Nonius OpenMolenN package.[8] CCDC reference number 163024. See http://www.rsc.org/suppdata/cc/b103824a/ for crystallographic data in CIF or other electonic format.

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