Molecular tectonics: from enantiomerically pure sugars to enantiomerically pure triple stranded helical coordination network†‡

Philippe Grosshans,[a] Abdelaziz Jouaiti,[a] Véronique Bulach,[a] Jean-Marc Planeix,[a] Mir Wais Hosseini*[a] and Jean-François Nicoud[b]

[a] *Laboratoire de Chimie de Coordination Organique, Institut Le Bel, Université Louis Pasteur, 4, rue Blaise Pascal, 67000 Strasbourg, France*

[b] *Groupe des Matériaux Organiques, Institut de Physique et Chimie des Matériaux de Strasbourg, CNRS (UMR 7504), et Université Louis Pasteur BP 43 23, rue du Loess, 67034 Strasbourg Cedex 2, France*

The self-assembly between a bis-monodentate tecton based on two pyridine units connected to an enantiomerically pure *iso*mannide stereoisomer and HgCl₂ leads to the formation of an enantiomerically pure triple stranded helical infinite coordination network which was structurally characterised by X-ray diffraction on single crystal.

The control of helicity at the molecular level is a fascinating area of research for chemists. Abiotic helical architectures may either be of the discrete type[1] or infinite networks. The latter class may be described as 1-D self-assembled molecular building blocks or tectons capable of mutual recognition. The majority of helical molecular assemblies in the crystalline phase reported to date are based on the use of achiral building blocks. In that case, two possibilities may occur. Either crystals are composed of both P and M helices (centric space group) affording thus an internal racemate or by a spontaneous resolution process, each crystal is enantiomerically pure (P or M helicity, chiral space group) but the mixture of crystals is a racemate. Let us focus on helical coordination networks which are formed by self-assembly processes, through mutual interconnection between organic and metallic tectons.[2] Continuing our effort in this area,[3] we systematically explore in the crystalline phase the possibility of generating enantiomerically pure helical coordination networks through the use of enantiomerically pure organic and/or metallic tectons. Here we report on the formation of a helical network based on the use of the enantiomerically pure organic tecton **1** (Scheme 1).

*Iso*mannide **5** and *iso*sorbide **6** are interesting scaffolds for the design of enantiomerically pure tectons such as **1–4**. Isomannide has been previously utilised in the design of crown ether type receptors and [2]catenanes.[4] These skeletons may be easily functionalised with a variety of monodentate units leading to bis-monodentate ligands with the two coordination sites oriented in a divergent fashion and thus allowing them to behave as tectons. Owing to the *cis*-junction of the two five membered rings, both compounds **5** and **6** adopt a "roof"-type shape. The two backbones differ by the stereochemistry of the C atoms bearing the OH group. In the case of **5**, the two OH groups point towards the concave face of the bicyclic structure, whereas for **6** they are pointing in opposite directions. The design of **1–4** is based on the functionalisation of **5** and **6** with two pyridine units as neutral coordination sites through the formation of ester junctions. Whereas **1** and **3** bearing two nicotinoyl and *iso*nicotinoyl units respectively are derived from *iso*mannide **5**, **2** and **4** bearing the same coordinating groups are generated from **6**.

The straightforward synthesis of **1–4** was achieved in *ca* 60% yield at room temperature upon esterification in dry tetrahydrofuran of **5** or **6** using *iso*nicotinoyl- (**7**) or nicotinoyl-chloride (**8**) in the presence of Et₃N. All four compounds were fully characterised both in solution by NMR spectroscopy and in the solid state by X-ray diffraction on single crystals (data not reported here).

Dealing with the metallic component, since the tecton **1** is neutral, we believed that a combination of a dicationic metal centre allowing linear bridging and two strongly coordinating anions would be of interest because it would lead to a double component system. For that reason HgCl₂ was chosen.

Upon slow diffusion at room temperature of a EtOH solution (2 ml) containing HgCl₂ (5 mg) into a CHCl₃ solution (1 ml) of **1** (5 mg), colourless crystals were obtained after several days and analysed by X-ray diffraction on a single crystal.§ The crystal (orthorhombic, space group $P2_12_12_1$) is exclusively composed of **1** and HgCl₂. As expected, the mutual interconnection between the organic tecton **1** and HgCl₂ leads to an enantiomerically pure helical strand with P chirality (Fig. 1a). The latter fact results from the predefined stereochemistry of *iso*mannide. For the organic moiety **1**, the two pyridine units connected to the *iso*mannide backbone through ester junctions ($d_{C-O} = 1.35$ Å and $d_{C=O} = 1.20$ Å) are almost parallel and divergently oriented towards the concave face of the bicyclic unit. The bridging of the organic tectons **1** by HgCl₂ units generates an infinite 1-D coordination network with helical geometry. The Hg²⁺ cation adopts a distorted square planar geometry with the two Cl⁻ anions ($d_{Hg-Cl} = 2.32$ Å) and the
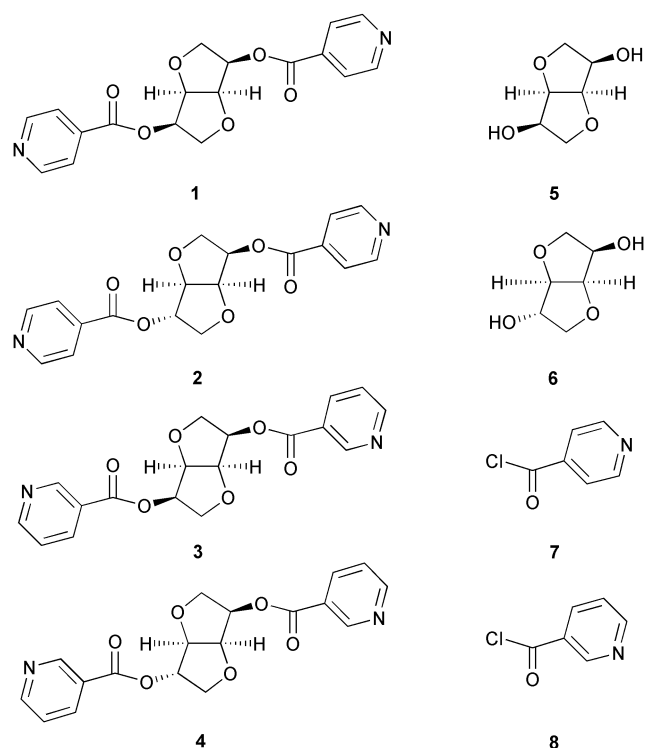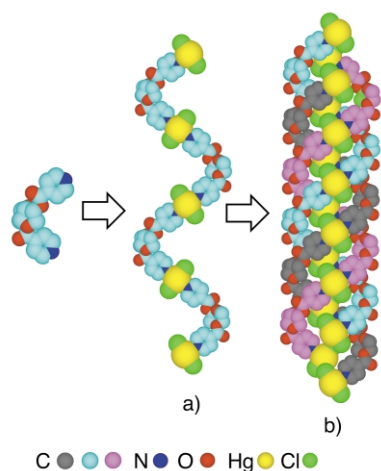

Scheme 1

Fig. 1 A perpendicular view in respect of a portion of the enantiomerically pure infinite helical 1-D coordination network (P helicity) formed upon bridging of consecutive tectons **1** by HgCl$_2$ (a) and a portion of the triple stranded helix formed between three single stranded helices through aromatic/aromatic interactions (b). H atoms are omitted and the C atoms belonging to different strands composing the triple helix are differentiated by colour for clarity.

two N atoms (d_{Hg-N} = 2.65–2.68 Å) in *trans* configuration (ClHgN angle varying between 89° and 91.3°, ClHgCl of 179° and NHgN angle of 168.9°).

Unexpectedly, the X-ray diffraction study revealed the formation of a triple stranded helical arrangement (Fig. 1b) resulting from interstrand interactions between pyridine units of different strands (distance between centroids of *ca* 3.73 Å). The triple stranded helices thus formed are not cylindrical but rather flat and arranged in a parallel fashion.

Furthermore, the triple stranded helical units are further interconnected through coordination bonding (d_{Hg-O} = 2.93 Å) between the O atoms of the carbonyl group of ester groups belonging to a triple stranded helices and Hg centres of the adjacent triple helices. When taking into account the lateral interconnection between triple helices, the coordination geometry around Hg^{2+} cation may be described as a distorted square based pyramid (OHgCl angle 88.6° and 92.2°, OHgN angle 79.0° and 112.0°) and the overall structure as a 3-D coordination network (Fig. 2).

In conclusion, using an enantiomerically pure organic tecton derived from *iso*mannide, the formation of an enantiomerically pure helical coordination network was demonstrated. Three infinite helical strands with P chirality self-assemble into a triple stranded non cylindrical architecture through aromatic/aromatic interactions. The triple stranded helices are packed parallel to each other and further interconnected through O–Hg interactions. The overall structure may be described as a 3-D network resulting from the interconnection of triple stranded helical 1-D networks. The formation of helical coordination networks using the other tectons **2–4** and other metallic centres are currently under investigation.
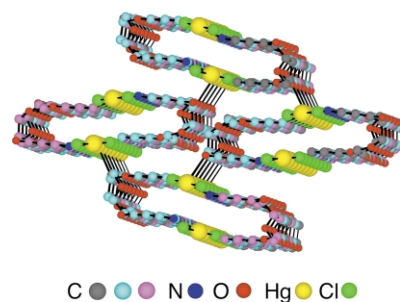
Fig. 2 A parallel view on the lateral packing of enantiomerically pure triple stranded helices and their interconnection through O–Hg bonding leading to a 3-D coordination network (See text). H atoms are omitted and the C atoms belonging to two different strands composing the triple helices are differentiated by colour for clarity.

Notes and references

§ **1**: (**1**-HgCl$_2$): (Colourless, 173 K), C$_{18}$H$_{16}$Cl$_2$Hg N$_2$O$_6$, M = 627.830, orthorhombic, a = 8.98190(10), b = 13.5846(2), c = 16.3968(2) Å, U = 2000.66(4) Å^3, Z = 4, space group $P2_12_12_1$, DC = 2.08 g cm^{-3}, Mo–Kα, μ = 7.998 mm^{-1}, 5470 data with $I > 2\sigma(I)$, R = 0.026, Rw = 0.0580. Data were collected on a Nonius Kappa CCD and structural determination was achieved using Nonius Maxus Package 4.3. CCDC 206101. See http://www.rsc.org/suppdata/cc/b3/b303238h/ for crystallographic data in .cif or other electronic format.

1 J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier and D. Moras, *Proc. Natl. Acad. Sci., USA.*, 1987, **84**, 2565; E. D. Constable, in *Comprehensive Supramolecular Chemistry*, Eds. J. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, Pergamon, 1996, **9** (Vol. Eds. J. P. Sauvage, M. W. Hosseini), 213; C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005; M. Albrecht, *Chem. Rev.*, 2001, **101**, 3457.

2 M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li and M. Schröder, *Angew. Chem., Int. Ed.*, 1997, **36**, 2327; L. Carlucci, G. Ciani, D. W. v. Gudenberg and D. M. Proserpio, *Inorg. Chem.*, 1997, **36**, 3812; M. Munakata, L. P. Wu and T. Kuroda-Sowa, *Adv. Inorg. Chem.*, 1999, **46**, 173; R. W. Saalfrank, H. Maid, F. Hampel and K. Peters, *Eur. J. Inorg. Chem.*, 1999, 1859; K. Nomiya S. Takahashi and R. Noguchi, *J. Chem. Soc., Dalton Trans.*, 2000, 1343; S. Sailaja and M. V. Rajasekharan, *Inorg. Chem.*, 2000, **39**, 4586; A. Erxleben, *Inorg. Chem.*, 2001, **40**, 2928; D. M. Ciurtin, N. G. Pshirer, M. D. Smith, U. H. F. Bunz and H.-C. zur Loye, *Chem. Mater.*, 2001, **13**, 2743; F. Tuna, J. Hamblin, G. Clarkson, W. Errington, N. W. Alcock and M. J. Hannon, *Chem. Eur. J.*, 2002, **8**, 4957; X.-M. Chen and G.-F. Liu, *Chem. Eur. J.*, 2002, **8**, 4811.

3 C. Kaes, M. W. Hosseini, C. E. F. Rickard, B. W. Skelton and A. White, *Angew. Chem. Int. Ed.*, 1998, **37**, 920; W. Jaunky, M. W. Hosseini, J.-M. Planeix, A. De Cian, N. Kyritsakas and J. Fischer, *Chem. Commun.*, 1999, 2313; B. Schmaltz, A. Jouaiti, M. W. Hosseini and A. De Cian, *Chem. Commun.*, 2001, 1242; A. Jouaiti, M. W. Hosseini and N. Kyritsakas, *Chem. Commun.*, 2002, 1898; A. Jouaiti, M. W. Hosseini and N. Kyritsakas-Gruber, *Chem. Commun.*, 2003, 472.

4 J. C. Metcalfe, J. F. Stoddart, G. Jones, T. H. Crawshaw, A. Quick and D. J. Williams, *Chem. Commun.*, 1981, 430; P. R. Ashton, A. M. Helss, D. Pasini, F. M. Raymo, A. N. Shipway, F. J. Stoddart and N. Spencer, *Eur. J. Org. Chem.*, 1999, 995.