



Preliminary communication / Communication

Molecular tectonics: design and structural analysis of enantiomerically pure tectons and helical coordination networks

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Received 7 September 2003; revised and accepted after revision 21 January 2004

This contribution is dedicated to the memory of Marie-Claire Dillenseger

Abstract

The synthesis of the four new enantiomerically pure coordinating tectons based on *isomannide* or *isosorbide* backbone bearing two pyridine units as coordination sites was achieved and their structure analysed by X-ray diffraction on single crystals. The junction between the pyridine units, connected to the sugar moieties at either position 3 or 4, was achieved by ester groups. Under self-assembly conditions, a mixture of the tecton based on *isomannide* bearing two nicotinoyl groups and HgCl₂ generates in the crystalline phase an enantiomerically pure single stranded helical assembly. As demonstrated by X-ray diffraction on single crystal, the infinite directional coordination networks are packed in the *syn*-parallel fashion, leading thus to a polar crystal.

To cite this article: P. Grosshans *et al.*, *C. R. Chimie* 7 (2004).

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Résumé

Quatre nouveaux tectons à base d'*isomannide* ou *isosorbide*, portant deux unités coordinantes du type pyridine connectées en position 3 ou 4 par des jonction ester, ont été synthétisés, et leur structure a été étudiée à l'état solide par diffraction des rayons X. Dans des conditions d'auto-assemblage, le tecton à base d'*isomannide* et portant deux groupes nicotinoyls conduit, en présence de HgCl₂, à la formation d'une hélice simple metalloorganique énantiomériquement pure. L'étude radiocristallographique par diffraction des rayons X sur monocristal montre que l'arrangement parallèle de ces réseaux de coordination monodimensionnels conduit à la formation d'un cristal polaire. **Pour citer cet article:** P. Grosshans *et al.*, *C. R. Chimie* 7 (2004).

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Keywords: Pyridine; Tecton; Ligand; Isomannide; Isosorbide; Mercury; Helix; Structure; Network

Mots clés: Pyridine; Tecton; Ligand; Isomannide; Isosorbide; Mercure; Hélice; Structure; Réseau

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1. Introduction

Molecular networks in the crystalline phase are infinite periodic molecular architectures resulting from mutual interconnection of molecular tectons [1]. Tectons are active molecular building units containing in their framework energetic and geometric information concerning the designed networks. These molecular assemblies are generated by self-assembly processes taking place between complementary tectons. Molecular tectonics [2] is a branch of supramolecular chemistry dealing with the design of tectons, networks and self-assembly [3] processes leading to the formation of finite or infinite molecular networks. The dimensionality of molecular networks is defined by the number of translations of the connecting nodes, which may be defined as a recognition pattern. Thus 1-, 2- and 3-D networks result from 1, 2 and 3 translations, respectively. The recognition pattern may be classified by the nature of the interaction between consecutive tectons. So far, three classes of networks have been defined. For the first category, called inclusion networks, the recognition pattern is essentially based on van der Waals interactions [4]. The second and third classes based on H- [5] and coordination- [6] bonds are the most frequently investigated.

Let us focus on 1-D coordination networks based on mutual bridging of organic and metallic tectons through the formation of coordination bonds. For these architectures, resulting from a single translation into one direction of space of one or several assembling nodes, in terms of geometry, four possibilities, i.e. linear (a), stair (b) and 'zigzag' (c) types and helical (d) may be considered (Fig. 1). We have previously demonstrated the possibility of generating a polar crystal based on the linear type arrangement using an enantiomerically pure tecton possessing C_2 chirality [7]. In terms of design, a further possibility, which may lead to the formation of a polar crystal, may be based on the use of enantiomerically pure 1-D coordination networks based on a chiral tecton presenting helicity. Pursuing our studies on the design and formation of coordination networks [8] and in particular helical structures [9–11], we have initiated a study dealing with the design of enantiomerically pure coordinating tectons and their assembly into helical structures. Helical assemblies based on coordination processes may either be of the discrete type, such as helicites [12] or infinite networks [13].

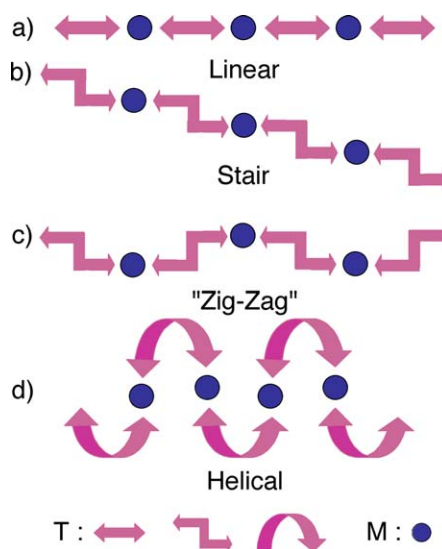


Fig. 1. Schematic representation of linear (a), stair (b), 'zigzag' (c) and helical (d) geometries for 1-D coordination networks.

Here we report the design, synthesis and structural analysis of a series of four tectons **1–4** (Scheme 1) based on *isomannide* or *isosorbide* scaffold bearing two pyridine units as well as an enantiomerically pure 1-D helical mercury coordination network.

2. Results and discussion

2.1. Design and synthesis of tectons

Isomannide **5** and *isosorbide* **6** are two readily available enantiomerically pure diols that may be used as backbones for the design of enantiomerically pure tectons. In particular, the functionalisation of these two scaffolds by two pyridine derivatives as monodentate coordinating units affords coordinating tectons of interest for the generation of coordination networks in the presence of appropriate metal centres. Although in both cases, due to the *cis*-junction of the two five membered rings, a 'roof'-type shape is generated for the backbones, they differ by the stereochemistry of the C atoms bearing the OH groups. Indeed, whereas for *isomannide* **5**, the two OH groups point towards the interior of the 'roof', for *isosorbide* **6** they point in opposite directions. Thus, for that reason, the double functionalisation of **5** and **6** by coordination sites leads to two constitutionally identical tectons, but differing by the orientation of the coordinating sites. Enantio-

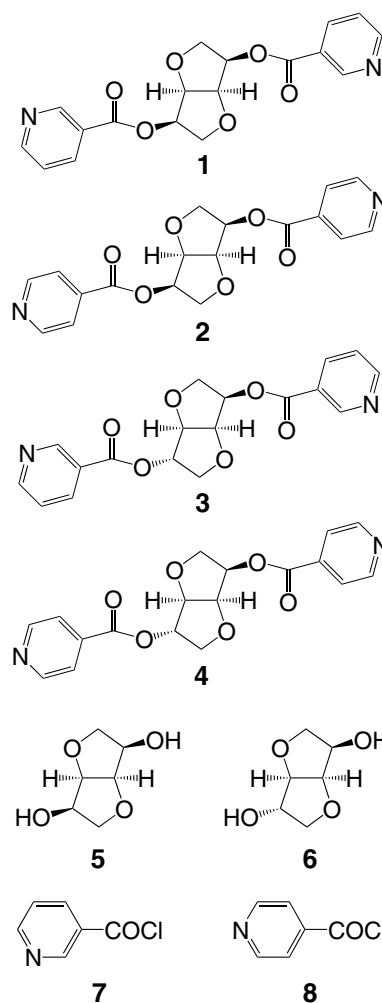
merically pure tectons **1–4** are of the bismonodentate type, based either on the *isomannide* (tectons **1** and **2**) or *isosorbide* (tectons **3** and **4**) backbones. Within each category, the tectons differ by the position of attachment of the pyridine derivative to the backbone. Thus, for tectons **1** and **3**, the position 3 of the six-membered ring (with respect to the N atom) is used, whereas for tectons **2** and **4**, the pyridine units are connected at position 4. In all cases, the junction between **5** or **6** and the pyridine moiety is ensured by ester groups.

Crown ether type receptors and [2]catenanes based on the *isomannide* skeleton have been reported [14].

The synthesis of tectons **1–4**, rather straightforward, was achieved at room temperature upon treatment of either **5** or **6** by commercially available nicotinoyl chloride **7** or *isonicotinoyl* chloride **8** as their hydrochloride salts in dry THF and in the presence of Et₃N. All four compounds were obtained as crystalline materials. In addition to classical characterisation methods, all four tectons were structurally characterised in the solid state by X-ray diffraction on single crystals (scheme 1).

2.2. Design and synthesis of coordination networks

For the design of coordination networks that may be defined by (oT, mT), one must consider both the organic tecton oT (shape, number, nature and disposition of coordinating sites, charge) and metallatecton mT (oxidation state, coordination sphere, number and disposition of available coordination sites). The latter may either be a metallic centre often cationic in nature, or a coordination complex possessing available coordination sites. When using a neutral organic tecton oT such as **1–4**, for the choice of the metallic tecton mT, two possibilities may be explored: (i) a combination of neutral oT and neutral mT, leading thus to a neutral coordination network of the type (oT, mTL). In that case, the mT is a neutral coordination complex of the type [Mⁿ⁺Lⁿ⁻], for which the positive charge on the metal is compensated by the negative charge of the auxiliary ligand L. The other possibility consists in the formation of a polycationic coordination network [(oT, mT)]^{x+} associated with non-coordinating anions that neither take part in the formation of the network nor are connected to the network by coordination bonds. In that case, the solid would be defined as [(oT, mT)]^{x+}, xA⁻ for mono charged anions or as [(oT, mT)]^{x+},



Scheme 1

$0.5 \times A^{2-}$] for doubly charged anions. Although the latter case has been frequently exploited [6], we have previously demonstrated the use of coordinating anions as a design principle for the generation of neutral coordination networks [7].

As stated above, tectons **1–4** are neutral bismonodentate construction units. In particular, the tecton **1**, because of the chiral nature of *isomannide*, is an enantiomerically pure unit suitable for the formation of helical coordination networks when associated with a metallatecton offering two available coordination sites. For that reason and based on our previous studies [11,15], HgCl₂, a neutral metallatecton presenting two available coordination sites, was considered.

Table 1
X-ray data for tectons **1–4** and for the helical coordination network formed between **1** and HgCl₂

	1	2	3	4	1–HgCl₂
Chemical Formula	C ₁₈ H ₁₆ N ₂ O ₆	C ₁₈ H ₁₆ N ₂ O ₆	C ₁₈ H ₁₆ N ₂ O ₆	C ₁₈ H ₁₆ N ₂ O ₆	C ₁₈ H ₁₆ N ₂ O ₆ Cl ₂ H
Formula weight	356.33	356.33	356.33	356.33	627.83
Crystal system	Tetragonal	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
Space group	<i>P</i> 4 ₁ 2 ₁ 2	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>C</i> 2
<i>a</i> (Å)	5.9173(5)	7.3349(3)	6.8647(2)	6.3552(2)	30.2492(11)
<i>b</i> (Å)	5.9173(3)	9.5189(4)	11.0211(4)	12.0559(4)	7.4892(6)
<i>c</i> (Å)	44.963(2)	23.2735(9)	21.1580(10)	22.0464(7)	8.7898(9)
<i>α</i> (deg)	90.00	90.00	90.00	90.00	90.00
<i>β</i> (deg)	90.00	90.00	90.00	90.00	92.365(7)
<i>γ</i> (deg)	90.00	90.00	90.00	90.00	90.00
<i>U</i> (Å ³)	1574.3(2)	1624.96(11)	1600.74(11)	1689.14(9)	1989.56(3)
<i>D</i> _{calc} (g cm ⁻³)	1.50	1.46	1.48	1.40	2.10
<i>Z</i>	4	4	4	4	4
Colour	colourless	colourless	colourless	colourless	colourless
Crystal dimensions (mm)	0.34 × 0.28 × 0.18	0.36 × 0.24 × 0.17	0.20 × 0.20 × 0.12	0.26 × 0.22 × 0.12	0.34 × 0.16 × 0.16
<i>μ</i> (Mo K α) (mm ⁻¹)	0.12	0.11	0.11	0.11	8.04
Temperature (K)	173.00	173.00	173.00	173.00	173.00
Number of data measured	2343.00	4732.00	4646.00	4884.00	7004.00
Number of data with <i>I</i> > 2 σ (<i>I</i>)	1687.00	3728.00	3804.00	3807.00	5407.00
<i>R</i>	0.040	0.044	0.043	0.042	0.039
<i>R</i> _w	0.080	0.11	0.096	0.091	0.115
GOF	1.013	1.089	1.076	1.013	1.093
CCDC No.	216 738	216 737	216 739	216 740	216 741

2.3. Solid-state structural studies

The X-ray diffraction study on single crystal of tectons **1–4** revealed the following features (Table 1). Dealing with tectons **1** and **3** (Fig. 2) bearing two nicotinoyl moieties, whereas **1** crystallises in the tetragonal system (space group *P*4₁2₁2), **3** crystallises in the orthorhombic system (*P*2₁2₁2₁). For the other two tectons **2** and **4** (Fig. 3) bearing two isonicotinoyl groups, they both crystallise in the orthorhombic system (*P*2₁2₁2₁). For all four cases, the crystal is exclusively composed of the organic tecton and no solvent molecule is present in the lattice. As expected, for tectons **1** and **2** based on the isomannide backbone, the two pyridine units are almost parallel and oriented towards the concave face of the bicyclic unit. For the other two tectons **3** and **4** based on the isosorbide scaffold, the two pyridine groups are oriented in the opposite directions (one towards the interior and the other towards the exterior of the concave skeleton). Except for the orientation of the pyridine units controlled by the backbones and the connecting positions, the other structural characteristics such as bond dis-

tances and angles are almost identical for all four tectons **1–4**. Indeed, for the ester junctions, *d*_{C–O} is ranging between 1.34 and 1.35 Å, *d*_{C=O} varies between 1.19 and 1.20 Å, the OCO angle varies between 123.4 and 124.7°. However, the orientation of the plane of the pyridine ring with respect to plane of the ester varies rather strongly (OCCC dihedral angle of (–10.4°, –10.4°) for **1**, (10.3°, –12.2°) for **2**, (–5.2°, –18.0°) for **3**, (19.6°, 3.2°) for **4**).

Upon diffusion at room temperature of a solution of the tecton **1** in CHCl₃ into a solution of HgCl₂ in EtOH, colourless crystals were obtained and studied by X-ray diffraction on single crystal. The crystal is exclusively composed of **1** and HgCl₂ and no solvent molecule is present in the lattice (Table 1). As expected, the mutual interconnection between the organic tecton **1** and HgCl₂ metallatecton leads to an enantiomerically pure neutral single stranded infinite helix with P helicity (Fig. 4). The observed P helicity results from the defined stereochemistry of the isomannide unit and consequently of the tecton **1**. The infinite helical network crystallises in the non-centrosymmetric polar space group *C*2 in the monoclinic system. For the tecton **1**,

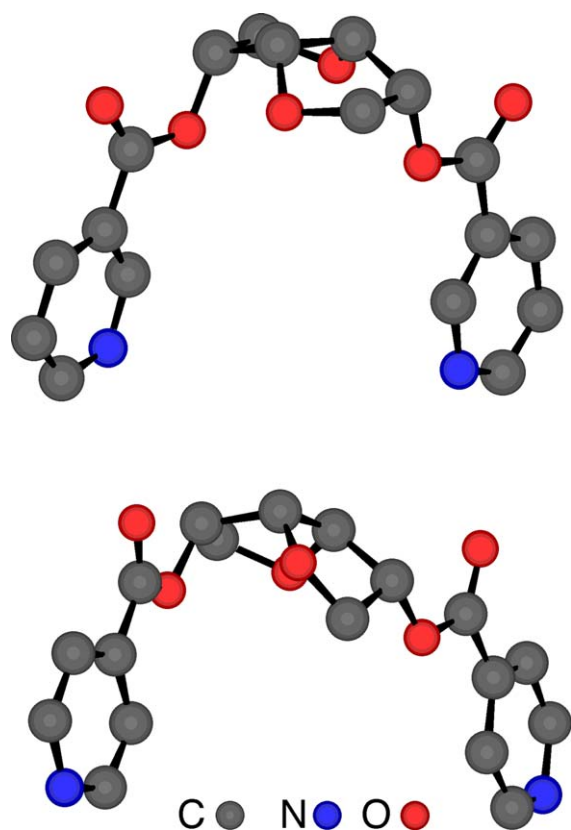


Fig. 2. Crystal structures of tectons **1** (top) and **3** (bottom). H atoms are omitted for clarity. For bond distances and angles, see text.

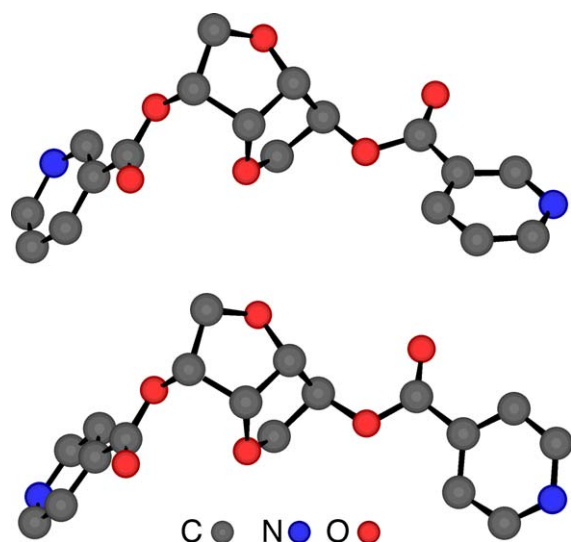


Fig. 3. Crystal structures of tectons **2** (top) and **4** (bottom). H atoms are omitted for clarity. For bond distances and angles, see text.

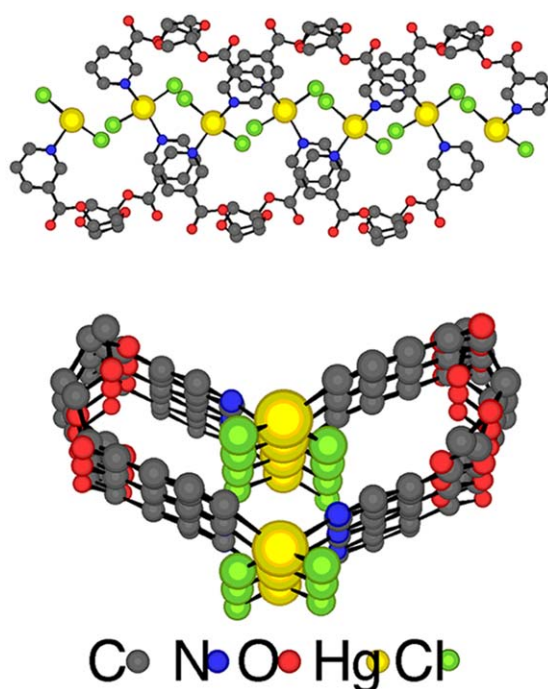


Fig. 4. Perpendicular (top) and along the helix axis (bottom) views of a portion of the enantiomerically pure infinite helical 1-D coordination network (P helicity) formed upon bridging of consecutive tectons **1** by HgCl_2 . H atoms are omitted for clarity. For bond distances and angles, see text.

the two pyridine units connected to the *isomannide* backbone through ester junctions (average $d_{\text{C-O}}$ of ca 1.33 Å and average $d_{\text{C=O}}$ of ca 1.20 Å, OCO angle of 124.2° and 125.2°) are almost parallel and convergently oriented towards the concave face of the backbone. The pyridine rings are tilted with respect to plane of the ester (OCCC dihedral angle of 0.0° and -9.3°. The infinite 1-D coordination network with helical geometry may either be regarded as resulting from bridging of the organic tectons **1** by HgCl_2 units or conversely as interconnection of HgCl_2 complexes by the organic tecton **1**. The coordination sphere around both crystallographically non-equivalent Hg^{2+} cations is composed of two N atoms belonging to two consecutive organic tectons **1** ($d_{\text{Hg-N}}$ varying between ca 2.37 Å and ca 2.43 Å) and two chloride anions (average $d_{\text{Hg-Cl}}$ of ca 2.37 Å). Both crystallographically non-equivalent Hg^{2+} cation adopts a distorted tetrahedral (Cl-Hg-N angle varying between 96.6° and 97.9°, Cl-Hg-Cl angle varying between 148.0° and 150.2° and N-Hg-N angle varying between 121.2° and 121.6°). The distance between two consecutive Hg^{2+}

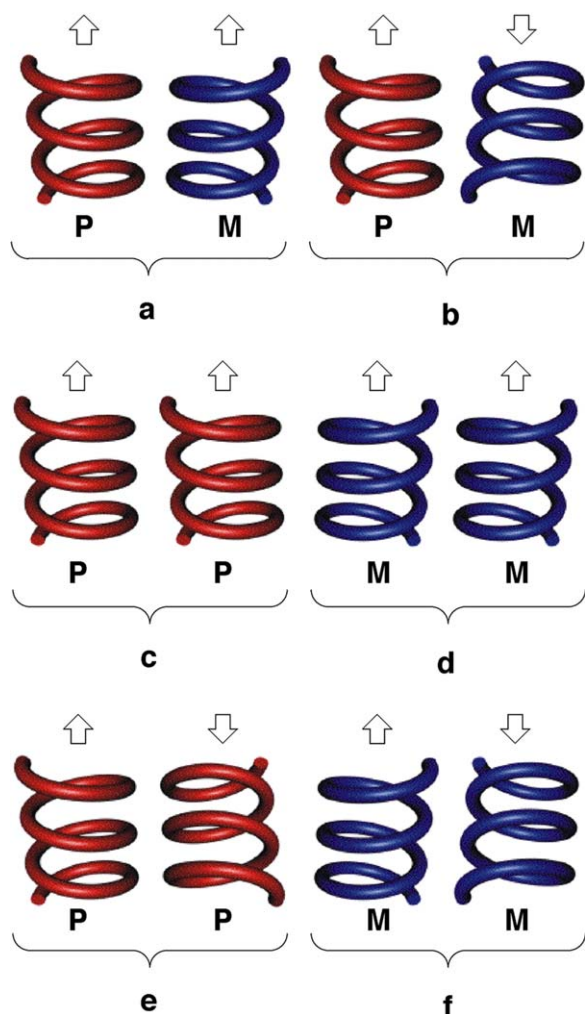


Fig. 5. Schematic representation of different possibilities of arrangement of infinite helical strands. Polar (a) and apolar (b) arrangements for a racemate (heterochiral mixture), polar (c and d) and apolar (e and f) for a homochiral system. The arrow represents the direction of polarity.

cations is 5.76 Å. The helix extends along the *c* axis. The fragment that determines the pitch (8.79 Å) of the helix is composed of two HgCl₂ and two tectons **1**.

Let us consider the parallel packing of infinite helical strands (Fig. 5). In principle, one may envisage several possibilities. For a racemate (presence of the same amounts of helices with P and M helicity: (P,M)), the *syn*-parallel arrangement will lead to a polar assembly (Fig. 5a), whereas the *anti*-parallel packing will generate a non-polar architecture (Fig. 5b). The prefix *syn* or *anti* is used in order to define the orientation of the polar axis of the helix. For the homochiral situation

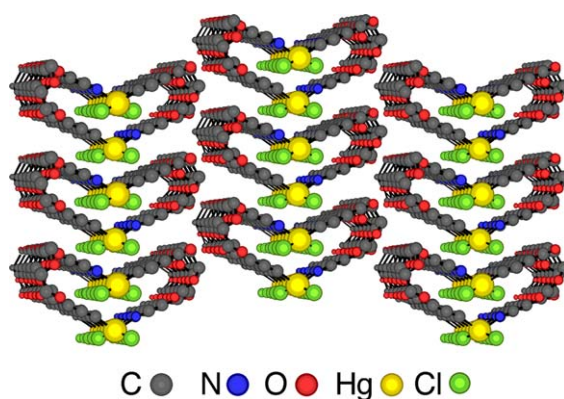


Fig. 6. A parallel view on the lateral packing of enantiomerically pure single stranded helices showing the *syn*-parallel arrangement of helical strands and the formation of a polar crystal. H atoms are omitted for clarity.

(exclusive presence of enantiomerically pure helices either with P or M helicity), again depending on the orientation of the polar axis of the helices, either polar (Fig. 5c and d) or apolar assemblies (Fig. 5e and f) may be formed. In the case of the enantiomerically pure helical arrangement obtained upon self-assembly of the tecton **1** and HgCl₂, the packing of the helical strands takes place in the *syn*-parallel mode (of the type c, Fig. 5) and, consequently, the crystal formed is polar (Fig. 6). The analysis of packing revealed no specific interaction between helical strands in the crystal.

The combination of **1** with HgCl₂ is rather different from the combination of **2** and HgCl₂. Indeed, using HgCl₂ as a metallatecton, whereas the tecton **1** leads to the formation of a single stranded helical architecture, the tecton **2** generates a triple helix [11].

2.4. Conclusion

The synthesis of four new pyridine containing tectons **1–4** based on isomannide (**1,2**) and isosorbide (**3,4**) skeletons was achieved and their structure elucidated in the solid state by X-ray diffraction on single crystals. Under self-assembly conditions and in the presence of HgCl₂, the tecton **1** based on the isomannide backbone bearing two nicotinoyl moieties generates in the solid state an enantiomerically pure 1-D coordination network of the helical type. The *syn*-parallel packing of the single stranded helices leads to the formation of a polar crystal. The formation of either chiral metallamacrocycles or infinite coordination networks using other metals is currently under investigation.

3. Experimental section

3.1. Synthesis of tectons

3.1.1. General

All commercially available reagents were purchased and used without further purification. ^1H and ^{13}C NMR spectra were recorded on Bruker spectrometers at 400 and 300 MHz and at 50 MHz, respectively. Microanalyses were performed by the Service de microanalyses de la fédération de recherche chimie, 'université Louis-Pasteur', Strasbourg, France.

Polarimetric measurements were performed on a JASCO DIP370 digital polarimeter. The optical rotation was measured at 20 °C at the concentration of 1.00 mol l⁻¹ in CHCl_3 .

3.1.2. General procedure for the synthesis of compounds 1–4

To a solution (150 ml) of **5** or **6** (1 g, 6.8 mmol) in dry THF, **7** or **8** (3.05 g, 17.1 mmol, 2.5 equiv) was added as its hydrochloride salt and the mixture was stirred at room temperature for 15 min. To the mixture Et_3N (4 ml) was added and stirring was further continued overnight. After evaporation to dryness, to the residue was added a saturated aqueous solution of Na_2CO_3 (40 ml) and the mixture extracted with CH_2Cl_2 (3 × 30 ml). The evaporation to dryness left a residue that was suspended in CH_2Cl_2 . The pure compounds **1–4** were obtained by filtration over alumina as white solids which were further recrystallised by slow evaporation of CHCl_3 /hexane 3:2 mixture containing the desired compound.

1 (1.46 g, 60% yield): mp 130 °C, $[\alpha]_{\text{D}} = +223.3$; anal. calc. for $\text{C}_6\text{H}_{16}\text{N}_2\text{O}_6$ ($m_w = 356.33$): C 60.67%; H 4.53%, N 7.86%, found: C 59.95%; H 4.60%, N 7.99%; $^1\text{H-NMR}$ (25 °C, CDCl_3): δ (ppm) 4.01 (m, 2H), 4.14 (m, 2H), 4.89 (m, 2H), 5.34 (m, 2H), 7.40 (m, 2H), 8.32 (m, 2H), 8.79 (m, 2H), 9.26 (dd, 2H, $J = 0.8$ Hz and 2.2 Hz); $^{13}\text{C-NMR}$ (25 °C, CDCl_3) δ (ppm): 70.6, 74.4, 80.6, 123.3, 125.3, 137.2, 151.0, 153.8, 164.6.

2 (1.5 g, 62% yield): mp 145 °C, $[\alpha]_{\text{D}} = +198.6$; anal. calc. for $\text{C}_6\text{H}_{16}\text{N}_2\text{O}_6$ ($m_w = 356.33$): C 60.67%; H 4.53%, N 7.86%, found: C 59.82%; H 4.61%, N 7.82%; $^1\text{H-NMR}$ (25 °C, CDCl_3): δ (ppm) 4.00 (m, 2H); 4.13 (m, 2H), 4.90 (m, 2H), 5.35 (m, 2H), 7.87 (dd, 4H, $J = 1.6$ and 4.4 Hz), 8.79 (dd, 4H, $J = 1.6$ and

4.4 Hz); $^{13}\text{C-NMR}$ (25 °C, CDCl_3) δ (ppm): 70.5, 74.7, 80.5, 122.8, 136.5, 150.7, 164.5.

3 (1.41 g, 58% yield): mp 129 °C, $[\alpha]_{\text{D}} = +32.0$; anal. calc. for $\text{C}_6\text{H}_{16}\text{N}_2\text{O}_6$ ($m_w = 356.33$): C 60.67%; H 4.53%, N 7.86%, found: C 59.82%; H 4.61%, N 7.82%; $^1\text{H-NMR}$ (25 °C, CDCl_3): δ (ppm) 4.08 (m, 4H), 4.67 (d, 1H, $J = 4.75$ Hz), 5.08 (t, 1H, $J = 5.1$ Hz), 5.41 (m, 2H), 8.29 (m, 2H), 9.20 (d, 1H, $J = 0.8$ Hz), 9.25 (d, 1H, $J = 2.2$ Hz); $^{13}\text{C-NMR}$ (25 °C, CDCl_3) δ (ppm): 70.5, 74.5, 80.6, 123.3, 125.3, 137.2, 151.0, 153.8, 164.6.

4 (1.29 g, 53% yield): mp 138 °C, $[\alpha]_{\text{D}} = +41.8$; anal. calc. for $\text{C}_6\text{H}_{16}\text{N}_2\text{O}_6$ ($m_w = 356.33$): C 60.67%; H 4.53%, N 7.86%, found: C 60.40%; H 4.46%, N 7.91%; $^1\text{H-NMR}$ (25 °C, CDCl_3): δ (ppm) 4.07 (m, 4H), 4.67 (d, 1H, $J = 4.7$ Hz), 5.06 (t, 1H, $J = 5.1$ Hz), 5.43 (q, 1H, $J = 5.2$ Hz), 5.49 (s, 1H), 7.80 (d, 2H, $J = 4.7$ Hz), 7.86 (d, 2H, $J = 4.7$ Hz), 8.78 (m, 4H); $^{13}\text{C-NMR}$ (25 °C, CDCl_3) δ (ppm): 70.7, 73.2, 75.1, 79.0, 81.0, 86.0, 122.8, 136.5, 150.7, 164.3.

3.2. Generation of networks

At room temperature, upon slow liquid/liquid diffusion of a solution of HgCl_2 (2 mg) in EtOH (2 ml) into a solution of the tecton **1** (5 mg) in chloroform (1 ml), colourless single crystals were obtained after several days.

3.3. X-ray structure analysis

X-ray diffraction data collection was performed at 173 K on a Kappa CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo $K\alpha$ radiation (see Table 1). All structures were solved by direct methods using the Nonius Maxus Package 4.3. All non-H atoms were refined anisotropically. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (see below).

Supplementary material

The supplementary material has been sent in electronic format to the Cambridge Crystallographic data Centre, 12 Union Road, Cambridge CB2 1EZ, UK as cif files No. CCDC 216737-216741, and can be obtained by contacting the CCDC.

Acknowledgements

We would like to thank M. Henry for helpful discussions and the ‘Université Louis-Pasteur’ as well as the French ‘Ministère de la Recherche et de la Technologie’ for financial support.

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