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Molecular tectonics: homochiral coordination networks based on combinations of a chiral neutral tecton with Hg(II), Cu(II) or Ni(II) neutral complexes as metallatectons†

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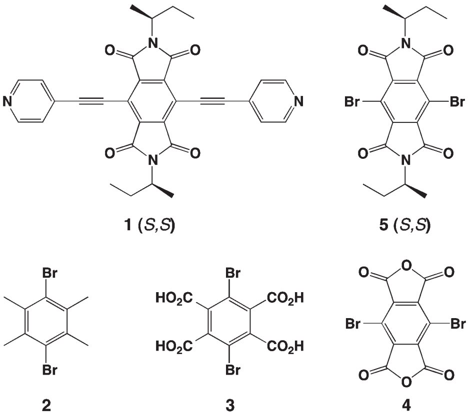
The use of compound **1** as an enantiomerically pure neutral and rigid organic linear tecton bearing two divergently oriented monodentate coordinating sites appended with two chiral centres of the same (*S*) configuration leads, in the presence of neutral metal complexes behaving either as a linear (Cu(hfac)$_2$, Cu(OAc)$_2$) or a V-shaped (HgCl$_2$) 2-connecting node or a 4-connecting square node (NiCl$_2$), to the formation of four homochiral 1- and 2-D coordination polymers.

Introduction

Molecular networks are extended periodic architectures displaying translational symmetry.[1–3] These infinite architectures are formed upon mutual interconnection of self-complementary or complementary molecular building blocks called tectons.[4–6] Coordination polymers[7] or coordination networks,[6] also called metal–organic frameworks,[8] form a subclass of molecular networks for which coordinating organic tectons are associated with metal cations or metal complexes. The latter category has attracted considerable interest over the last two decades[9] owing to the various effective or potential applications they offer in catalysis, storage, sensing or separation for example.[10,11] Although a large number of coordination networks has been reported over the last few years, despite the importance of chirality in biology and in chemistry, a relatively small number deals with chiral networks.[12–20] Among several possible design principles, chiral coordination networks may be generated by combining metal centres or metal complexes with chiral organic tectons. However, a challenge in this area remains the design and generation of enantiomerically pure architectures.

Herein we report on the combinations of the enantiomerically pure tecton **1** (see Scheme 1) with three different metal cations (Hg(II), Cu(II) or Ni(II)) associated with three different anions (Cl$^-$, hfac$^-$ and AcO$^-$) leading to the formation of four homochiral neutral coordination networks (**1**·HgCl$_2$, **1**·Cu(hfac)$_2$, **1**·Cu$_2$(AcO)$_4$ and **1**·NiCl$_2$).



Scheme 1

Experimental part

Characterization techniques

^{1}H- and ^{13}C-NMR spectra were recorded at 25 °C on a Bruker AV 300 spectrometer in deuterated solvents with the residual solvent peak used as the internal reference. Elemental analyses were performed on a Thermo Scientific Flash 2000 by the "Service Commun de Microanalyse" of the University of Strasbourg. Polarimetric measurements were performed on a Perkin Elmer (model 341) instrument.

Synthesis of tectons 1. 1,2,4,5-Tetramethylbenzene, (*S*)-(+)-*sec*-butylamine (Fluka, lot no. 1245162, optical rotation:

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+8.5°, purity (GC) 99.2%) and bis(triphenylphosphine)palladium(II) dichloride were commercially available and were used without further purification.

Compounds **2–4**[21a,b,g] and 4-ethynylpyridine[22] were prepared according to reported procedures. Their characterizations were consistent with reported data.

Synthesis of intermediate 5. To a suspension of dianhydride **4** (1 g, 2.66 mmol) in acetic acid (30 mL), (*S*)-(+)-2-aminobutane (0.8 mL, 7.98 mmol, 3 eq.) was added *via* a syringe. The reaction mixture was refluxed overnight before it was allowed to reach RT. The white precipitate was collected by filtration, washed with H_2O (50 mL) and dried under vacuum to yield compound **5** as a white solid (1.16 g, 90% yield). ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C) δ (ppm): 4.31 (m, 2H), 2.04 (m, 2H), 1.82 (m, 2H), 1.48 (d, 6H, ^3J = 7.0 Hz), 0.89 (t, 6H, ^3J = 7.3 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): δ (ppm): 163.6, 135.8, 114.1, 50.5, 26.6, 18.2, 11.3; Elemental analysis: calc. for $C_{18}H_{18}Br_2N_2O_4$: C 44.47%; H 3.73%; N 5.76%; found C 44.48%; H 3.73%; N 5.68%; $[\alpha]_D^{40}$: +21.4° (c = 0.5 in $CHCl_3$); m.p. > 330 °C.

Synthesis of tecton 1. A solution of compound **5** (500 mg, 1.03 mmol) along with 4-ethynylpyridine (318 mg, 3.09 mmol, 3 eq.) in Et_3N (30 mL) was degassed with argon for 15 min before cat. $PdCl_2(PPh_3)_2$ (145 mg, 0.21 mmol, 0.2 eq.) and CuI (40 mg, 0.21 mmol, 0.2 eq.) were added. The reaction mixture was heated to reflux for 48 h before it was allowed to reach RT. The mixture was evaporated to dryness and the resulting solid was washed with MeOH (30 mL). The crude product was further purified by column chromatography on silica gel (eluent CH_2Cl_2, 1% MeOH and 2% MeOH) affording tecton **1** (430 mg, 79% yield) as a yellowish solid. ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C) δ (ppm): 8.71 (d, 4H, ^3J = 5.9 Hz), 7.65 (d, 4H, ^3J = 5.9 Hz), 4.37 (m, 2H), 2.15 (m, 2H), 1.89 (m, 2H), 1.53 (d, 6H, ^3J = 6.8 Hz), 0.94 (t, 6H, ^3J = 7.4 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): δ (ppm): 164.9, 150.4, 136.9, 130.2, 126.4, 114.9, 101.8, 84.8, 50.6, 27.1, 18.7, 11.8; Elemental analysis: calc. for $C_{32}H_{26}N_4O_4$ C 72.44%; H 4.94%; N 10.56%; found C 71.96%; H 4.77%; N 10.34%; $[\alpha]_D^{20}$: +22.6° (c = 1.0 in $CHCl_3$); m.p. > 330 °C.

Preparation of crystalline materials

Crystals of tecton 1. Vapour diffusion at 25 °C of pentane contained in an external glass vial into a glass vial (height = 4.5 cm, diameter = 1.5 cm) containing tecton **1** (10 mg) in $CHCl_3$ (2 mL) produced colourless needle-like single crystals after two days.

Crystals of coordination polymers

General. Crystallizations were carried out by liquid–liquid diffusion techniques in glass crystallization tubes (height = 15 cm, diameter = 0.4 cm) at *ca.* 25 °C.

Crystals of 1·HgCl₂. Through a buffered layer of a 1 : 1 $CHCl_3$–EtOH mixture (0.1 mL), the diffusion of an EtOH solution (1 mL) of $HgCl_2$ (5 mg) into a $CHCl_3$ solution (1 mL) of tecton **1** (3 mg) afforded colourless single crystals after three days.

Crystals of 1·Cu(hfac)₂. Through a buffered layer of a 1 : 1 $C_2H_4Cl_2$–EtOH mixture (0.1 mL), the diffusion of an EtOH solution (1 mL) of $Cu(hfac)_2$ (5 mg) into a $C_2H_4Cl_2$ solution (1 mL) of tecton **1** (3 mg) afforded bluish-green single crystals after two days.

Crystals of 1·Cu₂(OAc)₄. Diffusion of an EtOH solution (1 mL) of $Cu(OAc)_2$ (5 mg) into a $CHCl_3$ solution (1 mL) of tecton **1** (3 mg) afforded bluish-green single crystals after five days.

Crystals of 1·NiCl₂. Through a buffered layer of a 1 : 1 $C_2H_2Cl_4$–EtOH mixture (0.1 mL), diffusion of an EtOH solution (1 mL) of $NiCl_2$ (5 mg) into a $C_2H_2Cl_4$ solution (1 mL) of tecton **1** (3 mg) afforded light-green single crystals after two days.

Single crystal analysis

Data were collected on a Bruker APEX8 CCD diffractometer equipped with an Oxford Cryosystem liquid N2 device at 173(2) K using a molybdenum microfocus sealed tube generator with mirror-monochromated Mo-Kα radiation (λ = 0.71073 Å), operated at 50 kV/600 mA. For both structures, diffraction data were corrected for absorption. Structures were solved using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-97. The hydrogen atoms were introduced at calculated positions and not refined (riding model).[23]

Crystallographic data for 1. $C_{32}H_{26}N_4O_4$, M = 530.67, *monoclinic*, space group $P2_1$, a = 5.1611(17) Å, b = 21.520(7) Å, c = 12.209(4) Å, α = 90°, β = 101.474(6)°, γ = 90°, V = 1328.9(7) Å^3, T = 173(2) K, Z = 2, D_c = 1.326 Mg m^{-3}, μ = 0.089 mm^{-1}, 11 214 collected reflections, 6034 [R(int) = 0.0652], GooF = 1.024, R_1 = 0.0791, wR_2 = 0.1813 for $I > 2\sigma(I)$ and R_1 = 0.1445, wR_2 = 0.2020 for all data.

Crystallographic data for 1·HgCl₂. $C_{32}H_{26}N_4HgCl_2$, M = 802.06, *orthorhombic*, space group $P2_12_12$, a = 21.6201(6) Å, b = 29.5433(9) Å, c = 5.0964(2) Å, $\alpha = \beta = \gamma$ = 90°, 3255.22(19) Å^3, T = 173(2) K, Z = 4, D_c = 1.637 Mg m^{-3}, μ = 4.933 mm^{-1}, 49 104 collected reflections, 7416 [R(int) = 0.0653], GooF = 1.029, R_1 = 0.0514, wR_2 = 0.1271 for $I > 2\sigma(I)$ and R_1 = 0.0732, wR_2 = 0.1372 for all data, Flack parameter = 0.037(13).

Crystallographic data for 1·Cu(hfac)₂. $C_{32}H_{26}N_4O_4Cu \cdot 2C_5HF_6O_2 \cdot 2C_2H_4Cl_2$, M = 1206.13, *triclinic*, space group $P1$, a = 6.4908(2) Å, b = 14.5434(5) Å, c = 15.0317(5) Å, α = 66.668(2)°, β = 82.427(2)°, γ = 80.980(2)°, V = 1283.01(7) Å^3, T = 173(2) K, Z = 1, D_c = 1.561 Mg m^{-3}, μ = 0.733 mm^{-1}, 36 928 collected reflections, 12 000 [R(int) = 0.0368], GooF = 1.058, R_1 = 0.0490, wR_2 = 0.1359 for $I > 2\sigma(I)$ and R_1 = 0.0645, wR_2 = 0.1509 for all data, Flack parameter = 0.018(10).

Crystallographic data for 1·Cu₂(OAc)₄. $C_{32}H_{26}N_4O_4Cu_2 \cdot 4C_2H_3O_2 \cdot 2CHCl_3$, M = 1371.30, *triclinic*, space group $P1$, a = 8.2342(5) Å, b = 19.7423(10) Å, c = 19.9269(12) Å, α = 65.3440(10)°, β = 89.542(2)°, γ = 86.931(2)°, V = 2939.4(3) Å^3, T = 173(2) K, Z = 2, D_c = 1.549 Mg m^{-3}, μ = 1.327 mm^{-1}, 26 531 collected reflections, 24 176 [R(int) = 0.0216], GooF = 1.031, R_1 = 0.0632, wR_2 = 0.1394 for $I > 2\sigma(I)$ R_1 = 0.1160, wR_2 = 0.1626 for all data, Flack parameter = 0.029(14).

Crystallographic data for 1·NiCl₂. $C_{64}H_{52}N_8O_8NiCl_2 \cdot 3C_2H_2Cl_4 \cdot 2H_2O$, M = 1730.29, *monoclinic*, space group $C2$, a =

24.5378(9) Å, b = 24.9529(11) Å, c = 19.2940(7) Å, $\alpha = \gamma = 90°$, β = 121.6010(10)°, V = 10 061.8(7) Å^3, T = 173(2) K, Z = 4, D_c = 1.142 Mg m^{-3}, μ = 0.612 mm^{-1}, 26 843 collected reflections, 26 843 [R(int) = 0.0458], GooF = 0.997, R_1 = 0.0957, wR_2 = 0.2411 for $I > 2\sigma(I)$ R_1 = 0.1472, wR_2 = 0.2605 for all data, Flack parameter = 0.07(2).

Results and discussion

Design of the enantiomerically pure tecton 1

Tecton **1** is a $C2$ chiral unit based on a diimide backbone derived from pyromellitic acid. Analogous diimide based derivatives have been used as monomers for the formation of covalent π-donor–acceptor polymers.[21a–f] As coordinating sites, two pyridyl groups are used. The connection between the backbone and pyridyl units is achieved through an ethynyl spacer using the *para* position of the aromatic ring. The chirality is introduced through both imide moieties using an alkyl fragment bearing an enantiomerically pure chiral centre of the S configuration. Compound **1** should behave as a rigid bis-monodentate chiral tecton in the presence of metal cations displaying at least two free coordination sites.

Synthesis of the enantiomerically pure C2-chiral tecton 1

The synthetic strategy followed is based on the use of compound **4** which allows, through sequential transformations, the introduction of both chiral centres using the two anhydride moieties and the two coordinating sites using the two bromine atoms.

The starting material for the synthesis of tecton **1** (Scheme 1) was the commercially available durene (1,2,4,5-tetramethyl benzene). The latter was transformed into the dibromo compound **2** by a double bromination process.[21a] Using an excess of $KMnO_4$, all four methyl groups of **2** were fully oxidized affording thus the tetracarboxylic derivative **3** in 38% yield.[21a,b] Upon refluxing the latter in a mixture of acetic acid and acetic anhydride, the bisanhydride derivative **4** was obtained in 68% yield.[21a,b,g] The condensation between compound **4** and (S)-(+)-2-aminobutane in acetic acid at 90 °C afforded the chiral compound **5** in 90% yield. Finally, the coordinating sites, *i.e.* 4-ethynyl-pyridines, were introduced by a $Pd(PPh_3)_2Cl_2$ catalysed Sonogashira coupling reaction at 90 °C between **5** and 4-ethynyl-pyridine in Et_3N along with a catalytic amount of CuI. The desired enantiomerically pure tecton **1** was obtained in 79% yield (see the Experimental section).

In addition to classical characterizations in solution, the structure of the enantiomerically pure tecton **1** was established in the solid state by X-ray diffraction on single crystal (see the Experimental section). Upon vapour diffusion of pentane into a solution of **1** in $CHCl_3$, needle-like single crystals were obtained. As expected, tecton **1** crystallises in a chiral space group ($P2_1$). No solvent molecules are present in the lattice. The pyridyl units are tilted with respect to the centre pyromellitic core by *ca.* 17.1 and 3.5° (Fig. 1a). The shortest distance between atoms belonging to two consecutive tectons **1** is *ca.* 2.46 Å. The length of the tecton *i.e.* the distance between the two N atoms of the pyridyl units is 16.47 Å. It is worth noting that in the crystalline phase, the two ethyl groups and thus the two methyl groups of the two chiral centres are *syn* oriented. Consecutive molecules are stacked in a parallel and staggered fashion. However, in consecutive stacks, the C–C triple bonds of the ethynyl moieties are located above and below the phenyl group of the pyromellitic backbone with distances in the 3.46–4.23 Å range (Fig. 1b).

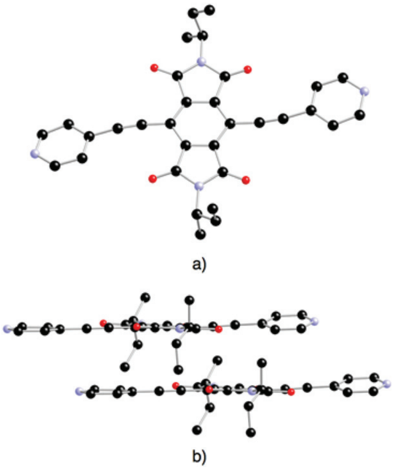

Fig. 1 X-Ray structure of tecton **1** (a) and views of the stacking of two consecutive molecules (b). H atoms are omitted for clarity. For bond distances and angles see text.

Choice of metallatectons

The chiral and enantiomerically pure compound **1** is a neutral tecton. Thus, its combination with metal cations may be either achieved using metal cations associated with non-coordinating anions or with neutral metal complexes for which anions are coordinated to the metal centre. Whereas for the first possibility, owing to the charge neutrality requirement, the anion must necessarily be present in the crystal, for the second case, one may take advantage of the binding of the anion by the metal centre to design neutral metal complexes as metallatectons. Indeed, for example for a metal cation such as Hg(II) adopting usually a tetrahedral coordination geometry (Fig. 2a),

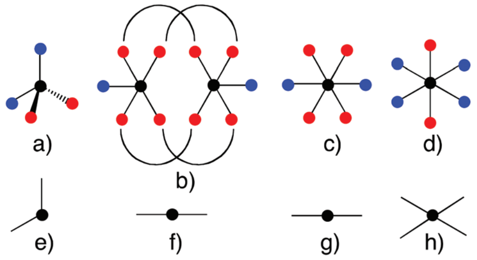

Fig. 2 Schematic representations of tetrahedral (a), dimeric complexes (b), and octahedral metal complexes (c and d) for which some of the coordination sites are blocked by coordinating anions (red spheres) leading to a V-shaped (e) and a linear 2-connecting node (f and g) and a 4-connecting node (h). The blue spheres represent free coordination sites.

one may use two coordinating monodentate anions such as chloride anions to block two coordination sites out of the four possible ones and thus generate a neutral metallatecton offering two free coordination sites as a V-shaped 2-connecting node (Fig. 2e). In a similar fashion, if not considering the M–M interaction, one may combine a pentacoordinated metal centre such as Cu(II) with four bridging anions such as the acetate anion (AcO^-) and thus generate a dimeric species of the paddlewheel type (Fig. 2b) behaving as a linear 2-connecting node (Fig. 2f). Another possibility for the formation of a linear 2-connecting node (Fig. 2g) is the use of a metal centre in the oxidation state 2 adopting an octahedral coordination geometry (Fig. 2c), for example Cu(II), and block four out of the six coordination sites by two monoanionic chelating ligands such as hexafluoroacetylacetonate ($hfac^-$). Finally, one may form a 4-connecting node (Fig. 2h) by blocking the two apical coordination sites on a metal centre such as Ni(II) adopting an octahedral coordination geometry by two monodentate coordinating anions such as chloride anions (Cl^-) (Fig. 2d).

Generation of enantiomerically pure coordination networks

Mercury 1D chiral coordination networks. Upon slow diffusion of an EtOH solution of $HgCl_2$ into a $CHCl_3$ solution of the organic tecton **1** through a buffered layer (EtOH–$CHCl_3$), colourless crystals were obtained after one week. The X-ray diffraction on single crystal investigation revealed that the crystal (chiral space group $P2_12_12$) is exclusively composed of tecton **1** and $HgCl_2$. The latter behaves as a 2-connecting V-shaped node leading thus to the formation of a 1D stair type mercury coordination network resulting from the bridging of consecutive organic tectons **1** by $HgCl_2$ complexes. Owing to the enantiomerically pure nature of tecton **1**, the 1D network is chiral (Fig. 3). For the organic tecton, pyridyl units are tilted with respect to the backbone by *ca.* 7.9 and 7.3°. Within the 1D chain, each Hg^{2+} cation, adopting a distorted T_d geometry (N–Hg–N and Cl–Hg–Cl angles of 94.48° and 157.04° respectively), is surrounded by two Cl^- anions (Cl–Hg distance of *ca.* 2.45 Å) and two N atoms (N–Hg distance of *ca.* 2.45 Å) belonging to the pyridyl moieties of two consecutive tectons **1** (Fig. 3a). Within the 1D network consecutive cations are distant by 21.45 Å.

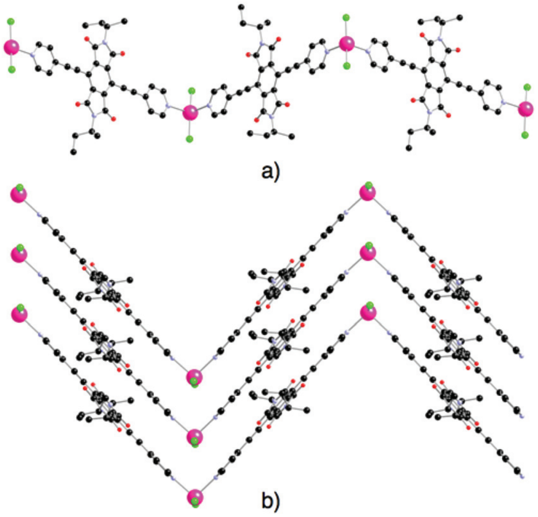

Fig. 3 Portion of the X-ray structure **1**·$HgCl_2$ showing the formation of the 1D stair type coordination network (a) and the packing of consecutive networks along the *a* axis (b). H atoms are not represented for clarity. For bond distances and angles see text.

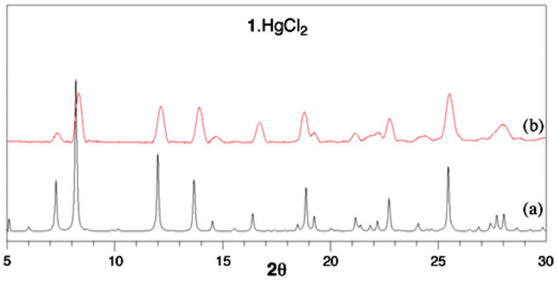

Fig. 4 Comparison of the simulated (a) and recorded (b) PXRD patterns for **1**·$HgCl_2$.

Along the *c* axis (Fig. 3b), the close staggered packing of consecutive 1D networks in a parallel fashion leads to a 3.28 Å distance between the nearly flat pyromellitic cores of consecutive layers. As for the free tecton **1**, the two ethyl groups of the two chiral centres are *syn* oriented.

The purity of crystals of **1**·$HgCl_2$ was established by PXRD on microcrystalline powder, which revealed good match between the simulated (Fig. 4a) and observed patterns (Fig. 4b).

Copper 1D chiral coordination networks. As expected, combinations of tecton **1** with two different Cu(II) complexes ($Cu(hfac)_2$ and $Cu(AcO)_2$) behaving as 2-connected linear nodes generate again two homochiral 1D linear coordination networks.

Upon slow diffusion of an EtOH solution of $Cu(hfac)_2$ into a $C_2H_4Cl_2$ solution of tecton **1** through a buffered layer composed of a $C_2H_4Cl_2$–EtOH mixture (see the Experimental part), bluish-green crystalline materials were obtained after *ca.* one week. The X-ray diffraction study on single crystal revealed the formation of a neutral 1D linear chiral coordination polymer (Fig. 5a) resulting from the bridging of consecutive tectons **1** by $Cu(hfac)_2$ complexes. The crystal (chiral space group $P1$) is composed of tecton **1**, Cu^{2+} cations, $hfac^-$ anions and $C_2H_4Cl_2$ solvent molecules. For the organic linker **1**, the pyridyl units are tilted with respect to the backbone by *ca.* 27.0 and 23.6°. The Cu(II) centre, in a distorted octahedral coordination geometry, is surrounded by four O atoms belonging to two $hfac^-$ anions occupying the apices of the square base of the octahedron (Cu–O distance in the 1.9–2.3 Å range) and two N atoms belonging to the pyridyl moiety of two consecutive tectons **1** occupying the two apical positions (N–Cu distances of *ca.* 2.0 Å and N–Cu–N angles of *ca.* 180.0°). Within the 1D network, consecutive Cu^{2+} cations are distant by 20.62 Å.

Consecutive 1D chains are packed in a staggered fashion (Fig. 5b) forming layers of stacked 1D coordination polymers. However in contrast with **1**·$HgCl_2$, no π–π interactions are

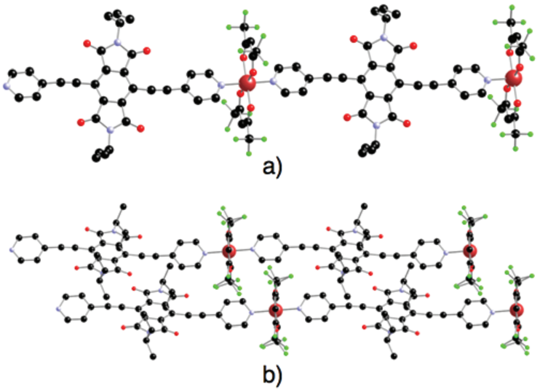

Fig. 5 Portion of the X-ray structure of **1**·Cu(hfac)$_2$ showing the formation of the 1D neutral and chiral linear coordination network resulting from bridging of consecutive tectons **1** by Cu(hfac)$_2$ behaving as a neutral 2-connecting linear node (a) and packing of consecutive chains along the *b* axis (b). H atoms and $C_2H_4Cl_2$ solvent molecules are not presented for clarity. For bond distances and angles see text.

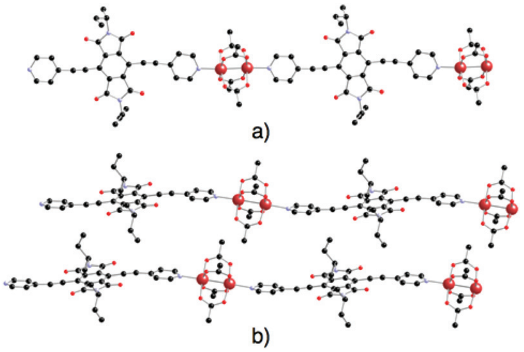

Fig. 6 Portions of the X-ray structure of **1**·Cu$_2$(AcO)$_4$ showing a view along the *a* axis of the 1D linear and chiral coordination network formed upon combining the organic chiral tecton **1** and Cu$_2$(AcO)$_4$ as a linear 2-connecting node (a) and the packing of consecutive chains viewed along the *c* axis (b). H atoms and $CHCl_3$ solvent molecules are not presented for clarity. For bond distances and angles see text.

observed, mainly due to the more crowded hfac anions. The $C_2H_4Cl_2$ solvent molecules occupy the interstices without any specific interaction with the organic and metalloorganic components.

Unfortunately, owing to the presence of solvent molecules in the crystal lattice, the removal of the mother liquor leads to the loss of $C_2H_4Cl_2$ molecules. Although the material remains crystalline, no good match between the simulated and observed powder diffraction patterns is obtained.

Upon slow diffusion of an EtOH solution of Cu(OAc)$_2$ into a $CHCl_3$ solution of **1**, blue crystals were obtained after *ca.* one week. X-Ray diffraction on single crystal revealed again the formation of a 1D homochiral linear coordination network resulting from bridging of consecutive tectons **1** by Cu$_2$(AcO)$_4$ dimers behaving as 2-connecting linear nodes (Fig. 6a). The crystal (chiral space group *P*1) is composed of the organic tecton **1**, Cu^{2+} cations, OAc^- anions and $CHCl_3$ solvent molecules. For the two crystallographically independent organic tectons **1**, the pyridyl units are tilted with respect to the backbone by *ca.* 6.9 and 19.3° and 10.3 and 8.7°. The Cu(II) centres, adopting a square based pyramidal coordination geometry, form a neutral dimer of the paddlewheel type (Cu$_2$(AcO)$_4$). Each metal centre is surrounded by four O atoms belonging to four bridging acetate anions (O–Cu distance in the 1.95–1.99 Å range) and one N atom belonging to the pyridyl moiety of tecton **1** (N–Cu distance in the 2.14–2.19 Å range). Within the 1D network, two paddlewheel motifs are distant by *ca.* 20.7 Å.

As for **1**·Cu(hfac)$_2$ discussed above, the 1D chains are packed in a staggered and parallel fashion (Fig. 6b). The $CHCl_3$ molecules are intercalated between consecutives chains without any specific interaction with the 1D networks.

Unfortunately, again owing to the presence of volatile $CHCl_3$ solvent molecules in the crystal, the removal of the mother liquor leads to the loss of the latter. Consequently, although the material remains crystalline, no good match between the simulated and observed powder diffraction patterns is obtained.

Nickel 2D chiral coordination networks. In order to generate a 2D chiral coordination network, tecton **1** was combined with NiCl$_2$ (see the Experimental section). The crystallisation process afforded light green crystals, which were analysed by X-ray diffraction on single crystal. The structural investigation revealed the formation of a 2D enantiomerically pure coordination network. The crystal (chiral space group *C*2) is composed of the organic tecton **1**, Ni^{2+} cations, Cl^- anions and highly disordered solvents molecules. Thus, the squeeze command[24] had to be applied to solve the structure.

The formation of the 2D grid-type neutral and chiral architecture results from the interconnection of four different tectons **1** by NiCl$_2$ complexes behaving as 4-connected nodes (Fig. 7a). Within the 2D network, the two pyridyl moieties of tecton **1** are tilted with respect to the backbone by *ca.* 13.6 and 85.8°. The Ni(II) centre, adopting a distorted octahedral geometry, is linked to four organic tectons occupying the apices of the square base of the octahedron through N–Ni bonds

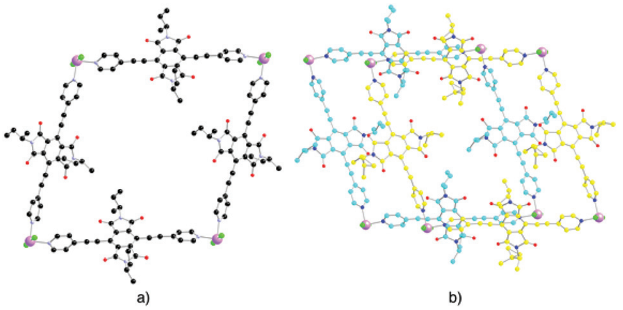

Fig. 7 Portions of the X-ray structure of **1**·NiCl$_2$ along the *a* axis showing the neutral 2D chiral grid resulting from the interconnection of tectons **1** by NiCl$_2$ neutral complexes acting as 4-connected nodes (a) and the staggered packing of two consecutive grids (b). H atoms and solvent molecules are not presented for clarity. For bond distances and angles see text.

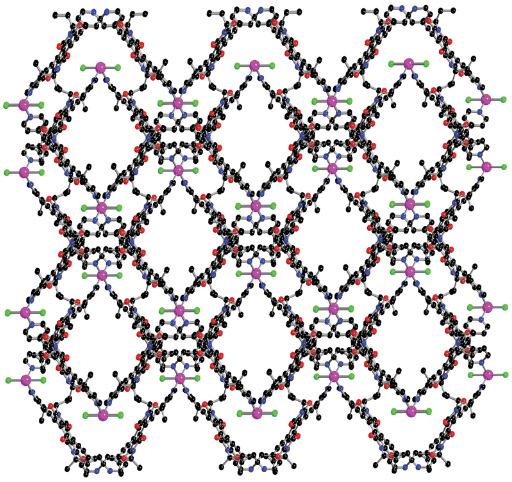

Fig. 8 Portions of the X-ray structure of **1**·$NiCl_2$ showing the packing of consecutive chiral 2D grid type networks leading to a porous chiral crystal. H atoms and solvent molecules are not presented for clarity. For bond distances and angles see text.

(distance in the 2.12–2.14 Å range). The two Cl^- anions are located on the apical positions with Cl–Ni distances in the 2.43–2.45 Å range. Within the 2D sheet, consecutive Ni^{2+} cations are distant by *ca.* 20.74 Å. Within the crystal, consecutive 2D networks are packed in a staggered fashion along the *a* axis (Fig. 7b). The distance between consecutive layers, with respect to the planes formed by the Ni(II) centres, is *ca.* 6.08 Å. The packing of consecutive 2D chiral networks, although in a staggered manner, leads to the formation of porous crystals with a solvent accessible void of 50.6% (Fig. 8).

Once again, owing to the presence of solvent molecules in the lattice, the removal of crystals from the mother liquor leads to the loss of solvent molecules. Again, although the material remains crystalline, no good match between the simulated and observed powder diffraction patterns is obtained.

Conclusions

Compound **1** is an enantiomerically pure neutral and rigid organic linear tecton bearing two divergently oriented monodentate coordinating sites appended with two chiral centres of the same (*S*) configuration. The latter are located orthogonal to the pyridyl coordinating sites. Combinations of the chiral and neutral tecton **1** (Fig. 9a) with neutral metal complexes behaving either as a linear ($Cu(hfac)_2$, $Cu(OAc)_2$) or a V-shaped ($HgCl_2$) 2-connecting node or a 4-connecting square node ($NiCl_2$) lead to four homochiral coordination polymers of different dimensionalities. Indeed, as expected, whereas for the two types of 2-connecting nodes linear (Fig. 9b) or stair-type (Fig. 9c) 1D chiral and neutral coordination networks are formed, for the 4-connecting node, a 2D chiral and neutral coordination network is obtained (Fig. 9d).

The combination of tecton **1** with other metal cations and metal complexes is currently under investigation. Furthermore, the use of tecton **1** for the generation of pillared 2- and 3-D coordination networks is under study.

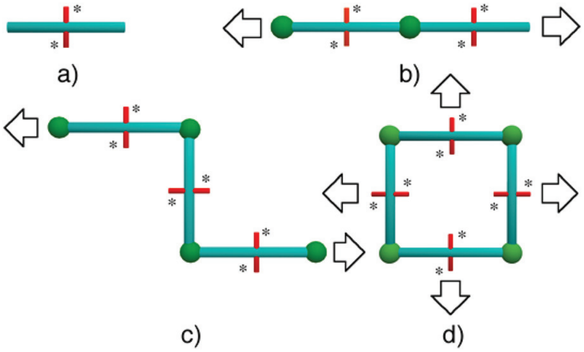

Fig. 9 Schematic representations of the *C*2-chiral linear tecton **1** bearing two chiral centres (a), linear coordination networks obtained upon combining **1** with $Cu(hfac)_2$ or $Cu(OAc)_2$ behaving as 2-connecting nodes (b), a stair type 1D network formed with $HgCl_2$ behaving as a bent connector (c) and a 2D network formed with $NiCl_2$ acting as a 4-connecting square planar node (d). * indicates the presence of the chiral centre.

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