Crystals formation of 1D coordination polymers based on chiral, achiral and racemic 1,2 cyclohexane scaffold

Abdelaziz Jouaïtia, Philippe Grosshans, Nathalie Kyritsakas, Sylvie Ferlay, Marc Henry, Mir Wais Hosseini

The enantiomerically pure ligands (1a, 1b) and the meso 1c based on the trans-1,2-cyclohexanediol and cis-1,2-cyclohexanediol respectively were used for the formation of zig-zag 1D coordination polymers, when combined with bent HgCl₂. A racemic mixture or 1a/1b in 1/1 ratio has also been studied. Four 1D Coordination Polymers have been obtained and their structures have been analysed using X-Ray diffraction on single crystals and also on powder. 1a-HgCl₂ (and isostructural 1b-HgCl₂) crystallizes in the non-centrosymmetric P 2₁2₁2₁ space group, 1c-HgCl₂ in the non-centrosymmetric P 2₁2₁2₁ space group and 1as,1bs-HgCl₂ crystallises in the centrosymmetric P 2₁/n space groups.

The analysis of the network energies, evaluated on a partial charges calculation method (PACHA), used here for the first time for a 1D coordination network, allows to evaluate energetical parameters like the Packing Energy (PE) for each crystalline compound, as well as the cooperativity Index (CI), illustrating the influence of chirality on the packing for this series of 1D Coordination Polymers. It has been shown that the use of the achiral ligand 1c requires the highest cooperativity between the chains.

Introduction

The interests in Coordination Polymers (CPs), coordination networks or MOFs, based on organic ligands and bridging metallic ions, do not only rely on their potential applications in electronics, magnetism, non-linear optics, and as porous materials and catalysts, but also on their intriguing variety of topologies and entanglement motifs that they may adopt. 3D and 2D Coordination Polymers have been widely classified from their topologies and concerning 1D CPs, they also have been extensively studied. Within this class of compounds, beside the classical linear chains, or zig-zag chains, the design of helical networks is of interest for potential applications in NLO for example. For the generation of such systems, the use of chiral components reveals to be a powerful approach. For piezo and pyroelectric properties of molecular compounds, for example, the formation of non-centrosymmetric crystals has proven to be very promising.

The formation of molecular networks remains still intriguing. The understanding of the packing and the parameters governing the crystal growth are of fundamental interest. The prediction of the recognition pattern between individual molecular components is rather mastered for simple components, but the prediction of packing remains difficult.

The discussion concerning molecular packing in a crystal can be based on symmetrical arguments: from a topological point of view, two very different kinds of symmetry operators act during the crystal growth process: (i) intramolecular point-group symmetry operators that describe different parts of the same molecules and (ii) intermolecular packing operators describing the arrangement between the different molecules.

Along this line, several approaches have been developed in order to control the packing in molecular crystals, like the use of non-symmetrical chiral components, for example. For this purpose, examples are based on the use of dissymmetric chiral ligand that can lead to a non-centrosymmetric packing (leading to Polar Crystals) of 1-D coordination networks.

In this context, using simple molecular components, we intend to understand the factors governing the crystal packing in a one-dimensional coordination polymer crystal and among these factors, the influence of the chirality on the crystal packing. This approach is based on the possibility to obtain...
chiral, racemic and achiral forms of analogous starting components and the use of a reliable recognition pattern between metallic species and the used ligand.

Along this line, we designed V shape ligands well suited for the formation of zig-zag 1D Coordination Polymers when combined with bent connectors like HgCl₂. A pair of bis monodentate chiral ligands (1a and 1b, see figure 1) bearing pyridine coordinating groups grafted through an ester junction, based on the chiral trans-1,2-cyclohexanediol is a good candidate for this study. 1a and 1b have been already reported and their combination with ZnSiF₅ for the formation of helical tubular crystals has been described. Combinations with other transition metals have also been studied. The related achiral ligand 1c has been designed following the same approach starting from the achiral cis-1,2-cyclohexanediol (the meso stereoisomer of the series).

![Figure 1: Both enantiomers of the chiral trans-1,2-cyclohexanediol derivatives 1a and 1b and the achiral cis-1,2-cyclohexanediol derivative 1c.](image)

In this work we have combined 1a, 1b and 1c and a racemic mixture of 1a/1b in 1/1 ratio with HgCl₂, acting as bent connector, forming thus four new 1D coordination polymers. After the structural description of the molecular systems, derived from X-Ray diffraction on single Crystals, a careful analysis of an estimation of the Packing Energy in the crystal has been considered in order to understand the packing of the formed zig-zag chains.

**Experimental**

**Characterization techniques**

1H-NMR and 13C-NMR spectra were recorded at room temperature on Bruker (400 or 500 MHz) NMR spectrometers by the shared NMR Service of the faculty of chemistry of the Strasbourg University.

Mass spectra (ESI) were recorded on a MicroTOF-Q (Bruker) equipped with an electrospray source.

Elemental analyses were performed by the Service de Microanalyses de la Fédération de Recherche Chimie, Université de Strasbourg, Strasbourg, France.

**Synthesis**

*General:* All reagents were purchased from commercial sources and used without further purification.

The synthesis of 1a and 1b was already reported. Bis-pyridin, 4,4’-[cis-1,2-cyclohexanediylbis(oxy)] (1c)

Under nitrogen and at room temperature, to a degassed solution of cis-1,2-cyclohexanediol (0.3 g, 3.6 mmol) in dry THF (40 ml), the Isonicotinoyl chloride hydrochloride (1.9 g, 10.7 mmol) was added and the mixture was stirred at room temperature for 15 min. Et₂N (5 ml) was added to the mixture and stirring was further continued for one day. After evaporation to dryness, saturated aqueous solution of Na₂CO₃ (40 ml) was added to the residue and the mixture extracted with CH₂Cl₂ (2 x 80 ml). The organic solvent was removed and the residue purified by short column chromatography [SiO₂, CH₂Cl₂] affording the pure products as a colorless powder. Yield 58 %.

1H-RMN (300 MHz, CDCl₃, 25 °C): δ (ppm) = 8.72 (d, 4H, J = 6 Hz); 7.74 (d, 4H, J = 6 Hz); 5.40 (m, 2H); 2.03 (m, 2H); 1.82 (m, 4H); 1.57 (m, 2H);

13C-RMN (125 MHz, CDCl₃, 25 °C): δ (ppm) = 21.5; 27.8; 72.5; 122.7; 137.4; 150.6; 164.2

(ESI): m/z calcld. for C₁₃H₁₀N₂O₄ [M-H]: 327.13; found: 327.13.

Anal. Calcld. for C₁₃H₁₀N₂O₄(1c): C = 66.25%; H = 5.56%; N = 8.58% ; Found C = 66.20%; H = 5.63%; N = 8.55%.

**Crytallisations conditions**

1a-HgCl₂, 1b-HgCl₂, or 1c-HgCl₂

A solution of compound 1b (1b or 1c) (3 mg, 9.2 x 10⁻³ mmol) in CHCl₃ (1 mL) is placed in a crystallization tube (20 x 4 mm). A solution of HgCl₂ (3 mg, 1 x 10⁻³ mmol) in EtOH (2 ml) is carefully added. At room temperature, slow diffusion produced colourless crystals suitable for X-ray diffraction after 36h (3.9 mg, 72 % yield for 1a-HgCl₂, 4 mg, 74 % yield for 1c-HgCl₂, and 3.8 mg, 70 % yield for 1c-HgCl₂).

10a₁b₂s-HgCl₂

A solution containing 1a (3 mg, 9.2 x 10⁻³ mmol) and 1b (3 mg, 9.2 x 10⁻³ mmol) in CHCl₃ (2 mL) is placed in a crystallization tube (20 x 4 mm). A solution of HgCl₂ (6 mg, 22 x 10⁻³ mmol) in EtOH (2 mL) is carefully added. At room temperature, slow diffusion produced colourless crystals suitable for X-ray diffraction after 36h (3.7 mg, 68 % yield).

The four solid-state samples were also analysed using XRPD on micromcrystalline samples.

**Structural studies**

**Single-Crystal Studies**

Data were collected at 173(2) K on a Bruker Apex-II-CCD diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. For all structures, diffraction data were corrected for absorption. Structures were solved using SHELXS-97 and refined by full matrix least-squares on F² using SHELXL-97. The hydrogen atoms were introduced at calculated positions and refined using a riding model. They can be obtained free of
charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/dat request/cif. CCDC: 1a-HgCl₂ (1946672), 1b-HgCl₂ (1946673), 1c-HgCl₂ (1949896) and 1a₂b₂HgCl₂ (1946675).

Powder diffraction studies (PXRD)

Diagrams were collected on a Bruker D8 diffractometer using monochromatized Cu-Kα radiation with a scanning range between 4 and 40° using a scan step size of 8°/mn. As already demonstrated and currently admitted, for all compounds, discrepancies in intensity between the observed and simulated patterns are due to preferential orientations of the microcrystalline powders.

Calculations

The PACHA formalism have been used for calculations of energetic parameters, and for this purpose, evaluations of the molecular volumes have been implemented using Gavezzotti’s algorithm[36] associated to a standard set of van der Waals radii.[17] For the computational details, see ESI.

Results and discussion

The coordination properties of chiral 1a-b, achiral 1c and the 1/1 1a/1b racemic mixture towards HgCl₂ have been investigated. The choice of the bent HgCl₂ is motivated by reliable recognition pattern that may arise between 1a-c and HgCl₂. The bis-monodentate 1a-b possess a V shape, more pronounced for 1c (using the cis-1,2-cyclohexanediol scaffold), combined with bent HgCl₂, may lead, to the formation of zig-zag chains, as schematically shown in figure 2. This event occurs through the formation of Hg-N coordination bonds, where the Hg²⁺ metallic cations present a N₂Cl₆ coordination sphere and a deformed tetrahedral geometry.

It is important to note that all the single-crystals were obtained using the diffusion technique method of a EtOH solution containing the metallic salt into a CHCl₃ solution containing 1a-c (see experimental section).

Description of 1D coordination networks with 1a-c

For generating coordination networks, both chiral ligands 1a and 1b were combined with HgCl₂. For 1a and 1b, isostructural chiral crystals, 1a-HgCl₂ and 1b-HgCl₂ crystals were obtained and characterized by X-ray diffraction on single crystal. Both enantiomERICALLY pure systems crystallize in an orthorhombic non-centrosymmetric space group P 2_12_12. (see experimental section and crystallographic table 1). The crystal is composed of the chiral organic ligands 1a (or 1b) and HgCl₂ connectors. No solvent molecules were found to be present in the crystal. As expected, the use of the chiral ligand bearing asymmetrical carbons leads to the formation of a chiral crystal.[38,39]

As expected, combination of the V-shape ligand (V angles 71.895° for 1a-HgCl₂ and 72.456° for 1b-HgCl₂) with HgCl₂ leads to the formation the Zig zag coordination polymers. In both compounds, the geometry around the metallic centres is a deformed tetrahedron, with bonds and angles presented in table 2.

<table>
<thead>
<tr>
<th></th>
<th>1a-HgCl₂</th>
<th>1b-HgCl₂</th>
<th>1c-HgCl₂</th>
<th>1a₂b₂HgCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg-N</td>
<td>2.416(5)</td>
<td>2.430(5)</td>
<td>2.416(16)</td>
<td>2.437(7)</td>
</tr>
<tr>
<td>Hg-Cl</td>
<td>2.348(16)</td>
<td>2.346(18)</td>
<td>2.346(5)</td>
<td>2.364(2)</td>
</tr>
<tr>
<td>ClHgCl</td>
<td>146.84(6)</td>
<td>146.80(8)</td>
<td>152.7(3)</td>
<td>149.8(3)</td>
</tr>
<tr>
<td>ClHgN</td>
<td>94.20(11)</td>
<td>94.20(11)</td>
<td>95.8(4)</td>
<td>95.77(16)</td>
</tr>
<tr>
<td>NHgN</td>
<td>85.54(15)</td>
<td>85.73(18)</td>
<td>84.8(9)</td>
<td>85.9(6)</td>
</tr>
</tbody>
</table>

Table 2: Main distances and angles for 1a-HgCl₂, 1b-HgCl₂, 1c-HgCl₂ and 1a₂b₂HgCl₂

The zig-zag chains are formed along the a axis, as shown in figure 3 and the chains are antiparallelly arranged in the xOy plane and form thus corrugate sheets, with very weak interactions (Cl-O distance of 4.043 (5)Å with Cl coordinated to Hg), and O from carbonyl ester junction of 1a), as shown in figure 3. In the xOy plane, the distance between two consecutives chains (metal to metal distances), along the b direction is equal to 6.251 (4) Å, whereas in the yOz plane, along the c direction, it is equal to 8.221 (6) Å (see table 3).

Figure 2: A schematic representation of the formation of Zig-zag chains resulting from the recognition, through the formation of coordination bonds, of HgCl₂ with 1a-c.
Figure 3. A portion of the 1D coordination networks 1a-HgCl$_2$ (or 1b-HgCl$_2$) along the $a$ (picture a) and $b$ (picture b) axes and corresponding packing obtained upon combining HgCl$_2$ with 1a (or 1b) (pictures c and d, in the xOz and xOy planes respectively). H atoms are omitted for clarity of the representation.

The combination of 1c with HgCl$_2$ leads to the formation of a chiral network 1c-HgCl$_2$, where the crystal is composed of the achiral organic ligand 1c and HgCl$_2$ in 1/1 stoichiometric amount (see experimental section and crystallographic table 1). As in the previous case, the crystal doesn’t contain any solvent molecule and the compound crystallize in an orthorhombic non-centrosymmetric space group $P 2_12_12$ (see crystallographic table 1), and is, as expected, a 1D coordination polymer. In the structure, the V angle displayed by 1c is equal to 90.340°. The geometry around the metallic centres is a deformed tetrahedron, with bonds and angles presented in table 2. As already mentioned in the literature, the use of an achiral ligand (1c) leads to the formation of a chiral crystal, resulting from the packing of the network. This is a well-known case for “induced chirality” in molecular networks, especially in helicoidal systems.$^{40,41}$

Figure 4. A portion of the 1D coordination networks 1c-HgCl$_2$ along the $a$ (picture a) and $b$ (picture b) axes and corresponding packing obtained upon combining HgCl$_2$ with 1c (pictures c and d, in the xOz and xOy planes respectively). H atoms are omitted for clarity of the representation.

The zig-zag chains are formed along the $a$ axis, as shown in figure 4 and the chains are parallelly arranged along the $c$ axis. In the xOy plane, the distance between two consecutives chains, along the $b$ direction is equal to 9.787 (5) Å. In this plane, there is a weak interaction between O (ester junction in 1c) and Cl (coordinated to Hg), with Cl-O distance of 3.547 (4) Å. In the xOz plane, the distance between two chains, along the $c$ direction, is equal to 5.886 (3) Å (see table 3).

In order to understand the packing of a racemic mixture, the 1/1 stoichiometric amount for 1a and 1b has been combined with HgCl$_2$. It leads to the formation of an achiral network of general formula 1a$_{0.5}$1b$_{0.5}$-HgCl$_2$. The compound crystallizes in a monoclinic centrosymmetric space group $P 2_1/n$ (see crystallographic table 1). This is a new example of formation of achiral crystals starting from a racemic composition of chiral ligands. The crystal is composed of the chiral organic ligands 1a and 1b in 1/1 stoichiometric amount, HgCl$_2$ connectors and CHCl$_3$ solvent molecules, that don’t present any specific
interactions with the network. The system is based on two zigzag chains running along the $b$ axis, containing respectively only 1a or 1b, as shown in figure 5, with V angle of 80.753° and 80.399° respectively. The crystal is achiral, due to the presence of pairs of helicoidal chains of opposite chirality. The geometry around the metallic centers is also a deformed tetrahedron, $\text{N}_2\text{Cl}_2$ with bonds and angles presented in table 2.

The purity of the 1a-HgCl$_2$, 1b-HgCl$_2$, 1c-HgCl$_2$ and 1a$_0.5$1b$_0.5$-HgCl$_2$ polycrystalline samples was investigated by PXRD on microcrystalline powder (see figures 6). For all compounds, a good match between the observed and calculated patterns from the XRD data was obtained, attesting a pure crystalline phase in the solid-state. It revealed that 1a$_0.5$1b$_0.5$-HgCl$_2$ doesn’t contain any 1a-HgCl$_2$ or 1b-HgCl$_2$ crystalline phase.

![Diagram](image)

**Figure 5.** A portion of the chiral 1D coordination network 1a$_0.5$1b$_0.5$-HgCl$_2$ (a) and corresponding packing (b) obtained upon combining HgCl$_2$ with 1a1b in racemic conditions. H atoms are omitted for clarity of the representation.

The energetic study of the crystal packing

Taking into account these structural considerations described above, some calculations have been performed in order to evaluate the Packing Energy (PE) of chiral crystals 1a-HgCl$_2$, 1b-HgCl$_2$ and 1c-HgCl$_2$ (compounds crystallising in a non-centrosymmetric and chiral space group), and 1a$_0.5$1b$_0.5$-HgCl$_2$ (compound crystallising in centrosymmetric space group) (see table 3). As already mentioned, the crystallisation in a non-centrosymmetric space group for 1a-HgCl$_2$ and 1b-HgCl$_2$ is the direct consequence of the chirality imposed by the ligand, whereas for 1c-HgCl$_2$ it results from the packing of the 1D system.

The use of a racemic mixture is at the origin of the observation of a centrosymmetric space group (P 21/n) in which 1a$_0.5$1b$_0.5$-HgCl$_2$ crystallises.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Space Group</th>
<th>V angle of 1a-c</th>
<th>Interchain distances ($\text{Å}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a-HgCl$_2$</td>
<td>P 2\text{I}$_2$/2\text{I}$_1$</td>
<td>71.895°</td>
<td>6.251 (4) \ 8.221 (6)</td>
</tr>
<tr>
<td>1b-HgCl$_2$</td>
<td>P 2\text{I}$_2$/2\text{I}$_1$</td>
<td>72.456°</td>
<td>6.251 (6) \ 8.222 (6)</td>
</tr>
<tr>
<td>1c-HgCl$_2$</td>
<td>P 2\text{I}$_2$/2\text{I}$_1$</td>
<td>90.340°</td>
<td>5.886 (3) \ 9.787 (6)</td>
</tr>
<tr>
<td>1a$_0.5$1b$_0.5$-HgCl$_2$</td>
<td>P 21/n centrosymmetric</td>
<td>80.753° 80.399°</td>
<td>5.839 (2) \ 8.166 (2)</td>
</tr>
</tbody>
</table>

**Table 3: Main characteristics for crystals 1a-HgCl$_2$, 1b-HgCl$_2$, 1c-HgCl$_2$ and 1a$_0.5$1b$_0.5$-HgCl$_2$**

In order to evaluate the energetic parameters, a force field approach can be used, but is not well adapted for extended...
networks. An estimation of the contribution of different recognition events and thus assembling nodes may also be obtained using a PACHA analysis (Partial Atomic Charges and Hardnesses Analysis).2,43,44 The PACHA analysis45 was successfully developed for analysing hydrogen bonds involving water,46 hydrogen bonded networks47 or extended MOFs48,49 and is well adapted for extended molecular networks, taking into account the symmetry operators governing the crystal structure.50

For analysing the packing in the solid state, three main factors, allowing an accurate description of the networks, will be analysed: i) Packing Efficiency51 $\xi$, ii) the Packing Energy (PE)50 in the crystal, which relies to the energy related to the energy required for 1D system to form the crystal and iii) the Cooperativity Index (CI)52 between the chains. The Cooperativity Index can be expressed as the tendency of the chains to cooperate in order to stabilize the packing energy of the crystal. A negative CI indicates a strong cooperativity between the components, stabilizing the system.

The first useful crystal structure descriptor should obviously be the Packing Efficiency $\xi$, derived from the Kitaigorskii equation ($\xi$=ZVm/Vcell, where $V_m$ is the molecular volume).51 This purely geometric descriptor is easily evaluated from the knowledge of a set of van der Waals atomic radii53 and of the unit-cell volume. It may provide useful indications concerning the “porosity” of the crystal.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Space Group</th>
<th>Packing Efficiency $\xi$%/</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a-HgCl$_2$</td>
<td>P 2$_1$/2$_1$</td>
<td>67.3</td>
</tr>
<tr>
<td>1b-HgCl$_2$</td>
<td>P 2$_1$/2$_1$</td>
<td>67.4</td>
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<tr>
<td>1c-HgCl$_2$</td>
<td>P 2$_1$/2$_1$</td>
<td>69.1</td>
</tr>
<tr>
<td>1a$<em>{0.5}$1b$</em>{0.5}$-HgCl$_2$</td>
<td>P 2$_1$/n</td>
<td>69.2</td>
</tr>
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</table>

Table 4: Packing Efficiency $\xi$ for crystals 1a-HgCl$_2$, 1b-HgCl$_2$, 1c-HgCl$_2$ and 1a$_{0.5}$1b$_{0.5}$-HgCl$_2$

These results (see table 4) show us that the Packing Efficiency is close to 70% for all the compounds and slightly smaller for 1a-HgCl$_2$ and 1b-HgCl$_2$, related to the non-centrosymmetric space group (use of a chiral ligand) in which the compounds are crystallising. For 1c-HgCl$_2$, it considers the chirality imposed by the packing and reveal to be slightly larger. For 1a$_{0.5}$1b$_{0.5}$-HgCl$_2$ $\xi$ was evaluated, considering the presence of solvent molecules (CHCl$_3$) in the voids. By artificially removing the solvents leads to a much lower value (57.4%), resulting also from the presence of an inversion centre in the crystal.

The proper and quantitative evaluation of energetic parameters guiding the formation of the molecular crystalline architecture is crucial,50 which is, in this case, mainly related to the Packing Energy (PE). Such analysis was carried out for the four crystalline structures reported here (1a-HgCl$_2$, 1b-HgCl$_2$, 1c-HgCl$_2$ and 1a$_{0.5}$1b$_{0.5}$-HgCl$_2$), using the PACHA analysis. The results, provided in Table 5, allowed the estimations of energy of the formed zig-zag chains, of the Packing Energy and finally the Cooperativity Index (CI),52 (for methodology and detailed calculations, see ESI).

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Chain Energy (kJmol$^{-1}$)</th>
<th>Network Energy (kJmol$^{-1}$)</th>
<th>Packing Energy (kJmol$^{-1}$)</th>
<th>Cooperativity Index (CI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a-HgCl$_2$</td>
<td>-536 (2)</td>
<td>-2267 (9)</td>
<td>-123 (9)</td>
<td>-2 (2)</td>
</tr>
<tr>
<td>1b-HgCl$_2$</td>
<td>-535 (2)</td>
<td>-2264 (9)</td>
<td>-124 (9)</td>
<td>-2 (2)</td>
</tr>
<tr>
<td>1c-HgCl$_2$</td>
<td>-534 (2)</td>
<td>-2314 (9)</td>
<td>-178 (9)</td>
<td>-33 (2)</td>
</tr>
<tr>
<td>1a$<em>{0.5}$1b$</em>{0.5}$-HgCl$_2$</td>
<td>-532 (2)</td>
<td>-2368 (9)</td>
<td>-214 (9)</td>
<td>-3 (2)</td>
</tr>
</tbody>
</table>

Table 5: Calculations of Chain Energy, Network Energy, Packing Energy and Cooperativity index for crystals 1a-HgCl$_2$, 1b-HgCl$_2$, 1c-HgCl$_2$ and 1a$_{0.5}$1b$_{0.5}$-HgCl$_2$

The calculation revealed that for all compounds, the Cooperativity Index is negative, reflecting an efficient cooperativity between the wires. Using pure enantiomers ligands (compounds 1a-HgCl$_2$ and 1b-HgCl$_2$), the resulting structures are characterized by a strong packing anisotropy between chiral chains associated to a weak cooperativity between chiral chains. 1a$_{0.5}$1b$_{0.5}$-HgCl$_2$, involving a racemic mixture and crystallising in a centro-symmetric space group, also displays a high packing anisotropy and a weak Cooperativity Index. The CI value of -33 kJmol$^{-1}$ for 1c-HgCl$_2$ reflects the use of achiral components in a network (ligand 1c), imposing a chiral packing.

In addition, the Hg-N coordination bond energy within the networks were evaluated (see ESI) and reveal to be weak, as expected for coordination networks.

Conclusions

The enantiomerically pure bis monodentate ligands (1a, 1b) and meso 1c based on the trans-1,2-cyclohexanediol and cis-1,2-cyclohexanediol respectively were used for the formation of zig-zag 1D Coordination Polymers, when combined with bent HgCl$_2$. The crystals 1a-HgCl$_2$ (and also isostructural 1b-HgCl$_2$) and 1c-HgCl$_2$ have and been obtained and the X-Ray analysis on single crystals reveals that the compounds crystallise in the chiral P 2$_1$/2$_1$2$_1$ and P 2$_1$/2$_1$2$_2$ space groups respectively. A head to tail packing of the chains is observed in 1a-HgCl$_2$ (isostructural 1b-HgCl$_2$). For the use of the achiral ligand 1c, the non centrosymmetry of the observed space group in 1c-HgCl$_2$, related to the packing.

Then a 1/1 racemic mixture of enantiomerically pure ligands 1a/1b was combined with HgCl$_2$ and the formed Coordination Polymer (1a$_{0.5}$1b$_{0.5}$-HgCl$_2$) crystallises in a centro-symmetric P 2$_1$/n space group.

The analysis of the networks revealed that the “Packing Efficiency” of the four compounds is close to 70%.

The analysis of the Packing Energies, based on a partial charges calculation method (PACHA), allows to derive the
Cooperativity Index for each compound, and clearly revealed that the cooperativity between the formed layers is stronger when achiral ligands are involved in the formed coordination network (compound 1c-HgCl₂). This energetical analysis is the first one reported for the crystal formation of 1D coordination polymers.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

45 The program can be free downloaded from https://complexmatter.unistra.fr/equipes-de-recherche/laboratoire-de-chimie-moleculaire-de-letat-solide/logiciels/.
Table 1: Crystallographic Parameters for 1a-HgCl₂, 1b-HgCl₂, 1c-HgCl₂, 1a₀.5b₀.5-HgCl₂ recorded at 173 K.

<table>
<thead>
<tr>
<th></th>
<th>1a-HgCl₂</th>
<th>1b-HgCl₂</th>
<th>1c-HgCl₂</th>
<th>1a₀.5b₀.5-HgCl₂</th>
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<tbody>
<tr>
<td>Formula</td>
<td>(R,R) C₁₈H₁₈Cl₂HgN₂O₄</td>
<td>(S,S) C₁₈H₁₈Cl₂HgN₂O₄</td>
<td>(S,R) C₁₈H₁₈Cl₂HgN₂O₄</td>
<td>(R,R)(S,S) 50% C₁₈H₁₈Cl₂HgN₂O₄, CHCl₃</td>
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<tr>
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Graphical abstract

1a (R,R) or 1b (S,S)  
1c (R,S)  
Racemate 1a (R,R) + 1b (S,S)  
+  
P  2_1 2_1 2_1  
P  2_1 2_1 2  
P  2_1 n
Crystals formation of 1D coordination polymers based on chiral, achiral and racemic 1,2 cyclohexane scaffold

Abdelaziz Jouaiti, Philippe Grosshans, Nathalie Kyritsakas, Sylvie Ferlay, Marc Henry, Mir Wais Hosseini

The enantiomerically pure ligands (1a, 1b) and the meso 1c based on the trans-1,2-cyclohexanediol and cis-1,2-cyclohexanediol respectively were used for the formation of zig-zag 1D coordination polymers, when combined with bent HgCl₂. A racemic mixture or 1a/1b in 1/1 ratio has also been studied. Four 1D Coordination Polymers have been obtained and their structures have been analysed using X-ray diffraction on single crystals and also on powder. 1a-HgCl₂ (and isoskeletal 1b-HgCl₂) crystallizes in the non-centrosymmetric P 2₁2₁2₁ space group, 1c-HgCl₂ in the non-centrosymmetric P 2₁2₁2₁ space group and 1a:1b:1c-HgCl₂ crystallises in the centrosymmetric P 2₁/n space groups.

The analysis of the network energies, evaluated on a partial charges calculation method (PACHA), used here for the first time for a 1D coordination networks, allows to evaluate energetical parameters like the Packing Energy (PE) for each crystalline compound, as well as the cooperativity Index (CI), illustrating the influence of chirality on the packing for this series of 1D Coordination Polymers. It has been shown that the use of the achiral ligand 1c requires the highest cooperativity between the chains.

Introduction

The interests in Coordination Polymers (CPs), coordination networks of MOFs, based on organic ligands and bridging metallic ions, do not only rely on their potential applications in electronics, magnetism, non-linear optics, and as porous materials and catalysts, but also on their intriguing variety of topologies and entanglement motifs that they may adopt. 3D and 2D Coordination Polymers have been widely classified from their topologies and concerning 1D CPs, they also have been extensively studied. Within this class of compounds, beside the classical linear chains or zig-zag chains, the design of helical networks is of interest for potential applications in NLO for example. For the generation of such systems, the use of chiral components reveals to be a powerful approach. For piezo and pyroelectric properties of molecular compounds, for example, the formation of non-centrosymmetric crystals has proven to be very promising.

The formation of molecular networks remains still intriguing. The understanding of the packing and the parameters governing the crystal growth are of fundamental interest. The prediction of the recognition pattern between individual molecular components is rather mastered for simple components, but the prediction of packing remains difficult.

The discussion concerning molecular packing in a crystal can be based on symmetrical arguments : from a topological point of view, two very different kinds of symmetry operators act during the crystal growth process: (i) intramolecular point-group symmetry operators that describe different parts of the same molecules and (ii) intermolecular packing operators describing the arrangement between the different molecules.

Along this line, several approaches have been developed in order to control the packing in molecular crystals, like the use of non-symmetrical chiral components, for example. For this purpose, examples are based on the use of disymmetric chiral ligand that can lead to a non-centrosymmetric packing (leading to Polar Crystals) of 1-D coordination networks.

In this context, using simple molecular components, we intend to understand the factors governing the crystal packing in a one-dimensional coordination polymer crystal and among these factors, the influence of the chirality on the crystal packing. This approach is based on the possibility to obtain...
chiral, racemic and achiral forms of analogous starting components and the use of a reliable recognition pattern between metallic species and the used ligand.

Along this line, we designed V shape ligands well suited for the formation of zig-zag 1D Coordination Polymers when combined with bent connectors like HgCl₂. A pair of bis monodentate chiral ligands (1a and 1b, see figure 1) bearing pyridine coordinating groups grafted through an ester junction, based on the chiral trans-1,2-cyclohexanediol is a good candidate for this study. 1a and 1b have been already reported and their combination with ZnSiF₆ for the formation of helical tubular crystals has been described. Combinations with other transition metals have also been studied.

The related achiral ligand 1c has been designed following the same approach starting from the achiral cis-1,2-cyclohexanediol (the meso stereoisomer of the series).

Figure 1: Both enantiomers of the chiral trans-1,2-cyclohexanediol derivatives 1a and 1b and the achiral cis-1,2-cyclohexanediol derivative 1c.

In this work we have combined 1a, 1b and 1c and a racemic mixture of 1a/1b in 1/1 ratio with HgCl₂, acting as bent connector, forming thus four new 1D coordination polymers. After the structural description of the molecular systems, derived from X-Ray diffraction on single Crystals, a careful analysis of an estimation of the Packing Energy in the crystal has been considered in order to understand the packing of the formed zig-zag chains.

Experimental

Characterization techniques

¹H-NMR and ¹³C-NMR spectra were recorded at room temperature on Bruker (400 or 500 MHz) NMR spectrometers by the shared NMR Service of the faculty of chemistry of the Strasbourg University. Mass spectra (ESI) were recorded on a MicroTOF-Q (Bruker) equipped with an electrospray source. Elemental analyses were performed by the Service de Microanalyses de la Fédération de Recherche Chimie, Université de Strasbourg, Strasbourg, France.

Synthesis

General: All reagents were purchased from commercial sources and used without further purification.

The synthesis of 1a and 1b was already reported.

Bis-pyridin, 4,4′-[cis-1,2-cyclohexanediylbis(oxy)] (1c)

Under nitrogen and at room temperature, to a degassed solution of cis-1,2-cyclohexanediol (0.3 g, 3.6 mmol) in dry THF (40 ml), the Isonicotinoyl chloride hydrochloride (1.9 g, 10.7 mmol) was added and the mixture was stirred at room temperature for 15 min. Et₂N (5 ml) was added to the mixture and stirring was further continued for one day. After evaporation to dryness, saturated aqueous solution of Na₂CO₃ (40 ml) was added to the residue and the mixture extracted with CH₂Cl₂ (2 x 80 ml). The organic solvent was removed and the residue purified by short column chromatography [SiO₂, CH₂Cl₂] affording the pure products as a colorless powder. Yield 58 %.

¹H-RMN (300 MHz, CDCl₃, 25 °C) : δ (ppm) = 8.72 (d, 4H, J = 6 Hz); 7.74 (d, 4H, J = 6 Hz); 5.40 (m, 2H); 2.03 (m, 2H); 1.82 (m, 4H); 1.57 (m, 2H);

¹³C-RMN (125 MHz, CDCl₃, 25 °C) : δ (ppm) = 21.5 ; 27.8 ; 72.5 ; 122.7 ; 137.4 ; 150.6 ; 164.2 (ESI): m/z calcld. for C₁₉H₁₄N₂O₄ [M-H]: 327.13; found: 327.13. Anal. Calcd. for C₁₉H₁₄N₂O₄ (1c): C = 66.25%; H = 5.56%; N = 8.58%; % ; Found C = 66.20%; H = 5.63%; N = 8.55%

Crystallisations conditions

1a-HgCl₂, 1b-HgCl₂ or 1c-HgCl₂

A solution of compound 1a (1b or 1c) (3 mg, 9.2 x 10⁻³ mmol) in CHCl₃ (1 mL) is placed in a crystallization tube (20 x 4 mm). A solution of HgCl₂ (3 mg, 11 x 10⁻³ mmol) in EtOH (2 mL) is carefully added. At room temperature, slow diffusion produced colourless crystals suitable for X-ray diffraction after 36h (3.9 mg, 72 % yield for 1a-HgCl₂, 4 mg, 74 % yield for 1c-HgCl₂ and 3.8 mg, 70 % yield for 1c-HgCl₂).

10a,b,1a,5a-HgCl₂

A solution containing 1a (3 mg, 9.2 x 10⁻³ mmol) and 1b (3 mg, 9.2 x 10⁻³ mmol) in CHCl₃ (2 mL) is placed in a crystallization tube (20 x 4 mm). A solution of HgCl₂ (6 mg, 22 x 10⁻³ mmol) in EtOH (2 mL) is carefully added. At room temperature, slow diffusion produced colourless crystals suitable for X-ray diffraction after 36h (3.7 mg, 68 % yield).

The four solid-state samples were also analysed using XRPD on microcrystalline samples.

Structural studies

Single-Crystal Studies

Data were collected at 173(2) K on a Bruker Apex-II-CCD diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. For all structures, diffraction data were corrected for absorption. Structures were solved using SHELX-97 and refined by full matrix least-squares on F² using SHELXL-97. The hydrogen atoms were introduced at calculated positions and refined using a riding model. They can be obtained free of...
charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif. CCDC: 1a-HgCl₂ (1946672), 1b-HgCl₂ (1946673), 1c-HgCl₂ (1949896) and 1aₙ1b₀.₅-HgCl₂ (1946675).

**Powder diffraction studies (PXRD)**

Diagrams were collected on a Bruker D8 diffractometer using monochromatic Cu-Kα radiation with a scanning range between 4 and 40° using a step size of 0.008/°mn. As already demonstrated and currently admitted, for all compounds, discrepancies in intensity between the observed and simulated patterns are due to preferential orientations of the microcrystalline powders.

**Calculations**

The PACHA formalism have been used for calculations of energetic parameters, and for this purpose, evaluations of the molecular volumes have been implemented using Gavezzotti’s algorithm associated to a standard set of van der Waals radii. 

For the computational details, see ESI.

**Results and discussion**

The coordination properties of chiral 1a-b, achiral 1c and the 1:1 1a/1b racemic mixture towards HgCl₂ have been investigated. The choice of the bent HgCl₂ is motivated by reliable recognition pattern that may arise between 1a-c and HgCl₂. The bis-monodentate 1a-b possess a V shape, more pronounced for 1c (using the cis-1,2-cyclohexaneadiol scaffold), combined with bent HgCl₂, may lead, to the formation of zig-zag chains, as schematically shown in figure 2. This event occurs through the formation of Hg-N coordination bonds, where the Hg²⁺ metallic cations present a N₃Cl₂ coordination sphere and a deformed tetrahedral geometry.

It is important to note that all the single-crystals were obtained using the diffusion technique method of a EtOH solution containing the metallic salt into a CHCl₃ solution containing 1a-c (see experimental section).

**Description of 1D coordination networks with 1a-c**

For generating coordination networks, both chiral ligands 1a and 1b were combined with HgCl₂. For 1a and 1b, isostructural chiral crystals, 1a-HgCl₂ and 1b-HgCl₂, crystals were obtained and characterized by X-ray diffraction on single crystal. Both enantiomerically pure systems crystallized in an orthorhombic non-centrosymmetric space group P 2₁2₁2₁ (see experimental section and crystallographic table 1). The crystal is composed of the chiral organic ligands 1a (or 1b) and HgCl₂ connectors. No solvent molecules were found to be present in the crystal. As expected, the use of the chiral ligand bearing asymmetrical carbons leads to the formation of a chiral crystal. As expected, combination of the V-shape ligand (V angles 71.895° for 1a-HgCl₂ and 72.456° for 1b-HgCl₂) with HgCl₂ leads to the formation the Zig zag coordination polymers. In both compounds, the geometry around the metallic centres is a deformed tetrahedron, with bonds and angles presented in table 2.

<table>
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<th></th>
<th>1a-HgCl₂</th>
<th>1b-HgCl₂</th>
<th>1c-HgCl₂</th>
<th>1a₀.₅₁b₀.₅-HgCl₂</th>
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<td>NHgN</td>
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Table 2: Main distances and angles for 1a-HgCl₂, 1b-HgCl₂, 1c-HgCl₂ and 1a₀.₅₁b₀.₅-HgCl₂

The zig-zag chains are formed along the a axis, as shown in figure 3 and the chains are antiparallely arranged in the xOy plane and form thus corrugate sheets, with very weak interactions (Cl-O distance of 4.043 (5)Å with Cl coordinated to Hg), and O from carbonyl ester junction of 1a, as shown in figure 3. In the xOy plane, the distance between two consecutives chains (metal to metal distances), along the b direction is equal to 6.251 (4) Å, whereas in the yOz plane, along the c direction, it is equal to 8.221 (6) Å (see table 3).
Figure 3. A portion of the 1D coordination networks 1a-HgCl$_2$ (or 1b-HgCl$_2$) along the a (picture a) and b (picture b) axes and corresponding packing obtained upon combining HgCl$_2$ with 1a (or 1b) (pictures c and d, in the xOz and xOy planes respectively). H atoms are omitted for clarity of the representation.

The combination of 1c with HgCl$_2$ leads to the formation of a chiral network 1c-HgCl$_2$, where the crystal is composed of the achiral organic ligand 1c and HgCl$_2$ in 1/1 stoichiometric amount (see experimental section and crystallographic table 1). As in the previous case, the crystal doesn’t contain any solvent molecule and the compound crystallize in an orthorhombic non-centrosymmetric space group $P$ 2$_1$2$_1$2 (see crystallographic table 1), and is, as expected, a 1D coordination polymer. In the structure, the V angle displayed by 1c is equal to 90.340°. The geometry around the metallic centres is a deformed tetrahedron, with bonds and angles presented in table 2. As already mentioned in the literature, the use of an achiral ligand (1c) leads to the formation of a chiral crystal, resulting from the packing of the network. This is a well-known case for “induced chirality” in molecular networks, especially in helicoidal systems.$^{40,41}$

Figure 4. A portion of the 1D coordination networks 1c-HgCl$_2$ along the a (picture a) and b (picture b) axes and corresponding packing obtained upon combining HgCl$_2$ with 1c (pictures c and d, in the xOz and xOy planes respectively). H atoms are omitted for clarity of the representation.

The zig-zag chains are formed along the a axis, as shown in figure 4 and the chains are parallelly arranged along the c axis. In the xOy plane, the distance between two consecutives chains, along the b direction is equal to 9.787 (5) Å. In this plane, there is a weak interaction between O (ester junction in 1c) and Cl (coordinated to Hg), with Cl-O distance of 3.547 (4) Å. In the xOz plane, the distance between two chains, along the c direction, is equal to 5.886 (3) Å (see table 3).

In order to understand the packing of a racemic mixture, the 1/1 stoichiometric amount for 1a and 1b has been combined with HgCl$_2$. It leads to the formation of an achiral network of general formula 1a$_{0.5}$1b$_{0.5}$-HgCl$_2$. The compound crystallizes in a monoclinic centrosymmetric space group $P$ 2$_1$/n (see crystallographic table 1). This is a new example of formation of achiral crystals starting from a racemic composition of chiral ligands. The crystal is composed of the chiral organic ligands 1a and 1b in 1/1 stoichiometric amount, HgCl$_2$ connectors and CHCl$_3$ solvent molecules, that don’t present any specific
interactions with the network. The system is based on two zigzag chains running along the b axis, containing respectively only 1a or 1b, as shown in figure 5, with V angle of 80.753° and 80.399° respectively. The crystal is achiral, due to the presence of pairs of helicoidal chains of opposite chirality. The geometry around the metallic centers is also a deformed tetrahedron, N2Cl2 with bonds and angles presented in table 2.

The purity of the 1a-HgCl2, 1b-HgCl2, 1c-HgCl2 and 1a0.51b0.5-HgCl2 polycrystalline samples was investigated by PXRD on microcrystalline powder (see figures 6). For all compounds, a good match between the observed and calculated patterns from the XRD data was obtained, attesting a pure crystalline phase in the solid-state. It revealed that 1a0.51b0.5-HgCl2 doesn’t contain any 1a-HgCl2 or 1b-HgCl2 crystalline phase.

Figure 5. A portion of the chiral 1D coordination network 1a0.51b0.5-HgCl2 (a) and corresponding packing (b) obtained upon combining HgCl2 with 1a1b in racemic conditions. H atoms are omitted for clarity of the representation.

Figure 6. Comparison of the simulated and recorded XRPD diagrams (a) for 1a-HgCl2, 1b-HgCl2 and 1c-HgCl2 (compounds crystallising in a non-centrosymmetric and chiral space group), and 1a0.51b0.5-HgCl2 (compound crystallising in centrosymmetric space group) (see table 3). As already mentioned, the crystallisation in a non-centrosymmetric space group for 1a-HgCl2 and 1b-HgCl2 is the direct consequence of the chirality imposed by the ligand, whereas for 1c-HgCl2 it results from the packing of the 1D system.

Energetical study of the crystal packing

Taking into account these structural considerations described above, some calculations have been performed in order to evaluate the Packing Energy (PE) of chiral crystals 1a-HgCl2, 1b-HgCl2 and 1c-HgCl2 (compounds crystallising in a non-centrosymmetric and chiral space groups), and 1a0.51b0.5-HgCl2 (compound crystallising in centrosymmetric space group) (see table 3). As already mentioned, the crystallisation in a non-centrosymmetric space group for 1a-HgCl2 and 1b-HgCl2 is the direct consequence of the chirality imposed by the ligand, whereas for 1c-HgCl2 it results from the packing of the 1D system.

The use of a racemic mixture is at the origin of the observation of a centrosymmetric space group (P 21/n) in which 1a0.51b0.5-HgCl2 crystallises.

Table 3: Main characteristics for crystals 1a-HgCl2, 1b-HgCl2, 1c-HgCl2 and 1a0.51b0.5-HgCl2

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Space Group</th>
<th>V angle of 1a-c</th>
<th>Interchain distances (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a-HgCl2</td>
<td>P 212121 Non centrosymmetric</td>
<td>71.895°</td>
<td>6.251 (4) 8.221 (6)</td>
</tr>
<tr>
<td>1b-HgCl2</td>
<td>P 212121 Non centrosymmetric</td>
<td>72.456°</td>
<td>6.251 (6) 8.222 (6)</td>
</tr>
<tr>
<td>1c-HgCl2</td>
<td>P 21212 Non centrosymmetric</td>
<td>90.340°</td>
<td>5.886 (3) 9.787 (6)</td>
</tr>
<tr>
<td>1a0.51b0.5-HgCl2</td>
<td>P 21/n centrosymmetric</td>
<td>80.753° 80.399°</td>
<td>5.839 (2) 8.166 (2)</td>
</tr>
</tbody>
</table>

In order to evaluate the energetic parameters, a force field approach can be used, but is not well adapted for extended
networks. An estimation of the contribution of different recognition events and thus assembling nodes may also be obtained using a PACHA analysis (Partial Atomic Charges and Hardnesses Analysis).\textsuperscript{12,43,44} The PACHA analysis\textsuperscript{45} was successfully developed for analysing hydrogen bonds involving water,\textsuperscript{46} hydrogen bonded networks\textsuperscript{47} or extended MOFs\textsuperscript{48,49} and is well adapted for extended molecular networks, taking into account the symmetry operators governing the crystal structure.\textsuperscript{50}

For analysing the packing in the solid state, three main factors, allowing an accurate description of the networks, will be analysed: i) Packing Efficiency\textsuperscript{51} \(\xi\), ii) the Packing Energy (PE)\textsuperscript{50} in the crystal, which relies to the energy related to the energy required for 1D system to form the crystal and iii) the Cooperativity Index (CI)\textsuperscript{52} between the chains. The Cooperativity Index can be expressed as the tendency of the chains to cooperate in order to stabilize the packing energy of the crystal. A negative CI indicates a strong cooperativity between the components, stabilizing the system.

The first useful crystal structure descriptor should obviously be the Packing Efficiency \(\xi\), derived from the Kitaigorodskii equation (\(\xi = V_m/V_{cell}\), where \(V_m\) is the molecular volume).\textsuperscript{51} This purely geometric descriptor is easily evaluated from the knowledge of a set of van der Waals atomic radii\textsuperscript{53} and of the unit-cell volume. It may provide useful indications concerning the “porosity” of the crystal.

<table>
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<th>Crystal</th>
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Table 4: Packing Efficiency \(\xi\) for crystals 1a-HgCl\textsubscript{2}, 1b-HgCl\textsubscript{2}, 1c-HgCl\textsubscript{2} and 1a\textsubscript{0.5}1b\textsubscript{0.5}-HgCl\textsubscript{2}

These results (see table 4) show us that the Packing Efficiency is close to 70\% for all the compounds and slightly smaller for 1a-HgCl\textsubscript{2} and 1b-HgCl\textsubscript{2}, related to the non-centrosymmetric space group (use of a chiral ligand) in which the compounds are crystallising. For 1c-HgCl\textsubscript{2}, it considers the chirality imposed by the packing and reveal to be slightly larger. For 1a\textsubscript{0.5}1b\textsubscript{0.5}-HgCl\textsubscript{2} \(\xi\) was evaluated, considering the presence of solvent molecules (CHCl\textsubscript{3}) in the voids. By artificially removing the solvents leads to a much lower value (57.4\%), resulting also from the presence of an inversion centre in the crystal.

The proper and quantitative evaluation of energetic parameters guiding the formation of the molecular crystalline architecture is crucial,\textsuperscript{50} which is, in this case, mainly related to the Packing Energy (PE). Such analysis was carried out for the four crystalline structures reported here (1a-HgCl\textsubscript{2}, 1b-HgCl\textsubscript{2}, 1c-HgCl\textsubscript{2} and 1a\textsubscript{0.5}1b\textsubscript{0.5}-HgCl\textsubscript{2}), using the PACHA analysis. The results, provided in Table 5, allowed the estimations of energy of the formed zig-zag chains, of the Packing Energy and finally the Cooperativity Index (CI).\textsuperscript{52} (for methodology and detailed calculations, see ESI).

The calculation revealed that for all compounds, the Cooperativity Index is negative, reflecting an efficient cooperativity between the wires. Using pure enantiomers ligands (compounds 1a-HgCl\textsubscript{2} and 1b-HgCl\textsubscript{2}), the resulting structures are characterized by a strong packing anisotropy between chiral chains associated to a weak cooperativity between chiral chains. 1a\textsubscript{0.5}1b\textsubscript{0.5}-HgCl\textsubscript{2}, involving a racemic mixture and crystallising in a centro-symmetric space group, also displays a high packing anisotropy and a weak Cooperativity Index. The CI value of -33 kJ mol\textsuperscript{-1} for 1c-HgCl\textsubscript{2} reflects the use of achiral components in a network (ligand 1c), imposing a chiral packing.

In addition, the Hg-N coordination bond energy within the networks were evaluated (see ESI) and reveal to be weak, as expected for coordination networks.

Conclusions

The enantiomerically pure bis monodentate ligands (1a, 1b) and \textit{meso} 1c based on the \textit{trans}-1,2-cyclohexanediol and \textit{cis}-1,2-cyclohexanediol respectively were used for the formation of zig-zag 1D Coordination Polymers, when combined with bent HgCl\textsubscript{2}. The crystals 1a-HgCl\textsubscript{2} (also isostructural 1b-HgCl\textsubscript{2} and 1c-HgCl\textsubscript{2}) and have been obtained and the X-Ray analysis on single crystals reveals that the compounds crystallise in the chiral \(P 2_12_12_1\) and \(P 2 2_12_2\) space groups respectively. A head to tail packing of the chains is observed in 1a-HgCl\textsubscript{2} (isostructural 1b-HgCl\textsubscript{2}). For the use of the achiral ligand 1c, the non centrosymmetry of the observed space group in 1c-HgCl\textsubscript{2}, related to the packing.

Then a 1/1 racemic mixture of enantiomerically pure ligands 1a/1b was combined with HgCl\textsubscript{2} and the formed Coordination Polymer (1a\textsubscript{0.5}1b\textsubscript{0.5}-HgCl\textsubscript{2}) crystallises in a centro-symmetric \(P 2_1/n\) space group.

The analysis of the networks revealed that the “Packing Efficiency” of the four compounds is close to 70\%.

The analysis of the Packing Energies, based on a partial charges calculation method (PACHA), allows to derive the
Cooperativity Index for each compound, and clearly revealed that the cooperativity between the formed layers is stronger when achiral ligands are involved in the formed coordination network (compound 1c-HgCl₂). This energetical analysis is the first one reported for the crystal formation of 1D coordination polymers.

Conflicts of interest
There are no conflicts to declare.

Acknowledgements
We thank the University of Strasbourg, the C.N.R.S., the International centre for Frontier Research in Chemistry (icFRC), the Labex CSC (ANR-10-LABX-0026 CSC) within the Investissement d’Avenir program ANR-10-IDEX-0002-02, the Ministère de l’Enseignement Supérieur et de la Recherche for financial support.

Notes and references

45. The program can be free downloaded from https://complex-matter.unistra.fr/ equipos-de-recherche/laboratoire-de- chimie-moleculaire-de-letat-solide/logiciels/.
Table 1: Crystallographic Parameters for 1a-HgCl₂, 1b-HgCl₂, 1c-HgCl₂ and 1a₀.51b₀.5-HgCl₂ recorded at 173 K.

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<th>1a-HgCl₂</th>
<th>1b-HgCl₂</th>
<th>1c-HgCl₂</th>
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<tr>
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<td>(S,S)C₁₈H₁₈Cl₂HgN₂O₄</td>
<td>(S,R)C₁₈H₁₈Cl₂HgN₂O₄</td>
<td>(R,R)(S,S) 50%C₁₈H₁₈Cl₂HgN₂O₄, CHCl₃</td>
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<td>0.038(19)</td>
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</table>
Graphical abstract

1a (R,R) or 1b (S,S)  
1c (R,S)  
Racemate 1a (R,R) + 1b (S,S)

+  

P 2_12_12  
P 2_12_2  
P 2_1n
Crystals formation of 1D coordination polymers based on chiral, achiral and racemic 1,2 cyclohexane scaffold

Abdelaziz Joua"
ti, Philippe Grosshans, Nathalie Kyritsakas, Sylvie Ferlay, Marc Henry, Mir Wais Hosseini

The enantiomerically pure ligands (1a, 1b) and the meso 1c based on the trans-1,2-cyclohexanediol and cis-1,2-cyclohexanediol respectively were used for the formation of zig-zag 1D coordination polymers, when combined with bent HgCl2. A racemic mixture or 1a/1b in 1/1 ratio has also been studied. Four 1D Coordination Polymers have been obtained and their structures have been analysed using X-Ray diffraction on single crystals and also on powder. 1a-HgCl2 (and isostructural 1b-HgCl2) crystallizes in the non-centrosymmetric P 2_1/c, space group, 1c-HgCl2 in the non-centrosymmetric P 21/c space group and 1a:1b:1a-HgCl2 crystallises in the centrosymmetric P 21/c space groups.

The analysis of the network energies, evaluated on a partial charges calculation method (PACHA), used here for the first time for a 1D coordination networks, allows to evaluate energetical parameters like the Packing Energy (PE) for each crystalline compound, as well as the cooperativity Index (CI), illustrating the influence of chirality on the packing for this series of 1D Coordination Polymers. It has been shown that the use of the achiral ligand 1c requires the highest cooperativity between the chains.

Introduction

The interests in Coordination Polymers (CPs), coordination networks2 or MOFs,3,4 based on organic ligands and bridging metallic ions, do not only rely on their potential applications in electronics, magnetism, non-linear optics, and as porous materials and catalysts,5,6,7,8,9,10,11 but also on their intriguing variety of topologies and entanglement motifs that they may adopt.12,13,14 3D and 2D Coordination Polymers have been widely classified from their topologies15 and concerning 1D CPs, they also have been extensively studied.16,17,18 Within this class of compounds, beside the classical linear chains16,19,20 or zig-zag chains16,21,22 the design of helical networks16,23,24,25,26,27,28 is of interest for potential applications in NLO for example. For the generation of such systems, the use of chiral components reveals to be a powerful approach.16 For piezo and pyroelectric properties of molecular compounds, for example, the formation of non-centrosymmetric crystals has proven to be very promising.29

The formation of molecular networks remains still intriguing. The understanding of the packing and the parameters governing the crystal growth are of fundamental interest. The prediction of the recognition pattern between individual molecular components is rather mastered for simple components, but the prediction of packing remains difficult.30,31 The discussion concerning molecular packing in a crystal can be based on symmetrical arguments: from a topological point of view, two very different kinds of symmetry operators act during the crystal growth process: (i) intramolecular point-group symmetry operators that describe different parts of the same molecules and (ii) intermolecular packing operators describing the arrangement between the different molecules.

Along this line, several approaches have been developed in order to control the packing in molecular crystals, like the use of non-symmetrical chiral components, for example. For this purpose, examples are based on the use of dissymmetric chiral ligand that can lead to a non-centrosymmetric packing (leading to Polar Crystals) of 1-D coordination networks.32

In this context, using simple molecular components, we intend to understand the factors governing the crystal packing in a one-dimensional coordination polymer crystal and among these factors, the influence of the chirality on the crystal packing. This approach is based on the possibility to obtain
chiral, racemic and achiral forms of analogous starting components and the use of a reliable recognition pattern between metallic species and the used ligand.

Along this line, we designed V shape ligands well suited for the formation of zig-zag 1D Coordination Polymers when combined with bent connectors like HgCl$_2$. A pair of bis monodentate chiral ligands (1a and 1b, see figure 1) bearing pyridine coordinating groups grafted through an ester junction, based on the chiral trans-1,2-cyclohexanediol is a good candidate for this study. 1a and 1b have been already reported and their combination with ZnSiF$_5$ for the formation of helical tubular crystals has been described. Combinations with other transition metals have also been studied.

The related achiral ligand 1c has been designed following the same approach starting from the achiral cis-1,2-cyclohexanediol (the meso stereoisomer of the series).

![Figure 1: Both enantiomers of the chiral trans-1,2-cyclohexanediol derivatives 1a and 1b and the achiral cis-1,2-cyclohexanediol derivative 1c.](image)

In this work we have combined 1a, 1b and 1c and a racemic mixture of 1a/1b in 1/1 ratio with HgCl$_2$, acting as bent connector, forming thus four new 1D coordination polymers. After the structural description of the molecular systems, derived from X-Ray diffraction on single Crystals, a careful analysis of an estimation of the Packing Energy in the crystal has been considered in order to understand the packing of the formed zig-zag chains.

**Experimental**

**Characterization techniques**

$^1$H-NMR and $^{13}$C-NMR spectra were recorded at room temperature on Bruker (400 or 500 MHz) NMR spectrometers by the shared NMR Service of the faculty of chemistry of the Strasbourg University.

Mass spectra (ESI) were recorded on a MicroTOF-Q (Bruker) equipped with an electrospray source. Elemental analyses were performed by the Service de Microanalyses de la Fédération de Recherche Chimie, Université de Strasbourg, Strasbourg, France.

**Synthesis**

**General:** All reagents were purchased from commercial sources and used without further purification.

The synthesis of 1a and 1b was already reported.

**Bis-pyridin, 4,4’-[cis-1,2-cyclohexanediybis(oxy)] (1c)**

Under nitrogen and at room temperature, to a degassed solution of cis-1,2-cyclohexanediol (0.3 g, 3.6 mmol) in dry THF (40 ml), the Isonicotinoyl chloride hydrochloride (1.9 g, 10.7 mmol) was added and the mixture was stirred at room temperature for 15 min. Et$_3$N (5 ml) was added to the mixture and stirring was further continued for one day. After evaporation to dryness, saturated aqueous solution of Na$_2$CO$_3$ (40 ml) was added to the residue and the mixture extracted with CH$_2$Cl$_2$ (2 x 80 ml). The organic solvent was removed and the residue purified by short column chromatography [SiO$_2$, CH$_2$Cl$_2$] affording the pure products as a colorless powder. Yield 58%.

$^1$H-NMR (300 MHz, CDCl$_3$, 25 ºC) : δ (ppm) = 8.72 (d, 4H, J = 6 HZ) ; 7.74 (d, 4H, J = 6 HZ) ; 5.40 (m, 2H) ; 2.03 (m, 2H) ; 1.82 (m, 4H) ; 1.57 (m, 2H);

$^{13}$C-NMR (125 MHz, CDCl$_3$, 25 ºC) : δ (ppm) = 21.5 ; 27.8 ; 72.5 ; 122.7 ; 137.4 ; 150.6 ; 164.2

(ESI): m/z calcd. for C$_{23}$H$_{23}$N$_3$O$_4$ [M+H]: 327.13; found: 327.13.

Anal. Calcd. for C$_{23}$H$_{23}$N$_3$O$_4$ (1c): C = 66.25%; H = 5.63%; N = 8.58% ; Found C = 66.20%; H = 5.63%; N = 8.55%

**Crystallisations conditions**

**1a-HgCl$_2$, 1b-HgCl$_2$ or 1c-HgCl$_2$**

A solution of compound 1a (1b or 1c) (3 mg, 9.2 x 10$^{-3}$ mmol) in CHCl$_3$ (1 mL) is placed in a crystallization tube (20 x 4 mm). A solution of HgCl$_2$ (3 mg, 11 x 10$^{-3}$ mmol) in EtOH (2 mL) is carefully added. At room temperature, slow diffusion produced colourless crystals suitable for X-ray diffraction after 36h (3.9 mg, 72 % yield for 1a-HgCl$_2$, 4 mg, 74 % yield for 1c-HgCl$_2$ and 3.8 mg, 70 % yield for 1c-HgCl$_2$).

**10a,10b,5s-HgCl$_2$**

A solution containing 1a (3 mg, 9.2 x 10$^{-3}$ mmol) and 1b (3 mg, 9.2 x 10$^{-3}$ mmol) in CHCl$_3$ (2 mL) is placed in a crystallization tube (20 x 4 mm). A solution of HgCl$_2$ (6 mg, 22 x 10$^{-3}$ mmol) in EtOH (2 mL) is carefully added. At room temperature, slow diffusion produced colourless crystals suitable for X-ray diffraction after 36h (3.7 mg, 68 % yield).

The four solid-state samples were also analysed using XRPD on microcrystalline samples.

**Structural studies**

**Single-Crystal Studies**

Data were collected at 173(2) K on a Bruker Apex-II-CCD diffractometer equipped with an Oxford Cryosystem liquid N$_2$ device, using graphite-monochromated Mo-K$_x$ ($\lambda$ = 0.71073 Å) radiation. For all 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 refined using a riding model. They can be obtained free of...
charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/daterequest/cif. CCDC: 1a-HgCl₂ (1946672), 1b-HgCl₂ (1946673), 1c-HgCl₂ (1949896) and 1a₁b₁₀s₅-HgCl₂ (1946675).

Powder diffraction studies (PXRD)

Diagrams were collected on a Bruker D8 diffractometer using monochromatic Cu-Kα radiation with a scanning range between 4 and 40° using a scan step size of 8°/mn. As already demonstrated and currently admitted, for all compounds, discrepancies in intensity between the observed and simulated patterns are due to preferential orientations of the microcrystalline powders.

Calculations

The PACHA formalism have been used for calculations of energetic parameters, and for this purpose, evaluations of the molecular volumes have been implemented using Gavezzotti’s algorithm36 associated to a standard set of van der Waals radii. For the computational details, see ESI.

Results and discussion

The coordination properties of chiral 1a-b, achiral 1c and the 1/1 1a/1b racemic mixture towards HgCl₂ have been investigated. The choice of the bent HgCl₂ is motivated by reliable recognition pattern that may arise between 1a-c and HgCl₂. The bis-monodentate 1a-b possess a V shape, more pronounced for 1c (using the cis-1,2-cyclohexanediol scaffold), combined with bent HgCl₂, may lead, to the formation of zig-zag chains, as schematically shown in figure 2. This event occurs through the formation of Hg-N coordination bonds, where the Hg²⁺ metallic cations present a N₃Cl₂ coordination sphere and a deformed tetrahedral geometry.

It is important to note that all the single-crystals were obtained using the diffusion technique method of a EtOH solution containing the metallic salt into a CHCl₃ solution containing 1a-c (see experimental section).

Description of 1D coordination networks with 1a-c

For generating coordination networks, both chiral ligands 1a and 1b were combined with HgCl₂. For 1a and 1b, isostructural chiral crystals, 1a-HgCl₂ and 1b-HgCl₂ crystals were obtained and characterized by X-ray diffraction on single crystal. Both enantiomERICALLY pure systems crystallize in an orthorhombic non-centrosymmetric space group P 2₁2₁2₁ (see experimental section and crystallographic table 1). The crystal is composed of the chiral organic ligands 1a (or 1b) and HgCl₂ connectors. No solvent molecules were found to be present in the crystal. As expected, the use of the chiral ligand bearing asymmetrical carbons leads to the formation of a chiral crystal.38,39

As expected, combination of the V-shape ligand (V angles 71.89⁰ for 1a-HgCl₂ and 72.45⁰ for 1b-HgCl₂) with HgCl₂ leads to the formation the Zig zag coordination polymers. In both compounds, the geometry around the metallic centres is a deformed tetrahedron, with bonds and angles presented in table 2.

![Figure 2: A schematic representation of the formation of Zig-zag chains resulting from the recognition, through the formation of coordination bonds, of HgCl₂ with 1a-c.](Image)

<table>
<thead>
<tr>
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<th>1a-HgCl₂</th>
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<th>1c-HgCl₂</th>
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Table 2: Main distances and angles for 1a-HgCl₂, 1b-HgCl₂, 1c-HgCl₂ and 1a₁b₁₀s₅-HgCl₂

The zig-zag chains are formed along the a axis, as shown in figure 3 and the chains are antiparallelly arranged in the xOy plane and form thus corrugate sheets, with very weak interactions (Cl-O distance of 4.043 (5)Å with Cl coordinated to Hg), and O from carbonyl ester junction of 1a, as shown in figure 3. In the xOy plane, the distance between two consecutives chains (metal to metal distances), along the b direction is equal to 6.251 (4)Å, whereas in the yOz plane, along the c direction, it is equal to 8.221 (6)Å (see table 3).
The combination of 1c with HgCl₂ leads to the formation of a chiral network 1c-HgCl₂, where the crystal is composed of the achiral organic ligand 1c and HgCl₂ in 1/1 stoichiometric amount (see experimental section and crystallographic table 1). As in the previous case, the crystal doesn’t contain any solvent molecule and the compound crystallize in an orthorhombic non-centrosymmetric space group P 2₁2₁2 (see crystallographic table 1), and is, as expected, a 1D coordination polymer. In the structure, the V angle displayed by 1c is equal to 90.340°. The geometry around the metallic centres is a deformed tetrahedron, with bonds and angles presented in table 2. As already mentioned in the literature, the use of an achiral ligand (1c) leads to the formation of a chiral crystal, resulting from the packing of the network. This is a well-known case for “induced chirality” in molecular networks, especially in helicoidal systems.40,41

The zig-zag chains are formed along the a axis, as shown in figure 4 and the chains are parallelly arranged along the c axis. In the xOy plane, the distance between two consecutives chains, along the b direction is equal to 9.787 (5) Å. In this plane, there is a weak interaction between O (ester junction in 1c) and Cl (coordinated to Hg), with Cl-O distance of 3.547 (4) Å. In the xOz plane, the distance between two chains, along the c direction, is equal to 5.886 (3) Å (see table 3).

In order to understand the packing of a racemic mixture, the 1/1 stoichiometric amount for 1a and 1b has been combined with HgCl₂. It leads to the formation of an achiral network of general formula 1a₀.₅1b₀.₅-HgCl₂. The compound crystallizes in a monoclinic centrosymmetric space group P 2₁/n (see crystallographic table 1). This is a new example of formation of achiral crystals starting from a racemic composition of chiral ligands. The crystal is composed of the chiral organic ligands 1a and 1b in 1/1 stoichiometric amount, HgCl₂ connectors and CHCl₃ solvent molecules, that don’t present any specific
interactions with the network. The system is based on two zigzag chains running along the b axis, containing respectively only 1a or 1b, as shown in figure 5, with V angle of 80.753° and 80.399° respectively. The crystal is achiral, due to the presence of pairs of helicoidal chains of opposite chirality. The geometry around the metallic centers is also a deformed tetrahedron, N₃Cl₂ with bonds and angles presented in table 2.

The purity of the 1a-HgCl₂, 1b-HgCl₂, 1c-HgCl₂ and 1a₀,₅₁b₀,₅-HgCl₂ polycrystalline samples was investigated by PXRD on microcrystalline powder (see figures 6). For all compounds, a good match between the observed and calculated patterns from the XRD data was obtained, attesting a pure crystalline phase in the solid-state. It revealed that 1a₀,₅₁b₀,₅-HgCl₂ doesn’t contain any 1a-HgCl₂ or 1b-HgCl₂ crystalline phase.

![Figure 5](image_url)

**Figure 5.** A portion of the chiral 1D coordination network 1a₀,₅₁b₀,₅-HgCl₂ (a) and corresponding packing (b) obtained upon combining HgCl₂ with 1a₁b₁ in racemic conditions. H atoms are omitted for clarity of the representation.

The crystal is achiral, due to the presence of pairs of helicoidal chains of opposite chirality. The system is based on two zigzag chains running along the b axis, containing respectively only 1a or 1b, as shown in figure 5, with V angle of 80.753° and 80.399° respectively. The crystal is achiral, due to the presence of pairs of helicoidal chains of opposite chirality. The geometry around the metallic centers is also a deformed tetrahedron, N₃Cl₂ with bonds and angles presented in table 2.

**Energetical study of the crystal packing**

Taking into account these structural considerations described above, some calculations have been performed in order to evaluate the Packing Energy (PE) of chiral crystals 1a-HgCl₂, 1b-HgCl₂ and 1c-HgCl₂ (compounds crystallising in a non-centrosymmetric and chiral space groups), and 1a₀,₅₁b₀,₅-HgCl₂ (compound crystallising in centrosymmetric space group) (see table 3). As already mentioned, the crystallisation in a non-centrosymmetric space group for 1a-HgCl₂ and 1b-HgCl₂ is the direct consequence of the chirality imposed by the ligand, whereas for 1c-HgCl₂ it results from the packing of the 1D system.

The use of a racemic mixture is at the origin of the observation of a centrosymmetric space group (P 2₁/n) in which 1a₀,₅₁b₀,₅-HgCl₂ crystallises.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Space Group</th>
<th>V angle of 1a-c</th>
<th>Interchain distances (Å)</th>
</tr>
</thead>
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<tr>
<td>1a-HgCl₂</td>
<td>P 2₁2₁2₁</td>
<td>71.895°</td>
<td>6.251 (4) 8.221 (6)</td>
</tr>
<tr>
<td>1b-HgCl₂</td>
<td>P 2₁2₁2₁</td>
<td>72.456°</td>
<td>6.251 (6) 8.222 (6)</td>
</tr>
<tr>
<td>1c-HgCl₂</td>
<td>P 2₁2₁2₁</td>
<td>90.340°</td>
<td>5.886 (3) 9.787 (6)</td>
</tr>
<tr>
<td>1a₀,₅₁b₀,₅-HgCl₂</td>
<td>P 2₁/n</td>
<td>80.753° 80.399°</td>
<td>5.839 (2) 8.166 (2)</td>
</tr>
</tbody>
</table>

**Table 3:** Main characteristics for crystals 1a-HgCl₂, 1b-HgCl₂, 1c-HgCl₂ and 1a₀,₅₁b₀,₅-HgCl₂.

In order to evaluate the energetic parameters, a force field approach can be used, but is not well adapted for extended
networks. An estimation of the contribution of different recognition events and thus assembling nodes may also be obtained using a PACHA analysis (Partial Atomic Charges and Hardnesses Analysis).

The Packing Energy (PE). Such analysis was carried out for the architecture is crucial parameters guiding the formation of the molecular crystalline structure are characterized by a strong packing anisotropy between chiral chains associated to a weak cooperativity between chiral chains. 1a0.51b0.5-HgCl2, involving a racemic mixture and crystallising in a centro-symmetric space group, also displays a high packing anisotropy and a weak Cooperativity Index. The CI value of -33 kJ mol⁻¹ for 1c-HgCl2 reflects the use of achiral components in a network (ligand 1c), imposing a chiral packing.

In addition, the Hg-N coordination bond energy within the networks were evaluated (see ESI) and reveal to be weak, as expected for coordination networks.

Conclusions

The enantiomerically pure bis monodentate ligands (1a, 1b) and meso 1c based on the trans-1,2-cyclohexanediol and cis-1,2-cyclohexanediol respectively were used for the formation of zig-zag 1D Coordination Polymers, when combined with bent HgCl2. The crystals 1a-HgCl2 (also isostructural 1b-HgCl2) and 1c-HgCl2 and have been obtained and the X-ray analysis on single crystals reveals that the compounds crystallise in the chiral P 212121 and P 21212 space groups respectively. A head to tail packing of the chains is observed in 1a-HgCl2 (isostructural 1b-HgCl2). For the use of the achiral ligand 1c, the non centro symmetry of the observed space group in 1c-HgCl2, related to the packing.

Then a 1/1 racemic mixture of enantiomerically pure ligands 1a/1b was combined with HgCl2 and the formed Coordination Polymer 1a0.51b0.5-HgCl2 crystallises in a centro-symmetric P 2/n space group.

The analysis of the networks revealed that the “Packing Efficiency” of the four compounds is close to 70%.

The analysis of the Packing Energies, based on a partial charges calculation method (PACHA), allows to derive the

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Space Group</th>
<th>Packing Efficiency ξ [%]</th>
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<tbody>
<tr>
<td>1a-HgCl2</td>
<td>P 212121</td>
<td>67.3</td>
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<td>1b-HgCl2</td>
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<td>1a0.51b0.5-HgCl2</td>
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<td>69.2</td>
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Table 4: Packing Efficiency ξ for crystals 1a-HgCl2, 1b-HgCl2, 1c-HgCl2 and 1a0.51b0.5-HgCl2,

1c-HgCl2 and 1a0.51b0.5-HgCl2, using the PACHA analysis. The results, provided in Table 5, allowed the estimations of energy of the formed zig-zag chains, of the Packing Energy and finally the Cooperativity Index (CI).

The calculation revealed that for all compounds, the Cooperativity Index is negative, reflecting an efficient cooperativity between the wires. Using pure enantiomers ligands (compounds 1a-HgCl2 and 1b-HgCl2), the resulting structures are characterized by a strong packing anisotropy between chiral chains associated to a weak cooperativity between chiral chains. 1a0.51b0.5-HgCl2, involving a racemic mixture and crystallising in a centro-symmetric space group, also displays a high packing anisotropy and a weak Cooperativity Index. The CI value of -33 kJ mol⁻¹ for 1c-HgCl2 reflects the use of achiral components in a network (ligand 1c), imposing a chiral packing.

In addition, the Hg-N coordination bond energy within the networks were evaluated (see ESI) and reveal to be weak, as expected for coordination networks.
Cooperativity Index for each compound, and clearly revealed that the cooperativity between the formed layers is stronger when achiral ligands are involved in the formed coordination network (compound 1c-HgCl₂). This energetical analysis is the first one reported for the crystal formation of 1D coordination polymers.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the University of Strasbourg, the C.N.R.S, the International centre for Frontier Research in Chemistry (icFRC), the Labex CSC (ANR-10-LABX-0026 CSC) within the Investissement d’Avenir program ANR-10-IDEX-0002-02, the Ministère de l’Enseignement Supérieur et de la Recherche for financial support.

Notes and references


45. The program can be free downloaded from https://complex-matter.unistra.fr/equipes/mater.unistra.fr/equipes-de-chimie-ionique/logiciels/.


<table>
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<tr>
<th>Formula</th>
<th>1a-HgCl₂</th>
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<td>C₁₈H₁₈Cl₂HgN₂O₄</td>
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</table>
Graphical abstract

1a (R,R) or 1b (S,S)  
1c (R,S)  
Racemate 1a (R,R) + 1b (S,S)

\[ \text{P} \text{2}_1 \text{2}_1 \text{2}_1 \]  
\[ \text{P} \text{2}_1 \text{2}_2 \text{2}_1 \]  
\[ \text{P} \text{2}_1 \text{n} \]