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

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## Abstract

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 HgCl<sub>2</sub>. 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-HgCl<sub>2</sub>** (and isostructural **1b-HgCl<sub>2</sub>**) crystallizes in the non-centrosymmetric *P* 2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> space group, **1c-HgCl<sub>2</sub>** in the non-centrosymmetric *P* 2<sub>1</sub>2<sub>1</sub>2 space group and **1a<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub>** crystallises in the centrosymmetric *P* 2<sub>1</sub>/*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.

## 1 Introduction

The interests in Coordination Polymers (CPs),<sup>i</sup> coordination networks<sup>ii</sup> or MOFs,<sup>iii,iv</sup> 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,<sup>v,vi,vii,viii,ix,x,xi</sup> but also on their intriguing variety of topologies and entanglement motifs that they may adopt.<sup>xii,xiii,xiv</sup> 3D and 2D Coordination Polymers have been widely classified from their topologies<sup>xv</sup> and concerning 1D CPs, they also have been extensively studied.<sup>xvi,xvii,xviii</sup> Within this class of compounds, beside the classical linear chains<sup>xix,xx,xxi</sup> or zig-zag chains<sup>xxii</sup> the design of helical networks<sup>xxiii,xxiv,xxv,xxvi,xxvii,xxviii</sup> 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.<sup>xvi</sup> For piezo and pyroelectric properties of molecular compounds, for example, the formation of non-centrosymmetric crystals has proven to be very promising.<sup>xxix</sup>

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.<sup>xxx,xxxi</sup> 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.

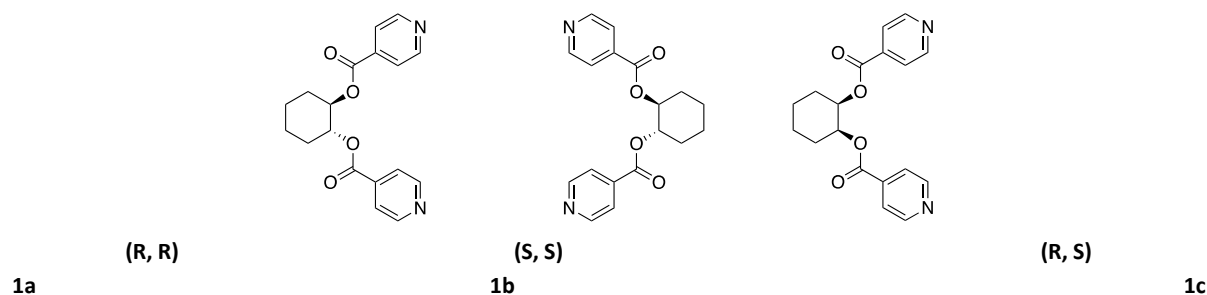
Along this line, several approaches have been developed in order to control the packing in molecular crystals, like the use of non-symmetrical chiral components, for example. For this purpose, examples are based on the use of dissymmetric chiral ligand that can lead to a non-centrosymmetric packing (leading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

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  $\text{HgCl}_2$ . 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  $\text{ZnSiF}_6$  for the formation of helical tubular crystals has been described.<sup>xxxiii</sup> Combinations with other transition metals have also been studied.<sup>xxxiv</sup>

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  $\text{HgCl}_2$ , 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

$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  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.<sup>xxxiii</sup>

### 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.  $\text{Et}_3\text{N}$  (5 ml) was added to the mixture and stirring was further continued for one day. After evaporation to dryness, saturated aqueous solution of  $\text{Na}_2\text{CO}_3$  (40 ml) was added to the residue and the mixture extracted with  $\text{CH}_2\text{Cl}_2$  (2 x 80 ml). The organic solvent was removed and the residue purified by short column chromatography [ $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2$ ] affording the pure products as a colorless powder. Yield 58 %.

$^1\text{H-RMN}$  (300 MHz,  $\text{CDCl}_3$ , 25 °C) :  $\delta$  (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);

$^{13}\text{C-RMN}$  (125 MHz,  $\text{CDCl}_3$ , 25 °C) :  $\delta$  (ppm) = 21.5 ; 27.8 ; 72.5 ; 122.7 ; 137.4 ; 150.6 ; 164.2

(ESI): m/z calcd. for  $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4$  [M-H]: 327.13; found: 327.13.

Anal. Calcd. for  $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4$  (**1c**): C = 66.25%; H = 5.56%; N = 8.58%, % ; Found C = 66.20%; H = 5.63%; N = 8.55%

### Crystallisations conditions

### **1a-HgCl<sub>2</sub>, 1b-HgCl<sub>2</sub> or 1c-HgCl<sub>2</sub>**

A solution of compound **1a** (**1b** or **1c**) (3 mg,  $9.2 \times 10^{-3}$  mmol) in CHCl<sub>3</sub> (1 mL) is placed in a crystallization tube (20 x 4 mm). A solution of HgCl<sub>2</sub> (3 mg,  $11 \times 10^{-3}$  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<sub>2</sub>**, 4 mg, 74 % yield for **1c-HgCl<sub>2</sub>** and 3.8 mg, 70 % yield for **1c-HgCl<sub>2</sub>**).

### **1a<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub>**

A solution containing **1a** (3 mg,  $9.2 \times 10^{-3}$  mmol) and **1b** (3 mg,  $9.2 \times 10^{-3}$  mmol) in CHCl<sub>3</sub> (2 mL) is placed in a crystallization tube (20 x 4 mm). A solution of HgCl<sub>2</sub> (6 mg,  $22 \times 10^{-3}$  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<sub>2</sub> device, using graphite-monochromated Mo-K $\alpha$  ( $\lambda = 0.71073$  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<sup>2</sup> using SHELXL-97. The hydrogen atoms were introduced at calculated positions and refined using a riding model.<sup>xxxv</sup> They can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* [www.ccdc.cam.ac.uk/datarequest/cif](http://www.ccdc.cam.ac.uk/datarequest/cif). CCDC: **1a-HgCl<sub>2</sub>** (1946672), **1b-HgCl<sub>2</sub>** (1946673), **1c-HgCl<sub>2</sub>** (1949896) and **1a<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub>** (1946675).

### **Powder diffraction studies (PXRD)**

Diagrams were collected on a Bruker D8 diffractometer using monochromatic Cu-K $\alpha$  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.

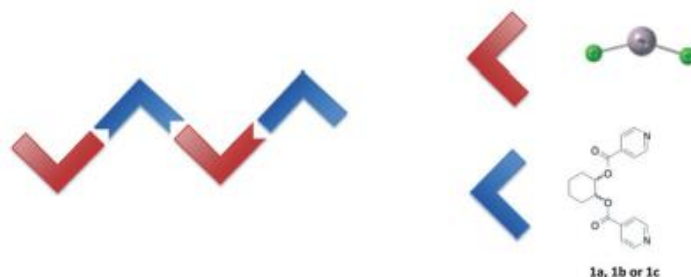
## **Calculations**

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<sup>xxxvi</sup> associated to a standard set of van der Waals radii.<sup>xxxvii</sup> 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 HgCl<sub>2</sub> have been investigated. The choice of the bent HgCl<sub>2</sub> is motivated by reliable recognition pattern that may arise between **1a-c** and HgCl<sub>2</sub>. The bis-monodentate **1a-b** possess a V shape, more pronounced for **1c** (using the *cis*-1,2-cyclohexanediol scaffold), combined with bent HgCl<sub>2</sub>, 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 Hg<sup>2+</sup> metallic cations present a N<sub>2</sub>Cl<sub>2</sub> 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 CHCl<sub>3</sub> solution containing **1a-c** (see experimental section).



**Figure 2:** A schematic representation of the formation of Zig-zag chains resulting from the recognition, through the formation of coordination bonds, of HgCl<sub>2</sub> with **1a-c**.

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

For generating coordination networks, both chiral ligands **1a** and **1b** were combined with HgCl<sub>2</sub>. For **1a** and **1b**, isostructural chiral crystals, **1a-HgCl<sub>2</sub>** and **1b-HgCl<sub>2</sub>** 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<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (see experimental section and crystallographic table 1). The crystal is composed of the chiral organic ligands **1a** (or **1b**) and HgCl<sub>2</sub> 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. <sup>xxxviii,xxxix</sup>

	<b>1a-HgCl<sub>2</sub></b>	<b>1b-HgCl<sub>2</sub></b>	<b>1c-HgCl<sub>2</sub></b>	<b>1a<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub></b>
Formula	(R,R) C <sub>18</sub> H <sub>18</sub> Cl <sub>2</sub> HgN <sub>2</sub> O <sub>4</sub>	(S,S) C <sub>18</sub> H <sub>18</sub> Cl <sub>2</sub> HgN <sub>2</sub> O <sub>4</sub>	(S,R) C <sub>18</sub> H <sub>18</sub> Cl <sub>2</sub> HgN <sub>2</sub> O <sub>4</sub>	(R,R)/(S,S) 50% C <sub>18</sub> H <sub>18</sub> Cl <sub>2</sub> HgN <sub>2</sub> O <sub>4</sub> , CHCl <sub>3</sub>
Molecular weight	597.83	597.83	597.83	717.20
Crystal system	orthorhombic	orthorhombic	orthorhombic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2	<i>P</i> 2 <sub>1</sub> / <i>n</i>
a(Å)	11.3240(9)	11.321(7)	18.3123(7)	11.6797(13)
b(Å)	12.502(4)	12.502(6)	18.3932(6)	12.746(2)
c(Å)	14.398(4)	14.40(2)	5.8857(3)	16.331(2)
α(deg)	90	90	90	90
β(deg)	90	90	90	100.554(10)
γ(deg)	90	90	90	90
V(Å <sup>3</sup> )	2038.4(8)	2038.0(8)	1982.43(14)	2390.1(6)
Z	4	4	4	4
Colour	Colourless	Colourless	Colourless	Colourless
Crystal dim (mm <sup>3</sup> )	0.100 x 0.110 x 0.120	0.080 x 0.100 x 0.110	0.09 x 0.08 x 0.06	0.120 x 0.120 x 0.130
Dcalc (gcm <sup>-3</sup> )	1.948	1.948	2.003	1.993
F(000)	1144	1144	1144	1376
μ (mm <sup>-1</sup> )	7.838	7.839	8.059	7.027
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Number of data meas.	6471	5816	15810	5182
Number of data with I > 2σ(I)	6471 [R(int) = 0.0325]	5816 [R(int) = 0.0423]	4345 [R(int) = 0.0388]	5182 [R(int) = 0.0750]
R	R1 = 0.0321, wR2 = 0.0551	R1 = 0.0287, wR2 = 0.0511	R1 = 0.0614, wR2 = 0.1397	R1 = 0.0477, wR2 = 0.0862
Rw	R1 = 0.0457, wR2 = 0.0588	R1 = 0.0361, wR2 = 0.0532	R1 = 0.0846, wR2 = 0.1454	R1 = 0.1137, wR2 = 0.1085
GOF	1.015	1.024	1.220	0.823
Largest peak in final difference (eÅ <sup>-3</sup> )	0.827 and -0.866	0.695 and -0.678	2.148 and -1.769	1.311 and -1.158
Flack parameter	0.002(6)	0.000(5)	0.038(19)	-

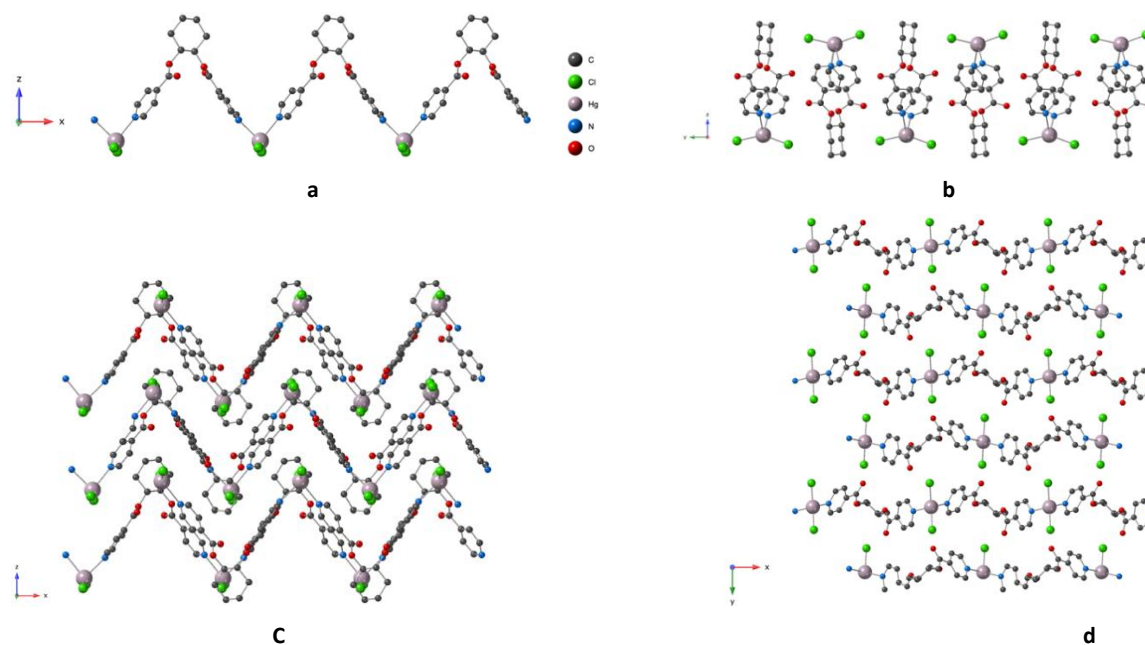
**Table 1:** Crystallographic Parameters for **1a-HgCl<sub>2</sub>**, **1b-HgCl<sub>2</sub>**, **1c-HgCl<sub>2</sub>** and **1a<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub>** recorded at 173 K.

As expected, combination of the V-shape ligand (V angles 71.895° for **1a-HgCl<sub>2</sub>** and 72.456° for **1b-HgCl<sub>2</sub>**) with HgCl<sub>2</sub> 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.

	<b>1a-HgCl<sub>2</sub></b>	<b>1b-HgCl<sub>2</sub></b>	<b>1c-HgCl<sub>2</sub></b>	<b>1a<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub></b>
Hg-N	2.419(5) 2.451(4)	2.430(5) 2.451(5)	2.416(16) 2.439(14)	2.437(7) 2.444(7)
Hg-Cl	2.3488(16) 2.3521(15)	2.3460(18) 2.3544(17)	2.346(5) 2.350(4)	2.364(2) 2.357(2)
ClHgCl	146.84(6)	146.80(8)	152.7(3) 149.8(3)	153.56(9)
ClHgN	94.20(11) 96.69(11) 105.86(10) 111.79(11)	94.20(11) 96.67(11) 105.97(10) 111.69(11)	95.8(4) 97.1(3) 104.2(4) 104.9(3)	95.77(16) 98.58(18) 101.93(17) 102.44(17)
NHgN	85.54(15)	85.73(18)	84.8(9) 85.9(6)	84.9(2)

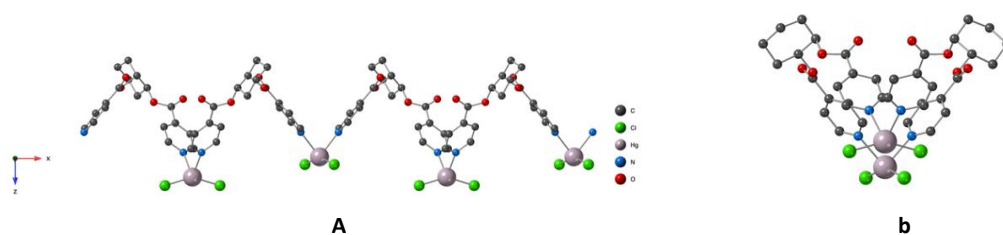
**Table 2:** Main distances and angles for **1a-HgCl<sub>2</sub>**, **1b-HgCl<sub>2</sub>**, **1c-HgCl<sub>2</sub>** and **1a<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub>**

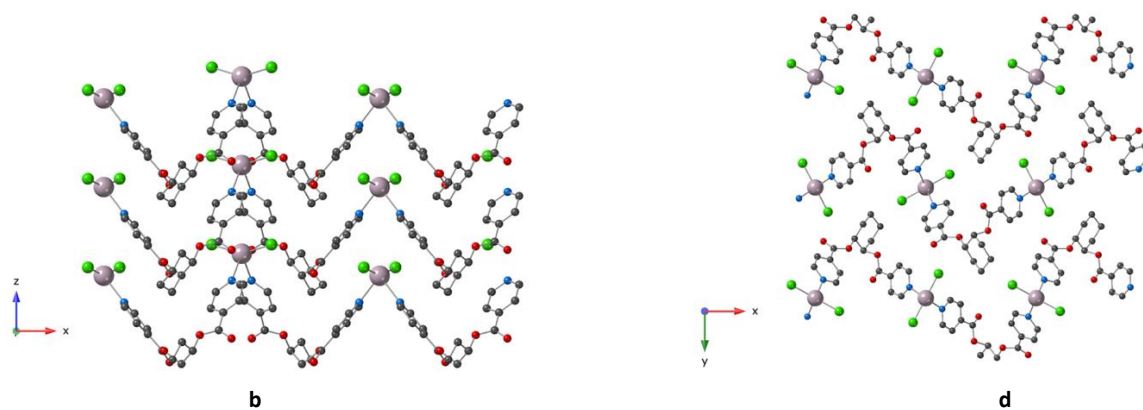
The zig-zag chains are formed along the  $a$  axis, as shown in figure 3 and the chains are antiparallely arranged in the  $xOy$  plane and form thus corrugate sheets, with very weak interactions (Cl-O distance of  $4.043(5)\text{Å}$  (with Cl coordinated to Hg), and O from carbonyl ester junction of **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  $6.251(4)\text{Å}$ , whereas in the  $yOz$  plane, along the  $c$  direction, it is equal to  $8.221(6)\text{Å}$  (see table 3).



**Figure 3.** A portion of the 1D coordination networks **1a-HgCl<sub>2</sub>** (or **1b-HgCl<sub>2</sub>**) along the  $a$  (picture a) and  $b$  (picture b) axes and corresponding packing obtained upon combining HgCl<sub>2</sub> 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<sub>2</sub> leads to the formation of a chiral network **1c-HgCl<sub>2</sub>**, where the crystal is composed of the achiral organic ligand **1c** and HgCl<sub>2</sub> 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  $90.340^\circ$ . 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.<sup>xl,xli</sup>

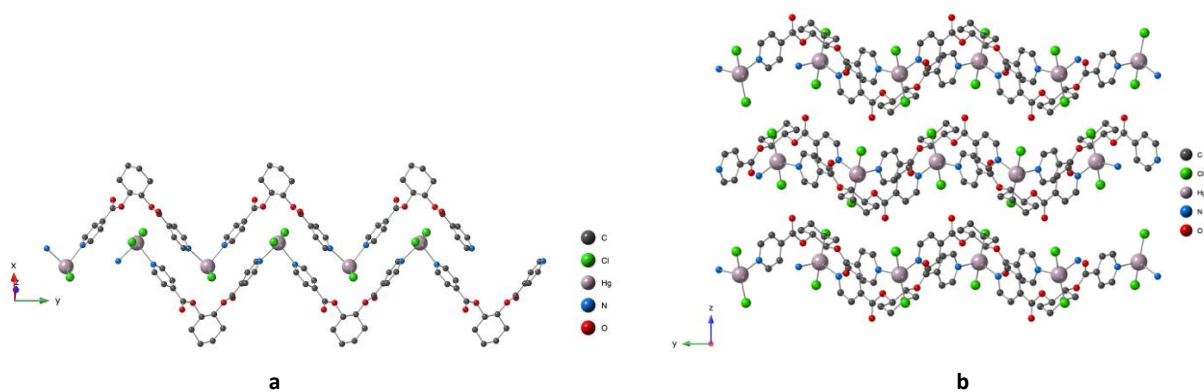




**Figure 4.** A portion of the 1D coordination networks **1c-HgCl<sub>2</sub>** along the *a* (picture a) and *b* (picture b) axes and corresponding packing obtained upon combining HgCl<sub>2</sub> with **1c** (pictures c and d, in the xOz and xOy planes respectively). H atoms are omitted for clarity of the representation.

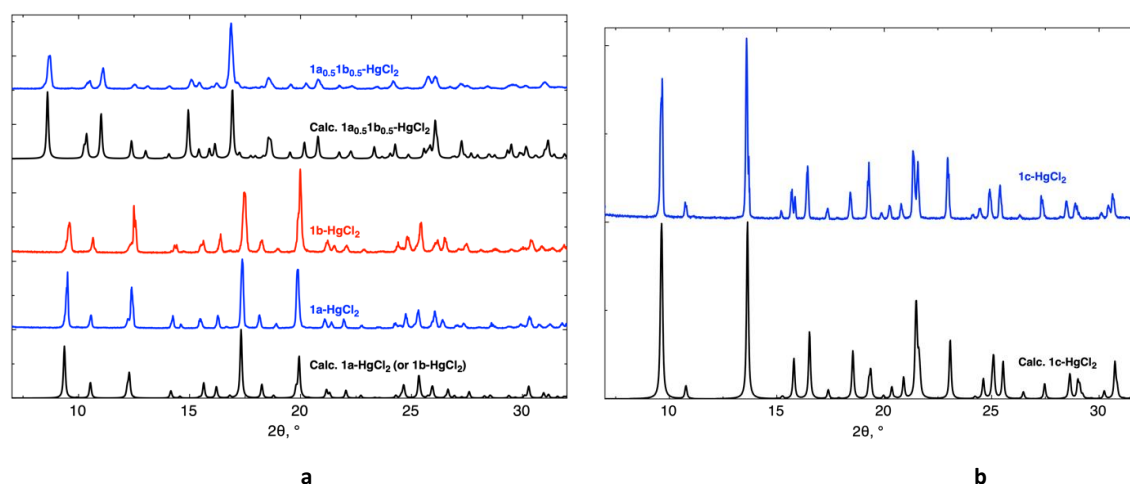
The zig-zag chains are formed along the *a* axis, as shown in figure 4 and the chains are parallelly arranged along the *c* axis. In the xOy plane, the distance between two consecutive chains, along the *b* direction is equal to 9.787 (5) Å. In this plane, there is a weak interaction between O (ester 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<sub>2</sub>. It leads to the formation of an achiral network of general formula **1a<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub>**. The compound crystallizes in a monoclinic centrosymmetric space group *P* 2<sub>1</sub>/*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<sub>2</sub> connectors and CHCl<sub>3</sub> solvent molecules, that don't present any specific interactions with the network. The system is based on two zig-zag 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, N<sub>2</sub>Cl<sub>2</sub> with bonds and angles presented in table 2.



**Figure 5.** A portion of the chiral 1D coordination network **1a<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub>** (a) and corresponding packing (b) obtained upon combining HgCl<sub>2</sub> with **1a+1b** in racemic conditions. H atoms are omitted for clarity of the representation.

The purity of the **1a-HgCl<sub>2</sub>**, **1b-HgCl<sub>2</sub>**, **1c-HgCl<sub>2</sub>** and **1a<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub>** 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<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub>** doesn't contain any **1a-HgCl<sub>2</sub>** or **1b-HgCl<sub>2</sub>** crystalline phase.



**Figure 6.** Comparison of the simulated and recorded XRPD diagrams (a) for **1a-HgCl<sub>2</sub>**, **1b-HgCl<sub>2</sub>** and **1a<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub>** and (b) for **1c-HgCl<sub>2</sub>**.

### **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-HgCl<sub>2</sub>**, **1b-HgCl<sub>2</sub>** and **1c-HgCl<sub>2</sub>** (compounds crystallising in a non-centrosymmetric and chiral space groups), and **1a<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub>** (compound crystallising in centrosymmetric space group) (see table 3). As already mentioned, the crystallisation in a non-centrosymmetric space group for **1a-HgCl<sub>2</sub>** and **1b-HgCl<sub>2</sub>** is the direct consequence of the chirality imposed by the ligand, whereas for **1c-HgCl<sub>2</sub>** 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 ( $P 2_1/n$ ) in which **1a<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub>** crystallises.

Crystal	Space Group	V angle of 1a-c	Interchain distances (Å)
<b>1a-HgCl<sub>2</sub></b>	$P 2_12_12_1$ Non centrosymmetric	71.895°	6.251 (4) 8.221 (6)
<b>1b-HgCl<sub>2</sub></b>	$P 2_12_12_1$ Non centrosymmetric	72.456°	6.251 (6) 8.222 (6)
<b>1c-HgCl<sub>2</sub></b>	$P 2_12_12$ Non centrosymmetric	90.340°	5.886 (3) 9.787 (6)
<b>1a<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub></b>	$P 2_1/n$ centrosymmetric	80.753° 80.399°	5.839 (2) 8.166 (2)

**Table 3:** Main characteristics for crystals **1a-HgCl<sub>2</sub>**, **1b-HgCl<sub>2</sub>**, **1c-HgCl<sub>2</sub>** and **1a<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub>**

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).<sup>xlii,xliii,xliv</sup> The PACHA analysis<sup>xlv</sup> was successfully developed for analysing hydrogen bonds involving water,<sup>xlvi</sup> hydrogen bonded networks<sup>xlvii</sup> or extended MOFs<sup>xlviii,xlix</sup> and is well adapted for extended molecular networks, taking into account the symmetry operators governing the crystal structure.<sup>1</sup>

For analysing the packing in the solid state, three main factors, allowing an accurate description of the networks, will be analysed: i) Packing Efficiency<sup>li</sup>  $\xi$ ; ii) the Packing Energy (PE)<sup>l</sup> 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)<sup>lii</sup> 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 ( $\xi = ZV_m/V_{\text{cell}}$ , where  $V_m$  is the molecular volume).<sup>ii</sup> This purely geometric descriptor is easily evaluated from the knowledge of a set of van der Waals atomic radii<sup>iii</sup> and of the unit-cell volume. It may provide useful indications concerning the “porosity” of the crystal.

Crystal	Space Group	Packing Efficiency $\xi$ /%
<b>1a-HgCl<sub>2</sub></b>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	67,3
<b>1b-HgCl<sub>2</sub></b>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	67,4
<b>1c-HgCl<sub>2</sub></b>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2	69,1
<b>1a<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub></b>	<i>P</i> 2 <sub>1</sub> /n	69,2

**Table 4:** Packing Efficiency  $\xi$  for crystals **1a-HgCl<sub>2</sub>**, **1b-HgCl<sub>2</sub>**, **1c-HgCl<sub>2</sub>** and **1a<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub>**

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<sub>2</sub>** and **1b-HgCl<sub>2</sub>**, related to the non-centrosymmetric space group (use of a chiral ligand) in which the compounds are crystallising. For **1c-HgCl<sub>2</sub>**, it considers the chirality imposed by the packing and reveal to be slightly larger. For **1a<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub>**  $\xi$  was evaluated, considering the presence of solvent molecules (CHCl<sub>3</sub>) 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,<sup>i</sup> 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<sub>2</sub>**, **1b-HgCl<sub>2</sub>**, **1c-HgCl<sub>2</sub>** and **1a<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub>**), 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),<sup>iii</sup> (for methodology and detailed calculations, see ESI).

Crystal	Chain energy (kJmol <sup>-1</sup> )	Network energy (kJmol <sup>-1</sup> )	Packing Energy (PE) (kJmol <sup>-1</sup> )	Cooperativity Index (CI) (kJmol <sup>-1</sup> )
<b>1a-HgCl<sub>2</sub></b>	-536 (2)	-2267 (9)	-123 (9)	-2 (2)
<b>1b-HgCl<sub>2</sub></b>	-535 (2)	-2264 (9)	-124 (9)	-2 (2)
<b>1c-HgCl<sub>2</sub></b>	-534 (2)	-2314 (9)	-178 (9)	-33 (2)
<b>1a<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub></b>	-532 (2)	-2368 (9)	-214 (9)	-3 (2)

**Table 5:** Calculations of Chain Energy, Network Energy, Packing Energy and Cooperativity index for crystals **1a-HgCl<sub>2</sub>**, **1b-HgCl<sub>2</sub>**, **1c-HgCl<sub>2</sub>** and **1a<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub>**

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<sub>2</sub>** and **1b-HgCl<sub>2</sub>**), the resulting structures are characterized by a strong packing anisotropy between chiral chains associated to a weak cooperativity between chiral chains. **1a<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub>**, 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<sup>-1</sup> for **1c-HgCl<sub>2</sub>** 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<sub>2</sub>. The crystals **1a-HgCl<sub>2</sub>** (and also isostructural **1b-HgCl<sub>2</sub>**) and **1c-HgCl<sub>2</sub>** and have been obtained and the X-Ray analysis on single crystals reveals that the compounds crystallise in the chiral *P* 2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> and *P* 2<sub>1</sub>2<sub>1</sub>2 space groups respectively. A head to tail packing of the chains is observed in **1a-HgCl<sub>2</sub>**

(isostructural **1b-HgCl<sub>2</sub>**). For the use of the achiral ligand **1c**, the non centrosymmetry of the observed space group in **1c-HgCl<sub>2</sub>**, related to the packing.

Then a 1/1 racemic mixture of enantiomerically pure ligands **1a/1b** was combined with HgCl<sub>2</sub> and the formed Coordination Polymer (**1a<sub>0.5</sub>1b<sub>0.5</sub>-HgCl<sub>2</sub>**) crystallises in a centrosymmetric *P* 2<sub>1</sub>/*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-HgCl<sub>2</sub>**). 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.

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Notes and referen

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