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Variations around 1D coordination polymers built from the triarylamine scaffold and Hg(II) or Cd(II)

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Abstract

Two tripodal ligands **1** and **2**, derived from triarylamine (tris[4-(pyridin-4-yl)phenyl]amine (**1**) and tris(4'-(pyridin-4-yl)-[1,1'-biphenyl]-4-yl)amine (**2**)), have been synthesized and used for the formation of new 1D coordination networks. The synthesis and complete characterization of **2** is described. Both ligands that present the same geometry but different metrics, have been combined with V shape metalloligands $M^{II}X_2$ ($M = \text{Hg}$ and $X = \text{Cl}$ or $M = \text{Cd}$ and $X = \text{I}$). The solid-state structures of the four new 1D coordination polymers (**1**- HgCl_2 , **1**- $\text{HgCl}_2 \cdot \text{CHCl}_3$, **2**- HgCl_2 and **2**- CdI_2) have been studied by X-ray diffraction on single crystals. The packing of networks and solvent molecules, when present within crystals, is mainly governed by π - π interactions.

Depending on the nature of the ligand and the metalloligand, two types of coordination modes are observed: (i) ligand **1** may behave as a V shape connector with one pyridyl group remaining uncoordinated, and tetracoordinated Hg(II) cation leading, in **1**- HgCl_2 , to a helicoidal arrangement; and (ii) ligands **1** and **2**, when assembled with HgCl_2 and CdI_2 lead to a ladder-like structure (**1**- $\text{HgCl}_2 \cdot \text{CHCl}_3$, **2**- HgCl_2 and **2**- CdI_2), resulting from the recognition of the T-shape ligand (**1** or **2**), whereas all the pyridyl groups are involved in the coordination with the pentacoordinated $M(\text{II})$ cation. The tuning of the geometrical parameters of the 1D ladder-like networks appears possible through the initial choice of ligands.

Key words:

Tripodal triarylamine based ligands; 1D coordination network; coordination chemistry, mercury and cadmium cations.

1. Introduction

Triarylamine derivatives are attractive redox-active¹ species displaying highly reversible one electron oxidation process leading to radicals. Due to their chemical stability and electron-rich character, they are used in optimized hole-transporting materials² or in organic emitting diodes,³ as well as dye sensitized solar cell for example.⁴ In addition, they were used in polymeric and supramolecular systems,⁵ with diverse functionalities such as optical waveguides, nanowires, etc.

We are interested in triarylamine derivatives for the generation of coordination networks. Coordination networks (CN),⁶ coordination polymers (CPs),⁷ or MOFs⁸ are molecular extended

architectures that may present different functionalities depending on their structures. CP derived from Triarylamines have also been reported.

The coordination abilities of triarylamine derivatives bearing coordinating sites have been thoroughly studied. Several complexes have been obtained,⁹ most of them based on terpyridyl appended species.¹⁰ Concerning the formation of coordination polymers based on the symmetrical triarylamine core, reports begin in 2013. The C3 geometry of the ligand allows the formation of high dimensional assemblies, when combined with metallic cations. Using the trisubstituted triarylamine scaffold bearing thiophenecarboxylic acid,¹¹ triazole,¹² carboxylic acid,¹³ benzoic acid¹⁴, or imidazole¹⁵, extended architectures, offering interesting features such as luminescence, catalysis or gas adsorption properties, have been described. Some other coordination polymers were obtained by breaking the C3 symmetry (di- or monosubstituted compounds).¹⁶ The pyridyl coordinating group has been also used in ligand **1** (tris[4-(pyridin-4-yl)phenyl]amine, figure 1) which leads to the formation of diverse coordination polymers with polythreated structures when combined with Cu(I)¹⁷ and Cd(II).¹⁸ The redox properties in the solid-state of the CP obtained with Zn(II),¹⁹ Cu(II)²⁰ are also reported. The use of ligand **1** with ancillary ligands and transition metals (Co(II), Ni(II), Fe(II), Cd(II), Cu(II), Zn(II)) has led to the formation of, most of the time, entangled porous compounds, presenting interesting gas adsorption behavior and also luminescent properties.^{15,21} Some of these architectures display chirality.²² Some of these compounds have been used for as electrode materials and/or supercapacitors.²³

No coordination networks based on Hg(II) cations, that may adopt various coordination spheres, and triarylamine scaffold ligands has been reported to date. In this contribution, we have explored the coordination ability of tripodal ligands **1** and **2** (figure 1) towards Hg(II) and Cd(II) cations. **1** and **2** differ by the length of the spacer between the coordinating pyridyl groups and the scaffold. Four new coordination networks based on ligands **1** and **2** are presented below, and their structures in the solid state are described.

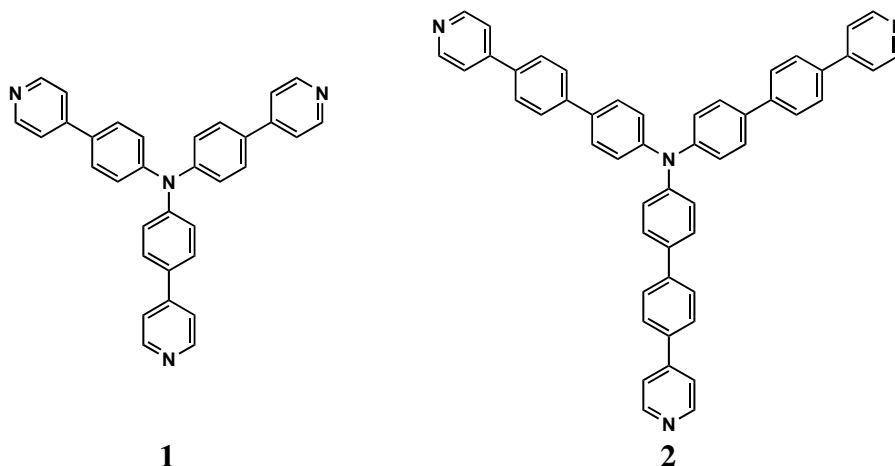


Figure 1: Tripodal ligands **1** and **2** based on the triarylamine core

2. Materials and Methods

2.1. Characterization techniques

¹H-NMR and ¹³C-NMR spectra were recorded at room temperature on a Bruker 300 MHz and 500 MHz spectrometers respectively.

Mass spectra (MS (ES+)) were obtained on a Bruker MicroTOF spectrometer.

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

2.2. Synthesis

All reagents were purchased from commercial sources and used without further purification. **1** was prepared following the already published procedure.²⁴ Tris(4'-bromo-[1,1'-biphenyl]amine (**2'**)) was prepared following the already reported method, using DMF instead of THF/H₂O.²⁵

2.2.1. tris(4'-(pyridin-4-yl)-[1,1'-biphenyl]-4-yl)amine **2**

A mixture of Tris(4'-bromo-[1,1'-biphenyl]amine (0.1 g, 0.14 mmol) (**2'**), K₂CO₃ (0.3 g, 2.1 mmol) and pyridine-4-ylboronic acid (0.30 g, 2.1 mmol) in 16 mL of a mixture THF/MeOH/H₂O (10/5/1) was degassed under argon for 20 minutes. Pd(PPh₃)₄ (0.01 g, 0.009 mmol) was added, and the mixture was then heated to reflux for 5 days under argon. Solvents were removed under vacuum and the residue was extracted with CH₂Cl₂ (3×50 mL). The combined organic layers were washed with brine, dried over MgSO₄, and evaporated to dryness. The residue was purified by silica gel column chromatography with CH₂Cl₂/MeOH mixture varying from 100/0 to 85/15 as eluent, to provide the target compound **2** as yellow solid (0.06 g, 60%).

¹H NMR (CD₂Cl₂, 500 MHz) : δ [ppm]: 8.64 (d, J = 5.2 Hz, 6H), 7.74 (s, 12H), 7.62 (d, J = 8.2 Hz, 6H), 7.56 (d, J = 5.2 Hz, 6H), 7.26 (d, J = 8.2 Hz, 6H).

¹³C NMR (CD₂Cl₂, 126 MHz) : δ [ppm]: 150.67, 147.83, 147.46, 141.46, 136.87, 135.02, 128.23, 127.76, 127.55, 124.92, 121.61.

MS (ESI-MS): m/z Calcd. for C₅₁H₃₆N₄ 704.29; found, 705.30 [M+H]⁺.

Anal. Calcd. for C₅₁H₃₆N₄ (H₂O)_{1.5} : C, 83.69%; H, 5.37%; N, 7.66%; Found: C, 83.68%; H, 5.34%; N, 7.15%.

2.2.2. Crystallization conditions

All crystallizations were performed at *ca.* 25 °C in a glass vial (height = 6.5 cm, diameter 0.4 cm).

General procedure for the obtention of crystals: CHCl₃ (2.0 ml) containing **1** or **2** (0.01 mmol) was placed in a tube; then, 3.0 ml of EtOH containing the metal salt (0.02 mmol) was layered at the top of this solution. The test tube was sealed and allowed to stand at room temperature. Upon slow diffusion at room temperature, colourless crystals suitable for X-ray analysis were obtained after *ca* a week.

1-HgCl₂ and **1-HgCl₂•CHCl₃**

3 mg of **1** was combined with 3 mg of HgCl₂.

Both compounds (**1-HgCl₂** and **1-HgCl₂•CHCl₃**) appeared in the same vial, and it was not possible to separate them; for this reason, further characterizations was not possible.

2-HgCl₂

3 mg of **2** was combined with 2.5 mg of HgCl₂, 60% yield.

2-CdI₂

3 mg of **2** was combined with 4 mg of CdI₂, 50% Yield.

Both compounds (**2-HgCl₂** and **2-CdI₂**) present a large quantity of solvents in the crystal, it was not possible to characterize them further: the structure collapses after a long exposure in the air, due to solvent loss.

2.3. Crystallography

During X-Ray diffraction measurements, the crystals have been protected by oil (Fomblin Y). Data were collected at 173(2) K on a Bruker APEX8 CCD Diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using graphite-monochromated Mo-K α ($\lambda = 0.71073$ Å) radiation. For both 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 not refined (riding model).²⁶ They can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif. CCDC: 1942809 (**1**-HgCl₂), 1942811 (**1**-HgCl₂•CHCl₃), 1942813 (**2**-HgCl₂) and 1942812 (**2**-CdI₂).

3. Results

Ligand **2**, that presents the same topology as ligand **1**, was designed while adding a phenyl spacer between the core and the pyridyl coordinating groups, in order to maintain rigidity (figure 1). **1** and **2** are both “rigid” tripodal N donor ligands, that may act as tris-monodentate connectors.

3.1. Synthesis of **2**

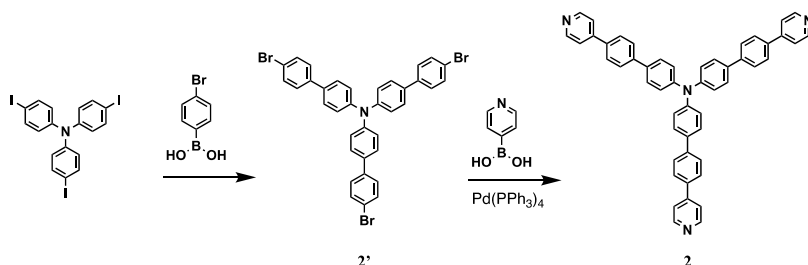


Figure 2: Synthetic pathway to obtain ligand **2**.

The synthetic strategy for obtaining ligand **2** (see the synthetic pathway on figure 2) is based on the use of tris(4-Bromobiphenyl)amine (**2'**) that was obtained starting from tris(4-iodophenyl)amine coupled with bromobenzeneboronic acid, then the Suzuki coupling reaction of **2'** with 4-pyridinylboronic acid leads to **2**. The total yield is equal to 6.6%, since the first step, due the presence of secondary reactions, has a yield equals to 11%, while the last step presents a 60% yield (see experimental section).

The coordination ability of both ligands **1** and **2**, was investigated, using the HgCl₂ and CdI₂ metal salts. Attempts to obtain single crystals using **1** or **2** combined with HgBr₂, HgI₂, CdBr₂ or CdCl₂ failed: only poor diffracting crystals were obtained with these combinations.

As shown in the experimental section, the diffusion technique was used for the formation of single crystals, that were analyzed using X ray diffraction on single crystals. Owing to small amount of crystals, or to their instability because of the solvent loss, they could not be further characterized.

3.2. Coordination properties of **1** and **2**

Four different crystals were obtained while performing the slow diffusion technique, starting from **1** or **2** and HgCl₂ (or CdI₂). These polymeric compounds represent the first coordination compounds obtained with **1** using Hg(II) salts. **1**-HgCl₂, **1**-HgCl₂•CHCl₃, **2**-HgCl₂ and **2**-CdI₂ were analysed using X-ray diffraction on single crystals and their structural analysis is presented below. For all crystals, the packing in the solid state results mainly from π - π interactions between the ligands (**1** and **2**) between consecutive chains.

Table 1: Crystallographic Parameters for **1**-HgCl₂, **1**-HgCl₂•CHCl₃, **2**-HgCl₂ and **2**-CdI₂ recorded at 173 K.

Formula	1 -HgCl ₂ C ₃₃ H ₂₄ Cl ₂ HgN ₄	1 -HgCl ₂ •CHCl ₃ C ₃₃ H ₂₄ Cl ₂ HgN ₄ , 1.25 CHCl ₃	2 -HgCl ₂ 2(C ₅ H ₃ Cl ₂ HgN ₄),4(C _{0.5} H _{0.5} Cl _{1.5} O) [+ solvent]	2 -CdI ₂ C ₁₀ H ₇ Cl ₂ Cd ₂ Cl ₆ I ₄ N ₈ [+ solvent]
Molecular weight	748.05	897.26	2310.76	2380.81
Crystal system	orthorhombic	triclinic	monoclinic	triclinic
Space group	<i>P bca</i>	<i>P</i> -1	<i>P</i> 2/c	<i>P</i> -1
<i>a</i> (Å)	11.8079(13)	8.6923(8)	12.669(2)	13.7385(13)
<i>b</i> (Å)	20.3210(16)	12.1251(11)	20.792(3)	21.0792(15)
<i>c</i> (Å)	23.0739(14)	17.5157(18)	21.234(3)	22.1930(17)
α (deg)	90	73.766(4)	90	104.522(5)
β (deg)	90	80.338(4)	104.749(5)	99.993(4)
γ (deg)	90	77.144(4)°	90	108.605(4)
<i>V</i> (Å ³)	5536.5(8)	1717.0(3)	5409.0(15)	5666.9(8)
<i>Z</i>	8	2	2	2
Colour	Colorless	Colorless	Colorless	Colorless
Crystal dim (mm ³)	0.090 x 0.090 x 0.110	0.100 x 0.120 x 0.140	0.050 x 0.050 x 0.060	0.080 x 0.090 x 0.100
<i>D</i> _{calc} (gcm ⁻³)	1.795	1.735	1.419	1.395
<i>F</i> (000)	2912	873	2284	2328
μ (mm ⁻¹)	5.784	4.961	3.203	1.950
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Number of data meas.	29129	18336	65004	154884
Number of data with $I > 2\sigma(I)$	6323 [R(int) = 0.0674]	9268 [R(int) = 0.0538]	15802 [R(int) = 0.1567]]	30086 [R(int) = 0.0504]
<i>R</i>	R1 = 0.0772, wR2 = 0.1160	R1 = 0.0482, wR2 = 0.0981	R1 = 0.0868, wR2 = 0.2100	R1 = 0.0952, wR2 = 0.2288
<i>R</i> _w	R1 = 0.1044, wR2 = 0.1236	R1 = 0.0836, wR2 = 0.1065	R1 = 0.1990, wR2 = 0.2608	R1 = 0.1453, wR2 = 0.2586
GOF	1.305	1.049	1.096	1.058
Largest peak in final difference (eÅ ⁻³)	1.939 and -1.622	1.436 and -1.439	3.521 and -1.957	2.161 and -1.598

3.2.1. **1**-HgCl₂

While crystallizing **1** with HgCl₂, two types of solvates were obtained in the same vial.

1-HgCl₂, of formula C₃₃H₂₄Cl₂HgN₄, reveals to crystallize in the orthorhombic *Pbca* system. The crystal is composed only of neutral ligand **1** and HgCl₂ (see crystallographic table 1). Ligand **1** acts as a tripodal ligand (V shape) interconnecting the V shape HgCl₂ metalloligand, which leads to an overall crenellated chain. One of the pyridyl nitrogen atoms of **1** remains uncoordinated, so that **1** behaves as a V shape connector. Two of the pyridyl nitrogen atoms of **1** are involved in coordination bonds with HgCl₂, and the metal center is thus in a deformed tetrahedral N₂Cl₂ environment as seen from the angles and distances reported in table 2. A helicoidal chain arises from this interconnection mode (figures 3a and b).

“U-shaped” units provide to the polymer a unique twisted shape leading to an helical architecture. The latter, running along the *b* axis, are entangled, leading to “4 chains achiral motives” held by π - π interactions as presented in figure 3c.

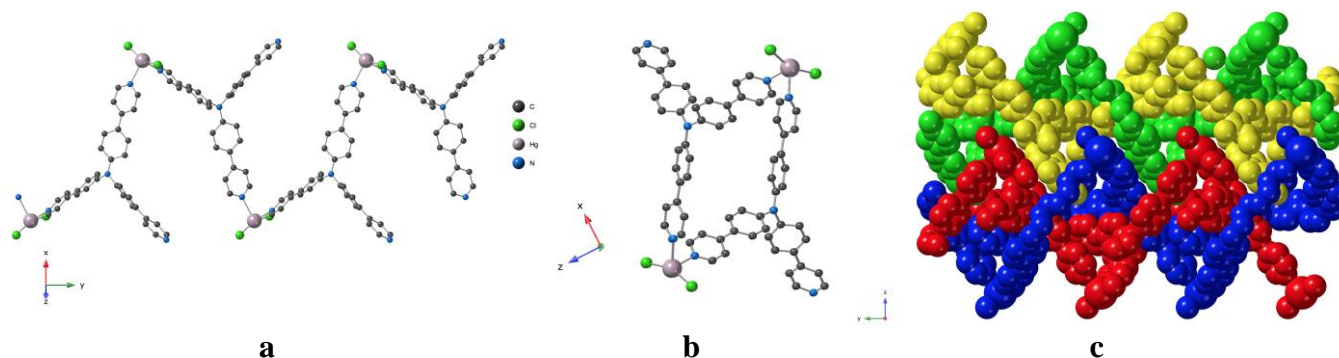


Figure 3: For the coordination compound **1**-HgCl₂, view of the 1D chain (a) and (b) packing of the chains in the unit cell along the *b* axis (c). Hydrogen atoms have been omitted for the sake of clarity.

3.2.2. **1**-HgCl₂•CHCl₃

A solvate form of **1**-HgCl₂, **1**-HgCl₂•CHCl₃, was also simultaneously observed.

1-HgCl₂•CHCl₃, of formula C₃₃H₂₄Cl₂HgN₄ • 1.25 CHCl₃, crystallizes in the triclinic *P*-1 system. The crystal is composed of neutral ligand **1**, HgCl₂ and CHCl₃ molecules (see crystallographic table 1). Ligand **1** acts as a tripodal entity (T shape) connecting the V shape HgCl₂ metalloligand, leading to a ladder-like chain (figure 4). In this case, all the pyridyl nitrogen atoms of **1** are involved in coordination bonds with HgCl₂ and the metal center adopts a pyramidal square planar with N₃Cl₂ environment, as seen from the angles and distances reported in table 2. There are no interactions between the solvent molecules and 1D arrays.

The chains are stacked along the *a* and *b* axis, through π -stacking interactions, as shown in figure 4 b.

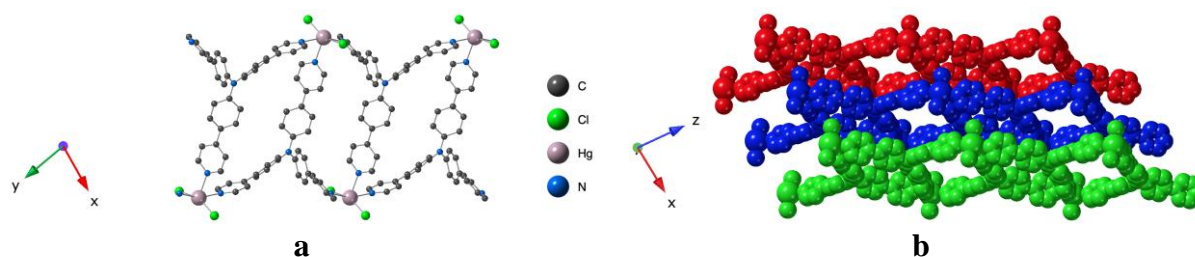


Figure 4: For the coordination compound **1**-HgCl₂•CHCl₃, view of the 1D chain in the *xOy* plane (a), and packing of the chains in the unit cell, in the *xOz* plane (b). Hydrogen atoms have been omitted for the sake of clarity

3.2.3. **2**-HgCl₂

The crystallization of **2** with HgCl₂ leads to the formation of a coordination network that crystallizes in a monoclinic *P2*/*c* system, with the formula C₃₃H₂₄Cl₂HgN₄, 1.25 CHCl₃ (see crystallographic table 1). Only a partial resolution of the solvent molecules present in the crystal was achieved, and, because of disordered solvent molecules, the structure was refined by applying the squeeze command.²⁷ As in the case

of $1\text{-HgCl}_2\cdot\text{CHCl}_3$, the formation of a ladder-like chain running along the c axis (figure 5a), was observed. The latter results from the mutual interconnection of **2** behaving as T shape and pentacoordinated Hg(II) in a pyramidal square planar N_3Cl_2 environment, as shown by angles and distances provided in Table 2.

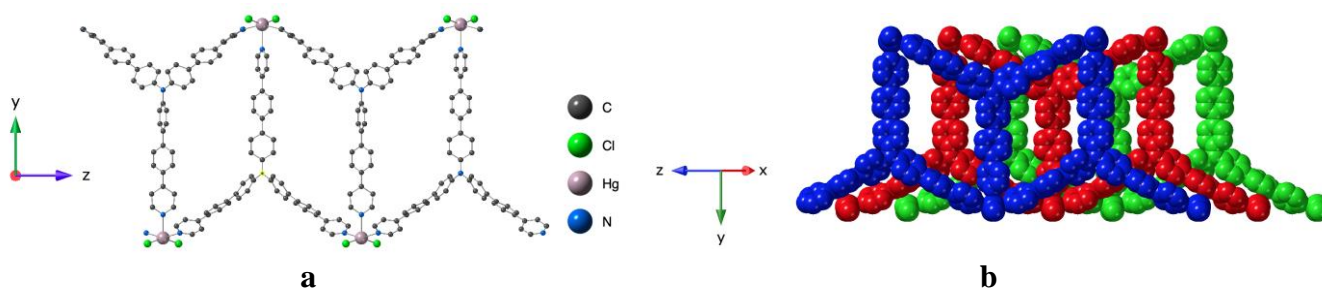


Figure 5: For the coordination compound 2-HgCl_2 , view of the 1D chain (a), and packing of chains in the unit cell (b). Hydrogen atoms have been omitted for the sake of clarity

The chains are stacked along the a axis, through π -stacking, as shown in figure 5 b.

In parallel to this study, the metal salt CdI_2 , which may also act as a V shape metalloligand, was investigated.

3.2.4. 2-CdI_2

The crystallization of **2** with CdI_2 leads to the formation of a coordination network that crystallizes in a triclinic $P\bar{1}$ system, with the formula $\text{C}_{104}\text{H}_{74}\text{Cd}_2\text{Cl}_6\text{I}_4\text{N}_8$ (see crystallographic table 1). Due to the presence of disordered solvent molecules, the squeeze command²⁷ was used to finalize data refinement and structural resolution.

As in the case of compound $1\text{-HgCl}_2\cdot\text{CHCl}_3$ and 2-HgCl_2 , a ladder-like chain running here along the c axis (figure 6a) was observed. The latter results from the interconnection of the T shape ligand **2** by the pentacoordinated Cd(II), in a pyramidal square planar N_3I_2 environment, as shown by angles and distances reported in Table 2. A disorder is observed for phenyl and pyridyl rings of **2** (not presented here).

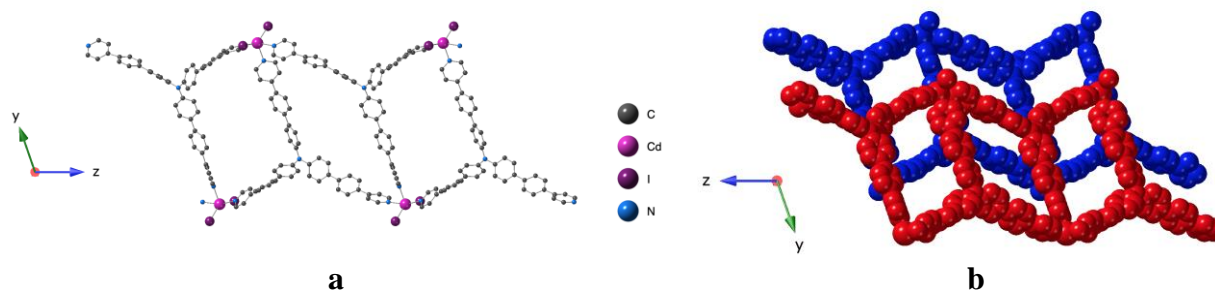


Figure 6: For the coordination compound 2-CdI_2 , view of the 1D chain, and packing of the chains in the unit cell. Hydrogen atoms have been omitted for the sake of clarity. Disorder on a phenyl ring and pyridyl ring is not represented for clarity.

The chains are stacked along the a axis, through π -stacking, as shown in figure 6 b.

Table 2: Useful distances for the geometry around M(II) ions for **1-HgCl₂**, **1-HgCl₂•CHCl₃**, **2-HgCl₂** and **2-CdI₂**

	1-HgCl₂	1-HgCl₂•CHCl₃	2-HgCl₂	2-CdI₂
d _{M-X} (Å)	2.333(3) 2.352(3)	2.3809(16) 2.3818(15)	2.384(3) 2.392(3)	2.7412(10) 2.7423(9) 2.7455(11) 2.7579(9)
d _{M-N} (Å)	2.427(7) 2.480(7)	2.417(4) 2.630(5) 2.637(5)	2.406(15) 2.537(8) 2.542(7) 2.567(12)	2.352(4) 2.359(7) 2.467(7) 2.473(7) 2.476(16) 2.51(2)
NMX (°)	94.2(2) 98.22(19) 100.0(2) 102.58(18)	90.98(12) 91.22(13) 92.02(13) 94.15(12) 102.96(12) 103.90(12)	90.7(2) 91.3(2) 94.5(2) 94.7(2) 103.73(8) 104.24(8)	90.86(18) 91.92(18) 94.25(18) 94.52(18) 107.22(17) 109.3(2) 112.11(17)
NMN (°)	87.0(3)	79.18(15) 82.74(16) 161.87(15)	78.1(2) 78.53(19) 156.3(4) 157.1(4)	82.9(2) 82.7(3)
XXM (°)	155.29(10)	153.14(6)	151.52(15) 152.54(16)	140.63(3) 141.37(3)

4. Discussion

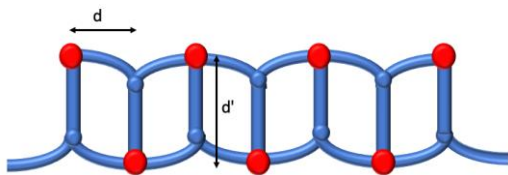
The four new structures were obtained under self-assembly conditions, revealing that it is possible, using ligands **1** and **2** offering the same topology (tripodal), to obtain the same connection pattern (ladder-like structure for **1-HgCl₂•CHCl₃**, **2-HgCl₂** and **2-CdI₂**).

No isostructural compounds were observed within this series, however, one may assume that **1-HgCl₂•CHCl₃** and **2-HgCl₂** or **2-CdI₂** are “isorecticular”, they present the same connectivity between their components. The solvent molecules, chlorinated solvent, appear to play a crucial role for the formation of the ladder-like structure (**1-HgCl₂•CHCl₃**, **2-HgCl₂** and **2-CdI₂**), CHCl₃ molecules were present and for the most flexible ligand **2**, they are highly disordered.

The fact that starting from **1** and HgCl₂, two different solvates were obtained: **1-HgCl₂** and **1-HgCl₂•CHCl₃** is an indication that the thermodynamical and kinetical compounds present the same stability. From a geometrical point of view, it is possible to transform **1-HgCl₂** into **1-HgCl₂•CHCl₃** by coordinating the free N atom of the pyridyl moiety in **1** to Hg(II), which leads to a penta coordination for Hg(II), as observed in **1-HgCl₂•CHCl₃**. In addition, the pentacoordination induces a constraint on ligand **1**, which is less flexible than **2**. For this reason, in the ladder-like chains, two of the Hg-N distances in **1-HgCl₂•CHCl₃** (see table 2) appear to be rather long (2.630(5) Å and 2.637(5) Å) compared to those found for **2-HgCl₂** (2.406(15) Å, 2.537(8) Å, 2.542(7) Å and 2.567(12) Å).

For the three architectures presenting a ladder-like structure (**1**-HgCl₂•CHCl₃, **2**-HgCl₂ and **2**-CdI₂), the structural parameters defining the ladder (*d* and *d'*) were measured and are presented in table 3.

Table 3: Structural parameters for **1**-HgCl₂•CHCl₃, **2**-HgCl₂ and **2**-CdI₂ presenting a ladder-like structure.



	<i>d</i> (Å)	<i>d'</i> (Å)
1 -HgCl ₂ • CHCl ₃	9.903	15.882
2 -HgCl ₂	13.644	22.787
2 -CdI ₂	13.731	22.565

From these data, it appears that, as expected, the increasing of the length of the coordinating arm in ligand **2** (compared to the one of ligand **1**), increases the length between steps of the ladder. This also increases the disorder for the ligand and also for the included solvents.

Using these combinations of metals cations Hg(type II) and Cd(II) and the two ligands **1** and **2**, one may tune the geometrical parameters of the ladder-type architecture.

5. Conclusion

Two tripodal ligands **1** and **2**, derived from triarylamine, were combined under mild conditions with metalloligands HgCl₂ and CdI₂. Four new coordination networks were observed and analyzed by X-Ray diffraction on single crystals. The latter investigations revealed the formation of one-dimensional networks in the solid state. Ligands **1** and **2** differ by the number of phenyl rings separating the coordinating sites (pyridyl) from the amine core. They display the same geometry but different rigidity and metrics. The short one, ligand **1**, forms with HgCl₂ two different solvates differing by the number of pyridyl moieties involved in the binding of Hg cation through Hg-N bonds. Using the longer one, ligand **2**, the combination either with HgCl₂ or CdI₂, leads to a ladder-like structure, the latter is also observed with **1**. The same type of assembling node between the analogous metalloligands HgCl₂ and CdI₂ and **1** and **2** was observed. This represents an example of the control of the geometrical parameters in 1D coordination compounds through the design of the ligand.

Other combinations of this series of ligands **1** and **2** are currently in progress using other metal salts and different chlorinated solvents.

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