Dalton Transactions

PAPER

Cite this: *Dalton Trans.*, 2014, **43**, 166

Molecular tectonics: enantiomerically pure 1D stair-type mercury coordination networks based on rigid bismonodentate C2-chiral organic tectons[†]

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Received 26th July 2013, Accepted 2nd October 2013 DOI: 10.1039/c3dt52036f Combinations of three enantiomerically pure organic chiral linear tectons bearing two divergently oriented pyridyl units as coordinating poles with HgCl₂ as a two-connecting V-shape metallatecton offering two free coordination sites lead to the formation of stair-type 1D enantiomerically pure mercury coordination networks.

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Introduction

In the last two decades, considerable attention has been paid to solid-state periodic materials combining organic moieties and metallic centres. These extended architectures, named coordination polymers,¹ coordination networks² or metalorganic frameworks,3 may be of interest in terms of applications such as for example separation, storage, catalysis and luminescent properties.4,5 For the design of coordination networks, one may apply the general concepts developed in molecular tectonics.⁶ For this approach, molecular networks⁷ are assemblies of self-complementary or complementary tectons⁸ bridging each other and thus displaying translational symmetry in one, two or three directions of space with the number of translations defining the dimensionality of the network (1-, 2- or 3-D). Coordination networks, a subclass of molecular networks, are generated upon mutual bridging of either organic coordinating tectons, offering at least two coordinating poles arranged in a divergent fashion, and metal centres or complexes possessing at least two free coordination sites. Alternatively, this type of periodic architecture may be formed by selfcomplementary metallatectons containing metal centres and divergently oriented complementary interaction sites or upon combining complementary organic and metallatectons.9

It is worth noting that, among the vast variety of coordination networks published to date, only a small number deals with chirality.¹⁰⁻¹⁷



Among the many examples of coordination networks documented in the literature,⁵ a large number has been obtained by serendipity consisting of mixing different components under different conditions and performing structural analysis on crystalline materials when formed. In order to gain more knowledge on design principles guiding the formation of coordination networks and thus to increase our predictive ability, it is worth carrying out systematic investigations by varying a small number of properly chosen parameters.

Here we report on the design and structural characterisation of three enantiomerically pure chiral organic tectons 1–3 (Scheme 1) and enantiomerically pure mercury 1D chiral coordination networks.

Results and discussion

For single- or poly-strand 1D networks in general and for 1D coordination networks in particular, four different geometrical categories may be defined (Fig. 1). For single strand 1D



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[†]Full experimental crystallographic data. CCDC 951926–951929. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52036f



Fig. 1 Schematic representations of the four geometric categories of single stranded 1-D coordination networks formed upon mutual bridging between organic coordinating tectons (in blue) and metal centres or metal complex (in red). For achiral organic tectons and metal complexes, whereas the first three types of architectures (linear (a), zigzag (b) and stair type (c)) are intrinsically achiral, the fourth category, the helical arrangement (d) is inherently chiral.

coordination networks composed of achiral organic tectons and metal centres, among the four possibilities, three *i.e.* linear (Fig. 1a), zigzag (Fig. 1b) and stair type (Fig. 1c) are intrinsically achiral and only the fourth category corresponding to a helical arrangement is inherently chiral (Fig. 1d).

Although several examples of chiral discrete or infinite helical architectures combining metal centres and organic ligands or tectons have been reported,^{14,17a-d,18} chiral assemblies belonging to the other three categories remain undocumented to date. In order to form 1D linear, stair- or zigzagtype chiral networks, one may either combine a chiral tecton with a metal centre or an achiral metal complex or use an achiral organic tecton and a chiral metal complex or finally combine a chiral organic tecton with a chiral metal complex. Another important issue associated with chiral networks concerns the formation of enantiomerically pure extended assemblies. This remains rather challenging and might be achieved either by the use of enantiomerically pure tectons or through spontaneous resolution which appears to be unpredictable so far. In this contribution we propose to use enantiomerically pure organic tectons and an achiral metal complex as a node.

Design of tectons

The three organic tectons 1–3 are based on a phenyl moiety as the backbone bearing two divergently oriented pyridyl monodentate coordinating sites at positions 1 and 4 and two appended OR groups directly attached to positions 2 and 5 of the phenyl moiety through two C–O bonds. Thus, compounds 1–3 are analogous tectons differing by the nature of the spacer used to connect the pyridyl group using its position 4 to the backbone and by chiral substituents located on positions 2 and 5 of the phenyl unit. Indeed, whereas for 1, the coordinating site is directly attached to the phenyl moiety, for tectons 2 and 3 an ethenyl and an ethynyl spacers have been used respectively.

All three tectons 1–3 are chiral entities (Scheme 1). The chirality arises from the presence of two homochiral asymmetric centres on the phenyl backbone. Whereas for the tecton 1, an OCHMeEt chiral centre is used, for both tectons 2 and 3, the chiral centre used was OCH₂CHMeEt. Furthermore, all three tectons 1–3 are enantiomerically pure. Whereas for the tecton 1, the (R,R) enantiomer was used, for the other two

Design of coordination networks

Since compounds 1–3 are neutral linear tectons offering two divergently oriented monodentate coordinating sites, in order to avoid the presence of anions in the crystal, they were combined with the HgCl₂ neutral complex which should behave as a two-connecting V-shape achiral node offering two free coordination sites. Mercury halides have been previously used as metallatectons by us¹⁷ and others.¹⁹

Owing to the chiral nature of tectons 1–3, their combination with an achiral V type node must lead to the formation of chiral stair type infinite architectures (Fig. 1c). Thus, for enantiomerically pure tectons 1–3, the formation of enantiomerically pure single strand 1D coordination networks is expected.

All three tectons 1-3 display another structural feature. Not only they are asymmetric but, owing to the location of the chiral substituents on position 2 and 5 of the phenyl moieties, they might adopt two opposite relative orientations (+, clockwise and – anticlockwise, Fig. 2a). As a result, within the 1D



Fig. 2 Owing to the acentric nature of tectons **1–3**, the latter may adopt two opposite relative orientations (a) (+ for clockwise and – for anticlockwise). Their interconnection into a 1D coordination polymer by metal centres behaving as two connecting node leads to three different arrangements. For only three consecutive units, they are (+,+,+, b), (-,-,-, c) and (+,-,+, d). For the packing of consecutive 1D networks within the same plane, four possibilities (+,+,+)-(+,+,+) (e), (-,-,-)-(-,-,-) (f), (+,+,+)-(-,-,-) (g) and (+,-,+)-(+,-,+) (h) may be expected.

coordination networks, different orientations can be observed for consecutive organic tectons. For example, considering a sequence of three organic tectons and two metallic nodes, the following three different arrangements may be expected: (i) (+,+,+) (Fig. 2b), (ii) (-,-,-) (Fig. 2c) and finally (iii) (+,-,+)(Fig. 2d).

Dealing with packing of the 1D stair type networks, again different packing of two consecutive networks in the same plane such as for example: (i) (+,+,+)-(+,+,+) (Fig. 2e), (ii) (-,-,-)-(-,-,-) (Fig. 2f), (iii) (+,+,+)-(-,-,-) (Fig. 2g) and (iv) (+,-,+)-(+,-,+) (Fig. 2h) may be expected.

Synthesis of tectons 1-3

Tectons 1-3 have been synthesised in three steps. The two chiral substituents were introduced on the phenyl backbone affording the precursors 4 and 5. In order to prepare the enantiomerically pure compounds, a substitution reaction between an enantiomerically pure activated alcohol and 2,5-dibromohydroquinone was carried out in DMF at 100 °C in the presence of Cs₂CO₃. The introduction of the two pyridyl units was achieved by a Pd catalysed coupling reaction. Compound 1¹⁴ was prepared under an inert atmosphere via a Suzuki coupling reaction between the dibromo compound 4 possessing the R,R stereochemistry and 4-pyridyl boronic acid in the presence of Pd(PPh₃)₄ and Cs₂CO₃ in DMF at 100 °C. Tecton 2 was synthesised in 72% yield via a Sonogashira coupling reaction at 100 °C between the S,S enantiomer of the dibromo derivative 5 and 4-vinylpyridine in the presence of catalytic amounts of Pd(OAc)₂ and PPh₃ in degassed Et₃N. Finally, tecton 3 was again obtained at 90 °C in 75% yield via a Sonogashira coupling reaction between the intermediate 5 and 4-ethynylpyridine in the presence of catalytic amounts of PdCl₂(PPh₃)₂ and CuI in degassed Et₃N.

All compounds have been characterised in solution by conventional techniques. Compounds **1** and **3** were further studied in the solid state by X-ray diffraction on single crystals.

The solid state structure of the tecton **1** was documented in our previous contribution.¹⁴ Single crystals of the tecton **3** were obtained by slow evaporation of a 1:1 CHCl₃–CH₃CN solution of **3**. As expected, due to the asymmetric nature of the tecton, **3** crystallizes in a chiral space group (*P*2₁). No solvent molecules are present in the crystal. The two pyridyl units are tilted with respect to the central phenyl group by *ca*. 14.94 and 7.27°. The bond distances and angles are close to values previously reported for analogous compounds. The length of the tectons, *i.e.* the distance between the two N atoms, is 16.49 Å (Fig. 3).

Generation of 1D enantiomerically pure coordination networks

Upon slow diffusion of an EtOH solution of $HgCl_2$ into a $CHCl_3$ solution of tectons **1**, **2** or **3** through a buffered layer of $CHCl_3$ -EtOH, single crystals were obtained after *ca*. one week. The solid-state structures of all three crystals **1**-HgCl₂ (Fig. 4), **2**-HgCl₂ (Fig. 5) and **3**-HgCl₂ (Fig. 6) were investigated by X-ray



Fig. 3 Crystal structure of the tecton **3**. H atoms are omitted for clarity. For bond distances and angles see text.



Fig. 4 Portions of the X-ray structure of $1-\text{HgCl}_2$ showing the formation of a stair-type 1D enantiopure network and relative orientations of consecutive organic tectons (a), the packing of consecutive 1D networks along the *b* axis (b) and the packing along the *a* axis showing the opposite relative orientations of consecutive networks (c). H atoms are not represented for clarity. For bond distances and angles see text.

diffraction on single crystals (see Experimental part for Crystallographic data).

As expected from the design of the enantiomerically pure tectons 1-3 and the choice of $HgCl_2$ behaving as an achiral V-shape node, enantiomerically 1D stair type coordination networks are formed in the crystalline phase (Fig. 4a, 5a and 6a).

For all three cases, the crystal (space group $P2_1$ for 1–HgCl₂, P1 for 2–HgCl₂ and C2 for 3–HgCl₂) is composed of the organic tectons 1, 2 or 3, Hg²⁺ cations and Cl⁻ anions. Whereas in the case of 2–HgCl₂ two CHCl₃ solvent molecules are present in the lattice, for 1–HgCl₂ and 3–HgCl₂, crystals are exclusively composed of the neutral organic tectons 1 and 3



Fig. 5 Portions of the X-ray structure of $2-HgCl_2$ showing the formation of a stair-type 1D enantiopure network and relative alternate orientations of consecutive organic tectons (a), the packing of consecutive 1D networks along the *b* axis (b) and the packing along the *a* axis showing the alternate relative orientations of consecutive networks (c). H atoms and solvent molecules are omitted for clarity. For bond distances and angles see text.



Fig. 6 Portions of the X-ray structure of $3-HgCl_2$ showing the formation of a stair-type 1D enantiopure network and relative orientations of consecutive organic tectons (a), the packing of consecutive 1D networks along the *b* axis (b) and the packing along the *a* axis showing the same relative orientations of consecutive networks (c). H atoms are not represented for clarity. For bond distances and angles see text.

and HgCl₂ complex. **1**–HgCl₂ was found to be stable in air at 25 °C and powder X-ray diffraction showed a good match between the simulated and observed patterns. Unfortunately,

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the crystals of 2-HgCl₂ and 3-HgCl₂ were unstable outside the mother liquor.

In all three cases, Hg(II) centre adopts a distorted tetrahedral coordination geometry and behaves as a two-connecting V-type node since two out of its four coordination sites are occupied by two Cl⁻ anions with the Cl–Hg distance in the 2.34–2.38 Å range and Cl–Hg–Cl angle in the 140–160° range. Consecutive organic tectons are bridged by HgCl₂ complexes through two Hg–N bonds between the metallic centre and two N atoms of pyridyl units belonging to two consecutive organic tectons (N–Hg distances in the 2.35–2.45 Å range and N–Hg–N angle in the 80–95° range).

For the tecton 1, the tilt angle (in the $30-40^{\circ}$ range) between the pyridine moieties and the central phenyl unit is more pronounced than for tectons 2 and 3 (in the $2-8^{\circ}$ range), which are almost planar. This is due to steric interactions between the pyridyl and phenyl units owing to their direct interconnection in 1, which is released when ethenyl or ethynyl spacers in the case of 2 and 3 respectively are introduced.

The distances between consecutive Hg^{2+} cations within the 1D networks are *ca*. 16.1 Å for 1·HgCl₂, 20.7 Å for 2·HgCl₂ and 21.3 Å for 3·HgCl₂.

For all three cases, the packing of consecutive 1D networks takes place in an eclipsed fashion along the *b* axis (Fig. 4b, 5b and 6b), whereas along the *a* axis the packing is achieved in a staggered manner (Fig. 4c, 5c and 6c).

As discussed above, within the 1D network, the chiral tecton may adopt two opposite relative orientations (Fig. 2a). For 1–HgCl₂, all consecutive tectons adopt either the clockwise (+) (Fig. 2b) or the anticlockwise (-) (Fig. 2c) relative orientation. In the crystal, consecutive 1D networks are composed of tectons 1 adopting the same but opposite (all + and all –) relative orientations (Fig. 2g and 4c).

For crystals composed of $2-HgCl_2$, within the 1D network, the alternate clockwise and anticlockwise (+ and -) relative orientations of consecutive organic tectons are observed (Fig. 2d, 5a). In consecutive 1D networks, the alternate (+,-) relative orientation of tectons 2 is obtained (Fig. 2d and 5c).

For 3-HgCl₂, within the 1D networks, the same clockwise (+) relative orientation of consecutive organic tectons is observed (Fig. 2b and 6a). In consecutive 1D networks, the same (+) relative orientation of tectons 3 is obtained (Fig. 2e and 6c).

Conclusion

Combinations of enantiomerically pure chiral compounds 1-3 behaving as linear bis-monodentate rigid tectons with HgCl₂ as a metallatecton offering two free coordination sites and behaving as a two-connecting V-shape node lead to the formation of stair-type 1D chiral coordination networks (Fig. 7). It is worth noting that the design principle allows us only to predict the connectivity pattern and the geometry of the 1D networks and not their packing leading to the formation of



Fig. 7 Schematic representations showing the shape, the packing and the relative orientation of enantiomerically pure organic tectons 1-3 within the 1D chiral mercury coordination networks.

crystals. In other words, the design allows to be deterministic in one dimension of space (translational symmetry in one direction of space) but not in the other two. Furthermore, owing to the peculiar structural feature of tectons 1–3, *i.e.* the location of the asymmetric centres at positions 2 and 5 on the phenyl backbone, the relative orientation of tectons within the 1D networks cannot be predicted. The same holds for the packing of consecutive 1D networks. Combinations of the same chiral organic tectons 1–3 with other metallatectons and metal centres to generate higher dimension chiral and enantiomerically pure networks are currently under investigation.

Experimental section

Synthesis

Compounds **1**, **4** and **5** were prepared according to published procedures.¹⁵

Synthesis of tecton 2. Into an oven dried Schlenk flask, compound 5 (500 mg, 1.22 mmol), 4-vinylpyridine (386 mg, 3.67 mmol, 3 eq.) and Et_3N (6 mL) were added. The mixture was degassed with argon for 15 min and a catalytic amount of $Pd(OAc)_2$ (55 mg, 0.25 mmol, 0.2 eq.) along with PPh₃ (128 mg, 0.49 mmol, 0.4 eq.) were added. The reaction mixture was sealed and heated to 100 °C for 48 h before it was allowed to reach RT. The residue was taken up in CH_2Cl_2 (30 mL) and evaporated to dryness. The solid residue was dissolved in CH_2Cl_2 and washed with brine (150 mL) followed by H_2O (150 mL). After drying of the organic phase over MgSO₄ and evaporation to dryness, tecton **2** was obtained as a yellow solid

after purification by column chromatography on silica gel (402 mg, 72%, eluent CH₂Cl₂, 1% MeOH, 2% MeOH and 3% MeOH). ¹H-NMR (300 MHz, CD₂Cl₂, 25 °C), δ (ppm): 8.56 (d, 4H, ³*J* = 6.2 Hz), 7.74 (d, 2H, ³*J* = 16.5 Hz), 7.40 (d, 4H, ³*J* = 6.2 Hz), 7.17 (d, 2H, ³*J* = 16.3 Hz), 7.17 (s, 2H), 3.99–3.85 (m, 4H), 2.02 (m, 2H), 1.70 (m, 2H), 1.44 (m, 2H), 1.13 (d, 6H, ³*J* = 6.8 Hz), 1.04 (t, 6H, ³*J* = 7.5 Hz). ¹³C-NMR (75 MHz, CD₂Cl₂, 25 °C), δ (ppm): 151.9, 150.6, 145.4, 127.9, 126.9, 121.1, 111.1, 74.6, 35.4, 26.7, 17.0, 11.6. Elemental analysis: calc. C 78.91%; H 7.95%; N 6.13% found C 78.85%; H 7.92%; N 6.07%. [*a*]_D²⁰: +12.7° (*c* = 1 in CHCl₃). Mp: 169 °C.

Synthesis of tecton 3. A mixture of compound 5 (500 mg, 1.22 mmol), 4-ethynylpyridine (380 mg, 3.67 mmol, 3 eq.) and Et₃N (30 mL) was degassed with argon for 15 min before a catalytic amount of PdCl₂(PPh₃)₂ (171 mg, 0.24 mmol, 0.2 eq.) and CuI (45 mg, 0.24 mmol, 0.2 eq.) were added. The reaction mixture was heated to reflux for 48 h before it was allowed to reach RT. The mixture was evaporated to dryness. The resulting residue was taken up in CH₂Cl₂ (150 mL) and washed with brine $(3 \times 150 \text{ mL})$ and H₂O (150 mL). The organic phase was dried over MgSO₄, evaporated to dryness and purified by column chromatography on silica gel (eluent CH₂Cl₂, 1% MeOH, 2% MeOH and 3% MeOH) affording the tecton 3 (413 mg, 75% yield) as a yellow solid. ¹H-NMR (300 MHz, CD_2Cl_2 , 25 °C), δ (ppm): 8.59 (d, 4H, ${}^{3}J$ = 6.0 Hz), 7.38 (d, 4H, ³J = 6.0 Hz), 7.06 (s, 2H), 3.93–3.81 (m, 4H), 1.97 (m, 2H), 1.69 (m, 2H), 1.40 (m, 2H), 1.11 (d, 6H, ${}^{3}J = 6.8$ Hz), 1.01 (t, 6H, ${}^{3}J =$ 7.5 Hz). ¹³C-NMR (75 MHz, CD₂Cl₂, 25 °C), δ (ppm): 155.5, 150.2, 131.6, 125.6, 117.1, 114.0, 92.6, 90.5, 74.6, 35.5, 26.5, 16.7, 11.6. Elemental analysis: calc.: C 79.61%; H 7.13%; N 6.19% found C 79.87%; H 7.06%; N 6.08%. $\left[\alpha\right]_{D}^{20}$: +10.6° $(c = 1 \text{ in CHCl}_3)$. Mp: 134 °C.

Characterization techniques

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

Crystallisation conditions for the generation of single crystals of Hg(n) based 1D-coordination polymer

General. All crystallisations described below were performed at 25 °C by a liquid–liquid diffusion technique in glass crystallisation tubes (height = 15 cm, diameter = 0.4 cm). All crystallizations have been repeated twice and the same types of crystals have been obtained.

1·HgCl₂. Through a buffered layer of a CHCl₃–EtOH mixture (0.2 mL, 1:1 (v:v)), diffusion of an EtOH solution (1 mL) of HgCl₂ (5 mg) into a CHCl₃ solution (1 mL) of tecton **1** (3 mg) afforded colourless needle shaped single crystals after a few days.

 $2 \cdot HgCl_2$. Through a buffered layer of a CHCl₃-EtOH mixture (0.2 mL, 1:1 (v:v)), diffusion of an EtOH solution (1 mL) of

 HgCl_2 (5 mg) into a CHCl_3 solution (1 mL) of tecton 2 (3 mg) afforded light-orange needle shaped single crystals after a few days.

3·HgCl₂. Through a buffered layer of a CHCl₃–EtOH mixture (0.2 mL, 1:1 (v:v)), diffusion of an EtOH solution (1 mL) of HgCl₂ (5 mg) into a CHCl₃ solution (1 mL) of tecton **3** (3 mg) afforded light-yellow needle shaped single crystals after a few days.

Crystallisation conditions for the preparation of microcrystalline powders of Hg(II) based 1D-coordination polymer

General. All crystallisations described below were performed at 25 °C by a liquid–liquid diffusion technique in capped glass vials (height = 6.5 cm, diameter = 2 cm).

1·HgCl₂. Through a buffered layer of a CHCl₃-EtOH mixture (2 mL, 1:1 (v:v)), the diffusion of an EtOH solution (3 mL) of HgCl₂ (15.0 mg) into a CHCl₃ solution (3 mL) of tecton **1** (10.0 mg) afforded a crystalline powder after one week which was filtrated and dried in air, leaving 13.9 mg of a solid.

2·HgCl₂. Through a buffered layer of a CHCl₃–EtOH mixture (2 mL, 1:1 (v:v)), diffusion of an EtOH solution (3 mL) of HgCl₂ (15.0 mg) into a CHCl₃ solution (3 mL) of tecton **2** (10.0 mg) afforded a crystalline powder after one week which was filtrated and dried in air, leaving 11.9 mg of a solid.

3·HgCl₂. Through a buffered layer of a CHCl₃–EtOH mixture (2 mL, 1:1 (v:v)), diffusion of an EtOH solution (3 mL) of HgCl₂ (15.0 mg) into a CHCl₃ solution (3 mL) of tecton **3** (10.0 mg) afforded a crystalline powder after one week which was filtrated and dried in air, leaving 11.5 mg of a solid.

X-ray diffraction

Single-crystals diffraction data were collected at 173(2) K using a Bruker APEX8 CCD Diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using graphite-monochromated Mo-K α (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 not refined (riding model).²⁰

Crystallographic data for 3. $C_{30}H_{32}N_2O_2$, M = 452.58, monoclinic, space group $P2_1$, a = 15.0970(10) Å, b = 4.9256(3) Å, c = 17.5598(12) Å, $\alpha = \gamma = 90^{\circ}$, $\beta = 100.365(2)^{\circ}$, V = 1284.47(15) Å³, T = 173(2) K, Z = 2, $D_c = 1.170$ Mg m⁻³, $\mu = 0.073$ mm⁻¹, 7494 collected reflections, 6071 [R(int) = 0.0186], GooF = 1.010, $R_1 = 0.0522$, w $R_2 = 0.1069$ for $I > 2\sigma(I)$ and $R_1 = 0.0831$, w $R_2 = 0.1237$ for all data, absolute structure parameter = 0.1(5).

Crystallographic data for 1·HgCl₂. $C_{48}H_{56}N_4O_4Hg_2Cl_4$, M = 1295.95, monoclinic, space group $P2_1$, a = 6.3226(2) Å, b = 17.6883(6) Å, c = 21.9405(8) Å, $\alpha = \gamma = 90^{\circ}$, $\beta = 90.7950(10)^{\circ}$, V = 2453.50(14) Å³, T = 173(2) K, Z = 2, Dc = 1.754 Mg m⁻³, $\mu = 6.514$ mm⁻¹, 57 047 collected reflections, 13 427 [R(int) = 0.0784], GooF = 1.010, $R_1 = 0.0434$, $wR_2 = 0.0550$ for $I > 2\sigma(I)$ and $R_1 = 0.0924$, $wR_2 = 0.0652$ for all data, absolute structure parameter = 0.006(5).

Crystallographic data for $2 \cdot \text{HgCl}_2$. C₆₀H₇₂N₄O₄Hg₂Cl₄, 2(CHCl₃), M = 1694.93, triclinic, space group P1, a = 5.0861(2) Å,

b = 14.8867(8) Å, *c* = 22.8798(11) Å, α = 98.776(4)°, β = 94.498(3)°, γ = 96.439(2)°, *V* = 1693.20(14) Å³, *T* = 173(2) K, *Z* = 1, *D*_c = 1.662 Mg m⁻³, μ = 4.970 mm⁻¹, 51 598 collected reflections, 15 956 [*R*(int) = 0.0622], GooF = 1.013, *R*₁ = 0.0558, w*R*₂ = 0.1200 for *I* > 2 σ (*I*) and *R*₁ = 0.0845, w*R*₂ = 0.1306 for all data, absolute structure parameter = 0.020(8).

Crystallographic data for 3·HgCl₂. $C_{30}H_{32}N_2O_2HgCl_2$, M = 724.07, monoclinic, space group *C*2, a = 21.3268(4) Å, b = 6.66500(10) Å, c = 22.7400(4) Å, $a = \gamma = 90^{\circ}$, $\beta = 116.166(2)^{\circ}$, V = 2901.08(9) Å³, T = 173(2) K, Z = 4, Dc = 1.658 Mg m⁻³, $\mu = 5.519$ mm⁻¹, 49 491 collected reflections, 7931 [*R*(int) = 0.0320], GooF = 1.038, $R_1 = 0.0170$, w $R_2 = 0.0376$ for $I > 2\sigma(I)$ and $R_1 = 0.0204$, w $R_2 = 0.0387$ for all data, absolute structure parameter = 0.009(6).

Acknowledgements

We thank the University of Strasbourg, the Institut Universitaire de France, the International centre for Frontier Research in Chemistry (icFRC, scholarship to P.L.), the C.N.R.S. and the Ministère de l'Enseignement Supérieur et de la Recherche for financial support.

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