Gradual increase in the dimensionality of cobalt and mercury coordination networks based on conformation of tetradentate tectons

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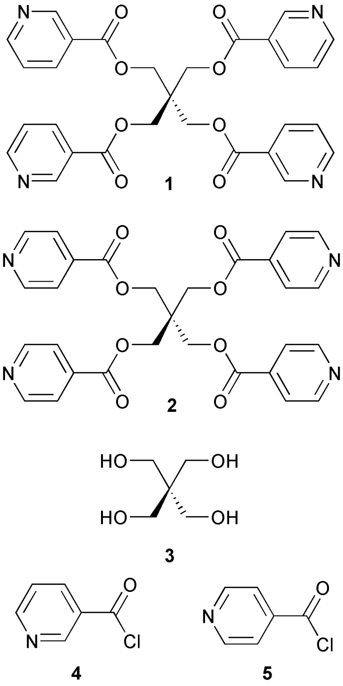
Neutral tetrakis-monodentate tectons **1** and **2**, based on the pentaerythritol skeleton and bearing four nicotinoyl or isonicotinoyl groups respectively as coordination sites, have been prepared and their ability to generate coordination networks was studied in the presence of $HgCl_2$ or $CoCl_2$ behaving as metallatectons offering either a "V" or a square type geometry respectively. Whereas in the case of the tecton **1** offering four coordination sites in the same plane (square type geometry) a 1-D coordination network was observed in the presence of neutral $HgCl_2$, in the presence of $CoCl_2$ metallatecton presenting four available coordination sites occupying the corners of a square, a 2-D neutral coordination network was obtained. For tecton **2**, possessing also four coordinating sites but occupying the apices of a pseudo tetrahedron, a 2-D network was obtained with $HgCl_2$, whereas in the presence of $CoCl_2$ a 3-D network was observed. In the latter case, a two-fold homo interpenetrating architecture was observed.

Coordination networks are metallo-organic molecular assemblies formed upon mutual bridging of organic tectons and metallic centres. The dimensionality (1-, 2- or 3-D) of these infinite architectures possessing translational symmetry is defined by the number of translations of the coordination patterns or assembling nodes connecting the organic and the metallic tectons. Coordination networks are attracting increasing interest over the years.[1] This is certainly due to the endless possibilities that combinations of organic tectons and metallic centres offer. Furthermore, in terms of possible applications, because of the variety of specific features such as coordination geometry, redox, optical and magnetic properties associated with metallic centres, their incorporation within the backbone of molecular networks (metals as structural nodes of the network) may lead to new materials with expected or not-predicted features.

Although, over the last decade, many examples of coordination networks have been reported,[1–19] nevertheless, the reliable *ab initio* design of these molecular assemblies remains often a challenge. For that reason, systematic investigations dealing with design principles are still needed.

We have been engaged in the design and characterisation in the crystalline phase of coordination networks for some time now.[20–34] Pursuing our effort in this direction, we have undertaken a systematic investigation of possibilities generated by combinations of tetradentate organic tectons offering four coordination sites in the same plane or out of the plane and metallic tectons possessing two or four available coordination sites and adopting a "V" or square type geometries.

Here we report the formation of four new coordination networks formed upon crystallisation of tectons **1** or **2** (Scheme 1) in the presence of $HgCl_2$ or $CoCl_2$.



Scheme 1

Both tectons **1** and **2** are based on the pentaerythritol **3** skeleton and bear four pyridine moieties as coordinating sites. The difference between the two is based on the connecting position of the pyridinoyl moiety to the backbone (position 3 for **1** and 4 for **2**). Thus, tectons **1** and **2** are positional isomers. Pyridine, probably one of the most often used ligands, was chosen in order to generate a neutral tecton. For both **1** and **2**, the junction between the pyridine units and the backbone is ensured by ester groups.

The straightforward and high yield syntheses of **1** and **2** were achieved upon condensing the hydrochloride salt of nicotinoyl chloride **4** or of isonicotinoyl chloride **5** respectively with pentaerythritol **3** in pyridine. Although compound **1** was described in a patent and obtained using a different method,[35] since no complete characterisation was reported, the syntheses of both tectons **1** and **2** are given in the experimental section.

For the design of coordination networks, with desired dimensionality (1-, 2-, 3-D), one must consider on one hand the stereochemical demands of the metal M (oxidation state, number, location and geometry of available coordination sites) and on the other hand the coordinating features of the organic tecton T (charge, number, location and geometry of coordinating sites). In other words, the design of coordination networks requires a match between the coordination and coordinating features of the metallic and organic tectons respectively.

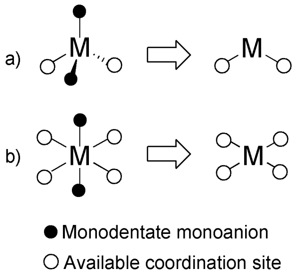
In this context, an organic tecton is a construction unit possessing at least two non-convergently oriented coordination poles. A coordination pole may be defined as a portion of space composed of converging coordination sites and may be of mono-, bi-, tri- or tetra-dentate type.[24] A tecton, in contrast to a ligand which binds a metal but does not allow the repetition of the coordination process, must be capable of coordinating the metal centre defining thus a coordination pattern and furthermore must allow the translation of the latter. In other words, coordination networks are obtained upon mutual bridging between the organic tecton and the metallic centre.

Let us consider the case of coordination networks with a 1/1 nuclearity engaging one metal centre and one organic tecton. Dealing with the metal centre, one may differentiate the situation for which the organic tecton satisfies the coordination demands of the metal leading thus to networks of the type $(\text{M–T})_n$ from the case $(\text{ML–T})_x$ for which only a part of the coordination sphere around the metal is occupied by the organic tecton while other coordination positions are engaged with a ligand (L) which does not take part in the formation of the network. In the first case, the metal will behave as an atomic metallic tecton whereas for the second case, the complex ML behaves as a metallatecton.

Coordination networks are often based on positively charged atomic metallic tectons (M^{n+}, $n = 1$, 2 or 3) or metallatectons (M^{n+}L complex). Based on charge neutrality, again one may consider different situations depending on the charge state of the organic tecton and ligand. For organic anionic tectons, if the positive charge ($n+$) of the cation is compensated by the negative charge ($n-$) of the tecton, the neutral coordination network will be described as a two component system $(\text{M}^{n+}\text{–T}^{n-})_x$. Furthermore, for anionic tectons (T^{m-}) ($m > 0$) with $m < n$, the charge compensation may be ensured by the ligand (L^{p-}, $p + m = n$). On the other hand, in the case of neutral tectons, the charge compensation may only be done by anions (A^{n-} or $n\text{A}^-$). For coordinating anions behaving thus as ligands, the network may be of the type $(\text{M}^{n+}\text{A}^{n-}\text{–T})_x$, or $(\text{M}^{n+}n\text{A}^-\text{–T})_x$. Finally, for non-coordinating anions, the solid, composed of cationic networks of the type $(\text{M}^{n+}\text{–T})_x$ and anions, may be described as $[(\text{M}^{n+}\text{–T})_x{\cdot}x\text{A}^{n-}]$ or as $[(\text{M}^{n+}\text{–T})_x{\cdot}xn\text{A}^-]$. For theses two cases, the anionic component does not take part in the backbone of the network and with respect to the latter may be regarded as "spectator".

When using neutral tectons, the two above mentioned cases are not equivalent in terms of design strategy. Indeed, whereas for non-coordinating anions the system leading to the network will be composed of three components (M^{n+}, T and A^{n-} or $n\text{A}^-$), for coordinating anions, the number of components may be reduced from three to two ($\text{M}^{n+}\text{A}^{n-}$ or $\text{M}^{n+}n\text{A}^-$ complexes and T). These concepts have been previously demonstrated.[26]

The use of coordinating anions as ligands opens some further possibilities in terms of design principles. Indeed, for a given metal cation with defined stereochemical demands, the occupation of certain coordination sites around the metal centre by the coordinating anion leads to geometrical simplification. For example in the case of a dicationic metal centre requiring a tetrahedral coordination geometry, upon coordination of two monodentate anions a neutral metallatecton possessing a "V" type geometry and offering two available coordination sites will be obtained (Scheme 2). In the same manner, a dication adopting an octahedral coordination geometry, when associated with two monodentate anions occupying the two apical positions will lead to a neutral metallatecton offering four available coordination sites located in all four corner of a square (Scheme 2). Applying the above mentioned principles, HgCl_2 and CoCl_2 were considered as neutral metallatectons offering "V" and square type geometries respectively. The choice of Cl^- anion as ligand was based on its ability to coordinate to cationic metal centres.



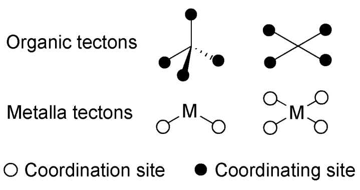
Scheme 2

The investigation presented here reports an exploration of different possibilities which may be generated when neutral metallatectons offering either a "V" or a square type geometries are combined with neutral organic tetradentate tectons such as **1** and **2** for which the coordinating sites may be located either in the same plane (square type geometry) or out of the plane (pseudotetrahedral geometry) (Scheme 3).

At room temperature, upon slow diffusion of a tetrachloroethane solution (2 ml) of **1** (4 mg) into a isopropanol solution (4 ml) of HgCl_2 (5 mg), colourless single crystals were obtained after *ca.* 48 hours and studied by X-ray diffraction which revealed the following features. The combination of **1** offering four coordinating sites occupying the corners of a square with HgCl_2 possessing two available coordination sites in "V" type disposition leads to the formation of a 1-D neutral coordination network resulting from the mutual bridging between **1** and HgCl_2 (Fig. 1). The crystal (monoclinic system, $P2_1/n$ as the space group, $Z = 4$) is composed of neutral networks and $\text{C}_2\text{H}_2\text{Cl}_4$ and H_2O solvent molecules. These molecules occupy the empty space with no specific interactions with the networks.

The coordination sphere around Hg^{2+} cations is composed of two Cl^- anions (average Hg–Cl distance of *ca.* 2.35 Å) and two N atoms (average Hg–N distance of *ca.* 2.44 Å) belonging to two consecutive tectons **1**. The coordination geometry around the metal is a distorted tetrahedron (average Cl–Hg–Cl and N–Hg–N angles of *ca.* 152° and *ca.* 101° respectively). The 1-D networks are packed in parallel fashion.

Under the same conditions, the slow diffusion at room temperature of a tetrachloroethane solution (2 ml) of **2** (4 mg) into an isopropanol solution (4 ml) of HgCl_2 (5 mg) affords again colourless single crystals after *ca.* 48 hours which were also studied by X-ray diffraction. The combination of **2** offering four coordinating sites occupying the apices of a pseudo



Scheme 3

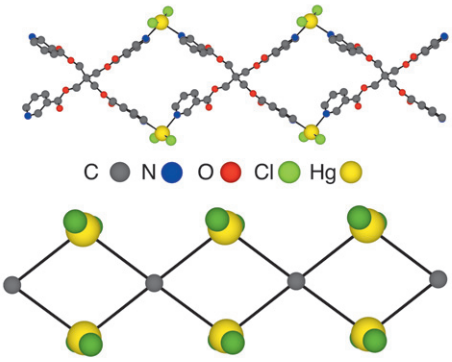


Fig. 1 A portion of the neutral 1-D network obtained upon self-assembly of the tecton **1** with HgCl$_2$ (top) and the topological simplification made by connecting the central C atom of the tecton to mercury atoms (bottom). Solvent molecules and H atoms are not represented for clarity. For bond distances and angles see text.

tetrahedron with HgCl$_2$ leads to the formation of a neutral 2-D coordination network resulting again from the mutual bridging between **2** and HgCl$_2$ (Fig. 2). The crystal (monoclinic system, $C2/c$ as the space group, $Z = 4$) is composed of neutral networks and C$_2$H$_2$Cl$_4$ solvent molecules with no specific interactions between them.

The coordination sphere around Hg^{2+} cations is again composed of two Cl$^-$ anions (average Hg–Cl distance of *ca.* 2.33 Å) and two N atoms (average Hg–N distance of *ca.* 2.45 Å) belonging to two tectons **1**. The coordination geometry around the metal is a distorted tetrahedron (average Cl–Hg–Cl and N–Hg–N angles of *ca.* 154° and *ca.* 92° respectively). The 2-D networks are packed parallel to each other generating thus channels which are occupied by solvent molecules.

Dealing with CoCl$_2$ possessing four available coordination sites located within the square base of the octahedron, again the formation of networks was studied in the presence of both tectons **1** and **2**. Upon slow diffusion at room temperature of a chloroform solution (2 ml) of **1** (4 mg) into a ethanol solution (4 ml) of CoCl$_2$ (5 mg) pink single crystals were obtained after *ca.* 48 hours and studied by X-ray diffraction (Fig. 3). The combination of **1** and CoCl$_2$ generates a 2-D neutral coordination network resulting from the mutual bridging between **1** and CoCl$_2$. The crystal (orthorhombic system, $Pccn$ as the space group, $Z = 4$) is composed of neutral network and CHCl$_3$ solvent molecules. These molecules occupy the empty space with no specific interactions with the networks.

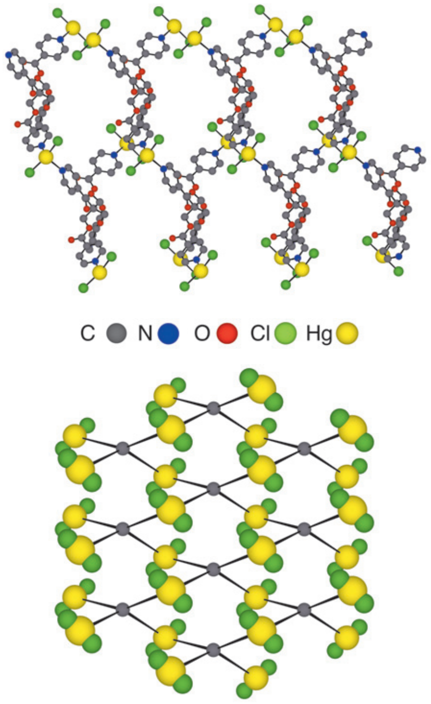


Fig. 2 A portion of the neutral 1-D network obtained upon self-assembly of the tecton **2** with HgCl$_2$ (top) and the topological simplification made by connecting the central C atom of the tecton to mercury atoms (bottom). Solvent molecules and H atoms are not represented for clarity. For bond distances and angles see text.

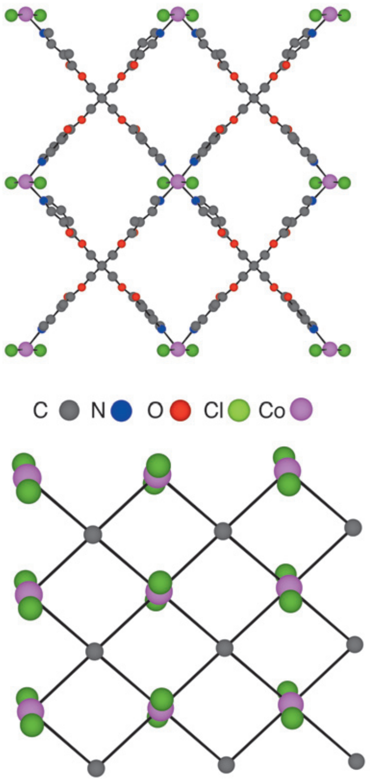


Fig. 3 A portion of the neutral 2-D network obtained upon self-assembly of the tecton **1** with CoCl$_2$ (top) and the topological simplification made by connecting the central C atom of the tecton to mercury atoms (bottom). Solvent molecules and H atoms are not represented for clarity. For bond distances and angles see text.

The coordination sphere around Co^{2+} cations is composed of two Cl$^-$ anions (average Co–Cl distance of *ca.* 2.44 Å) and four N atoms (average Co–N distance of *ca.* 2.23 Å) belonging to four tectons **1**. The coordination geometry around the metal is a distorted octahedron (average Cl–Co–Cl angles of *ca.* 175° and N–Co–N *trans* angle of *ca.* 176° and N–Co–N *cis* angle varying between 85° and 93°). The packing of the 2-D networks in the crystal generates channels which are filled with solvent molecules.

Finally, upon slow diffusion at room temperature of a chloroform solution (2 ml) of **2** (4 mg) into a ethanol solution (4 ml) of CoCl$_2$ (5 mg) pink single crystals were obtained again after *ca.* 48 hours and studied by X-ray diffraction. The tecton **2** leads in the presence of CoCl$_2$ to the formation of a neutral 3-D coordination network resulting from the mutual bridging between **2** and CoCl$_2$ (Fig. 4). The crystal (tetragonal system, $P4_2/n$ as the space group, $Z = 2$) is composed of neutral 3-D networks and CHCl$_3$ and H$_2$O solvent molecules. The solvent molecules, occupying the empty space, are disordered and for that reason a rather high R (0.143) factor is obtained.

The coordination sphere around Co^{2+} cations is again composed of two Cl$^-$ anions (average Co–Cl distance of *ca.* 2.4 Å) and four N atoms (average Co–N distance of *ca.* 2.2 Å) belonging to four tectons **2**. The coordination geometry around the metal is a distorted octahedron (average Cl–Co–Cl

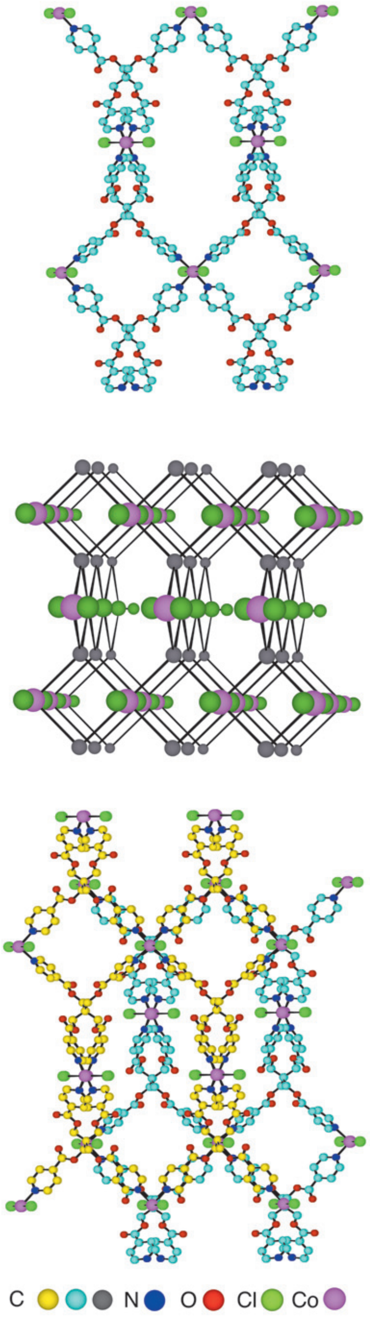


Fig. 4 A portion of the neutral 3-D network obtained upon self-assembly of the tecton **2** with CoCl$_2$ (top), the topological simplification made by connecting the central C atom of the tecton to mercury atoms (middle) and the interpenetration of two 3-D networks (bottom). In order to illustrate the interpenetration of the two 3-D networks, the C atoms of the two independent networks are differentiated by colour. Solvent molecules and H atoms are not represented for clarity. For bond distances and angles see text.

angles of *ca.* 179° and N–Co–N *trans* angle of *ca.* 175° and N–Co–N *cis* angle varying between *ca.* 86° and 89°). Probably for better packing reasons, a two-fold homo interpenetrating architecture is observed. This is not unprecedented since many 3-D networks lead to interpenetrating structures.[36]

In summary, the neutral tectons **1**, possessing four monodentate pyridines as coordination sites located in the same plane (square type geometry for the N atoms), leads to a neutral 1-D coordination network in the presence of the neutral HgCl$_2$ metallatecton offering two available coordination sites occupying the extremities of a "V" (Fig. 5a). The same tecton, in the presence of CoCl$_2$, offering four coordination sites occupying the corners of a square, forms a neutral 2-D coordination network (Fig. 5b). For the tecton **2**, possessing also four coordinating sites but occupying the apices of a pseudo tetrahedron (Td type geometry for the N atoms), a 2-D network is observed with HgCl$_2$ (Fig. 5c), whereas in the presence of CoCl$_2$, a neutral 3-D network is obtained (Fig. 5d).

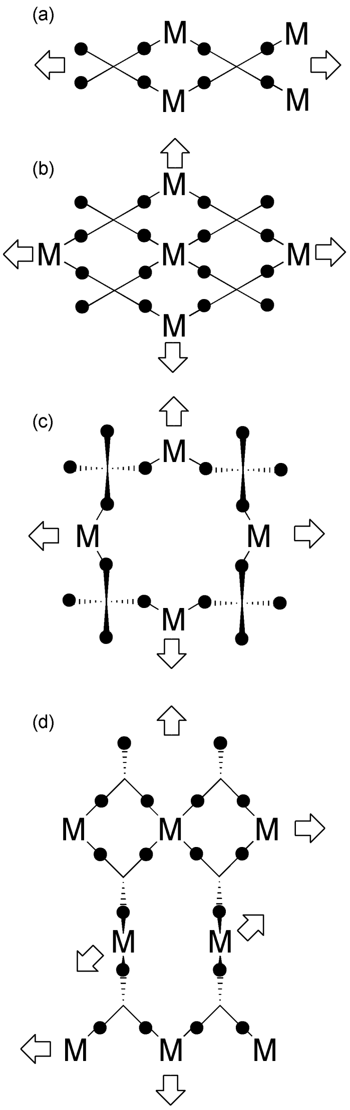


Fig. 5 Schematic representation of the formation of neutral coordination networks based on the mutual bridging between the tecton **1** possessing four coordination sites located in the same plane and HgCl$_2$ metallatecton offering two available coordination sites occupying the extremities of a V (a) and CoCl$_2$ metallatecton offering four coordination sites occupying the corners of a square (b), and the tecton **2**, possessing four coordinating sites but occupying the apices of a pseudo tetrahedron with HgCl$_2$ (c) and CoCl$_2$ (d).

Further studies using combinations of tectons **1** and **2** and other metallic tectons are currently under investigation.

Experimental

General procedure for the synthesis of 1 and 2

To a degassed solution of pyridine (35 ml), pentaerythritol **3** (0.5 g, 3.7 mmol) and the hydrochloride salt of nicotinoyl chloride **4** or isonicotinoyl chloride **5** (3.3 g, 1.84 mmol) was added and the mixture refluxed for 5 h. After evaporation to dryness, to the residue Na$_2$CO$_3$ saturated H$_2$O (50 ml) was added and the mixture extracted three times with CH$_2$Cl$_2$ (50 ml). The organic solvent was removed and the residue suspended in ether (20 ml) was filtered and the solid further washed with ether (2 × 10 ml) affording the pure compounds **1** (2.0 g, 97%) or **2** (1.8 g, 87%) as white powders.

1: m.p. 145 °C, ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm): 4.72 (s, 8H, CH_2), 7.37 (m, 4H), 8.24 (dd, 4H, $J = 1.5$ Hz and 5.3 Hz), 8.79 (d, 4H, 3.8 Hz), 9.20 (s, 4H); ^{13}C-NMR (50 MHz, $CDCl_3$, 25 °C): δ (ppm): 43.3, 63.2, 123.4, 125.1, 137.0, 150.8, 153.9, 164.6; Anal. Calc. for $C_{29}H_{24}O_8N_4$: C 62.59, H 4.35, N 10.07, Found: C 61.94, H 4.47, N 9.97%.

2: m.p. 142 °C, ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm): 4.70 (s, 8H, CH_2), 7.77 (dd, 8H, $J = 1.5$ Hz and 5.4 Hz), 8.77 (dd, 8H, $J = 1.5$ Hz and 5.4 Hz); ^{13}C-NMR (50 MHz, $CDCl_3$, 25 °C): δ (ppm): 43.3, 63.4,122.6, 136.1, 150.8, 164.5; Anal. Calc. for $C_{29}H_{24}O_8N_4$: C 62.59, H 4.35, N 10.07, Found: C 61.72, H 4.39, N 10.26%.

Crystal structure characterisation

X-Ray diffraction data collection was carried out on a Kappa CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo-Kα radiation. For all structures, diffraction data were corrected for absorption and analysed using the OpenMolen package.[37] All non-H atoms were refined anisotropically. CCDC reference numbers 202740–202743. See http://www.rsc.org/suppdata/nj/b3/b301351k/ for crystallographic data in CIF or other electronic format.

Crystallographic data for (1-HgCl$_2$)$_n$. (Colourless crystals, 173 K): $C_{29}H_{24}Cl_4Hg_2N_4O_8 \cdot 0.5C_2H_2Cl_4 \cdot H_2O$, $M = 1201.47$, monoclinic, $a = 14.7630(3)$, $b = 13.2294(3)$, $c = 20.6902(4)$ Å, $\beta = 91.285(5)°$, $U = 4039.9(1)$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.98$ g cm^{-3}; $\mu = 8.040$ mm^{-1}, 6214 data with $I > 3\sigma(I)$, $R = 0.060$, $Rw = 0.074$.

Crystallographic data for (2-HgCl$_2$)$_n$. (Colourless, 173 K): $C_{29}H_{24}Cl_4Hg_2N_4O_8 \cdot 2C_2H_2Cl_4$, $M = 1435.23$, monoclinic, $a = 24.2740(6)$, $b = 10.8173(3)$, $c = 20.6707(6)$ Å, $\beta = 123.094(5)°$, $U = 4547.2(2)$ Å^3, space group $C2/c$, $Z = 4$, $D_c = 2.10$ g cm^{-3}; $\mu = 7.501$ mm^{-1}, 3397 data with $I > 3\sigma(I)$, $R = 0.038$, $Rw = 0.053$.

Crystallographic data for (1-CoCl$_2$)$_n$. (Pink, 173 K): $C_{29}H_{24}Cl_2CoN_4O_8 \cdot 3CHCl_3$, $M = 1044.51$, orthorhombic, $a = 12.2414(2)$, $b = 13.1257(2)$, $c = 27.1081(4)$ Å, $U = 4355.6(1)$ Å^3, space group $Pccn$, $Z = 4$, $D_c = 1.59$ g cm^{-3}; $\mu = 1.120$ mm^{-1}, 4594 data with $I > 3\sigma(I)$, $R = 0.080$, $Rw = 0.093$.

Crystallographic data for (2-CoCl$_2$)$_n$. (Pink, 173 K): $C_{58}H_{48}Cl_4Co_2N_8O_{16} \cdot 2CHCl_3 \cdot 7H_2O$, $M = 1737.61$, tetragonal, $a = 13.0678(9)$, $b = 13.0678(9)$, $c = 25.914(1)$ Å, $U = 4425.3(5)$ Å^3, space group $P4_2/n$, $Z = 2$, $D_c = 1.30$ g cm^{-3}; $\mu = 0.743$ mm^{-1}, 2101 data with $I > 3\sigma(I)$, $R = 0.143$, $Rw = 0.173$.

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