Molecular tectonics: control of dimensionality in Tetramercapto-thiocalixarenes based coordination networks

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Supporting Information Placeholder

ABSTRACT: Combinations of tetramercapto-tetrathiocalix[4]arene pyridyl appended positional isomers with HgCl₂ leads to the formation of neutral coordination networks with their dimensionality imposed by the position of the N atom on the pyridyl group. The *ortho* isomer leads to the formation of a 1D network, the *meta* isomer generates a 2D assembly and finally, the *para* isomer affords a diamond-like 3D coordination architecture.

The increasing interest in Coordination Polymers (CPs) also called MOFs arises from their applications in separation, storage and catalysis for example.¹ The design and preparation of this type of infinite architectures displaying translational symmetry may be based on the molecular tectonics approach which considers both the organic moiety and the metallic centre or complex as complementary tectons.² Among many types of organic tectons, those based on macrocycles such as azacrown ethers,³ porphyrins⁴ and cucurbit[n]urils,⁵ calix[4]arenes⁶ are interesting backbones since they are preorganised entities with, in some cases, restricted conformational space. Within the calix[4]arene⁶ family, tertthiocalix[4]arenes (TCA)⁷ for which all four CH₂ groups connecting the aromatic moieties are substituted by S atoms particularly interesting for the design of organic tectons since they offer four additional thioether junctions which may take part in the coordination of metal centres.¹⁰ Using TCA derivatives in 1,3-alternate conformation bearing peripheral coordinating sites such as nitrile,¹¹ carboxylate¹² or benzonitrile groups¹³ and propoxy groups¹⁴ variety of 1-, 2- and 3-D coordination networks have been obtained using Ag⁺ cation as connector. Tetramercapto-tetrathiocalix[4]arene **1** (Scheme 1) is an analogue of TCA for which the four OH moieties are replaced by four SH groups.¹⁵ The latter offers 8 sulphur atoms which may be involved in binding of metal cations. Few examples of functionalization of the lower rim of **1** have been described.^{16,17} The coordination propensity of **1** has been studied and only few discrete complexes have been reported for Ir(II) and Rh(II)¹⁸, Mo(II), Ni(II) and W(II)¹⁹ and Hg(II).¹⁰ A specific Hg(II) extracting agent based on an analogue of **1** bearing only two SH groups has been also reported.²⁰

In this contribution, we report on the design, synthesis and structural characterisation of three new organic tectons **2-4** (Scheme 1) and their combinations with HgCl₂ leading to mercury coordination networks in the crystalline phase.

Tectons **2-4**, based on the parent compound **1** locked in the 1,3-alternate conformation (Scheme 1 right) bearing four monodentate pyridyl group as coordinating sites, are positional isomers and differ by the position of the N atom on the pyridyl moiety. Whereas compounds **2** and **3**, owing to the distance between the N and S atoms, should behave as tetrakis monodentate units, compound **4**, offering four NCCH₂S

moieties, can behave as a chelating ligand.

Scheme 1: Tetramercaptotetrathiocalix[4]arene TMTCA **1**, tectons **2-4** and a schematic representation of their 1,3-A conformation. Black circle indicates the junction between pyridyl moieties X and the calix backbone. S atoms are shown by yellow spheres.

The starting material for the preparation of tectons **2-4** was compound **1**.¹⁵ As for the tetrathiocalix[4]arene pyridyl appended analogues,²¹ compounds **2-4** have been obtained at 25 °C in 53, 41 and 51 % yield respectively upon condensation between the parent compound **1** and X-(chloromethyl)pyridine (X = 4 for **2**, 3 for **3** and 2 for **4**) in dry acetone in the presence of Cs₂CO₃. In all cases, only the 1,3-A conformation was isolated from the reaction mixture (see SI). Structures of **2-4** have been studied by X-ray diffraction on single crystals (see crystallographic table in SI). Crystals were obtained upon slow diffusion (or evaporation) of CH₃CN (or MeOH) into a CHCl₃ solution of tecton **2-4** (see SI). As expected, the 1,3-A conformation was established for all three compounds (Fig. 1). Whereas crystals of **4** contain CHCl₃ molecules, **2** and **3** crystallise in the absence of solvent. For all three cases, the metrics for the macrocyclic part is close to those observed for the parent compound **1**.¹⁵ Among the three structures, only for **2**, two out the four *tert*-butyl groups are found to be disordered. Whereas for **2** and **3** the pyridyl groups are oriented almost perpendicular to the main plane formed by the four S atoms connecting the aromatic rings (tilt angle between 75.9 and 83.7°) for **4**, the tilt angle is considerably smaller (40.7°).

Figure 1: The solid state structures of **2** (left), **3** (middle) and **4** (right) showing the 1,3-A conformation adopted by all three tectons. H atoms and solvent molecules are omitted for clarity.

For the formation of coordination networks, HgCl₂ was chosen as the neutral metallic partner. The latter was shown to act as a neutral deformed tetrahedral node offering two free

coordination sites in a V-type disposition²² although examples with extended coordination sphere have been also reported.²³ Combinations of **2-4** with HgCl_2 have been explored by slow evaporation at 25 °C of a CHCl_3 solution containing the organic part into a CH_3OH solution of HgCl_2 (see SI). In all cases, crystals suitable for X-ray diffraction have been obtained reproducibly (see SI). For **2**- HgCl_2 and **3**- HgCl_2 , the purity of the crystalline material was established by PXRD on microcrystalline powders which revealed a good match between the observed and simulated patterns (see SI). For **4**- HgCl_2 , owing to the decomposition of the microcrystalline powder, probably due to the loss of CHCl_3 solvent molecules, no good quality PXRD pattern could be obtained. In all three cases, the structural investigation revealed the formation of neutral Hg coordination networks **2**- HgCl_2 , **3**- HgCl_2 and **4**- HgCl_2 discussed below.

In the case of **2**- HgCl_2 , the crystal (Triclinic, *P*-1, $\text{Hg}_4\text{Cl}_8(\text{C}_{64}\text{H}_{68}\text{N}_4\text{S}_8)(\text{CHCl}_3)_2$) is composed of tecton **2**, Hg^{2+} cation, Cl^- anion and CHCl_3 solvent molecules. The tecton/ Hg^{2+} ratio is $\frac{1}{2}$. Each Hg^{2+} , surrounded by a N_2Cl_2 set ($d_{\text{Hg-N}}$ and $d_{\text{Hg-Cl}}$ in the 2.398(5) - 2.508(5) Å and 2.3377(16) - 2.3632(14) Å range respectively) in a deformed tetrahedral coordination geometry (NHgN , ClHgN and ClHgCl angles in the 82.04(16)-85.24(16)°, 90.91(12)-106.36(12)° and 150.18(6)-159.81(6)° range respectively), is linked to two consecutive tectons **2** through Hg-N bonds. Tecton **2** binds four Hg^{2+} cations through its four N_{py} atoms occupying the apices of a deformed tetrahedron (Fig. 2).

Figure 2: A portion of the 1D neutral coordination network formed upon bridging of consecutive tectons **2** by HgCl_2 along the *a* axis. H atoms and CHCl_3 solvent molecules are omitted for clarity. For bond distances and angles see text.

The connectivity mode leads to the formation of a 1-D neutral network resulting from the bridging of consecutive tectons **2** by HgCl_2 acting as a V shape connector. Owing to the distance between the N atoms of the pyridyl groups and the S atoms of the thiacalix backbone, no S- Hg^{2+} bond is formed. The CHCl_3 molecules occupy the interstices in the crystal without any specific interaction with framework.

For the combination of the tecton **3** and HgCl_2 , the crystal (Triclinic, *P*-1, $\text{Hg}_4\text{Cl}_8(\text{C}_{64}\text{H}_{68}\text{N}_4\text{S}_8)_2$) is exclusively composed of **3**, Hg^{2+} and Cl^- . The **3**/ Hg^{2+} ratio is $\frac{1}{2}$. Each tecton **3** binds four Hg^{2+} and each cation bridges two consecutive tectons **3** (Fig. 3). Hg^{2+} , acting again as a V shape connector as in the case of **2**- HgCl_2 , is surrounded by a N_2Cl_2 set of atoms ($d_{\text{Hg-N}}$ and $d_{\text{Hg-Cl}}$ in the range of 2.365(8) - 2.41(9) Å and 2.358(4) - 2.393(4) Å range respectively) and adopts a distorted *Td* coordination geometry (NHgN , ClHgN and ClHgCl angles in the 91.0(4)-100.5(4)°, 96.2(3)-105(2)° and 140.7(2)-150.19(15)° range respectively). The connectivity pattern leads to the formation of a 2D architecture resulting from the bridging of consecutive tectons **3** by HgCl_2 units through pyridyl-Hg bonds. As in the case of **2**- HgCl_2 , the S atoms do not participate in the binding of Hg^{2+} cation. The packing of consecutive sheets takes place along the *b* axis.

Figure 3: A portion of the 2D neutral coordination network formed upon bridging of consecutive tectons **3** by HgCl_2 in the *abc* plane. H atoms are omitted for clarity. For bond distances and angles see text.

Finally, in the case of **4**- HgCl_2 , the crystal (monoclinic, *C*2/*c*, $(\text{Hg}_4\text{Cl}_8)_{0.5}(\text{C}_{64}\text{H}_{68}\text{N}_4\text{S}_8)_{0.5}(\text{CHCl}_3)$) is composed of **4**, Hg^{2+} , Cl^- and CHCl_3 solvent molecule. The tecton/ Hg^{2+} ratio is $\frac{1}{4}$ (Fig. 4 left). HgCl_2 forms a tetranuclear (Hg_4Cl_8) species through two μ_3 -Chloro bridging modes between the cationic centres by two Cl^- anions. (Fig. 4 right). This type of mercury polynuclear complex, although rare, has already been described in the literature.²⁴

The crystal is as 3-D pseudo diamond-type coordination network resulting from the interconnection of consecutive tectons **4** by pseudo rectangular $\text{Hg}_4\text{N}_4\text{S}_4\text{Cl}_8$ complexes. The distance between Hg^{2+} cations within the tetranuclear unit of 4.225(4) Å is close to those reported for similar neutral $\text{Hg}_n\text{Cl}_{2n}$ species.²⁵ The organic tecton **4**, in marked contrast with tectons **2** and **3** which behave as tetradentate units, acts as a hexadentate N_4S_2 neutral connector. The latter offers two monodentate pyridyl sites and two chelates of the NCCH_2S type. Indeed, only two out of the four ArSCH_2S S atoms participate in the coordination of Hg^{2+} with a Hg-S distance of *ca* 3.1 Å, whereas the other two are located at *ca* 4.1 Å. The four N atoms of the pyridyl units occupy the apices of a tetrahedron. The S atoms connecting the aromatic moieties are not involved in the binding of Hg^{2+} . The interconnection between the two partners thus occurs through both N-Hg(II) and S-Hg(II) coordination bonds. Within the 3D network, two types of Hg^{2+} cation differing both by their geometry and surrounding are present. Those with a distorted tetrahedral coordination geometry (ClHgCl and NHgCl angles in the 90.24(5)-153.59(9)° and 89.20(11)-153.59(9)° range respectively) are bound to one N and three Cl atoms ($d_{\text{Hg-N}}$ of 2.431(5) Å and $d_{\text{Hg-Cl}}$ of 2.3399(16), 2.3411(13) and 2.8430(12) Å). The other ones with a distorted octahedral environment (NHgCl , ClHgCl SHgCl and NHgS angles of 94.69(11)-155.48(12)°, 84.14(11)-107.54(5)°, 80.29(5)-164.60(12)° and 71.78(4)-96.29(5)° respectively and SHgS of 61.85(7)°) are surrounded by one N, two S and three Cl atoms with $d_{\text{Hg-N}}$ of 2.189(4) Å, $d_{\text{Hg-Cl}}$ of 2.3366(12), 2.6381(12) and 3.041(4) Å and $d_{\text{Hg-S}}$ of 3.125(5) and 3.168(5) Å. The CHCl_3 molecules occupy the interstices in the crystal without any specific interaction with framework.

Figure 4: A portion of the 3D neutral coordination network (left) formed upon bridging of consecutive tectons **4** by the tetranuclear mercury complex (right). H atoms and CHCl_3 solvent molecules are omitted for clarity. For bond distances and angles see text.

In conclusion, we have demonstrated that compound **1** is a suitable backbone for the design of tectons **2-4** which are positional isomers differing by the position of the N atom on the pyridyl group. Their association with HgCl_2 leads to the formation of Hg coordination networks with either HgCl_2 or a tetranuclear Hg_4Cl_8 moieties as bridging units interconnecting consecutive organic tectons. Interestingly, the dimensionality of the network (1D for **2**, 2D for **3** and 3D for **4**) may be controlled by the location of the N atom on the pyridyl unit. The formation of infinite networks and/or discrete polynuclear species based on the parent compound **1** and the the pyridyl appended tectons **2-4** is currently under investigation.

ASSOCIATED CONTENT

Supporting Information. Crystallographic table for **2-4** and $2\text{-HgCl}_2\text{-4-HgCl}_2$, complete experimental section, XRPD diagrams for **2** and 3-HgCl_2 . CCDC 926008-926013.

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SYNOPSIS TOC.

Combinations of tetramercapto-tetrathiacalix[4]arene pyridyl appended positional isomers with HgCl_2 leads to the formation of three new neutral coordination networks with imposed 1-3 D dimensionality by the position of the N atom on the pyridyl group.

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