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Molecular Tectonics: Control of the Dimensionality in Tetramercaptothiacalixarenes Based Coordination Networks

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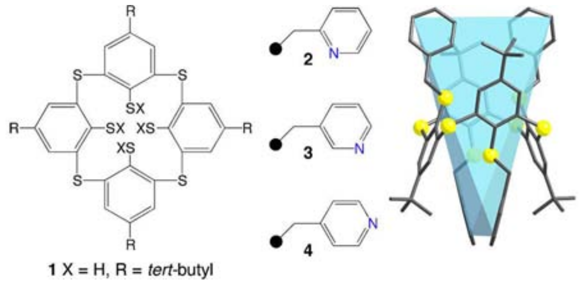
Supporting Information

ABSTRACT: Combinations of tetramercaptotetrathiacalix[4]arene pyridyl-appended positional isomers with $HgCl_2$ lead to the formation of neutral coordination networks with their dimensionality imposed by the position of the N atom on the pyridyl group.

The increasing interest in coordination polymers, also called metal–organic frameworks, arises from their applications in separation, storage, and catalysis, for example.[1] The design and preparation of these types of infinite architectures displaying translational symmetry may be based on the molecular tectonics approach,[2] which considers both the organic moiety and the metallic center or complex as complementary tectons.[3] Among many types of organic tectons, those based on macrocycles such as azacrown ethers,[4] porphyrins,[5] cucurbit[*n*]urils,[6] and calix[4]arenes[7] are interesting backbones because they are preorganized entities with, in same cases, restricted conformational space. Within the calix[4]arene[8] family, tetrathiacalix[4]arenes (TCAs),[9] for which all four CH_2 groups connecting the aromatic moieties are substituted by S atoms, are particularly interesting for the design of organic tectons because they offer four additional thioether junctions that may take part in the coordination of metal centers.[10] Using TCA derivatives in an 1,3-alternate (1,3-A) conformation bearing peripheral coordinating sites such as nitrile,[11] carboxylate,[12] or benzonitrile groups[13] and propoxy groups,[14] a variety of 1-, 2-, and 3D coordination networks have been obtained using the Ag^+ cation as a connector. Tetramercaptotetrathiacalix[4]arene (**1**; Scheme 1) is an analogue of TCA in which the four OH moieties are replaced by four SH groups.[15] The latter offers eight S atoms, which may be involved in binding of the metal cations. Few examples of the functionalization of the lower rim of **1** have been described.[16,17] The coordination propensity of **1** has been studied, and only a 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 also been reported.[20]

In this contribution, we report on the design, synthesis, and structural characterization of three new organic tectons **2–4** (Scheme 1) and their combinations with $HgCl_2$, leading to mercury coordination networks in the crystalline phase.

Scheme 1. 1, Tectons 2–4, and a Schematic Representation of Their 1,3-A Conformation[a]



[a]Black circles indicate the junctions between pyridyl moieties X and the calix backbone. S atoms are shown by yellow spheres.

Tectons **2–4**, based on the parent compound **1** locked in the 1,3-A 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 **2** and **3**, owing to the distance between the N and S atoms, should behave as tetrakis-monodentate units, **4**, offering four $NCCH_2S$ moieties, can behave as a chelating ligand.

The starting material for the preparation of tectons **2–4** was compound **1**.[15] As for the TCA 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 Cs_2CO_3. In all cases, only the 1,3-A conformation was isolated from the reaction mixture (see the Supporting Information, SI). Structures of **2–4** have been studied by X-ray diffraction (XRD) on single crystals (see the crystallographic table in the SI). Crystals were obtained upon the slow diffusion (or evaporation) of CH_3CN (or MeOH) into a $CHCl_3$ solution of tectons **2–4** (see the SI). As expected, the 1,3-A conformation was established for all three compounds (Figure S1, SI). Whereas crystals of **4** contain $CHCl_3$ molecules, **2** and **3** crystallize in the absence of solvent. For all three cases,

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the metrics for the macrocyclic part are 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 perpendicularly 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°).

For the formation of coordination networks, $HgCl_2$ 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 disposition,[22] although examples with an extended coordination sphere have been also reported.[23] Combinations of **2**−**4** with $HgCl_2$ have been explored by the slow evaporation at 25 °C of a $CHCl_3$ solution containing the organic part into a CH_3OH solution of $HgCl_2$ (see the SI). In all cases, crystals suitable for XRD have been obtained reproducibly (see the SI). For **2**-$HgCl_2$ and **3**-$HgCl_2$, the purity of the crystalline material was established by powder XRD (PXRD) on microcrystalline powders, which revealed a good match between the observed and simulated patterns (see the SI). For **4**-$HgCl_2$, owing to decomposition of the microcrystalline powder, probably because of 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 mercury coordination networks **2**-$HgCl_2$, **3**-$HgCl_2$, and **4**-$HgCl_2$ discussed below.

In the case of **2**-$HgCl_2$, the crystal [triclinic, $P\bar{1}$, $Hg_2Cl_4(C_{64}H_{68}N_4S_8)\cdot(CHCl_3)_2$] is composed of tecton **2** and Hg^{2+} cation, Cl^- anion, and $CHCl_3$ solvent molecules. The tecton/Hg^{2+} ratio is 1:2. Each Hg^{2+}, surrounded by a N_2Cl_2 set [d_{Hg-N} and d_{Hg-Cl} in the 2.398(5)−2.508(5) and 2.3377(16)−2.3632(14) Å ranges, respectively] in a deformed tetrahedral coordination geometry [N−Hg−N, Cl−Hg−N, and Cl−Hg−Cl angles in the 82.04(16)−85.24(16)°, 90.91(12)−106.36(12)°, and 150.18(6)−159.81(6)° ranges, 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 apexes of a deformed tetrahedron (Figure 1).

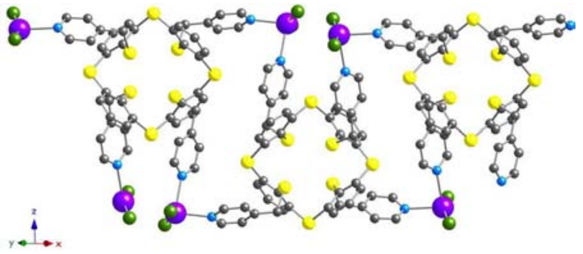

Figure 1. Portion of the 1D neutral coordination network formed upon bridging of consecutive tectons **2** by $HgCl_2$ along the *a* axis. H atoms and $CHCl_3$ solvent molecules are omitted for clarity.

The connectivity mode leads to the formation of a 1D neutral network, resulting from the bridging of consecutive tectons **2** by $HgCl_2$ acting as a V-shaped 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 the framework.

For a combination of the tecton **3** and $HgCl_2$, the crystal [triclinic, $P\bar{1}$, $Hg_4Cl_8(C_{64}H_{68}N_4S_8)_2$] is exclusively composed of **3**, Hg^{2+}, and Cl^-. The **3**/Hg^{2+} ratio is 1:2. Each tecton **3** binds four Hg^{2+}, and each cation bridges two consecutive tectons **3** (Figure 2). Hg^{2+}, acting again as a V-shaped connector as in the case of **2**-$HgCl_2$, is surrounded by a N_2Cl_2 set of atoms [d_{Hg-N} and d_{Hg-Cl} in the 2.365(8)−2.41(9) and 2.358(4)−2.393(4) Å ranges, respectively] and adopts a distorted T_d coordination geometry [N−Hg−N, Cl−Hg−N, and Cl−Hg−Cl angles in the 91.0(4)−100.5(4)°, 96.2(3)−105(2)°, and 140.7(2)−150.19(15)° ranges, 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 the Hg^{2+} cation. The packing of consecutive sheets takes place along the *b* axis.

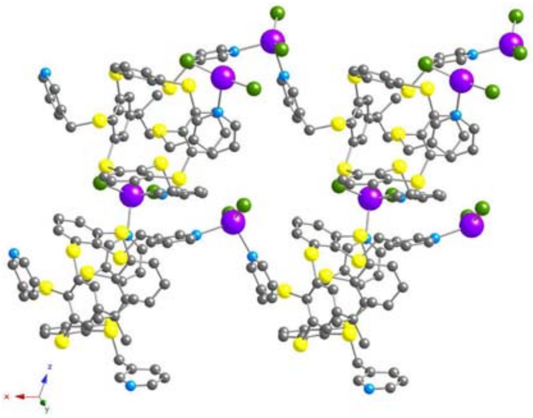

Figure 2. Portion of the 2D neutral network formed upon bridging of tectons **3** by $HgCl_2$ in the *abc* plane. H atoms are omitted for clarity.

Finally, in the case of **4**-$HgCl_2$, the crystal [monoclinic, $C2/c$, $(Hg_4Cl_8)_{0.5}(C_{64}H_{68}N_4S_8)_{0.5}\cdot(CHCl_3)$] is composed of **4** and Hg^{2+}, Cl^-, and $CHCl_3$ solvent molecules. The tecton/Hg^{2+} ratio is 1:4 (Figure 3, left). $HgCl_2$ forms a tetranuclear (Hg_4Cl_8) species through two μ_3-chloro bridging modes between the cationic centers by two Cl^- anions (Figure 3, right). This type of mercury polynuclear complex, although rare, has already been described in the literature.[24]

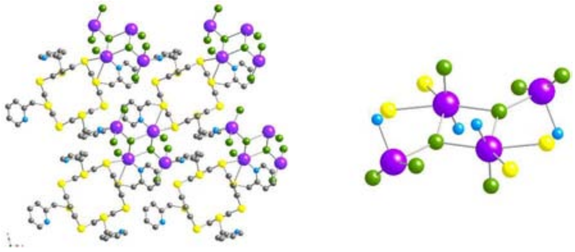

Figure 3. Portion of the 3D coordination network (left) formed upon bridging of consecutive tectons **4** by the tetranuclear mercury complex (right). H atoms and $CHCl_3$ solvent molecules are omitted for clarity.

The crystal is a 3D pseudo-diamond-type coordination network, resulting from the interconnection of consecutive tectons **4** by pseudorectangular $Hg_4N_4S_4Cl_8$ complexes. The distance between Hg^{2+} cations within the tetranuclear unit of 4.225(4) Å is close to those reported for similar neutral Hg_nCl_{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 $ArSCH_2$ 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 apexes 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+} cations differing by both their geometry and surroundings are present. Those with a distorted tetrahedral coordination geometry [Cl−Hg−Cl and N−Hg−Cl angles in the 90.24(5)−153.59(9)° and 89.20(11)−153.59(9)° ranges, respectively] are bound to one N and three Cl atoms [d_{Hg-N} of 2.431(5) Å and d_{Hg-Cl} of 2.3399(16), 2.3411(13), and 2.8430(12) Å]. The other ones with a distorted octahedral environment [N−Hg−Cl, Cl−Hg−Cl, S−Hg−Cl, and N−Hg−S 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 S−Hg−S of 61.85(7)°] are surrounded by one N, two S, and three Cl atoms with d_{Hg-N} of 2.189(4) Å, d_{Hg-Cl} of 2.3366(12), 2.6381(12), and 3.041(4) Å, and d_{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 the framework.

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 mercury coordination networks with either $HgCl_2$ or 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 pyridyl-appended tectons **2**−**4** is currently under investigation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic table for **2**−**4** and **2**-$HgCl_2$−**4**-$HgCl_2$, a complete experimental section, solid-state structures of **2**, **3**, and **4**, and PXRD diagrams for **2** and **3**-$HgCl_2$. This material is available free of charge via the Internet at http://pubs.acs.org. The atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre as CCDC 926008−926013. The coordinates can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

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Notes

The authors declare no competing financial interest.

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