

## Molecular Tectonics: 1D Tubular Type and 3D Diamond Like Mercury(II) Coordination Polymers Based on Pyridyl Appended *p*-*tert*-Butyltetra-thiacalix[4]arene

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*Dedicated to Academician of Russian Academy of Sciences Oleg G. Sinyashin  
on the occasion of his 60<sup>th</sup> Anniversary*

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*1D Tubular-type and 3D diamond-like coordination polymers are formed upon combining pyridyl appended p-tert-butyltetra-thiacalix[4]arene in 1,3-alternate conformation tectons 4 and 5 with mercury(II) chloride.*

**Keywords:** Molecular tectonics, coordination polymer, tetrathiacalix[4]arene, mercury.

## Молекулярная тектоника: 1D тубулярная структура и 3D алмазоподобная структура координационных полимеров на основе взаимодействия тетразамещённых пиридинных производных *p*-*tert*-бутилтетратиакаликс[4]арена и катионов ртути(II)

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*Взаимодействие хлорида ртути(II) с тетразамещёнными пиридинными производными p-tert-бутилтетратиакаликс[4]арена 4 и 5 в конформации 1,3-альтернат привело к получению двух новых координационных полимеров: 1D тубулярного типа и 3D алмазоподобного типа.*

**Ключевые слова:** Молекулярная тектоника, координационный полимер, тетраатиакаликс[4]арен, ртуть.

## Introduction

*Molecular tectonics*<sup>[1]</sup> is a strategy dealing with the design and analysis of extended periodic architectures like molecular networks in the crystalline phase. This approach relies on concepts such as molecular recognition developed in supramolecular chemistry.<sup>[2]</sup> Thus, molecular networks are designed and generated through translations of recognition events taking place between molecular building blocks or *tectons*.<sup>[3]</sup> This strategy is a powerful approach for the design of crystalline periodic molecular architectures that may display functional features if the tectons possess of specific properties or if their arrangement in space leads to emergence of properties, such as porosity for example.

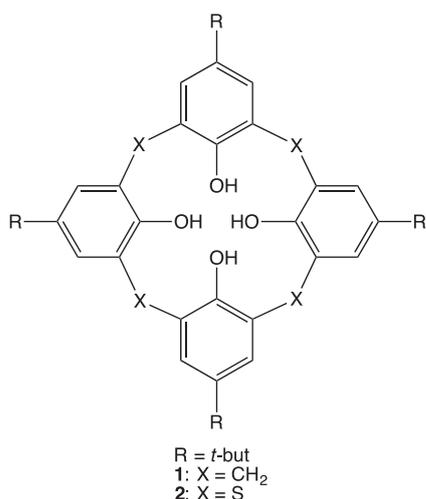
Coordination polymers,<sup>[4]</sup> a subclass of molecular networks, may be designed using concepts developed in molecular tectonics. Coordination networks are extended periodic assemblies resulting from the bridging by metal cations (or metal complexes as metallatectons) of coordinating organic tectons through establishment of coordination bonds. The rational design of coordination networks, still not completely mastered and operational, continues to attract considerable interest and requires

experimental investigations to unravel subtleties governing self-assembly processes.

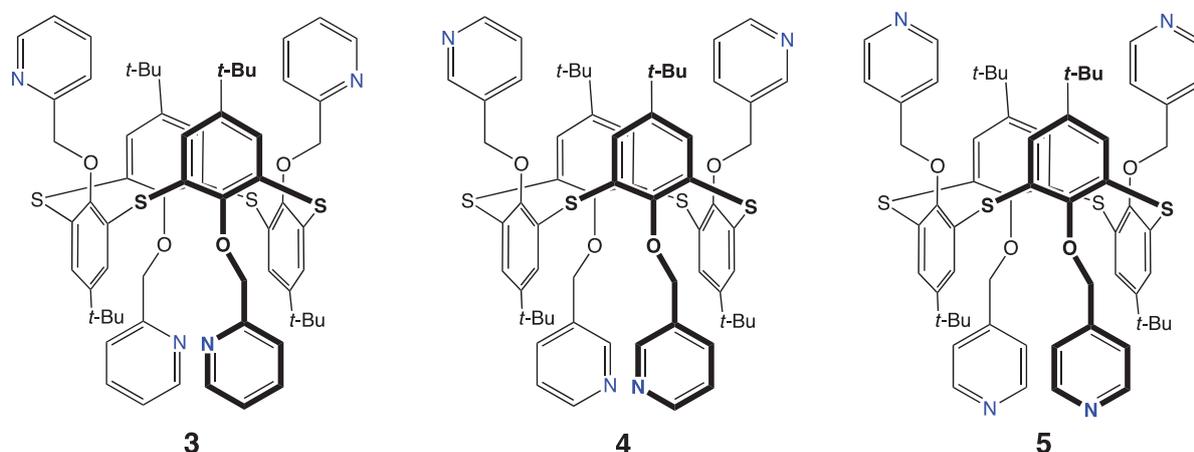
Calix[4]arene<sup>[5]</sup> (**1**, Figure 1), a macrocyclic organic entity, is composed of four phenol moieties connected by the CH<sub>2</sub>-groups. For steric reasons, this platform is not planar but adopts four limit conformations (cone, partial cone, *1,2-alternate* and *1,3-alternate*). Among these, the *1,3-alternate* conformer is particularly well suited for the design of coordinating tectons since such conformation allows to position up to four coordinating sites (two above and two below the main plane of the macrocyclic backbone). This design principle has been widely exploited for the generation of molecular networks variety, in particular, 1D-3D coordination networks based on combinations of calix[4]arene derivatives in cone or *1,3-alternate* conformation bearing coordinating groups such as cyano,<sup>[6]</sup> carboxyl,<sup>[7-9]</sup> thiocrown,<sup>[10-14]</sup> have been reported.

Thiocalix[4]arene (TCA) for which the bridging methylene groups are replaced by S atoms (**2**, Figure 1),<sup>[15]</sup> and tetramercaptothiocalixarenes (TMTCA) for which both the bridging methylene groups and the O atoms are replaced by S atoms,<sup>[16]</sup> are structural analogues of calix[4]arene. However, for both TCA and TMTCA, the presence of bridging S atoms not only leads to an enhancement of the size of the macrocycle cavity but also provides additional coordinating sites. Tetrasubstituted thiocalix[4]arene derivatives bearing cyano,<sup>[17-19]</sup> carboxyl,<sup>[20-22]</sup> pyridyl,<sup>[23-28]</sup> coordinating groups were combined with metal cations for the formation of coordination networks displaying a variety of dimensionalities (1D-3D). In contrast to CA, for these sulfur containing tectons, only the *1,3-alternate* conformation has been used. The tetrasubstitution of the *1,3-alternate* conformer leads to a S<sub>4</sub> symmetry in which the four coordinating sites occupy the apices of a tetrahedron. We have previously shown that TCA pyridyl based tectons **3**, **4**, **5** (Figure 2), differing by the position of the N atom on the pyridyl moiety, lead to the formation of silver coordination networks. Furthermore, it has been demonstrated that the dimensionality of the resulting network may be controlled either by the localization of the N atoms or by the nature of the counter ions.<sup>[23,27]</sup>

Here, we report on the preparation of two new coordination networks obtained by combining pyridyl TCA



**Figure 1.** Calix[4]arene (CA) **1** and thiocalix[4]arene (TCA) **2**.



**Figure 2.** Pyridyl TCA based tectons **3**, **4**, **5**.<sup>[23]</sup>

derivatives in *1,3-alternate* conformation **4** (N atom of the pyridyl in *meta* position) and **5** (N atom of the pyridyl in *para* position) (Figure 2) with  $\text{HgCl}_2$ , acting as V-shape two-connecting metallatecton.

## Experimental

Compounds **3**, **4**, **5** have been synthesized as previously reported.<sup>[23]</sup>

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

Data for X-ray analysis were collected at 173(2) K on a Bruker APEX8 CCD Diffractometer equipped with an Oxford Cryosystem liquid  $\text{N}_2$  device, using graphite-monochromated Mo-K $\alpha$  ( $\lambda = 0.71073$  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  $F^2$  using SHELXL-97. The hydrogen atoms were introduced at calculated positions and not refined (riding model).<sup>[29]</sup> They can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/datarequest/cif. CCDC: 1433709-1433710.

## Crystallisation Conditions

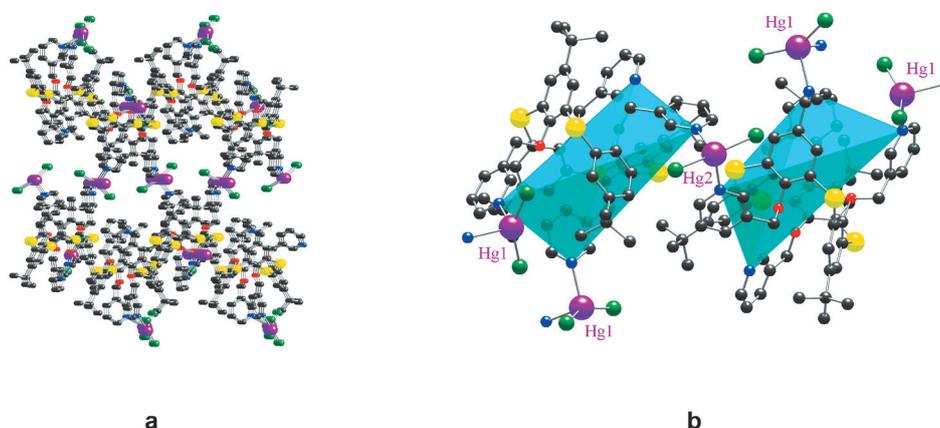
**4-HgCl<sub>2</sub>**: Formula  $\{\text{Hg}_3\text{Cl}_6(\text{C}_{64}\text{H}_{68}\text{N}_4\text{O}_4\text{S}_4)_2 \cdot 2(\text{CHCl}_3)\}$ . In a crystallization tube (4 mm diameter, 15 cm height), a solution of the compound **4** (5 mg, 0.0046 mmol) in  $\text{CHCl}_3$  (1 ml) was layered with a 1/1  $\text{CHCl}_3/\text{iso-PrOH}$  mixture (1 ml). A solution of  $\text{HgCl}_2$  (2.5 mg, 0.0092 mmol) in MeOH (1 ml) was carefully added. Slow diffusion at room temperature produced after one month colourless crystals suitable for X-ray diffraction studies. Found, %: C, 48.86; H, 4.35; N, 3.40.  $\text{Hg}_3\text{Cl}_6(\text{C}_{64}\text{H}_{68}\text{N}_4\text{O}_4\text{S}_4)_2(\text{CHCl}_3)_2$ . Calculated, %: C, 48.43; H, 4.31; N, 3.48.

**5-HgCl<sub>2</sub>**: Formula  $\{\text{Hg}_2\text{Cl}_4(\text{C}_{64}\text{H}_{68}\text{N}_4\text{O}_4\text{S}_4)_4 \cdot 4\text{CHCl}_3\}$ . In a crystallization tube (4 mm diameter, 15 cm height), a solution of compound **5** (5 mg, 0.0046 mmol) in  $\text{CHCl}_3$  (1 ml) was layered with a 1/1  $\text{CHCl}_3/\text{iso-PrOH}$  mixture (1 ml). A solution of  $\text{HgCl}_2$  (2.5 mg, 0.0092 mmol) in MeOH (1 ml) was carefully added. Slow diffusion at room temperature produced after *ca* one month colourless crystals suitable for X-ray diffraction studies. Found, %: C, 38.90; H, 3.55; N, 2.51.  $\text{Hg}_2\text{Cl}_4(\text{C}_{64}\text{H}_{68}\text{N}_4\text{O}_4\text{S}_4)(\text{CHCl}_3)_4$ . Calculated, %: C, 38.78; H, 3.45; N, 2.66.

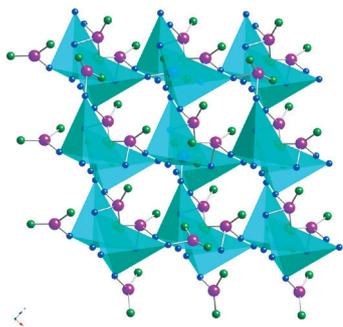
## Results and Discussion

With the aim of generating coordination networks, compounds **3**, **4**, and **5** (Figure 2) were combined under self-assembly conditions with  $\text{HgCl}_2$ . Although for compound **3** no crystalline material was obtained, for tectons **4** and **5**, colorless single crystals were obtained upon slow diffusion, through a  $\text{CHCl}_3/\text{iso-PrOH}$  layer, of MeOH solution of  $\text{HgCl}_2$  into a  $\text{CHCl}_3$  solution of **4** or **5** (see Experimental). X-Ray diffraction on single crystals revealed that whereas the use of the tecton **4** leads to the formation of the 3D mercury coordination network, for tectons **5** the 1D coordination networks is generated in the crystalline phase. In both cases,  $\text{Hg}^{2+}$  cation, adopting a distorted tetrahedral geometry with two of the four apices occupied by two  $\text{Cl}^-$  anions, behaves as a V-type two-connecting node.

As mentioned above, the combination of **4** with  $\text{HgCl}_2$  leads to a neutral 3D coordination polymer **4-HgCl<sub>2</sub>** ( $\{\text{Hg}_3\text{Cl}_6(\text{C}_{64}\text{H}_{68}\text{N}_4\text{O}_4\text{S}_4)_2 \cdot 2\text{CHCl}_3\}$ ) with a **4**/ $\text{Hg}$  ratio of 2/3 (Figure 3a, Table 2). **4-HgCl<sub>2</sub>** crystallizes in the *Fdd2* orthorhombic space group. Within the crystal, two crystallographically independent  $\text{Hg}^{2+}$  cations ( $\text{Hg1}$  and  $\text{Hg2}$ ) with the same distorted tetrahedron geometry and  $\text{N}_2\text{Cl}_2$  environment are present. For bond distances and angles, see Table 1. Both types of  $\text{Hg}^{2+}$  cations bridge two adjacent tectons **4** *via* the pendent pyridyl moieties. S atoms of **4** are not involved in the coordination with  $\text{Hg}^{2+}$  cations. Among the four coordinating pyridyl units, only three take part in the formation of the extended 3D architecture. Each neutral  $\text{HgCl}_2$  metallatecton is surrounded by two organic tectons **4** and each tecton **4** is surrounded by three  $\text{HgCl}_2$  units. The 3D diamond-like structure **4-HgCl<sub>2</sub>** may be described as: i) the generation of a “superpolyhedrons” resulting from the bridging of two adjacent tectons **4**, for which the N atoms of the pyridyl units occupy the apices of a distorted tetrahedron, by a  $\text{Hg2}$  type cation through N-Hg coordination bonds between the metal center and N atoms of the pyridyl moieties (Figure 3b); ii) the interconnection of “superpolyhedrons” through N-Hg bonds between the two remaining two pyridyl moieties of **4** with  $\text{Hg1}$  type cations (Figure 4). Although crystal of **4-HgCl<sub>2</sub>** contain two  $\text{CHCl}_3$  molecules occupying the pores,



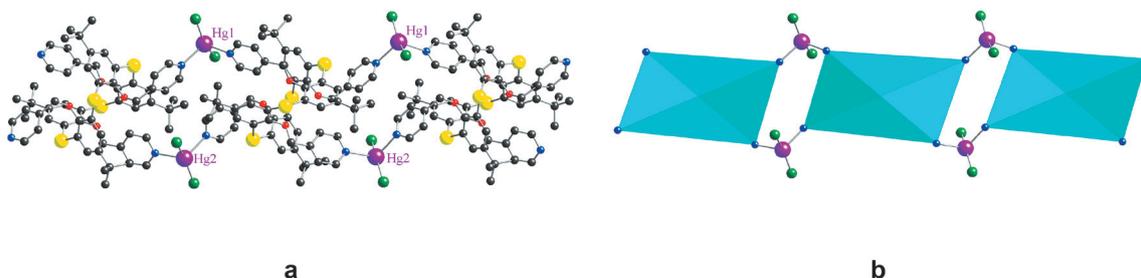
**Figure 3.** 3D coordination network **4-HgCl<sub>2</sub>** generated upon combining the organic tecton **4** and  $\text{HgCl}_2$  as a two connecting metallatecton: a) a portion of crystal structure; b) structure of a “superpolyhedron” resulting from the bridging of two tectons **4** by a  $\text{Hg1}$  type cation and the propensity of the subunit to bind  $\text{Hg1}$  type cations leading to the formation of the 3D architecture. Solvents molecules and H atoms are omitted for clarity.



**Figure 4.** Polyhedral representation of the crystal structure of the 3D diamond-like coordination polymer **4-HgCl<sub>2</sub>** in the xOz plane.

**Table 1.** Main characteristics (bond distances and angles) for **4-HgCl<sub>2</sub>** and **5-HgCl<sub>2</sub>**.

	<b>4-HgCl<sub>2</sub></b>	<b>5-HgCl<sub>2</sub></b>
d(Hg1-N <sub>py</sub> ), Å	2.395(10) 2.43(5)	2.398(4) 2.423(4)
d(Hg2-N <sub>py</sub> ), Å	2.414(7)	2.407(4) 2.414(4)
d(Hg1-Cl <sub>x</sub> ), Å	2.319(6) 2.380(5)	2.3565(15) 2.3892(14)
d(Hg2-Cl <sub>x</sub> ), Å	2.364(2)	2.3535(15) 2.3926(15)
∠(N <sub>py</sub> -Hg1-N <sub>py</sub> ), °	93.8(15)	107.79(14)
∠(N <sub>py</sub> -Hg2-N <sub>py</sub> ), °	89.0(3)	113.66(14)
∠(Cl <sub>x</sub> -Hg1-N <sub>py</sub> ), °	98.4(9) 95.5(3)	104.34(11) 94.84(11) 100.43(11) 93.30(11)
∠(Cl <sub>x</sub> -Hg2-N <sub>py</sub> ), °	99.74(19) 94.73(19)	100.90(12) 91.48(12) 102.93(11) 91.28(11)
∠(Cl <sub>x</sub> -Hg1-Cl <sub>y</sub> ), °	149.6(2)	151.54(6)
∠(Cl <sub>x</sub> -Hg2-Cl <sub>y</sub> ), °	159.67(11)	155.29(5)



**Figure 5.** 1D coordination polymer **5-HgCl<sub>2</sub>** obtained upon combining the organic tecton **5** and HgCl<sub>2</sub>: a) a portion of the crystal structure showing the presence of two crystallographically nonequivalent Hg atoms (Hg1 and Hg2) and their bridging role in the formation of the extended coordination network, b) a polyhedral representation of the tubular type architecture showing the bridging of consecutive tectons **5** by HgCl<sub>2</sub> metallatecton in the yOz plane. Solvents molecules and H atoms are omitted for clarity.

no specific interactions between them and the framework could be spotted.

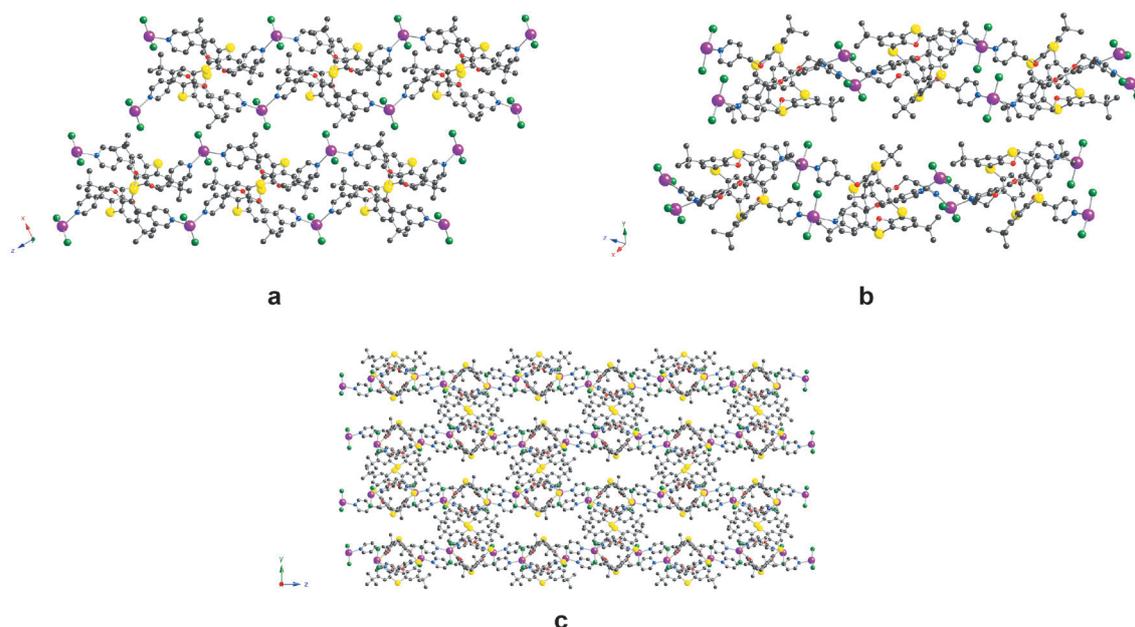
Unfortunately, probably owing to the loss of CHCl<sub>3</sub> solvents molecules, crystals of **4-HgCl<sub>2</sub>** were found to be unstable outside of the crystallization solution and thus all attempts to record the XRPD diagrams failed.

In marked contrast with the 3D architecture discussed above, tecton **5** (Figure 2), also bearing four pyridyl groups but differing from the tecton **4** by the position of the N atom on pyridyl units (*meta* in the case of **4** and *para* for tecton **5**), leads to the formation of a neutral 1D tubular type coordination polymer in the presence of HgCl<sub>2</sub> (Figure 5, Table 3). **5-HgCl<sub>2</sub>** ( $\{\text{Hg}_2\text{Cl}_4(\text{C}_{64}\text{H}_{68}\text{N}_4\text{O}_4\text{S}_4)4\text{CHCl}_3\}$ ) crystallizes in the P2<sub>1</sub>/n monoclinic space group. The crystal is composed of **5**, HgCl<sub>2</sub> and CHCl<sub>3</sub> molecules, with a 1/2 **5**/HgCl<sub>2</sub> ratio. Each HgCl<sub>2</sub> is surrounded by two organic tectons **5** and each tecton **5** is surrounded by four HgCl<sub>2</sub> units. In marked contrast with the above discussed 3D network **4-HgCl<sub>2</sub>**, all four pyridyl units belonging to tecton **5** participate in binding of neutral V-shaped HgCl<sub>2</sub> species *via* four N atoms of the divergently disposed pyridyl moieties.

As in the case of **4-HgCl<sub>2</sub>**, the two crystallographically independent Hg<sup>2+</sup> cations are adopting a distorted tetrahedral coordination geometry and are surrounded by two N atoms belonging to pyridyl moieties of the same tecton **5** and two chlorine anions (for bond distances and angles see Table 1). As in the previous case, the sulfur atoms of **5** do not interact with Hg<sup>2+</sup> cations. The tubular type architecture is analogous to previously reported studies on other macrocycle based tectons such as metacyclophanes,<sup>[30]</sup> or calixarenes<sup>[31]</sup> bearing monodentate binding sites. The same type of 1D network has been also obtained using pyridyl appended tetramercaptothiacalix[4]arene.<sup>[26]</sup>

In the crystal, the 1D networks are packed in a parallel fashion along (0,1,0) crystallographic plane and form layers (Figure 6a). The latter are stacked in an antiparallel fashion along the *b* axis (Figure 6b), leading thus to formation of square shaped channels along the *a* axis (Figure 6c). The latter are filled with CHCl<sub>3</sub> molecules without any specific interactions with the coordination network.

Again, as in the case of **4-HgCl<sub>2</sub>**, because of the instability of crystals in the air, no XRPD diagram of compound **5-HgCl<sub>2</sub>** could not be recorded at room temperature.



**Figure 6.** Crystal packing of **5-HgCl<sub>2</sub>**: a) parallel packing of 1D tubular networks, b) antiparallel arrangement of layers resulting from the packing of 1D networks along *b* axis, c) formation of square channels along *a* axis. Solvents molecules and H atoms are omitted for clarity.

**Table 2.** Crystal data for  $\{\text{Hg}_3\text{Cl}_6(\text{C}_{64}\text{H}_{68}\text{N}_4\text{O}_4\text{S}_4)_2 \cdot 2(\text{CHCl}_3)\} \cdot 4\text{-HgCl}_2$ .

Empirical formula	$\{\text{Hg}_3\text{Cl}_6(\text{C}_{64}\text{H}_{68}\text{N}_4\text{O}_4\text{S}_4)_2 \cdot 2(\text{CHCl}_3)\}$
Formula weight	3224.13
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	<i>Fdd2</i>
Unit cell dimensions	<i>a</i> = 22.2654(6) Å $\alpha$ = 90°. <i>b</i> = 69.809(2) Å $\beta$ = 90°. <i>c</i> = 19.4799(6) Å $\gamma$ = 90°.
Volume	30278.1(16) Å <sup>3</sup>
Z	8
Density (calculated)	1.415 Mg/m <sup>3</sup>
Absorption coefficient	3.408 mm <sup>-1</sup>
F(000)	12880
Crystal size	0.09×0.07×0.06 mm <sup>3</sup>
Theta range for data collection	1.42 to 30.09°.
Index ranges	-21 ≤ <i>h</i> ≤ 29, -98 ≤ <i>k</i> ≤ 97, -27 ≤ <i>l</i> ≤ 27
Reflections collected	136672
Independent reflections	21188 [R(int) = 0.0683]
Completeness to theta = 30.09°	97.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8216 and 0.7490
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	21188 / 31 / 770
Goodness-of-fit on F <sup>2</sup>	1.041
Final R indices [I > 2σ(I)]	R1 = 0.0770, wR2 = 0.2034
R indices (all data)	R1 = 0.1265, wR2 = 0.2286
Absolute structure parameter	0.042(7)
Largest diff. peak and hole	1.251 and -0.946 e·Å <sup>-3</sup>

**Table 3.** Crystal data for  $\{\text{Hg}_2\text{Cl}_4(\text{C}_{64}\text{H}_{68}\text{N}_4\text{O}_4\text{S}_4) \cdot 4\text{CHCl}_3\} \cdot 5\text{-HgCl}_2$ .

Empirical formula	$\{\text{Hg}_2\text{Cl}_4(\text{C}_{64}\text{H}_{68}\text{N}_4\text{O}_4\text{S}_4) \cdot 4\text{CHCl}_3\}$
Formula weight	2105.92
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P2(1)/n</i>
Unit cell dimensions	<i>a</i> = 14.6095(5) Å $\alpha$ = 90°. <i>b</i> = 21.1405(7) Å $\beta$ = 95.3600(10)°. <i>c</i> = 26.3307(9) Å $\gamma$ = 90°.
Volume	8096.7(5) Å <sup>3</sup>
Z	4
Density (calculated)	1.728 Mg/m <sup>3</sup>
Absorption coefficient	4.467 mm <sup>-1</sup>
F(000)	4144
Crystal size	0.09×0.06×0.06 mm <sup>3</sup>
Theta range for data collection	1.83 to 30.08°.
Index ranges	-20 ≤ <i>h</i> ≤ 20, -29 ≤ <i>k</i> ≤ 21, -37 ≤ <i>l</i> ≤ 35
Reflections collected	66564
Independent reflections	23486 [R(int) = 0.0776]
Completeness to theta = 30.08°	98.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7754 and 0.6893
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	23486 / 0 / 895
Goodness-of-fit on F <sup>2</sup>	1.088
Final R indices [I > 2σ(I)]	R1 = 0.0530, wR2 = 0.0906
R indices (all data)	R1 = 0.1098, wR2 = 0.1061
Largest diff. peak and hole	1.808 and -1.511 e·Å <sup>-3</sup>

## Conclusion

Combinations of tetrapyrrolyl appended thiacalix[4]-arene in *1,3-alternate* conformation **3–5** as coordinating organic tectons with HgCl<sub>2</sub>, a V-shape two-connecting metal-

latecton, were explored. Whereas no crystalline material could be obtained using the tecton **3**, the other two tectons **4** and **5** lead to the formation of neutral mercury coordination networks in the solid state. Tectons **3** (*ortho*), **4** (*meta*) and **5** (*para*) are positional isomers and differ by the position of the N atom on the pyridyl coordinating moiety. The dimensional-

ity of the extended architectures appears to be dependent on the localization of the N atom. Indeed, whereas tectons **4** leads to the formation of a neutral 3D diamond-like architecture, tectons **5** forms 1D tubular coordination network. Although for all three tectons **3–5**, one may impose the overall *1,3-alternate* conformation, these species are not rigid and thus may adopt different shapes. Furthermore, owing to the presence of -OCH<sub>2</sub> spacer used to connect the pyridyl units to the thiacalix backbone, tectons **3–5** may behave as different rotamers leading to a variety of orientation of the pyridyl coordinating sites, in particular in the case of tectons **3** (N atom at the *ortho* position) and **4** (N atom at the *meta* position). Consequently, for such flexible tectons, it is virtually impossible to predict the formation, the dimensionality as well as the geometry of coordination networks. For that reason, it is compulsory to experimentally investigate the formation of networks by exploring different metal centers and complexes as well as crystallization conditions.

Based on tectons **3–5**, the generation of other types of coordination networks using other metal cations or metallatectons is currently under investigation.

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