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Introduction

Coordination networks or MOFs are infinite periodic assemblies resulting from the interconnection of organic coordinating units by metal centres or metal complexes.¹ This type of molecular architecture is mainly generated in the solid state using self-assembly processes such as crystallisation. Since ca. two decades, coordination networks have been increasingly attracting attention as molecular materials owing to chemical (catalysis, separation, storage, porosity) and/or physical properties (electronics, optics, magnetism, etc.).² Thus, the design, formation and characterisation of coordination networks are of current interest.³ Molecular tectonics,⁴⁻⁶ an approach at the intersection between supramolecular and/or coordination chemistry, solid state and materials chemistry, deals with the design and/or analysis of molecular crystals for which the components are linked by reversible interactions. For this approach, molecular crystals are considered as periodic architectures composed of building blocks and nodes. Building blocks, called tectons, are active construction units operating by self-assembly processes⁷ and nodes, *i.e.* connecting points between tectons, are specific interaction patterns between

Molecular tectonics: pyridyl containing thiacalix[4]arene based tectons for the generation of 2- and 3-D silver coordination networks†

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Three new organic tectons (2–4) based on the *p-tert*-butylthiacalix[4]arene backbone, blocked in the 1,3alternate conformation, bearing four pyridyl coordinating moieties, have been synthesised and characterised in the solid state. The ligands are positional isomers and differ by the position of the N atom on the pyridyl unit (*ortho* for 2, *meta* for 3 and *para* for 4). Their combination with the Ag⁺ cation leads, reproducibly, to the formation of 2- and 3-D infinite silver coordination networks. Independent of the nature of the anion, the combination of 2 offering four (N,S) type chelates with the Ag⁺ cation affords an unprecedented diamond type 3D network. Both 3 and 4, behaving as tetrakis monodentate ligands, lead to the formation of 2-D architectures.

> tectons. Thus, molecular crystals may be described as molecular networks displaying translational symmetry which results from repetition of recognition processes.⁸ Coordination networks or coordination polymers¹ represent a particular class of hybrid molecular networks composed of two types of tectons, *i.e.* ligands offering at least two divergently disposed coordinating sites and metal centres or complexes displaying at least two divergently oriented free coordination sites. The interconnection between the two types of tectons is ensured by coordination processes. As stated above, the design of new coordination networks or explorations of combinations of new organic tectons and metal centres or complexes is a topic of current interest.

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Calix[4]arene is an interesting backbone for the design of receptors and ligands.9 Indeed, this cyclic molecule not only offers four phenolic units, but also, because of the non-planar nature of the macrocycle due to steric hindrance and owing to possible rotations around the CH₂ groups connecting the aromatic moieties, it adopts four distinct conformations (cone (C), partial cone (CP), 1,2-alternate (1,2-A) and 1,3-alternate (1,3-A)). However, for the unsubstituted derivative, the conformers interconvert in solution, although, owing to the formation of H-bonds between the OH groups, the cone conformer dominates in some solvents. Concerning the coordination ability of calix[4]arene derivatives to bind metal centres or main group elements, the cone conformer, offering four OH groups positioned on the same face of the macrocyclic backbone, was used for the preparation of discrete fused architectures based on Si,^{10a} Ti^{10b} or Si and Ti,^{10c} Al,^{10d} Zn,^{10e} Eu^{10f} or Nb.^{10g}

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As stated above, the calix[4]arene backbone may be equipped with peripheral coordinating sites. In particular, the 1,3-alternate conformer offering divergently oriented connecting sites is suitable for the generation of extended coordination networks. For example, an infinite 1D coordination network was generated in the crystalline phase by us upon a combination of a blocked 1,3-alternate conformer of calix[4]arene bearing four CN groups at the upper rim.¹¹ An example of an infinite 1D braided helical architecture based on the formation of H bonds between a blocked 1,3-alternate conformer of calix[4]arene bearing four pyridyl units and 4,4'-biphenol was also reported.¹²

The [1,1,1,1]-*metac*yclophane, an analogue of calix[4]arene inherently locked in the 1,3-alternate conformation for steric reasons, has been widely used by us for the formation of a variety of 1-, 2- and 3-D coordination networks.¹³

Thiacalix[4]arene^{9b,14} (TCA) is an analogue of calix[4]arene for which the CH₂ groups connecting the phenol moieties are replaced by S atoms. As for calix[4]arene, thiacalix[4]arene also displays the same four conformations in solution. In the crystalline phase, again as for the parent calix[4]arene, thiacalix[4]arene adopts the cone conformation.¹⁵ The main difference between the two molecules resides in the propensity of thiacalix[4]arene to bind metal centres.¹⁶ This feature has been first demonstrated by us¹⁷ and subsequently by others for discrete polynuclear metallic species.18 Furthermore, the formation of periodic infinite 1-, 2- and 3-D silver coordination networks using thiacalix[4]arene derivatives in the 1,3-alternate conformation bearing four nitrile groups,19 and carboxylate units²⁰ and four benzonitrile groups²¹ respectively have been reported by us. Another example of a 1D silver network based on a thiacalix[4]arene bearing ether groups has also been reported by others.²² Recently, the formation of periodic architectures resulting from combinations of thiacalix[4]arene derivatives in the 1,3-alternate conformation bearing carboxylate moieties, Co(II) salts and bispyridyl auxiliary ligands has been published.23

In this contribution, we report on the design, synthesis and structural characterisation of three new organic tectons 2-4 (Scheme 1) based on positional isomers of *p*-tert-butylthiacalix-[4]arene 1 locked in the 1,3-alternate conformation bearing



Scheme 1 *p-tert*-Butyl thiacalix[4]arene **1**, tectons **2–4** and a schematic representation of their 1,3-A conformation. The black and blue circles represent the connecting position of the pyridyl groups to the calix backbone and the OCH_{2^-} pyridyl unit respectively.

four pyridyl groups as coordinating sites and on 2- and 3-D coordination networks generated upon their combinations with different silver salts.

Experimental part

Characterization techniques

¹H-NMR and ¹³C-NMR spectra were recorded at room temperature on a Bruker (300 MHz) NMR spectrometer.

FT-IR spectra were recorded on a Perkin Elmer spectrometer.

Mass spectra (MS (ES⁺)) were obtained on a MALDI-TOF Dynamo Finnigan mass spectrometer using 1,8,9-trihydroxy-anthracene or p-nitroaniline as the matrix.

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

Single-crystal studies

Data were collected at 173(2) K on 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 F^2 using SHELXL-97. The hydrogen atoms were introduced at calculated positions and not refined (riding model).²⁴

Synthesis

General: All reagents were purchased from commercial sources and used without further purification. *p-tert*-Butylthiacalix[4]-arene **1** was prepared according to the literature.¹⁴

25,26,27,28-TETRA[(2-PYRIDYLMETHYL)OXY]-5,11,17,23-TETRA-TERT-BUTYL-2,8,14,20-TETRATHIACALIX[4]ARENE (2). A mixture of 2-(chloromethyl)pyridine hydrochloride (2.28 g, 13.9 mmol), Cs₂CO₃ (9.05 g, 27.7 mmol) and a catalytic amount of KI in dry acetone (150 mL) was stirred at room temperature for 1 h under argon. Then *p-tert*-butylthiacalix[4]arene 1 (0.5 g, 0.69 mmol) was added and the mixture was refluxed for 40 h under argon. After cooling, the reaction mixture was filtrated. The filtrate was evaporated to dryness. The yellow solid was precipitated by addition of acetonitrile (100 mL). This solid was recrystallised from the CH₂Cl₂-CH₃CN mixture (1/10, 100 mL) affording the pure product 2 (0.30 g, 46%) in the 1,3-A conformation.

mp = 270 °C (decomp.). ¹H-NMR (CDCl₃): δ = 0.84 (36H, s, t-Bu), 5.21 (8H, s, ArOCH₂), 6.66 (4H, d, Py–H), 7.09 (8H, s, Ar– H), 7.07 (4 H, t, Py–H), 7.36 (4H, m, Py–H), 8.49 (4H, d, Py–H). ¹³C-NMR (CDCl₃): δ = 31.2, 34.3, 71.7, 122.4, 128.6, 128.7, 137.1, 146.8, 148.7, 156.4, 157.9. FTIR (KBr): ν = 2963, 1590, 1571, 1476, 1431, 1266, 1086, 1026, 759 cm⁻¹. MS (MALDI-TOF), *m*/*z*: 1085.9 (calculated 1085.51). Anal. Calcd for C₆₄H₆₈N₄O₄S₄: C, 70.81%; H, 6.31%; N, 5.16%. Found: C, 70.07%; H, 6.35%; N, 5.12%. 25,26,27,28-TETRA[(3-PYRIDYLMETHYL)OXY]-5,11,17,23-TETRA-*TERT*-BUTYL-2,8,14,20-TETRATHIACALIX[4]ARENE (3). A mixture of *p*-tertbutylthiacalix[4]arene 1 (0.3 g, 0.416 mmol) with Cs₂CO₃ (1.36 g, 4.17 mmol) in dry acetone (40 mL) was refluxed for 2 h under argon. Then a solution of 3-(chloromethyl)pyridine [prepared by stirring 3-(chloromethyl)pyridine hydrochloride (0.85 g, 5 mmol) with Cs₂CO₃ (1.63 g, 5 mmol) in dry acetone (20 mL) at room temperature for 1 h under argon] was added with a catalytic amount of KI. The reaction mixture was refluxed for 14 h. After cooling, the solid was filtrated. The filtrate was evaporated and the yellow solid was precipitated by adding acetonitrile (40 mL) to the residue. This solid was recrystallised from the CH₂Cl₂-CH₃CN mixture (1/10, 50 mL) affording the pure product **3** (0.20 g, 50%) in 1,3-A conformation.

mp = 269 °C (decomp.). ¹H-NMR (CDCl₃): δ = 0.86 (36H, s, t-Bu), 5.19 (8H, s, ArO*CH2*), 7.03 (8H, s, Ar–*H*), 7.05 (4H, d, Py– *H*), 7.33 (4H, m, Py–*H*), 8.14 (4H, s, Py–*H*), 8.47 (4H, d, Py–*H*). ¹³C-NMR (CDCl₃): δ = 31.1, 34.3, 67.8, 123.2, 128.3, 128.5, 133.4, 135.1, 147.1, 148.7, 149.2, 155.7. FTIR (KBr): ν = 2961, 1594, 1577, 1479, 1424, 1264, 1087, 1016, 710 cm⁻¹. MS (MALDI-TOF), *m*/*z*: 1085.8 (calculated 1085.51). Anal. Calcd for C₆₄H₆₈N₄O₄S₄: C, 70.81%; H, 6.31%; N, 5.16%. Found: C, 69.96%; H, 6.32%; N, 5.21%.

25,26,27,28-Tetra[(4-pyridylmethyl)oxy]-5,11,17,23-tetra-tert-BUTYL-2,8,14,20-TETRATHIACALIX[4]ARENE (4). A mixture of p-tertbutylthiacalix[4]arene 1 (1.0 g, 1.38 mmol) and Cs₂CO₃ (9.0 g, 27.6 mmol) in dry acetone (100 mL) was refluxed for 2 h under argon. Then a catalytic amount of KI and a solution of 4-(chloromethyl)pyridine, prepared by stirring at room temperature and under argon a mixture of 4-(chloromethyl)pyridine hydrochloride (4.52 g, 27.6 mmol) and Cs₂CO₃ (9.0 g, 27.6 mmol) in dry acetone (50 mL) during 1 h, were added. The reaction mixture was stirred for 40 h at room temperature. The solid was filtrated and washed with hot chloroform (100 mL). The organic phase was evaporated to dryness. To the residue, methanol (5 mL), water (100 mL), acetonitrile (5 mL) and acetone (5 mL) were added. Upon standing overnight, a white solid was formed which was filtrated and washed with hot methanol (100 mL) affording the compound 4 in 1,2-A conformation (0.20 g, 13%). The filtrate was collected and evaporated to dryness affording the desired compound 4 in 1,3-A conformation (0.75 g, 50%).

Compound 4 in 1,2-A conformation: ¹H-NMR (CDCl₃): δ = 1.16 (36H, s, *t*-Bu), 4.65 (8H, s, ArO*CH2*), 6.45 (8H, d, Py–*H*), 7.31 (4H, d, Ar–*H*), 7.75 (4H, d, Ar–*H*), 8.12 (8H, d, Py–*H*).

Compound 4 in 1,3-A conformation: mp = 240 °C (decomp.). ¹H-NMR (CDCl₃): δ = 0.86 (36H, s, *t*-Bu), 5.12 (8H, s, ArO*CH2*), 6.87 (8H, d, Py–*H*), 7.11 (8H, s, Ar–*H*), 8.39 (8H, d, Py–*H*). ¹³C-NMR (CDCl₃): δ = 31.1, 34.3, 69.5 122.2, 128.8, 129.2, 146.6, 147.5, 149.7, 156.3. FTIR (KBr): ν = 2964, 1606, 1437, 1415, 1382, 1263, 1244, 1228, 1085, 1019, 993, 881, 820, 805, 800, 758, 731, 646 cm⁻¹. MS (MALDI-TOF), *m/z*: 1085.7 (calculated 1085.51). Anal. Calcd for C₆₄H₆₈N₄O₄S₄: C, 70.81%; H, 6.31%; N, 5.16%. Found: C, 69.89%; H, 6.59%; N, 4.89%.

Crystallisation conditions

2: 1.0 mL of methanol was mixed with a solution of compound 2 (5 mg, 4.6×10^{-3} mmol) in CHCl₃ (0.5 mL). Slow evaporation at room temperature produced, after one day, colourless crystals suitable for X-ray diffraction (3 mg, 60% yield).

3: 1.0 mL of methanol was mixed with a solution of compound 3 (5 mg, 4.6×10^{-3} mmol) in CH₂Cl₂ (0.5 mL). Slow evaporation at room temperature produced colourless crystals suitable for X-ray diffraction after one day (2.5 mg, 50% yield).

4: In a crystallization tube (20 × 4 mm), 1.0 mL of acetonitrile was carefully added to a solution of compound 4 (5 mg, 4.6×10^{-3} mmol) in CHCl₃ (0.5 mL). Slow diffusion at room temperature produced colourless crystals suitable for X-ray diffraction after 7 days (3 mg, 60% yield).

2-AgPF₆: In a crystallization tube $(20 \times 4 \text{ mm})$, a solution of compound 3 (5 mg, $4.6 \times 10^{-3} \text{ mmol}$) in CHCl₃ (1 mL) was layered with a CHCl₃-iso-PrOH (1/1) mixture (0.1 mL). A solution of AgPF₆ (2.3 mg, 9.2×10^{-3} mmol) in MeOH (1 mL) was carefully added. Slow diffusion at room temperature and in the dark produced colourless crystals suitable for X-ray diffraction after several days (2 mg, 26% yield). Anal. Calcd for (C₆₄H₆₈N₄O₄S₄)(AgPF₆)₂(H₂O)₂: C, 47.24%; H, 4.46%; N, 3.44%. Found: C, 48.18%; H, 4.78%; N, 3.68%.

2-AgSbF₆: In a crystallization tube (20×4 mm), a solution of compound 2 (5 mg, 4.6×10^{-3} mmol) in CHCl₃ (1 mL) was layered with a CHCl₃-iso-PrOH (1/1) mixture (0.1 mL). A solution of AgSbF₆ (3.2 mg, 9.2×10^{-3} mmol) in MeOH (1 mL) was carefully added. At room temperature, slow diffusion in the dark produced colourless crystals suitable for X-ray diffraction after several days (2.3 mg, 33% yield). Anal. Calcd for ($C_{64}H_{68}N_4O_4S_4$)(AgSbF₆)₂(H₂O)₂: C, 36.32%; H, 3.25%; N, 0.46%. Found: C, 36.56%; H, 3.40%; N, 0.52%.

2-AgBF₄: In a crystallization tube (20×4 mm), a solution of compound 2 (5 mg, 4.6×10^{-3} mmol) in CHCl₃ (1 mL) was layered with a CHCl₃-iso-PrOH (1/1) mixture (0.1 mL). A solution of AgBF₆ (1.8 mg, 9.2×10^{-3} mmol) in MeOH (1 mL) was carefully added. At room temperature, slow diffusion in the dark produced colourless crystals suitable for X-ray diffraction after several days (1.8 mg, 22% yield). Anal. Calcd for (C₆₄H₆₈N₄O₄S₄)(AgBF₄)₂(H₂O)₂: C, 47.24%; H, 4.45%; N, 3.44%. Found: C, 46.50%; H, 4.56%; N, 3.48%.

3-AgPF₆: In a crystallization tube $(20 \times 4 \text{ mm})$, a solution of compound 3 (5 mg, $4.6 \times 10^{-3} \text{ mmol}$) in CHCl₃ (1 mL) was layered with a CHCl₃-iso-PrOH (1/1) mixture (0.1 mL). A solution of AgPF₆ (2.3 mg, $9.2 \times 10^{-3} \text{ mmol}$) in MeOH (1 mL) was carefully added. Slow diffusion in the dark at room temperature produced colourless crystals suitable for X-ray diffraction after several days (2.6 mg, 30% yield). Anal. Calcd for (C₆₄H₆₈N₄O₄S₄)(Ag(PF₆))₂(H₂O)_{0.5}(CHCl₃)₂: C, 43.11%; H, 3.89%; N, 3.05%. Found: C, 43.33%; H, 4.20%; N, 3.05%.

3-AgSbF₆: In a crystallization tube (20×4 mm), a solution of compound 3 (5 mg, 4.6×10^{-3} mmol) in CHCl₃ (1 mL) was layered with a CHCl₃-iso-PrOH (1/1) mixture (0.1 mL). A solution of AgSbF₆ (3.2 mg, 9.2×10^{-3} mmol) in MeOH (1 mL) was carefully added. Slow diffusion in the dark at room

temperature produced colourless crystals suitable for X-ray diffraction after several days (2 mg, 25% yield). Anal. Calcd for $(C_{64}H_{68}N_4O_4S_4)(AgSbF_6)_2(CHCl_3)_{4.5}$: C, 36.32%; H, 3.25%; N, 0.46%. Found: C, 36.56%; H, 3.40%; N, 2.52%.

3-AgBF₄: In a crystallization tube $(20 \times 4 \text{ mm})$, a solution of compound 3 (5 mg, 4.6×10^{-3} mmol) in CHCl₃ (1 mL) was layered with a CHCl₃-iso-PrOH (1/1) mixture (0.1 mL). A solution of AgBF₄ (1.8 mg, 9.2×10^{-3} mmol) in MeOH (1 mL) was carefully added. Slow diffusion in the dark at room temperature produced colourless crystals suitable for X-ray diffraction after several days (2.4 mg, 28% yield). Anal. Calcd for (C₆₄H₆₈N₄O₄S₄)(AgBF₄)₂(CHCl₃)_{3.5}(H₂O)_{0.5}: C, 42.63%; H, 3.84%; N, 2.94%. Found: C, 42.61%; H, 4.18%; N, 3.05%.

4-AgPF₆: In a crystallization tube (20×4 mm), a solution of compound 4 (5 mg, 4.6×10^{-3} mmol) in a CHCl₃–DMF mixture (1/1) (1 mL) was layered with a DMF–MeOH (1/1) mixture (0.2 mL). A solution of AgPF₆ (2.3 mg, 9.2×10^{-3} mmol) in MeOH (1 mL) was carefully added. Slow diffusion in the dark at room temperature produced colourless crystals suitable for X-ray diffraction after several days (2.5 mg, 29% yield). Anal. Calcd for ($C_{64}H_{68}N_4O_4S_4$)AgPF₆·CHCl₃·C₃H₇NO·CH₃OH: C, 53.03%; H, 5.16%; N, 4.48%. Found: C, 51.64%; H, 4.96%; N, 4.32%.

Results and discussion

The aim of this investigation was to explore the role played by the connecting position of the pyridyl group (*ortho*, *meta* and *para* for 2, 3 and 4 respectively) to the *p-tert*-butylthiacalix[4]arene backbone on the connectivity and dimensionality of silver coordination networks generated under self-assembly conditions. In particular, owing to the proximity of the N atom of the pyridyl groups to the S atoms connecting the aromatic moieties of the calix platform in tecton 2, one may expect a chelate effect resulting from the simultaneous binding of the cation by both N and S atoms.

The design of tectons 2-4 (Scheme 1) is based on the p-tertbutylthiacalix[4]arene backbone 1 locked in the 1,3-alternate conformation bearing four pyridyl units as monodentate coordinating sites. The imposed conformation allows locating the binding sites above and below the main plane of the macrocyclic platform in an alternate manner. This divergent disposition is suitable for the generation of coordination networks through interconnection of consecutive metal centres offering free coordination sites. Tectons 2-4 are positional isomers and differ only in the position of the connection between pyridyl units and the thiacalix backbone (ortho, meta and para for 2, 3 and 4 respectively). The junction between both parts is ensured by ether groups. We have previously reported the synthesis and structural analyses of different conformers of thiacalix[4]arene²⁵ and tetramercaptothiacalix[4] arene²⁶ bearing four pyridyl groups (*ortho* and *meta* positions) using ester junctions.²⁷ The synthesis of calix[4]arene analogues of compounds 2-4 has been published²⁸ and only discrete complexes have been reported.29



Fig. 1 Schematic representations of the six extreme possible rotamers of **2** locked in 1,3-alternate conformation. The extreme rotamers differ by the orientation of the N atoms of the pyridyl units towards the interior (i) or exterior (o) of the backbone. The same holds for compound **3**.

It is worth noting that for all three tectons 2–4, the 1,3-alternate conformation is imposed by construction, owing to the ether junctions connecting the pyridyl coordinating units to the thiacalix backbone. However, depending on the orientation of the pyridyl groups, both compounds 2 and 3 may exist as six different rotamers ($X_{i,i,i,i}$, $X_{i,i,i,o}$, $X_{i,o,o,o}$, $X_{i,o,i,o}$ and $X_{o,o,o,o}$, with X = 2 or 3) (Fig. 1). In solution, owing to the non-hindered rotation around the single C–O bond, these rotamers freely interconvert, whereas in the crystalline phase and in the presence of connecting metal centres, depending on the orientation of the pyridyl coordinating sites, different connectivity patterns and thus architectures may be formed.

Ligands 2–4 were obtained in 46%, 50% and 50% yield respectively upon condensation in dry acetone of *p-tert*butylthiacalix[4]arene 1, prepared following a published procedure,¹⁴ with X-(chloromethyl)pyridine hydrochloride (X = 2 for 2, 3 for 3 and 4 for 4) under alkaline conditions using Cs_2CO_3 . For compounds 2 and 3, the condensation was performed under reflux, whereas for compound 4, it was performed at room temperature. In the latter case, both 1,3alternate and 1,2-alternate conformers were obtained. Owing to the low solubility of the 1,2-alternate conformer in MeOH, the pure 1,3-A conformer could be obtained by simple filtration. The synthesis of conformers of compounds 2 and 4 has already been described using refluxing THF.³⁰ However under these reactions, the cone and 1,2-alternate conformers were isolated.

Structural investigations of the free tectons 2-4

Solid state structures of free tectons 2–4 were studied using X-ray diffraction methods on single crystals (crystallographic Tables 1 and 2). The latter were obtained upon slow diffusion of MeOH into a CHCl₃ solution of 1–3 (see the experimental section).

Formula	2 C ₆₄ H ₆₈ N ₄ O ₄ S ₄ ·(CH ₃ OH) ₂	$\begin{array}{l} 2\text{-}AgPF_{6} \\ C_{32}H_{34}N_{2}O_{2}S_{2}\text{-}Ag\text{-} \\ (PF_{6})\text{-}(H_{2}O) \end{array}$	$\begin{array}{l} \textbf{2-AgBF}_4\\ C_{32}H_{34}N_2O_2S_2\textbf{\cdot}Ag\textbf{\cdot}(BF_4)\textbf{\cdot}(H_2O) \end{array}$	$\begin{array}{l} \textbf{2-AgSbF}_6\\ C_{32}H_{34}N_2O_2S_2\textbf{\cdot}Ag\textbf{\cdot}(SbF_6)\textbf{\cdot}(H_2O) \end{array}$
Molecular weight	1149.55	1627.18	755.43	904.37
Crystal system	Monoclinic	Tetragonal	Tetragonal	Tetragonal
Space group	C2/c	$I\bar{4}2d$	I42d	I42d
a (Å)	22.5022(14)	23.7715(9)	23.2001(5)	24.1812(17)
b (Å)	19.9845(12)	23.7715(9)	23.2001(5)	24.1812(17)
c (Å)	28.2241(18)	14.1007(5)	14.3622(3)	13.9842(10)
α (°)	90	90	90	90
$\beta(\circ)$	107.0190(10)	90	90	90
γ (°)	90	90	90	90
$V(Å^3)$	12136.4(13)	7968.1(5)	7730.4(3)	8177.0(10)
Z	8	8	8	8
Colour	Colourless	Colourless	Colourless	Colourless
Crystal dim (mm ³)	0.11 imes 0.08 imes 0.05	$0.09 \times 0.07 \times 0.06$	0.07 imes 0.06 imes 0.05	0.06 imes 0.05 imes 0.04
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.258	1.356	1.298	1.469
F(000)	4896	3312	3088	3600
$\mu (\mathrm{mm}^{-1})$	0.211	0.710	0.679	1.299
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Number of data meas.	31 654	37 022	43 137	32 754
Number of data with $I > 2\sigma(I)$	13979[R(int)=0.0571]	5599 [R(int) = 0.0677]	5685 [R(int) = 0.0585]	5763 [R(int) = 0.1184]
R	$R_1 = 0.0814,$	$R_1 = 0.0957,$	$R_1 = 0.0931,$	$R_1 = 0.1316,$
	$wR_2 = 0.2011$	$wR_2 = 0.2846$	$wR_2 = 0.2705$	$wR_2 = 0.3527$
R _w	$R_1 = 0.1545,$	$R_1 = 0.1194,$	$R_1 = 0.1358,$	$R_1 = 0.2252,$
	$wR_2 = 0.2418$	$wR_2 = 0.3051$	$wR_2 = 0.3056$	$wR_2 = 0.3868$
GOF	1.022	1.153	1.107	1.002

Table 1 Crystallographic parameters recorded at 173 K for 2, 2-AgPF₆, 2-AgBF₄ and 2-AgSbF₆

In agreement with solution NMR studies, all three compounds adopt the 1,3-alternate conformation in the crystalline phase. Whereas crystals of compounds 2 (Fig. 2a) and 4 (Fig. 2c) are solvates and contain MeOH and CHCl₃ molecules respectively, for compounds 3 (Fig. 2b) no solvent molecule is found in the crystal (see crystallographic Tables 1 and 2). Compounds 2 and 4 present two and one disordered *tert*-butyl groups respectively. For all three derivatives 2–4, the C–O_{Phenol} and C–S distances are in the 1.3704(4)–1.456(5) and 1.770(4)– 1.780(4) Å range respectively. Whereas for 2, the methanol molecule is H-bonded to the N atom of one of the pyridyl units $(d_{N-O} = 2.836(4) Å)$, for 4, no specific interactions with the chloroform molecule are detected.

In the crystalline phase, whereas compound 2 is present as its $2_{o,o,o,o}$ rotamer, in contrast, compound 3 is present as its $3_{i,i,i,i}$ rotamer (Fig. 1).

The description of the localisation and orientation of the N atoms of the pyridyl units may be done by considering the polyhedron formed by the four N atoms. In the solid state, the polyhedron for 2 is close to a deformed tetrahedron (Fig. 2a), whereas for the other two compounds 3 (Fig. 2b) and 4 (Fig. 2c) the adopted geometry is closer to a deformed rectangle. Interestingly, when combined with the silver cation, it seems that the shape of the polyhedron is rather conserved (see below).

Structural investigations of coordination networks formed between the silver cation and tectons 2–4

The propensity of all three tectons 2-4 to form coordination networks was explored using the silver cation. The choice of the latter, a d^{10} cation, was based on its rather loose coordination demand both in terms of coordination number and geometry. In order to study the reproducibility of generated architectures and the role played by the anion on the type of connectivity between the organic tecton and the cation,³¹ different silver salts (AgX (X = BF₄, PF₆ or SbF₆)) have been used for 2 and 3. For 4, only the PF₆⁻ anion was used.

For all three tectons 2–4, suitable crystals have been obtained at room temperature upon slow liquid–liquid diffusion of either a CH_2Cl_2 or $CHCl_3$ solution containing the organic tecton and a CH_3OH , DMF or H_2O solution of the silver salt (see the experimental section). Structural studies have been performed by X-ray diffraction techniques on single crystals (crystallographic Tables 1 and 2).

Since for all structures, C–C, C–O and C–S bond distances were close to those observed for the free tectons 2–4, they will not be discussed.

2-AgX (X = BF_4 , PF_6 and SbF_6)

Interestingly, independent of the nature of the anion, in all three cases, structural investigations revealed the formation of an unprecedented diamond type 3-D silver coordination network crystallising in the same space group and displaying similar connectivity patterns between 2 and the Ag⁺ cation.

For 2-AgBF₄, the crystal is composed of the neutral tecton 2, Ag^+ cations, one BF_4^- anion and water molecules. The tecton $2/Ag^+$ stoichiometry is 1/2. The silver cation acts as a V shaped connector between two adjacent tectons 2. The latter, offering four chelating units each composed of one N and one S atom, binds four Ag^+ cations. This connectivity between tectons 2 and silver cations leads to the formation of a diamond type network (Fig. 3).

Table 2	Crystallographic parameters	recorded at 173 K for 3	, 4 and for 3 -AgPF ₆	, 3-AgBF ₄ , 3-AgSbF ₆ and 4-AgPF ₆
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Formula	$3 \ C_{64} H_{68} N_4 O_4 S_4$	$\begin{array}{l} 3\text{-}AgPF_{6}\ (C_{64}H_{68}N_{4}O_{4}S_{4})_{4} \\ Ag_{8}(PF_{6})_{8}\text{\cdot}(H_{2}O)_{2}\text{\cdot}(CHCl_{3})_{8} \end{array}$	$\begin{array}{l} \textbf{3-AgBF}_4 \ (C_{64}H_{68}N_4O_4S_4)_2 \\ (AgBF_4)_4 \cdot (CHCl_3)_7 \cdot (H_2O)_3 \end{array}$	$\begin{array}{l} \textbf{3-AgSbF}_6(C_{64}H_{68}N_4O_4S_4)_8 \cdot \\ (AgSbF_6)_{16} \cdot (CHCl_3)_{36} \end{array}$	$\begin{array}{c} 4 \\ \mathbf{C}_{64}\mathbf{H}_{68}\mathbf{N}_4\mathbf{O}_4\mathbf{S}_4{\boldsymbol{\cdot}}\mathbf{CHCl}_3 \end{array}$	4-AgPF ₆ ($C_{64}H_{68}N_4O_4S_4$) AgPF ₆ ·CHCl ₃ ·C ₃ H ₇ NO·CH ₃ OH		
Molecular weight	1085.46	7355.55	3853.30	18482.91	1204.83	1562.81		
Crystal system	Tetragonal	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic		
Space group	I4(1)/a	Сс	P2(1)/c	P2(1)/c	$P\bar{1}$	P2(1)/n		
a(Å)	19.446(2)	27.8405(11)	22.6083(13)	27.5820(9)	11.0521(2)	14.8181(3)		
b (Å)	19.446(2)	14.2705(4)	28.6805(14)	28.4143(7)	14.4897(3)	32.1705(6)		
c (Å)	15.0141(16)	22.4525(6)	27.2831(13)	25.5819(9)	0.2847(4)	15.1669(3)		
$\alpha(\circ)$	90	90	90	90	79.7800(10)	90		
$\beta(\circ)$	90	102.331(2)	100.757(2)	108.6540(10)	88.9880(10)	93.7100(10)		
γ (°)	90	90	90	90	74.2200(10)	90		
$V(Å^3)$	1085.46	8714.5(5)	17380.0(16)	18995.9(10)	3074.80(10)	7215.0(2)		
Z	4	1	4	1	2	4		
Colour	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless		
Crystal dim (mm ³)	0.11 imes 0.09 imes 0.09	$0.07 \times 0.06 \times 0.05$	0.08 imes 0.06 imes 0.05	$0.09 \times 0.07 \times 0.06$	0.12 imes 0.09 imes 0.08	0.08 imes 0.08 imes 0.06		
D_{calc} (g cm ⁻³)	1.270	1.402	1.473	1.616	1.301	1.439		
F(000)	2304	3716	7792	9132	1268	3232		
$\mu (mm^{-1})$	0.219	0.835	0.933	1.504	0.336	0.598		
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073		
Number of data	6235	52 532	199 983	202 931	46 446	84 333		
meas.								
Number of data	3047 [R(int) = 0.0313]	$20\ 104\ [R(int) = 0.0568]$	50328[R(int)=0.0992]	51700[R(int)=0.1033]	14517[R(int)=0.0276]	20904[R(int)=0.0364]		
with $I > 2\sigma(I)$								
R	$R_1 = 0.0669,$	$R_1 = 0.0895,$	$R_1 = 0.1203,$	$R_1 = 0.0952, wR_2 = 0.2517$	$R_1 = 0.0775,$	$R_1 = 0.0608,$		
	$wR_2 = 0.1387$	$wR_2 = 0.2517$	$wR_2 = 0.2682$	1 , 2	$wR_2 = 0.2103$	$wR_2 = 0.1664$		
R_{w}	$R_1 = 0.0779,$	$R_1 = 0.1566,$	$R_1 = 0.2355,$	$R_1 = 0.2189, wR_2 = 0.3034$	$R_1 = 0.1003,$	$R_1 = 0.0831,$		
	$wR_2 = 0.1449$	$wR_2 = 0.3078$	$wR_2 = 0.3059$. , 2	$wR_2 = 0.2299$	$wR_2 = 0.1833$		
GOF	1.076	1.130	1.042	1.061	1.097	1.026		



Fig. 2 The solid state structures of **2** (left), **3** (middle) and **4** (right) showing the adopted 1,3-A conformation and the polyhedron formed by the four N atoms of the pyridyl units. H atoms, solvent molecules and disordered *tert*-butyl groups for compounds **2** and **4** are not presented for clarity. For bond distances and angles see text.



Fig. 3 A portion of the 3D diamond type architecture generated upon combining tecton **2** with AgBF₄ salt showing the connectivity pattern between consecutive tectons **2** and Ag⁺ cations, the surrounding of the latter and BF₄⁻ anions which were found to be disordered over two positions. H atoms and water molecules are not represented for clarity. For bond distances and angles see text.

A more detailed analysis revealed that the Ag⁺ cation is penta-coordinated with its coordination sphere composed of two N atoms ($d_{AgN} = 2.294(7)$ Å) of two pyridyl moieties and two S atoms ($d_{AgS} = 2.8784(18)$ and 2.8785(18) Å) belonging to two consecutive tectons 2, and a F atom of the BF₄⁻ anion ($d_{AgF} = 2.317(11)$ Å). The cation adopts a distorted trigonal bipyramidal coordination geometry (NAgN, SAgS and NAgF angles of 114.1(4), 157.51(7) and 122.95(18)° respectively) (Fig. 3). The water molecule present in the crystal is not interacting with the cation ($d_{AgO} =$ 3.642(7) Å).

The diamond type architecture displays two types of channels: a rather restricted square type formed by the thiacalix[4]arene backbone and a larger one resulting from the interconnection of consecutive tectons 2 by silver cations. The large channels are partially occupied by BF_4^- anions and water molecules.

Since the structures of $2\text{-}AgPF_6$ and $2\text{-}AgSbF_6$ are rather similar, only the latter case will be discussed hereafter. However, it should be noted that for $2\text{-}AgPF_6$, the metallic cations and the water molecules were found to be disordered over two positions.



Fig. 4 A portion of the diamond type architecture generated upon combining tecton **2** with AgSbF₆ showing the connectivity pattern between consecutive tectons **2** and Ag⁺ cations, the coordination sphere around the cation and the localisation of SbF₆⁻ anions. H atoms are not represented for clarity. For bond distances and angles see text.

For 2-AgSbF₆, except for the substitution of BF₄⁻ by the SbF₆⁻ anion, the composition of the crystal and the tecton/ metal ratio are the same as for 2-AgBF₄ (Fig. 4). However, in the present case, the water molecule is bound to the metal centre. The coordination sphere around the Ag⁺ cation is thus composed of two N atoms ($d_{AgN} = 2.247(8)$ Å) of two pyridyl moieties and two S atoms (with a rather Ag–S distance of 3.261(14) Å) belonging to two consecutive tectons 2, and an O atom of the water molecule ($d_{AgO} = 2.426(18)$ Å).

3-AgX ($X = BF_4$, PF_6 and SbF_6)

The three crystalline materials differ by their solvent contents. Indeed, whereas for 3-AgBF₄ and 3-AgPF₆, the crystal contains both CHCl₃ and H₂O molecules, for 3-AgSbF₆, only CHCl₃ molecules are present in the lattice. For 3-AgBF₄, one of the two crystallographically independent BF_4^- anions is disordered over two positions (Fig. 5a). For both 3-AgPF₆ and 3-AgSbF₆, one of the crystallographically independent XF_6^- anions is also disordered over two positions (Fig. 5b and c). Interestingly, again as in the case of tecton 2 discussed above, independent of the nature of the anion, the combination of tecton 3 with the silver cation leads to the formation of 2-D networks with similar connectivity patterns (see Fig. 5 and crystallographic Table 2).

Owing to the similarity between the three cases, only the detailed description of 3-AgPF₆ is given below.

The crystal is composed of the neutral ligand 3, Ag^+ cations, PF_6^- anions, water and chloroform molecules. The $3/Ag^+$ ratio is 1/2. Each Ag^+ cation is bound to two N atoms of pyridyl moieties belonging to two adjacent tectons 3. Each tecton 3 is linked to four Ag^+ cations (Fig. 5b). The silver cation is tris coordinated adopting a T type coordination geometry and behaves as a linear connector. Its coordination sphere is composed of two N atoms (d_{Ag-N} of 2.083(10), 2.124(11), 2.136(12) and 2.137(9) Å) and one O



Fig. 5 Portions of 2-D networks generated upon combining tecton **3** with AgBF₄ (a), AgPF₆ (b) and AgSbF₆ (c) showing the connectivity between consecutive tectons **3** and Ag⁺ cations, the coordination sphere around the Ag⁺ cation and the localisation of anions. H atoms and CHCl₃ solvent molecules are not represented for clarity. For bond distances and angles see text.

atom of a water molecule ($d_{Ag-O} = 2.723(10)$ Å). The O and S heteroatoms of tecton 3 do not interact with the cation. The overall connectivity described above leads to the formation of 2D silver coordination networks displaying rectangular type cavities filled with chloroform molecules and PF₆⁻ anions.

Consecutive sheets are packed along the *z* axis with an antiparallel arrangement (Fig. 6). The same type of packing is observed for 3-AgBF₄ and 3-AgSbF₆.



Fig. 6 A portion of the structure of 3-AgPF₆ showing the packing of consecutive 2-D networks. H atoms, SbF₆⁻ anions and CHCl₃ solvent molecules are not represented for clarity.

4-AgPF₆

The crystal is composed of the neutral ligand 4, the Ag⁺ cation, the PF₆⁻ anion, methanol and DMF molecules coordinated to the Ag⁺ cation and chloroform molecules without any specific interaction with the framework. The tecton/Ag⁺ stoichiometry is 1/1. In marked contrast with 3, for which all four pyridyl units are involved in the connectivity pattern between the organic and metallic tectons, the ligand 4 behaves as a tri-connecting tecton, *i.e.* among its four coordinating pyridyl units, only three participate in the formation of the coordination network (Fig. 7). Each silver cation is bound to three tectons 4. The cation is tetra-coordinated with a strongly distorted tetrahedral coordination geometry. Its coordination sphere is composed of three N atoms of pyridyl moieties belonging to three different tectons 4 (d_{Ag-N} of 2.234(3), 2.303(3) and 2.457(3) Å) and an O atom of a DMF molecule (d_{Ag-O} of 2.553(3) Å). However, the methanol molecule present in the crystal is located in the proximity of the cation with a d_{Ag-O} distance of 3.000(3) Å. As in the case of 3, the O and S heteroatoms of tecton 4 are not involved in any type of interaction with the cation. The connectivity pattern described above leads to the formation of a porous 2-D cationic silver coordination network (Fig. 7a). The empty space is occupied by PF_6^- anions, MeOH and CHCl3 molecules.

The 2D networks are packed as parallel eclipsed stacks along the [101] plane, as shown in Fig. 7b.

Conclusions

The new organic tectons 2–4 are positional isomers based on the *p-tert*-butylthiacalix[4]arene, in the 1,3-alternate conformation, bearing four pyridyl coordinating moieties. They differ by the position of the N atom on the pyridyl unit (*ortho* for 2, *meta* for 3 and *para* for 4). Among the three tectons, owing to the proximity between N and S atoms, only the compound 2 may behave as a tetrakis N,S type chelate. The other two tectons 3 and 4 should act as tetrakis monodentate units. Depending on the localisation of the N atom on the pyridyl unit, the combination of tectons 2–4 with the Ag⁺ cation leads to the formation of 2- and 3-D infinite coordination networks.



Fig. 7 A portion of the crystal structure of the **4**-AgPF₆ 2-D silver coordination network showing (a) the connectivity, the surrounding of the silver cations and the localisation of anions and MeOH molecules and (b) the packing of consecutive 2D sheets along the [101] plane. H atoms and CHCl₃ solvent molecules are not presented for clarity. For bond distances and angles see text.

As expected, tecton 2, behaving as a tetrakis chelate, leads to the formation of a diamond type 3D network, unprecedented for calix based tectons. The formation of the latter is independent of the nature of the anion (BF_4^- , PF_6^- or SbF_6^-), showing thus the robustness of the connectivity pattern (Fig. 8).

In principle, both tectons 3 and 4 should behave as tetrakis monodentate entities. However, to our surprise, whereas tecton 3 behaves as a 4 connecting tecton (Fig. 9), for tecton 4, only three out of the four pyridyl units participate in the connectivity pattern between the organic tecton and silver cations (Fig. 10).

Unfortunately, for all reported cases, the crystalline materials are not stable outside of the solvent systems used for their formation. This was demonstrated by XRPD and TGA investigations which revealed a slow transformation of crystals in air and upon increasing the temperature. Using the same tectons, the formation of other types of coordination networks using other metal cations and complexes is currently under investigation.

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Fig. 8 A simplified presentation of a portion of the diamond type architecture generated upon combining tecton **2** with $AgSbF_6$ showing the connectivity pattern between consecutive tectons **2** and Ag^+ cations. The 3-D architecture results from interconnection of consecutive tectons **2** behaving as a tetrahedral building block by silver cations acting as a V shaped connector.



Fig. 9 A simplified presentation of a portion of the 2-D network generated upon combining tecton **3** with AgSbF₆ showing the connectivity pattern between consecutive tectons **3** and Ag⁺ cations. The formation of the sheet type architecture results from interconnection of consecutive tectons **3** behaving as a strongly deformed tetrahedral four connecting node by silver cations acting as an almost linear connector.



Fig. 10 A simplified presentation of a portion of the 2-D network generated upon combining tecton **4** with $AgPF_6$ showing the connectivity pattern between consecutive tectons **4** and Ag^+ cations. The formation of the 2-D architecture results from interconnection of consecutive tectons **4** behaving as a three connecting node by silver cations acting as a V shaped connector.

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