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ARTICLE TYPE

Molecular tectonics: generation of grid and porous diamondoid coordination networks by combining metal halides with tetrathiacalix[4]arene and tetrathiatetramercaptothiacalix[4]arene pyridyl appended tectons

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Combinations of neutral tetrakis *meta*-pyridyl appended calix[4]arene derivatives in 1,3-A conformation as tectons **3** (Tetrakis-*meta*-pyridyl-tetrathiacalix[4]arene) and **4** (Tetrakis-*meta*-pyridyltetrathiatetramercaptocalix[4]arene) with MX_2, behaving as a neutral metallatecton, lead to the formation of 2- and 3-D neutral coordination networks. In all cases, the metal centre adopts a distorted octahedral geometry with the two anions occupying the two apical positions. For the compound **3**-CdX_2 (X = Cl or Br), **4**-$CdBr_2$ and **4**-$FeCl_2$ similar porous diamondoid 3D networks, resulting from tetrakis monodentate behaviour of the organic tectons, are formed. In marked contrast, for **4**-CoX_2 (X = Cl or Br), only two out of the four pyridyl units take part in the connectivity pattern leading thus to the formation of 2D grid type architectures.

Introduction

Crystal engineering[1] is a research area bridging the gap between solid state and supramolecular chemistry.[2] By considering crystals, compact periodic assemblies, as supermolecules[3] for which the components are held together by attractive intermolecular interactions, this approach is concerned with both the design of crystals and the description of the connectivity between components and packing processes.

Although at the early stage, crystal engineering was mainly concerned with organic molecular crystals,[4,5,6,7] over the last two decades it has been generalized to other types of molecular crystals by the *molecular tectonics* approach.[8,9,10] For the latter, crystals are seen as extended periodic molecular networks[11,12,13] resulting from specific association processes between self complementary or complementary tectons.[14,15] Among the many possible intermolecular or ion-molecule interactions that can be considered for designing recognition patterns, the use of coordination bonds defines a specific class of crystals called coordination polymers,[16] coordination networks[17] or metal organic frameworks.[18] The latter type of crystalline materials is attracting considerable interest.[19] The generation of coordination networks requires combinations of organic tectons and metal centres or metal complexes behaving as bridging units.

Calix[4]arene (CA) is a macrocyclic unit resulting from the interconnection of four phenolic moieties by four CH_2 groups.[20] This backbone, owing to possible rotations around the C-CH_2-C bonds, exists in four interconvertible conformations (cone, partial cone, 1,2-alternate and 1,3-alternate). The replacement of the four CH_2 moieties by four S atoms leads to tetrathiacalix[4]arene (TCA, **1**, figure 1).[21] The latter was transformed into its tetrasulfone[22] or tetrasulfinyl[23] derivatives upon oxidation. Furthermore, for both CA and TCA backbones, the OH groups may be replaced by SH groups leading thus to tetramercaptocalix[4]arene[24,25] and tetramercaptotetrathiacalix[4]arene[26] (TMCA, **2**, figure 1).[27] CA derivatives in cone conformation offering four OH groups positioned on the same face of the macrocyclic backbone, have been used for the formation of discrete complexes[28] and fused dimeric species with a variety of metal cations.[29] For the generation of periodic extended architectures, the 1,3-alternate (1,3-A) conformer of CA, TCA and TMCA bearing peripheral coordinating sites derivatives are of particular interest since they display four divergently oriented sites occupying the apices of a tetrahedron.

Using a calix[4]arene derivative blocked 1,3-alternate conformation and bearing four CN groups, a 1D coordination network was generated in the presence of Ag^+ cations in the crystalline phase.[30] The formation of extended assemblies resulting from combinations of CA based tectons bearing carboxylate groups with Ag(I)[31] or Cu(II), Zn(II), Co(II) or Cd(II) cations has been described.[32] The combination of a CA bearing pyridyl moieties with Cu(II) cation was found to lead to extended networks.[33]

TCA has been also used for the formation of discrete polynuclear species.[34,35,36] Furthermore, periodic infinite 1-, 2- and 3-D silver coordination networks based on thiacalix[4]arene derivatives in 1,3-alternate conformation equipped with four nitrile groups,[37] carboxylate units[38] or benzonitrile groups[39] have been described. Another type of 1D silver network based on a TCA derivative, bearing ether junctions, has also been reported.[40] The formation of coordination networks resulting from a combination of TCA and Cu(I) cation has been described.[41] TCA derivatives bearing carboxylate groups have been combined with metal cations and auxiliary ligands to generate infinite architectures.[42]

However, dealing with TMCA, only few examples of coordination networks, resulting from combinations of its pyridyl appended derivatives in 1,3-alternate conformation with Hg(II)[43] or Ag(I)[44] cations have been reported.

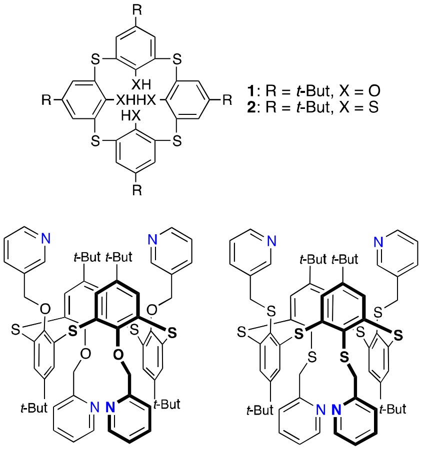

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Figure 1: Tetrathia- and tetrathiatetramercapto- calix[4] arene precursors **1** and **2** and tetra *meta*-pyridyl appended tectons **3** and **4** in 1,3-A conformation.

As stated above, the majority of extended networks based on the use of TCA and TMCA derivatives in 1,3-alternate conformation reported to date concerns the use of Ag^+ and Hg^{2+} cations as connecting metal centres. Surprisingly, only few extended networks based on octahedral transition metals have been reported. Our aim was to explore several of this type of connecting centres (Fe, Co and Cd) with both calix[4]arene derivatives **3** and **4**.

It is worth noting that tecton **3** or **4** (Fig. 1), owing to the presence of O, S and N atoms, might, in principle, behave as a dodecadentate unit displaying either a (4O,4S,4N) or a (8S, 4N) set of coordinating sites towards metal cations. Furthermore, owing to the nature of junctions (single bond) between the calix backbone and the coordinating pyridyl units (ether for **3** and thioether for **4**) and the location of the N atom on the pyridyl ring (*meta* position), both tectons may display many different rotamers resulting from the orientation of the pyridyl moieties. With our present level of knowledge, the prediction of connectivity patterns resulting from combinations of tecton **3** or **4** with transition metal cations is impossible. However, the formation of extended architectures may be investigated experimentally by imposing the nature of the metal centre, the solvent, the temperature and the concentration the organic tectons and metallic salts.

Here, we report on combinations of tectons **3** and **4** (Fig. 1), two different *meta*-pyridyl appended TCA and TMTCA neutral derivatives in 1,3-A imposed conformation, with octahedral MX_2 (M = Cd, Co or Fe and X = Cl or Br) salts behaving as metallatectons. Owing to the strong coordinating propensity of used halides (Cl^- or Br^-), MX_2 centres should behave as 4-connecting nodes. Indeed, the chosen metal cations in the oxidation state II should adopt an octahedral coordination geometry with the two apical positions occupied by the two halides leading thus to four free coordination sites located in the corners of the square base of the octahedron for the bridging of coordinating tectons **3** or **4**.

Experimental section

General: All reagents were purchased from commercial sources and used without further purification. The synthesis of **3**[43b] (25,26,27,28-tetra[(3-pyridylmethyl)oxy]-5,11,17,23-tetra-tert-butyl-2,8,14,20-tetrathiacalix[4]arene) and **4**[43a] (25,26,27,28-tetra[(3-pyridylmethyl)thio]-5,11,17,23-tetra-tert-butyl-2,8,14,20-tetrathiacalix[4]arene (in *1,3*-A conformation) has already been reported.

Characterization techniques

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 N_2 device, using graphite-monochromated Mo-Kα (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).[45] They can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/datarequest/cif. CCDC: 970400-970403.

Powder X-ray Diffraction

Powder diffraction studies (PXRD) diagrams were collected on a Bruker D8 diffractometer using monochromatic Cu-Kα radiation with a scanning range between 3.8 and 40° using a scan step size of 2°/mn.

As already demonstrated and currently admitted, for all the compounds, discrepancies in intensity between the observed and simulated patterns are due to preferential orientations of the microcrystalline powders.

Crystallisation conditions

3-$CdBr_2$: In a crystallization tube (4 mm diameter, 15 cm height), a solution of compound **3** (5 mg, 4.6 μmol) in $CHCl_3$ (1 mL) was layered with a $CHCl_3$/*iso*-PrOH (1/1) mixture (1 mL). A solution of $CdBr_2{\cdot}4H_2O$ (3.2 mg, 9.3 μmol) in MeOH (1 mL) was carefully added. Slow diffusion at room temperature produced after several days colourless crystals suitable for X-ray diffraction studies. Formula: $Cd(C_{64}H_{68}N_4O_4S_4)Br_2{\cdot}4CHCl_3$. Anal. Calcd.: C, 44.50%; H, 3.75%; N, 3.05%; Found: C, 45.57%; H, 4.28%; N, 2.87%.

3-$CdCl_2$: The same procedure as described for **3**-$CdBr_2$ was applied using $CdCl_2{\cdot}4H_2O$ (3.2 mg, 12.5 μmol).

Formula: $Cd(C_{64}H_{68}N_4O_4S_4)Cl_2{\cdot}3CHCl_3$. Anal. Calcd.: C, 49.46%; H, 4.40%; N, 3.44%; Found: C, 49.57%; H, 4.34%; N, 3.34%.

4-$CdBr_2$: A solution of compound **4** (5 mg, 4.35 μmol) in $CHCl_3$ (1 mL) was mixed with a solution of $CdBr_2{\cdot}4H_2O$ (3 mg, 8.7 μmol) in MeOH (1 mL). Slow evaporation at room temperature produced after several days colourless crystals suitable for X-ray diffraction studies.

Formula: $Cd(C_{64}H_{68}N_4S_8)Br_2 \cdot 2CHCl_3$. Anal. Calcd.: C, 47.73%; H, 4.25%; N, 3.37%; Found: C, 47.91%; H, 4.29%; N, 3.35%.

4-$FeCl_2$: Under argon, a solution of compound **4** (3 mg, 2.61 □mol) in degassed $CHCl_3$ (1 mL) was mixed with a solution of $FeCl_2$ (0.7 mg, 5.5 □mol) in degassed MeOH (1 mL). After 2 days, the solution was placed in ether chamber. Slow vapour diffusion of ether into the solution produced after several days yellow crystals suitable for X-ray diffraction studies.

Formula: $Fe_2(C_{64}H_{68}N_4S_8)_2Cl_2 \cdot 4CH_3OH$. Anal. Calcd.: C, 60.74%; H, 5.86%; N, 4.29%; Found: C, 60.25%; H, 5.56%; N, 4.29%.

4-$CoBr_2$: A solution of compound **4** (3 mg, 2.61 □mol) in $CHCl_3$ (1 mL) was mixed with a solution of $CoBr_2 \cdot 6H_2O$ (1.2 mg, 5.1 □mol) in MeOH (1 mL) and was first left for 2 days. Then, slow vapour diffusion of ether produced after several days blue crystals suitable for X-ray diffraction studies.

Formula: $Co(C_{64}H_{68}N_4S_8)_2Br_2$. Anal. Calcd.: C, 61.05%; H, 5.44%; N, 4.45%; Found: C, 62.12%; H, 5.48%; N, 4.39%.

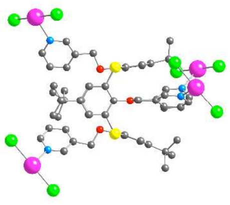
4-$CoCl_2$: The same procedure as described for **4**-$CoBr_2$ was applied using $CoCl_2 \cdot 6H_2O$ (1.1 mg, 4.6 □mol).

Formula: $Co(C_{64}H_{68}N_4S_8)_2Cl_2 \cdot 2H_2O \cdot 1MeOH$. Anal. Calcd.: C, 62.04%; H, 5.81%; N, 4.49%; Found: C, 61.78%; H, 5.70%; N, 4.41%.

Results

3-$CdBr_2$

The combination of **3** with $CdBr_2$ leads to the formation of a neutral 3D coordination network of formula $CdBr_2(C_{64}H_{68}N_4O_4S_4) \cdot 4CHCl_3$. Crystals (monoclinic, *C2/c*), in addition to the organic tecton **3** and $CdBr_2$ salt, contain four $CHCl_3$ solvent molecules (see table 1). The **3**/$CdBr_2$ ratio is 1/1. The coordination geometry around Cd^{2+} cation is a slightly deformed octahedron. Owing to the presence of the two halide anions occupying the two apical position (d_{Cd-Br} = 2.7067(6) Å), the Cd^{2+} cation acts as a square 4-connecting node and thus bridges four adjacent tectons **3** through four Cd-N bonds (d_{Cd-N} of 2.395(5) and 2.414(5) Å). The NCdN and NCdBr angles vary between 84.46(16) and 179.996(1)°, 88.98(12) and 91.02(12) respectively whereas the BrCdBr angle is 180°. On the other hand, the organic tecton **3** behaves as a tetrakis monodentate unit with the four N atoms of the pyridyl moieties outwardly oriented and occupying the apices of a deformed tetrahedron (Fig. 2a). The overall connectivity pattern leads to the formation of a diamond network (figure 2b). It is worth noting that the S atoms of the thiacalix moiety **3** are not engaged in any type of coordination scheme with Cd(II) metal centres.



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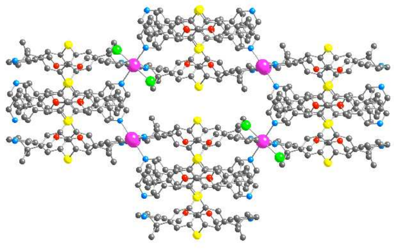

b

Figure 2: For **3**-$CdBr_2$: a) a portion of the X-ray structure showing the binding of four $CdBr_2$ centres by the four pyridyl moieties of **3** and the localization of the N atoms on the apices of a tetrahedron and b) a portion of the 3D crystal structure, viewed along the *b* axis showing the octahedral coordination geometry of Cd(II) cation. H atoms and $CHCl_3$ solvent molecules are omitted for clarity. For bond distances and angles see text.

The chloroform molecules are located in the cavities of the diamondoid network without specific interactions with the network.

The purity of the **3**-$CdBr_2$ phase was established by PXRD on microcrystalline powder which revealed a good match between the observed (Fig. 3a) and simulated patterns from the XRD data (Fig. 3b).

Interestingly, when replacing $CdBr_2$ by $CdCl_2$, an *iso*structural microcrystalline phase **3**-$CdCl_2$ is obtained. The latter phase was characterised by PXRD on microcrystalline powder (Fig. 3c) which revealed a similar pattern as those observed and simulated for **3**-$CdBr_2$ phase.

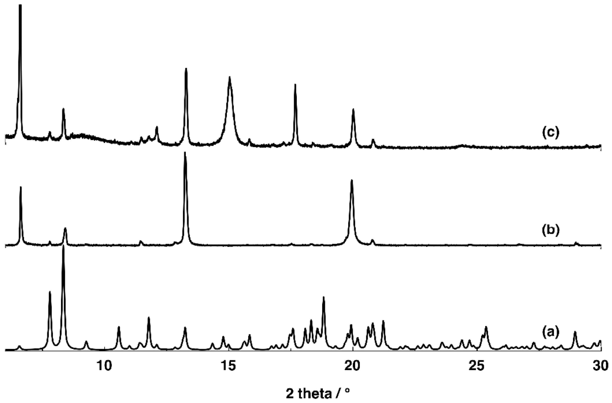

Figure 3: Comparison of the simulated (a) and recorded (b) PXRD patterns for **3**-$CdBr_2$ and for **3**-$CdCl_2$ (c). Discrepancies in intensity between the observed and simulated patterns are due to preferential orientations of the microcrystalline powders.

4-$CdBr_2$

In order to investigate the role played by the substitution of the O atoms in the tetrathiacalix[4]arene derivative **3** by S atoms in tetramercaptotetrathiaxalix[4]arene based tecton **4**, the latter was also combined with $CdBr_2$. The structural study revealed again the formation of a neutral 3D coordination network of formula $CdBr_2(C_{64}H_{68}N_4S_8) \cdot 2CHCl_3$ (figure 4). The crystal (triclinic, *P-1*), in addition to tecton **4** and $CdBr_2$ contains two $CHCl_3$ solvent molecules (see table 1). Again, the **4**/Cd^{2+} ratio is 1/1. For the organic tecton **4**, as in the case of **3**-$CdBr_2$, all four pyridyl units are outwardly oriented. Consequently, compound **4** behaves as a tetrakis monodentate tecton and bridges four consecutive $CdBr_2$ centres. Two types of crystallographically independent Cd^{2+}

cations, adopting both a slightly distorted octahedral coordination geometry, are found. The metal centres, behaving as a square 4-connecting node, are surrounded by four N atoms belonging to four pyridyl moieties of four different tectons **4** occupying the corners of the square base of the octahedron with Cd-N distances varying between 2.382(3) and 2.473(3) Å and two Br atoms in axial positions with Cd-Br distances of 2.6986(3) and 2.7198(3) Å. The NCdN and NCdBr angles are varying between 85.03(9)° and 180.0°, and 88.22(6) and 91.78(6)° respectively and the BrCdBr angle is equal to 179.999(15)°.

The 3D diamond type network displays channels along the *c* axis. They are filled with $CHCl_3$ molecules without any specific interaction with the coordination network. Again, it is worth noting that, as in the case of **3**, none of the eight S atoms of the organic tecton **4** participate in the binding of the metal cation.

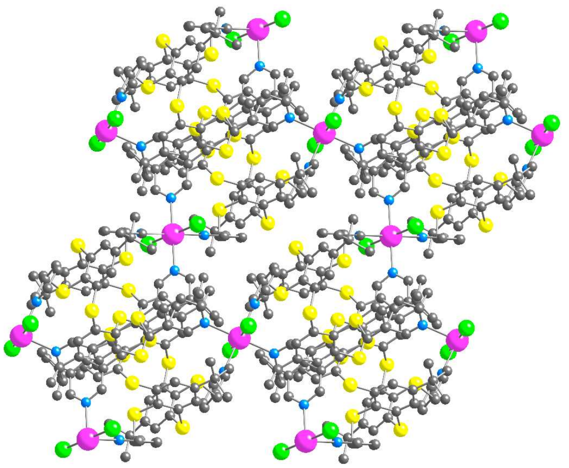

Figure 4: The view along the *c* axis of a portion of the structure of the diamondoid network formed by **4**-$CdBr_2$. H atoms and chloroform molecules are omitted for clarity. For bond distances and angles see text.

The purity of the **4**-$CdBr_2$ phase was established by PXRD on microcrystalline powder which revealed a rather good match between the observed and simulated patterns from the XRD data of **4**-$CdBr_2$ (figure 5).

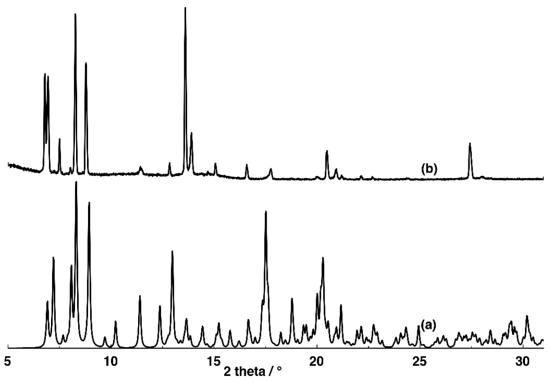

Figure 5: Comparison of the simulated (a) and recorded (b) PXRD patterns for **4**-$CdBr_2$. Discrepancies in intensity between the observed and simulated patterns are due to preferential orientations of the microcrystalline powders.

4-$FeCl_2$

The combination of tecton **4** with $FeCl_2$ again leads to the formation of a neutral 3D coordination network of formula $(FeCl_2C_{64}H_{68}N_4S_8)_2{\cdot}CH_3OH$ (Fig. 6). Crystals (triclinic, *P-1*) (see table 1) contain the organic tecton **4**, $FeCl_2$, and one CH_3OH solvent molecule. The **4**/$FeCl_2$ ratio is again 1/1. The coordination pattern is similar to the one found for **3**-$CdBr_2$ presented above. Again, for the tecton **4**, all four pyridyl units are outwardly oriented leading thus to a tetrakis monodentate connecting unit. Within the crystal, two types of crystallographically independent Fe^{2+} cations, adopting both a slightly distorted octahedral coordination geometry, are present. The coordination sphere around Fe(II) is composed of four N atoms in the equatorial plane with Fe-N distances varying between 2.225(2) and 2.3179(19) Å and two Cl atoms in axial positions with Fe-Cl distances of 2.6986(3) and 2.4056(6) Å. The NFeN and NFeCl angles are varying between 88.89(7) and 180,0°, and 88.64(6) and 91.36(6) ° respectively and the ClFeCl angle is equal to 180.00(3)°. As in the case of **3**-$CdBr_2$, $FeCl_2$ acts as a square four connecting node and bridges four consecutive tectons **4**. The 3D diamond type network displays channels along the *a* axis. The latter are filled with MeOH molecules as shown in figure 6. The methanol molecules form dimers through hydrogen bonds with O-O distance of 1.738Å.

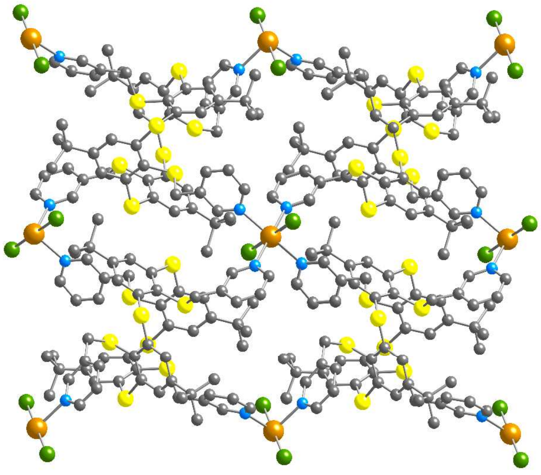

Figure 4: A view along the *a* axis of a portion of the 3D crystal structure of **4**-$FeCl_2$. H atoms and MeOH solvent molecules are omitted for clarity. For bond distances and angles see text.

Again, the rather high purity of **4**-$FeCl_2$ was established by PXRD on microcrystalline powder which revealed a good match between the observed and simulated patterns from the XRD data (figure 7).

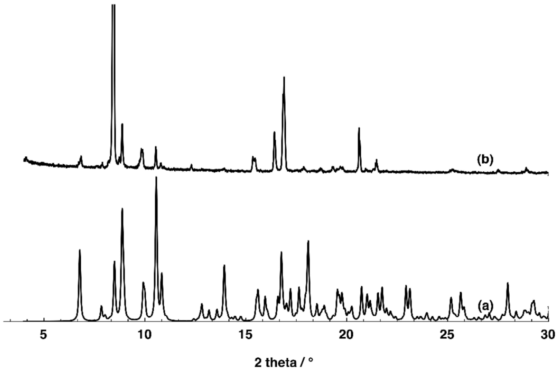

Figure 5: Comparison of the simulated (a) and recorded (b) PXRD patterns for **4**-$FeCl_2$. Discrepancies in intensity between the observed and simulated patterns are due to preferential orientations of the microcrystalline powders.

4-$CoBr_2$

In contrast to the case of $CdBr_2$ and $FeCl_2$, the combination of the tecton **4** with $CoBr_2$ leads to the formation of a neutral 2D coordination network of formula $CoBr_2(C_{64}H_{68}N_4S_8)_2{\cdot}2CH_3OH{\cdot}H_2O$ (see table 1). The crystal (monoclinic, *C2*) is composed of the organic tecton **4**, $CoCl_2$, MeOH and H_2O solvent molecules. In marked contrast with the above mentioned three cases (**3**-$CdBr_2$, **4**-$CdBr_2$ **3**-$FeCl_2$), the **4**/Co^{2+}ratio is 2/1 leading to a different connectivity pattern.

For the present case, compound **4** behaves as a bis mondentate tecton. Indeed, among its four pyridyl units, only two take part in the binding of Co(II) centre (Fig. 8a) leading thus to the formation of a 2D grid type coordination network. Co^{2+} cation, adopting a distorted octahedral coordination geometry, is surrounded by four N atoms and two Br^- anions. The square base of the octahedron is occupied by four N atoms of four pyridyl moieties belonging to four different tectons **4** with Co-N distances of 2.145(4) and 2.210(4) Å. The two apical positions are occupied by two Br atoms with a Cd-Br distance of 2.6673(5) Å. The, NCoN and NCoBr angles vary between 90.51(14) and 172.63(14)°, 86.05(10) and 94.96(10)° respectively and the BrCoBr angle is equal to 170.87(4)°.

Again, the S atoms of the tecton **4** do not participate in the connectivity pattern of the 2D network.

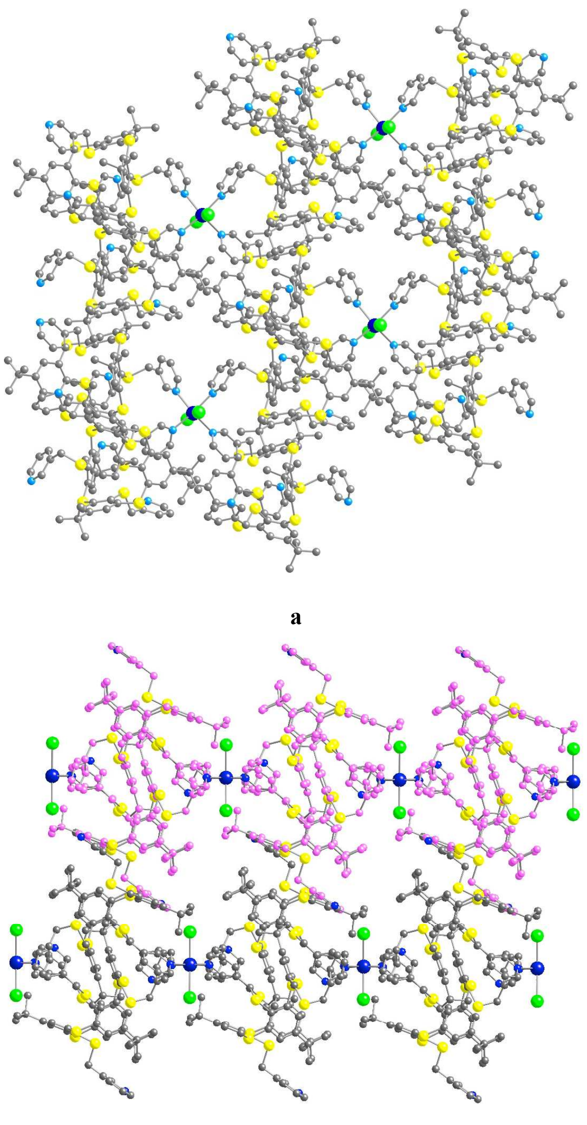

Figure 6: Portions of the structure of **4**-$CoBr_2$: forming a 2D grid type architecture (a) and of the packing of consecutive 2D networks along *c* axis (b). H atoms and solvent molecules are omitted for clarity. For bond distances and angles see text.

In the crystal, 2D network are stacked in a parallel fashion along *c* axis (figure 8b). Two different MeOH molecules are present in the crystal. One type is H-bound to the N atom of the free pyridyl unit ($d_{N\text{-}O}$ = 2.802 Å), whereas the second type lies in the interstices without any specific interaction with framework. The same holds for the water molecule.

The purity of the **4**-$CoBr_2$ phases was established by PXRD on microcrystalline powder which revealed a good match between the simulated from the XRD data of **4**-$CoBr_2$ (Fig. 9a) and the observed patterns (Fig. 9b).

Interestingly, as in the case of **3**-$CdBr_2$, an *iso*structural phase is obtained upon using $CoCl_2{\cdot}6H_2O$ instead of $CoBr_2{\cdot}6H_2O$. **4**-$CoCl_2$ was characterized by PXRD on microcrystalline powder which revealed a good match between the observed (Fig. 9c) and simulated (Fig. 9a) and observed (Fig. 9b) patterns for **4**-$CoBr_2$.

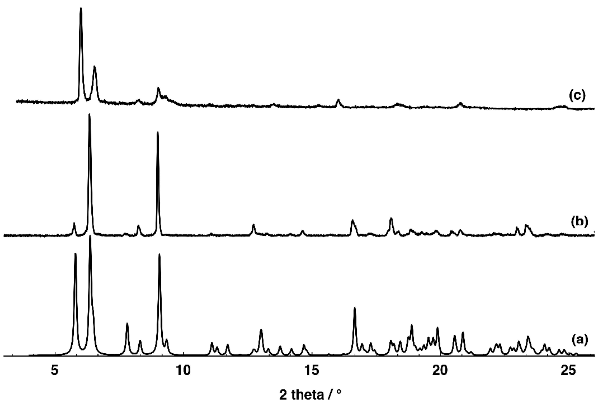

Figure 7: Comparison of PXRD data of the simulated (a) and recorded (b) patterns for **4**-$CoBr_2$ and for **4**-$CoCl_2$(c). Discrepancies in intensity between the observed and simulated patterns are due to preferential orientations of the microcrystalline powders.

Conclusion

Tectons **3** and **4** are organic neutral tetrakis *meta*-pyridyl appended *p-tert*-butyltetrathiacalix[4]arene and *p-tert*-butyltetrathiatetramercaptoclaix[4]arene derivatives in 1,3-A conformation respectively. Their combinations with MX_2, behaving as a neutral octahedral metallatecton, lead to the formation of unprecedented 2- and 3-D neutral coordination networks (Fig. 10). For all studied metal halide salts (Cd^{2+}, Fe^{2+} and Co^{2+}, X = Cl^- or Br^-), the metal centre adopts a distorted octahedral geometry with the two anions occupying the two apical positions. In none of the investigated cases, the four S atoms of **3** or the eight S atoms of **4** take part in the binding of the metal centre. For compound **3**, behaving as a tetrakis monodentate tecton, *iso*structural porous diamondoid 3D networks are formed in the presence of both $CdCl_2$ and $CdBr_2$. Interestingly, for tecton **4**, the same type of porous 3D architecture is obtained with $CdBr_2$ and $FeCl_2$. In all cases, crystals are solvates and the solvent molecules are located within the cavities of the porous 3D networks. Whereas the 3D networks **3**-CdX_2 (X = Cl or Br) and **4**-$FeCl_2$ display similar metrics, for **4**-$CdBr_2$ a deformation is observed. The latter results from the different orientation of the pyridyl moieties. However, in marked contrast, combinations of CoX_2 (X = Cl or Br) with compound **4**, behaving as a bis monodentate tecton since among its four pyridyl units only two take part in the connectivity pattern, lead to the formation of 2D grid type architectures. The reason why in the case of CoX_2 a different connectivity pattern is observed remains unexplained.

Using other metal salts and complexes, the propensity of tectons **3** and **4** to form extended periodic coordination networks is currently under investigation.

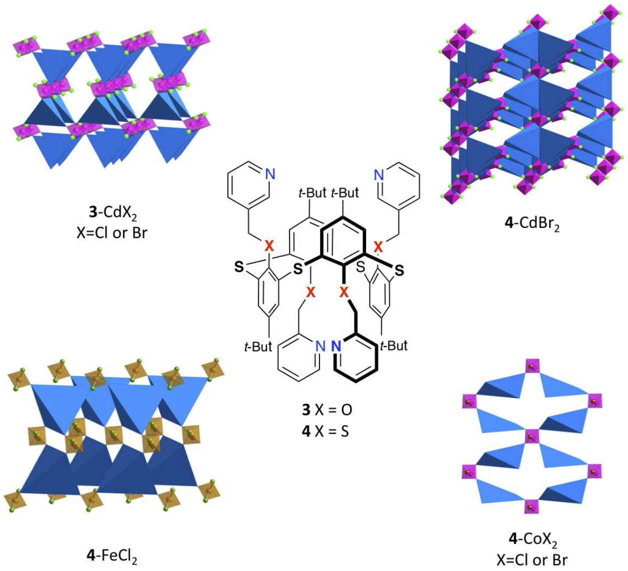

Figure 8: Polyhedral representations of 2D grid type and 3D diamondoid porous networks obtained upon combining tectons **3** and **4** with metal halide salts.

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Notes and references

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Table 1 : Crystallographic Parameters for **3**-$CdBr_2$, **4**-$CdBr_2$, **4**-$FeCl_2$, **4**-$CoBr_2$**4** and recorded at 173 K.

Formula	**3**-$CdBr_2$ $(C_{64}H_{68}N_4O_4S_4)CdBr_2\ (CHCl_3)_4$	**4**-$CdBr_2$ $(C_{64}H_{68}N_4S_8)$ $CdBr_2\ (CHCl_3)_2$	**4**-$FeCl_2$ $(C_{64}H_{68}N_4S_8)_2$ $(FeCl_2)_2\ CH_3OH$	**4**-$CoBr_2$ $(C_{64}H_{68}N_4S_8)_2CoBr_2$, $(CH_3OH)_2\ H_2O$
Molecular weight	1835.16	1660.66	2584.95	2600.26
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	C2/c	P-1	P-1	C2
a(Å)	27.1683(11)	13.9112(2)	11.4791(4)	28.1970(8)
b(Å)	15.3846(5)	14.4800(3)	14.2338(4)	15.6401(4)
c(Å)	19.2713(9)	20.8500(4)	21.6211(5)	15.4989(4)
α(deg)	90	74.7320(10)	87.8170(10)	90
β(deg)	98.162(2)	82.4040(10)	81.1830(10)	100.242(2)
γ(deg)	90	66.7770(10)	66.3810(10)	90
V(Å^3)	7973.3(6)	3721.48(12)	3197.45(16)	6726.2(3)
Z	4	2	1	2
Colour	colourless	colourless	yellow	colourless
Crystal dim (mm3)	0.08 x 0.06 x 0.04	0.07 x 0.05 x 0.05	0.08 x 0.07 x 0.05	0.14 x 0.11 x 0.10
Dcalc (gcm-3)	1.529	1.482	1.342	1.284
F(000)	3704	1684	1354	2718
μ (mm^{-1})	1.830	1.848	0.624	1.022
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Number of data meas.	65819	101938	60060	102470
Number of data with I> 2σ(I)	11034 [R(int) = 0.0455]	19836 [R(int) = 0.0598]	16744 [R(int) = 0.0235]	19261 [R(int) = 0.0632]
R	R1 = 0.0811, wR2 = 0.2313	R1 = 0.0432, wR2 = 0.1015	R1 = 0.0486, wR2 = 0.1368	R1 = 0.0603, wR2 = 0.1503
Rw	R1 = 0.1103, wR2 = 0.2548	R1 = 0.0847, wR2 = 0.1181	R1 = 0.0607, wR2 = 0.1480	R1 = 0.1022, wR2 = 0.1734
GOF	1.051	1.004	1.033	1.032
Largest peak in final difference (eÅ-3)	1.661 and -1.099	0.545 and -0.839	2.092 and -1.060	2.447 and -0.713

Graphical abstract

Combinations of tetrakis *meta*-pyridyl appended tetrathia- or tetrathiamercapto-calix[4]arene derivatives in 1,3-A conformation with MX_2 (M = Cd, Co or Fe, X = Cl or Br) behaving as a neutral metallatecton, lead to the formation of 2D grid type and 3D porous diamondoid coordination networks.