ARTICLE

Molecular Tectonics: high dimensional coordination networks based on a methylenecarboxylate appended tetramercaptotetrathiacalix[4]arene in 1,3-Alternate conformation

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The combination, under mild conditions, of the methylenecarboxylic appended tetramercaptotetrathiacalix[4]arene (TMTCA) derivative **4**, blocked in 1,3-Alternate conformation, with acetate salts of octahedral Copper(II), Manganese(II), Nickel(II) and Zinc(II), leads to the formation, in the crystalline state, of high dimensional coordination networks. Depending on the nature of the used metal cations and bases (pyridine or non-coordinating Et₃N), six new different high-dimensional coordination polymers have been evidenced, presenting 4 different coordination patterns. All the compounds present a metal/4 ratio equal to 2/1. The formation of a 2D grid-like compound (**4**-Zn₂(Py)₄) as well as three different pseudo-diamandoid-like 3D compounds (**4**-Co₂(Py)₆(H₂O), **4**-Ni₂(Py)₆(H₂O), **4**-Mn₂(Py)₄(MeOH)₂, **4**-Mn₂(DMF)₂(MeOH)₄ and **4**-Zn₂(MeOH)₄) is observed.

Introduction

Novel coordination polymers (CPs)¹ or coordination networks (CNs)² and Metal Organic Frameworks (MOFs)³ are of constantly increasing interest owing to their applications in several domains such as storage, catalysis and separation.⁴ These classes of solid-state extended architectures also display specific physical properties in the field of electronics, optics, magnetism or conduction, for example. Although since *ca* two decades a large variety of architectures has been reported, their design still remains attracting and highly challenging.⁵ The formation of these periodic crystalline materials results from mutual interconnection of organic ligands and metal centres or metal complexes. For some times now, we are developing an approach called *molecular tectonics*⁶ based on self-assembly processes⁷ between complementary tectons⁸ or building blocks. For this approach, molecular crystals are considered as infinite molecular networks formed upon interconnection of tectons by any type of reversible intermolecular interactions. This approach allows the rationale formation of well-defined coordination polymers, due to the judicious design of the organic ligand and the choice of metallic cation.

The family of calix[4]arene CA (**1**, Figure 1),⁹ its sulphur analogue tetrathiacalix[4]arene TCA (**2**, Figure 1) and tetramercaptotetrathiacalix[4]arene¹¹ (TMTCA, **3**, Figure 1) are versatile macrocyclic scaffolds for the formation of new

coordination networks. TCA and TMTCA are inherently coordinating, due to the presence of sulphur atoms in their macrocyclic ring. Several coordination networks have been obtained using these unmodified scaffolds.¹² Diverse organic coordinating groups can be anchored either at the lower or upper rim of the macrocyclic unit. Another significantly important ability of these macrocycles is flexibility to be adopted in four different conformation which may be separated. Among them, for the formation of high dimensionality polymers, the 1,3-Alternate conformation appears the most intriguing.

Figure 1: Calix[4]arene CA **1**, tetrathiacalix[4]arene TCA **2**, tetramercaptotetrathiacalix[4]arene **3** and precursor **4**

tetramethylenecarboxylic acid appended ligand **4**, blocked in *1,3*-Alternate conformation.

In general, for the formation of coordination polymers, different coordinating groups have been used:¹³ one can notice N donor or O donor ligands. Among them, carboxylic(ate) ligands are of particular interest. Macrocyclic compounds bearing carboxylate coordinating groups have been intensively used for the design of new coordination polymers: using tetrasubstituted porphyrine with carboxylate moieties, series of coordination compounds have been obtained,¹⁴ but concerning calixarene derivatives, several coordination polymers of various dimensionalities have been reported:¹⁵ for example the upper rim has been decorated with carboxylate moieties of calix[4]arene (**1**) in *cone* conformation leading to mono,¹⁶ di¹⁷ and tetrasubstituted¹⁸ species combined with transition metals (Cu(II), Zn(II), Co(II) or Cd(II)), alkali cations (Rb(I)) or lanthanides (Yb(III), Eu(III) and Y(III)), leading to polymeric compounds. The lower rim substituted calixarene derivatives has also been used for the formation of carboxylate based ligands: di¹⁹ and tetrasubstituted²⁰ calix[4]arene in *cone* and *1,3*-Alternate conformation, were used for the formation of extended networks. Concerning the use of thiacalix[4]arene (**2**), only tetrasubstituted species in *1,3*-Alternate conformation have been reported,²¹ combined with different transition metals, some of the networks presenting interesting gas adsorption properties. For the formation of different coordination polymers, TMTCA backbone (**3**) has been used only with the following coordinating groups:¹⁵ cyano,²² pyridine²³ or pyrazolyl²⁴ coordinating groups, has been reported, and we recently reported the formation of a coordination polymer based on a tetrasubstituted TMTCA derivative appended with benzoate coordinating groups and combined with transition metals, leading to 1D coordination networks.²⁵ Nevertheless, the coordination abilities of TMTCA appended with carboxylic(ate) coordinating groups remains only rarely investigated.

Along this line, we designed a new TMTCA based ligand for the formation of coordination polymers: the tetrasubstituted **4**, blocked in *1,3*-Alternate conformation, and appended with methylenecarboxylic moieties. Compound **4**, presented in figure 1, has been already reported by us, for the formation of hydrogen bonded molecular networks.²⁶

Here we will discuss the influence of the nature of the base and the nature of the used divalent octahedral transition metal, combined, in mild conditions with **4**, on the obtained six new high dimensional coordination networks, presenting four different coordination patterns. Most of the molecular networks involving carboxylate ligands are obtained using hydrothermal or solvothermal, but through this contribution, we intent to demonstrate the control of the dimensionality of the formed networks, using mild conditions for the combination of **4** with metals.

Experimental section

Characterization techniques

Elemental analysis were performed by the Analysis Service of the Faculty of Chemistry.

Synthesis

General: All reagents were purchased from commercial sources and used without further purification. Compound **2** (25,26,27,28-tetrakis[(carboxyl)methylenethio]-5,11,17,23-tetra-*tert*-butyl-2,8,14,20-tetrathiacalix[4]arene) in *1,3*-Alternate conformation was prepared following a reported procedure.²⁶

Crystallization conditions

4-Zn₂(Py)₄: In a crystallization tube (length 20 cm, diameter 4 mm), a pyridine solution (1 ml) of **4** (5 mg, 0.005 mmol) was carefully layered with a Py/*i*-PrOH mixture (1 ml, 1/1). Then a MeOH solution (1 ml) containing Zn(OAc)₂·2H₂O (2.2 mg, 0.01 mmol) was added. Upon slow diffusion at room temperature, colourless crystals suitable for X-ray analysis were obtained after *ca* a week. Formula: C_{76.50}H_{82.50}N_{5.50}O_{8.75}S₈Zn₂, Anal. Calcd.: C, 57.12%; H, 5.19%; N, 4.81%; Found: C, 56.95 %; H, 5.28 %; N, 4.96 %.

4-Co₂(Py)₆(H₂O)₂: In a crystallization tube (length 20 cm, diameter 4 mm), a pyridine solution (1 ml) of **4** (5 mg, 0.005 mmol) was carefully layered with a Py/MeOH mixture (1 ml, 1/1). Then a MeOH solution (1 ml) containing Co(OAc)₂·4H₂O (2.4 mg, 0.01 mmol) was added. Upon slow diffusion at room temperature, pale pink crystals suitable for X-ray analysis were obtained after *ca* 2 weeks. Formula: C₈₁H₉₈Co₂N₆O₁₃S₈, Anal. Calcd.: C, 55.98%; H, 5.68%; N, 4.84%; Found: C, 56.12 %; H, 5.72 %; N, 4.89 %.

4-Ni₂(Py)₆(H₂O)₂: In a crystallization tube (length 20 cm, diameter 4 mm), a pyridine solution (1 ml) of **4** (5 mg, 0.005 mmol) was carefully layered with a Py/MeOH mixture (1 ml, 1/1). Then a MeOH solution (1 ml) containing Ni(OAc)₂·4H₂O (2.4 mg, 0.01 mmol) was added. Upon slow diffusion at room temperature, pale green crystals suitable for X-ray analysis were obtained after *ca* 2 weeks. Formula: C_{80.75}H_{93.25}N_{6.25}Ni₂O_{11.50}S₈, Anal. Calcd.: C, 56.74%; H, 5.50%; N, 5.12%; Found: C, 56.86 %; H, 5.56 %; N, 5.16 %.

4-Mn₂(Py)₄(MeOH)₂: In a crystallization tube (length 20 cm, diameter 4 mm), a pyridine solution (1 ml) of **4** (5 mg, 0.005 mmol) was carefully layered with a Py/*i*-PrOH mixture (1 ml, 1/1). Then a MeOH solution (1 ml) containing Mn(OAc)₂·4H₂O (2.4 mg, 0.01 mmol) was added. Upon slow diffusion at room temperature, colourless crystals suitable for X-ray analysis were obtained after *ca* a week. Formula: C₉₀H₁₀₀Mn₂N₈O₁₁S₈, Anal. Calcd.: C, 58.87%; H, 5.49%; N, 6.10%; Found: C, 58.54 %; H, 5.56 %; N, 6.16 %.

4-Mn₂(DMF)₂(MeOH)₄: In a crystallization tube (length 20 cm, diameter 4 mm), a DMF solution (0.5 ml) of **4** (5 mg, 0.005

mmol) and 0.4 ml of 0.05 M solution of NEt_3 (0.02 mmol) in DMF was carefully layered with a DMF/MeOH mixture (1 ml, 1/1). Then a MeOH solution (1 ml) containing $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (2.4 mg, 0.01 mmol) was added. Upon slow diffusion at room temperature, colourless crystals suitable for X-ray analysis were obtained after *ca* a month. Formula: $\text{C}_{29}\text{H}_{41}\text{MnNO}_7\text{S}_8$, Anal. Calcd.: C, 49.84%; H, 5.91%; N, 2.00%; Found: C, 49.54 %; H, 6.05 %; N, 2.12 %.

4-Zn₂(MeOH)₄: In a crystallization tube (length 20 cm, diameter 4 mm), a DMF solution (0.5 ml) of **4** (5 mg, 0.005 mmol) and 0.4 ml of 0.05 M solution of NEt_3 (0.02 mmol) in DMF was carefully layered with a DMF/MeOH mixture (1 ml, 1/1). Then a MeOH solution (1 ml) containing $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.9 mg, 0.01 mmol) was added. Upon slow diffusion at room temperature, colourless crystals suitable for X-ray analysis were obtained after *ca* a month. Formula: $\text{C}_{26}\text{H}_{32}\text{O}_6\text{S}_4\text{Zn}$, Anal. Calcd.: C, 49.24%; H, 5.09 %; Found: C, 48.95 %; H, 5.15 %.

Structural studies

Single-Crystal Studies

Data were collected at 173(2) K on a Bruker Apex-II-CCD diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using graphite-monochromated Mo-K α ($\lambda = 0.71073$ 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 refined using a riding model.²⁷ They can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif. CCDC: 1563044-1563049.

Results and discussion

Synthesis of the networks

All crystals **4-Zn₂(Py)₄**, **4-Co₂(Py)₆(H₂O)₂**, **4-Ni₂(Py)₆(H₂O)₂**, **4-Mn₂(Py)₄(MeOH)₂**, **4-Mn₂(DMF)₂(MeOH)₄** and **4-Zn₂(MeOH)₄** (see experimental part and crystallographic table 1) were obtained under mild conditions by slow diffusion techniques using DMF/MeOH, py/MeOH or py/*i*-PrOH mixtures containing **4** and a base (NEt_3 (4 eq.) or pyridine (as solvent)) which were layered with a MeOH solution containing $\text{M}^{\text{II}}(\text{OAc})_2 \cdot n\text{H}_2\text{O}$ (M = Co, Ni, Mn or Zn, $n = 2$ or 4). The choice of the metals was based on their preferred octahedral coordination geometry and their affinity for oxygen donor atoms. As it may be expected, the use of the pyridine as base and solvent obviously leads to its presence in the coordination sphere of the metal.

The obtained compounds present coordination patterns leading to 2D and 3D compounds, resulting mainly from the divergent disposition of the four coordinating carboxylate groups towards the mean plane of the macrocyclic backbone, blocked in *1,3*-Alternate conformation and the nature and geometry of the used divalent first row transition metal.

For all the obtained crystals and microcrystalline powders, the purity of the crystalline phase could not be established by PXRD, since all the compounds partially decompose in the air, probably by the loss of solvent molecules. Further thermal analysis or gas adsorption measurements could not be investigated.

Structural description of networks

There are four types of different compounds that are reported here, starting from divalent first row transition metals combined with **4** (i) a bidimensionnal compound **4-Zn₂(Py)₄**, (ii) two isomorphous and isometric 3D compounds **4-Co₂(Py)₆(H₂O)₂** and **4-Co₂(Py)₆(H₂O)₂**, (iii) a 3D compound **4-Mn₂(Py)₄(MeOH)₂** and (iv) two isomorphous and isometric 3D compounds **4-Mn₂(DMF)₂(MeOH)₄** and **4-Zn₂(MeOH)₄**.

For all the compounds, a total deprotonation of ligand **4** into **4⁴⁻** was observed, where all the carboxylic moieties behave as carboxylate monodentate coordinating groups (excepting **4-Zn₂(MeOH)₄**), as shown by the C-O distances in the 1.203(8)-1.293(6) Å range (see table 2) for all coordination polymers. As a consequence, for all the reported compounds a metal/**4** ratio of 2/1 is observed. All **4⁴⁻** ligands, are surrounded by four metallic cations and all metals are surrounded by two **4⁴⁻** ligands, and all carboxylate groups bared by **4⁴⁻** are involved in coordination bonds (either in mono- or bidentate coordination mode).

Except for **4-Mn₂(DMF)₂(MeOH)₄** and also for **4-Zn₂(MeOH)₄** for which the squeeze command²⁸ was applied during the refinement process, positions of used solvent molecules were found and refined in all compounds: Pyridine, CH₃OH and H₂O. Water molecules are providing from the metallic salts used for the synthesis, and also from the used solvents. For **4-Ni₂(Py)₆(H₂O)₂**, one of the *tert*-butyl group is found to be disordered.

For all the reported coordination networks, the metrics for the macrocyclic backbone **4** are close to the one observed for the already reported compound,²⁶ and will not be described here in detail. In all the reported structures, ligand **4** adopts a deformed tetrahedral shape, with a maximum side of 10 Å, depending on the flexibility of the carboxylated pendant arms.

4-Zn₂(Py)₄

When **4**, in a Py/*i*-PrOH 1/1 mixture, is combined, under self-assembly conditions, with methanolic solution of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and using pyridine as a base, the formation of **4-Zn₂(Py)₄** were observed. X-ray diffraction on single crystals revealed the following formula (see experimental part and crystallographic table 1): $\text{C}_{48}\text{H}_{54}\text{O}_8\text{S}_8\text{Zn}_2(\text{C}_5\text{H}_5\text{N})_4 \cdot 1.5(\text{C}_5\text{H}_5\text{N}) \cdot 0.75(\text{CH}_3\text{OH})$. The obtained compound crystallizes in the monoclinic $P2_1/c$ space group and positions of solvent molecules (MeOH and pyridine) were found and refined in the lattice. Four pyridine molecules are coordinated to two zinc cations. The 2D resulting coordination network arises from the observed deformed square planar shape of the tetrasubstituted ligands, presenting four coordination sites interconnected with zinc cations, acting as linear connectors (see figure 2 a and b). All carboxylate groups are involved in the coordination with zinc cations, displaying a monodentate mode of coordination (figure 2c).

Figure 2: For $4\text{-Zn}_2(\text{Py})_4$, (a) a portion of the 2D coordination network viewed in the yOz plane, (b) the environment of the deformed tetrahedral zinc cations, (c) the environment of **4** and (d) the packing of the 2D arrays, together with solvent molecules, viewed in the xOz plane. H atoms (for a-d) and solvent molecules (for a, b and c) are omitted for clarity. For bond distances and angles see text and table 2.

The geometry around the divalent Zn metal centers, is a deformed tetrahedron with N_2O_2 environment (figure 2b), with two nitrogen atoms belonging to two pyridine auxiliary ligands and two oxygen atoms from carboxylate units belonging to two adjacent ligands. The Zn-N and Zn-O_{carboxyl} distances are in the 2.038(4)-2.074(5) and 1.941(3)-1.975(3) Å range respectively. The NZnN angles are equal to 104.16(19)° and 104.85(16)°, the OZnO angles are equal to 104.74(13)° and 133.50(18)°, and the OZnN are in the 97.56(16)-122.97(16)° range (see table 2 for precise values).

The formed 2D layers are stacked along the Ox axis, as shown in figure 2d, with the solvent molecules (MeOH and pyridine) located in the interstices. There is an interaction between MeOH and free pyridine molecules, with O-N distance of 2.798(18) Å, between a MeOH and an oxygen atoms from carboxylate group with O-O distance of 2.801(15) Å and between two methanol molecules, with O-O distance of 3.037(15) Å.

$4\text{-Ni}_2(\text{Py})_6(\text{H}_2\text{O})_2$ AND $4\text{-Co}_2(\text{Py})_6(\text{H}_2\text{O})_2$

The combination of **4** in a Py/*i*-PrOH 1/1 mixture with a methanolic solution of $\text{M}^{\text{II}}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (M = Co or Ni), using pyridine as base, leads to the formation of crystals of two isomorphous and isometric compounds: $4\text{-Co}_2(\text{Py})_6(\text{H}_2\text{O})_2$ and $4\text{-Ni}_2(\text{Py})_6(\text{H}_2\text{O})_2$. After X-Ray analysis of the single crystals, it was established that both compounds present the following formula (see experimental part and crystallographic table 1): $\text{C}_{48}\text{H}_{54}\text{S}_8\text{O}_8\text{Co}_2(\text{C}_5\text{H}_5\text{N})_6(\text{H}_2\text{O})_2$, $3(\text{CH}_3\text{OH})$, H_2O and $\text{C}_{48}\text{H}_{54}\text{S}_8\text{O}_8\text{Ni}_2(\text{C}_5\text{H}_5\text{N})_6(\text{H}_2\text{O})_2$, $0.25(\text{C}_5\text{H}_5\text{N})_{0.25} \text{CH}_3\text{OH}$. They crystallize in the monoclinic $C2/c$ space group and positions of solvent molecules (MeOH and water for $4\text{-Co}_2(\text{Py})_6(\text{H}_2\text{O})_2$, and pyridine and MeOH for $4\text{-Ni}_2(\text{Py})_6(\text{H}_2\text{O})_2$) were found and refined in the lattice. Both isometric and isomorphous compounds form solvates.

In the crystal, six pyridine molecules are coordinated to two

cobalt (or nickel) cations, together with two molecules of water (figure 3b). The 3D pseudo diamondoid-like network results from the interconnection of deformed tetrahedra formed by coordinating ligands **4** with cobalt (or nickel) cations, acting as linear connectors (see figure 3a), and binuclear cations acting as square planar connectors. As in the previous case, the carboxylate groups are involved in monodentate coordination mode with cobalt (or nickel) cations (figure 3b).

Figure 3: For $4\text{-Ni}_2(\text{Py})_6(\text{H}_2\text{O})_2$, (a) a portion of the 3D coordination network in polyhedral representation (blue deformed tetrahedra are representing **4**⁺ and green deformed octahedra are representing the Ni^{2+} (or Co^{2+} cations), (b) the environment of the deformed octahedral Ni^{2+} (or Co^{2+}) cations and of **4**⁺ and (c) interpenetration of two (in red and in green) 3D coordination networks. Some of the H atoms and solvent molecules are omitted for clarity. Disordered tertibutyl group for $4\text{-Ni}_2(\text{Py})_6(\text{H}_2\text{O})_2$ was not represented. For bond distances and angles see text and table 2.

The geometry around the divalent cobalt or nickel cations, is a deformed octahedron with N_3O_3 environment (figure 3b), with three nitrogen atoms belonging to three pyridine ligands and two oxygen atoms from carboxylate units belonging to two different ligands. An additional oxygen atom comes from a coordinating water molecule. The Co(Ni)-N and Co(Ni)-O_{carboxyl} distances are in the 2.103(6)-2.193(5) Å (2.073(7)-2.198(6) Å) and 2.013(4)-2.089(4) Å (2.047(5)-2.074(4) Å) range, respectively. The Co(Ni)-O_{water} distances are equal to 2.109(4) and 2.357(12) Å (2.080(5) and 2.204(10) Å). For both compounds $4\text{-Co}_2(\text{Py})_6(\text{H}_2\text{O})_2$ and $4\text{-Ni}_2(\text{Py})_6(\text{H}_2\text{O})_2$,

NCo(Ni)N angles are in the 83.3(3)-179.04(19)° range, the OCo(Ni)N angles in the 86.3(2)-177.5(2) range, and the OCo(Ni)O in the 88.49(16)-177.9(2) range (see table 2 for precise values).

There are two identical interpenetrated 3D networks in the crystal, as shown in figure 3c, so that the structure is compact. Some solvent molecules are located between the interpenetrated networks with interactions between them and with the network. For **4**-Ni₂(Py)₆(H₂O)₂, there is a hydrogen bond between uncoordinated MeOH and pyridine molecules, with a short O-N distance of 2.358(25) Å, between MeOH and oxygen atoms from carboxylate groups with O-O distances of 2.648(7), 2.722(8) and 2.754(2) Å. For **4**-Co₂(Py)₆(H₂O)₂, there are hydrogen bonds between (i) MeOH and water molecule located on the cobalt cations, with a O-O distance of 2.722(5) Å and (ii) MeOH and oxygen atoms from carboxylate groups with O-O distances of 2.643(6) and 2.750(7). There is also an hydrogen bond between uncoordinated methanol and water molecules with a O-O distance of 2.800(7) Å.

4-Mn₂(Py)₄(MeOH)₂

When **4**, in a Py/*i*-PrOH 1/1 mixture, is combined, under self-assembly conditions, with Mn(OAc)₂ 2H₂O using pyridine as base, crystals of a coordination polymer **4**-Mn₂(Py)₄(MeOH)₂ presenting the following formula were analysed using X-Ray diffraction (see experimental part and crystallographic table 1): 2(C₂₄H₂₇S₄O₄Mn(C₅H₅N)₂(CH₃OH)), 4(C₅H₅N), H₂O. The compound crystallizes in the monoclinic *C2/c* space group and the position of solvent molecules (water and pyridine) were found and refined in the lattice.

Figure 4: For **4**-Mn₂(Py)₄(MeOH)₂, (a) the environment of the deformed octahedral dimeric (Mn²⁺)₂ units and (b) a portion of the 3D coordination network in polyhedral representation (blue deformed tetrahedra are representing **4**⁴⁻ and brown deformed octahedra are representing the Mn (II) cations). H atoms are omitted for clarity. For bond distances and angles see text and table 2.

Four pyridine molecules are coordinated to manganese cations, together with two MeOH molecules. The 3D pseudo diamond-like network results from the interconnection of deformed tetrahedral coordinating ligands **4** with dimeric units formed by the metallic cations, acting as deformed square planar connectors (see figure 4b), leading to the formation of pores. Two of the carboxylate groups are involved in a monodentate coordination mode with manganese cations, and two are involved in bis-monodentate coordinating mode, bridging the dimeric manganese units, as shown in figure 4a.

In the dimeric metallic unit, the geometry around the two equivalent manganese cations, is a deformed octahedron with N₂O₄ environment (figure 4a), with two nitrogen atoms belonging to two pyridine ligands, located in *cis* position, and three oxygen atoms from carboxylate units belonging to three different ligands: which two bridges two metals and another one connected to the side position of dimeric metal unit. An additional oxygen molecule comes from a coordinating methanol molecule. The Mn-N distances are equal to 2.263(2) and 2.329(2) Å and Mn-O_{carboxyl} distances are equal to 2.1521(19), 2.1654(19) and 2.1679(18) Å. The Mn-O (MeOH) distance is equal to 2.193(2) Å. The NMnN angle between two pyridine located in *cis* position, is equal to 96.59(9)°. The OMnN angles are in the 86.82(9)-178.68(8)° range, and the OMnO are in the 88.21(8)-171.82(7)° range (see table 2 for precise values). It is important to note that the described dimeric units display a Mn-Mn distance equals to 4.750(7) Å.

Some water and pyridine solvent molecules are laying within the 3D network, especially in the formed pores of the diamondoid-like network, showing hydrogen bonds between them and water (short O-N distance between water and pyridine molecules is 2.887(5) Å) and without any specific interaction with the network.

4-Mn₂(DMF)₂(MeOH)₄ OR 4-Zn₂(MeOH)₄

The combination of **4** in a MeOH/DMF 1/1 mixture, with a MeOH solution of M^{II}(OAc)₂ 2H₂O (M = Zn or Mn), using 4

eq. of NEt_3 as base, afforded crystals of two isomorphous and isometric compounds $4\text{-Mn}_2(\text{DMF})_2(\text{MeOH})_4$ and $4\text{-Zn}_2(\text{MeOH})_4$. The following formula (see experimental part and crystallographic table 1) of obtained crystals: $\text{C}_{24}\text{H}_{27}\text{S}_4\text{O}_4\text{Mn}(\text{C}_3\text{H}_7\text{NO})(\text{CH}_3\text{OH})_2$ and $\text{C}_{24}\text{H}_{27}\text{S}_4\text{O}_4\text{Zn}(\text{CH}_3\text{OH})_2$ have been revealed using X-Ray diffraction on single crystals. Both compounds crystallize in the monoclinic $C2/c$ space group and for $4\text{-Mn}_2(\text{DMF})_2(\text{MeOH})_4$ no positions of solvent molecules were found and refined in the lattice, whereas for $4\text{-Zn}_2(\text{MeOH})_4$, the squeeze command was applied. In this case, methanol molecules are present in the coordination sphere of the metals. In the case of $4\text{-Mn}_2(\text{DMF})_2(\text{MeOH})_4$, an additional DMF molecule is present in the coordination sphere of the metal. Both compounds $4\text{-Mn}_2(\text{DMF})_2(\text{MeOH})_4$ and $4\text{-Zn}_2(\text{MeOH})_4$ are isomorphous and isometric. They behave as different solvates and they display an analogous coordination pattern, especially in terms of coordination sphere of the metal. The 3D pseudo diamond-like network results from the interconnection of deformed tetrahedral coordinating ligands **4** and, as in the previous case, dimeric units formed by the metallic cations, acting as deformed square planar connectors (see figure 5b), leading to the formation of a porous network.

Figure 5: For $4\text{-Mn}_2(\text{DMF})_2(\text{MeOH})_4$ and $4\text{-Zn}_2(\text{MeOH})_4$ (a) the environment of the deformed octahedral dimeric $(\text{Zn}^{2+})_2$ units, (b) the environment of the deformed octahedral dimeric $(\text{Mn}^{2+})_2$ units and (c) a portion of the 3D coordination network in polyhedral representation (blue deformed tetrahedra are representing **4**⁺ and brown deformed octahedra are representing the Mn^{2+} cations). H atoms are omitted for clarity. For bond distances and angles see text and table 2.

In the dimeric metallic units of $4\text{-Mn}_2(\text{DMF})_2(\text{MeOH})_4$ and $4\text{-Zn}_2(\text{MeOH})_4$, the metallic cations Mn and Zn are both in an octahedral environment with an O_6 surrounding; they present a comparable size and metrics. Both compounds contain two methanol molecules in their coordination sphere, together with two carboxylate groups coming from two different ligands **4**, involved in bis-monodentate coordinating mode, bridging the dimeric manganese units by one oxygen atom, as shown in figure 4a. But both compounds are slightly differing, since in the case of $4\text{-Zn}_2(\text{MeOH})_4$ an additional bidentate coordinating group is completing the coordination sphere, while for $4\text{-Mn}_2(\text{DMF})_2(\text{MeOH})_4$ this carboxylate group is bonded in a monodentate fashion, the last position of the coordination sphere is occupied by a DMF coordinating ligand pointing into the cavities of the formed diamond-like network.

The $\text{Mn-O}_{\text{carboxyl}}$ and $\text{Zn-O}_{\text{carboxyl}}$ distances are in the 1.956(5)–2.263(3) Å range. The $\text{Mn-O}_{\text{MeOH}}$ and $\text{Zn-O}_{\text{MeOH}}$ distances are equal to 2.228(3) and 1.976(7) Å, respectively, and the Mn-O_{DMF} distance is equal to 2.240(3) Å. For both compounds $4\text{-Mn}_2(\text{DMF})_2(\text{MeOH})_4$ and $4\text{-Zn}_2(\text{MeOH})_4$, the OMn(Zn)O angles are varying in the 77.18(10)–165.89(14)° range (see table 2 for precise values).

Both compounds $4\text{-Mn}_2(\text{DMF})_2(\text{MeOH})_4$ and $4\text{-Zn}_2(\text{MeOH})_4$, in the dimeric units, present the short Mn–Mn and Zn–Zn distances of 3.505(2) and 3.219(1) Å, respectively.

In $4\text{-Mn}_2(\text{DMF})_2(\text{MeOH})_4$ no solvent molecules were found in the pores of the compact structure.

Discussion

The use of ligand **4** (figure 1), offering four divergently oriented carboxylic acid moieties, that are fully deprotonated into carboxylate coordinating sites (**4**⁴⁻), afforded four different types of high dimensional coordination polymers when combining with transition

metals.

The formation of four different types of networks is a consequence of the low flexibility of **4**, blocked in 1,3-Alternate conformation and behaving either as slightly deformed tetrahedral (**4**-Zn₂(Py)₄, 2D) or as significantly deformed tetrahedral connectors (all other compounds), leading to high-dimensional 2D and 3D compounds, respectively. In the formed coordination networks, the metallic species reveals to be either in a deformed tetrahedral (**4**-Zn₂(Py)₄) or deformed octahedral environment (all other compounds). But these species act either as linear mononuclear connectors (for **4**-Zn₂(Py)₄, **4**-Co₂(Py)₆(H₂O)₂ and **4**-Ni₂(Py)₆(H₂O)₂) or as deformed square planar binuclear connectors (for **4**-Mn₂(Py)₄(MeOH)₂, **4**-Mn₂(DMF)₂(MeOH)₄ and **4**-Zn₂(MeOH)₄). As already stated, the formation of 2D grids can result from the combination of rectangular or tetrahedral ligands with linear connectors (schematic representation figure 6a) whereas the formation of 3D diamond-like networks may results either from the interconnection of two types of deformed tetrahedra or from the interconnection of tetrahedra with linear or square planar connectors (schematic representation figures 6 c and b).²⁹ It is interesting to note that, since **4**-Mn₂(Py)₄(MeOH)₂, **4**-Mn₂(DMF)₂(MeOH)₄ and **4**-Zn₂(MeOH)₄ are formed, based on the same coordination pattern, through the formation of Mn₂ or Zn₂ binuclear coordination units, they are isomorphous and present 3D pores that have analogous metrics. The calculated void space per unit size of the pores are 10x6 Å² for **4**-Mn₂(Py)₄(MeOH)₂, 6x4 Å² for **4**-Mn₂(DMF)₂(MeOH)₄ and 6x6 Å² for Zn₂(MeOH)₄. The voids space per unit cell are equal to: 8124.96 Å³ (87.21%) for **4**-Mn₂(Py)₄(MeOH)₂, 5870.72 Å³ (87.21%) for **4**-Mn₂(DMF)₂(MeOH)₄, 5814.20 Å³ (87.36%) for Zn₂(MeOH)₄ (calculated by PLATON).

In addition, both metallic cations have already shown their propensity to form short M-M bonds in their homometallic dimeric units.

All the parameters governing the formation of the high dimensional networks are gathered in table 3.

Table 3: Parameters governing the formation of the high dimensional **4**-Zn₂(Py)₄, **4**-Co₂(Py)₆(H₂O)₂, **4**-Ni₂(Py)₆(H₂O)₂, **4**-Mn₂(Py)₄(MeOH)₂, **4**-Mn₂(DMF)₂(MeOH)₄ and **4**-Zn₂(MeOH)₄

	4 -Zn ₂ (Py) ₄	4 -Co ₂ (Py) ₆ (H ₂ O) ₂ 4 -Ni ₂ (Py) ₆ (H ₂ O) ₂	4 -Mn ₂ (Py) ₄ (MeOH) ₂	4 -Mn ₂ (DMF) ₂ (MeOH) ₄ 4 -Zn ₂ (MeOH) ₄
Environment of Metal	Td	Oh	Oh	Oh
Coordination sphere	N2O2	N3O3	N2O4	O6
Nature of the metallic connector	Linear (mononuclear)	Linear (mononuclear) or deformed square planar binuclear connectors	deformed Tetrahedral (binuclear)	deformed Tetrahedral (binuclear)
Coordination modes of carboxylate	monodentate	monodentate	monodentate	Monodentate/bidentate (Zn)
Dimensionality	2D	3D pseudo diamondoid-like	3D pseudo diamondoid-like	3D pseudo diamondoid-like
Schematic representation	Figure 6a	Figure 6b	Figure 6c	Figure 6c

Figure 6: For the observed high-dimensional networks, schematic representation of (a) 2D grids resulting from the combination of rectangular (or losange-like) ligands with linear connectors, (b) 3D pseudo diamondoid-like networks resulting from the combination of 7tetrahedral with linear connectors and (c) 3D pseudo diamondoid-like networks resulting from the combination of two types of deformed 7tetrahedral.

Conclusion

The use of the tetramercaptotetrathiacalix[4]arene TMTCA, blocked in 1,3-Alternate conformation and appended with four methylenecarboxylate coordinating groups **4** successfully leads, in mild conditions, to the formation of coordination networks, when the latter was combined with transition metals at the oxidation state (II) such as Co, Mn, Ni and Zn. Depending on

the nature of the used metal and on the nature of the synthetic conditions (use of coordinating Pyridine or non-coordinating Et₃N as base), four types of different high-dimensional coordination polymers have been evidenced. The nature (connectivity and geometry) of the extended architectures essentially depends on nature of the metal: 2D for metal cations adopting a tetrahedral environment (4-Zn₂(Py)₄), and pseudo diamond-like 3D networks, with sometimes, the formation of binuclear metallic units in the frameworks in the case of 4-Mn₂(Py)₄(MeOH)₂, 4-Mn₂(DMF)₂(MeOH)₄ and 4-Zn₂(MeOH)₄. It is important to note, that due to their low accessibility and the low affinity of the used metals, the sulphur atoms don't enter into the coordination sphere of the metals.

One may conclude that despite the inherent rigidity of the organic ligand **4**, the topology of the resulting coordination patterns depends significantly either on the nature of the used metallic cations or on the used solvent molecules involved in the coordination process. As a consequence, the predictability of the obtained coordinating patterns appears rather low. Further investigation including the preparation of new coordination polymers using other solvent systems as well as other metallic cations will be continued.

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Notes and references

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Table 1: Crystallographic Parameters for **4-Zn₂(Py)₄**, **4-Co₂(Py)₆(H₂O)**, **4-Ni₂(Py)₆(H₂O)**, **4-Mn₂(Py)₄(MeOH)₂**, **4-Mn₂(DMF)₂(MeOH)₄** and **4-Zn₂(MeOH)₄** recorded at 173 K.

Formula	4-Zn₂(Py)₄ C ₄₈ H ₅₄ O ₈ S ₈ Zn ₂ (C ₅ H ₅ N) ₄ , 1.5(C ₅ H ₅ N), 0.75(CH ₃ OH)	4-Co₂(Py)₆(H₂O)₂ C ₄₈ H ₅₄ S ₈ O ₈ Co ₂ (C ₅ H ₅ N) ₆ (H ₂ O), 3(CH ₃ OH), H ₂ O	4-Ni₂(Py)₆(H₂O)₂ C ₄₈ H ₅₄ S ₈ O ₈ Ni ₂ (C ₅ H ₅ N) ₆ (H ₂ O), 0.25(C ₅ H ₅ N) _{0.25} , CH ₃ OH	4-Mn₂(Py)₄(MeOH)₂ 2(C ₂₄ H ₂₇ S ₄ O ₄ Mn(C ₅ H ₅ N) ₂ (CH ₃ OH)), 4(C ₅ H ₅ N), H ₂ O	4-Mn₂(DMF)₂(MeOH)₄ C ₂₄ H ₂₇ S ₄ O ₄ Mn(C ₃ H ₇ NO)(CH ₃ OH) ₂	4-Zn₂(MeOH)₄ C ₂₄ H ₂₇ O ₄ S ₄ Zn ₂ (CH ₃ OH) ₂
Molecular weight	1603.19	1737.99	1709.26	1836.13	698.81	634.12
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	15.6172(11)	24.4001(12)	24.5031(8)	23.1233(11)	19.0093(9)	18.6752(10)
<i>b</i> (Å)	25.956(2)	45.643(3)	45.605(2)	19.3037(10)	19.6552(9)	19.4783(10)
<i>c</i> (Å)	22.5235(10)	19.8706(10)	19.9347(9)	21.8209(12)	19.0680(6)	19.3185(9)
<i>α</i> (deg)	90	90	90	90	90	90
<i>β</i> (deg)	92.578(2)	122.247(2)	122.2980(10)	106.950(2)	107.8880(10)	108.722(2)
<i>γ</i> (deg)	90	90	90	90	90	90
<i>V</i> (Å ³)	9120.9(10)	18716.4(18)	18829.7(13)	9317.0(8)	6780.0(5)	6655.5(6)
<i>Z</i>	4	8	8	4	8	8
Colour	Colourless	Light pink	Light green	Colourless	Colourless	Colourless
Crystal dim (mm ³)	0.050 x 0.060 x 0.060	0.040 x 0.050 x 0.060	0.060 x 0.060 x 0.070	0.050 x 0.050 x 0.060	0.07 x 0.04 x 0.04	0.040 x 0.040 x 0.060
<i>D</i> _{calc} (gcm ⁻³)	1.167	1.234	1.206	1.309	1.369	1.266
<i>F</i> (000)	3346	7296	7180	3848	2936	2640
<i>μ</i> (mm ⁻¹)	0.759	0.590	0.632	0.511	0.679	1.022
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Number of data meas.	24310	26484	22682	117823	18922	9009
Number of data with <i>I</i> > 2σ(<i>I</i>)	24310 [R(int) = 0.0860]	26484 [R(int) = 0.0760]	----	13616 [R(int) = 0.0450]	9115 [R(int) = 0.0420]	9009 [R(int) = 0.0385]
<i>R</i>	R1 = 0.0815, wR2 = 0.2212	R1 = 0.1025, wR2 = 0.2683	R1 = 0.1203, wR2 = 0.2951	R1 = 0.0598, wR2 = 0.1586	R1 = 0.0634, wR2 = 0.1606	R1 = 0.0833, wR2 = 0.2075
<i>R</i> _w	R1 = 0.1505, wR2 = 0.2472	R1 = 0.2334, wR2 = 0.2991	R1 = 0.2185, wR2 = 0.3364	R1 = 0.0838, wR2 = 0.1735	R1 = 0.1127, wR2 = 0.1890	R1 = 0.1191, wR2 = 0.2273
GOF	1.039	1.021	1.013	1.165	1.028	1.114
Largest peak in final difference (eÅ ⁻³)	1.646 and -0.617	1.064 and -1.033	1.083 and -0.995	1.774 and -1.231	1.213 and -0.805	1.995 and -1.695

Table 2: Useful angles and distances in **4-Zn₂(Py)₄**, **4-Co₂(Py)₆(H₂O)₂**, **4-Ni₂(Py)₆(H₂O)₂**, **4-Mn₂(Py)₄(MeOH)₂**, **4-Mn₂(DMF)₂(MeOH)₄** and **4-Zn₂(MeOH)₄**.

	4-Zn₂(Py)₄	4-Co₂(Py)₆(H₂O)₂	4-Ni₂(Py)₆(H₂O)₂	4-Mn₂(Py)₄(MeOH)₂	4-Mn₂(DMF)₂(MeOH)₄	4-Zn₂(MeOH)₄
d(CO _{carbonyl})	1.211(5) 1.218(7) 1.220(6) 1.240(6) 1.258(5) 1.261(6) 1.272(7) 1.285(6)	1.203(8) 1.222(8) 1.228(7) 1.251(7) 1.257(8) 1.263(6)	1.196(9) 1.219(9) 1.231(8) 1.246(8) 1.257(9) 1.264(8) 1.265(8) 1.331(9)	1.243(4) 1.248(3) 1.255(3) 1.258(3)	1.239(5) 1.241(4) 1.249(5) 1.287(4)	1.214(9) 1.225(6) 1.265(8) 1.293(6)
d(M-N _N), Å	2.038(4) 2.047(5) 2.050(5) 2.074(5)	2.103(6) 2.159(7) 2.164(5) 2.172(8) 2.189(4) 2.193(5)	2.073(7) 2.0870(13) 2.125(5) 2.130(5) 2.147(5) 2.198(6)	2.263(2) 2.329(2)	-	-
d(M-O _{carbonyl}), Å	1.941(3) 1.944(3) 1.949(3) 1.975(3)	2.013(4) 2.041(4) 2.046(6) 2.089(4)	2.047(5) 2.051(6) 2.055(4) 2.074(4)	2.1521(19) 2.1654(19) 2.1679(18)	2.082(3) 2.122(3) 2.221(2) 2.263(3)	1.956(5) 2.026(3) 2.153(3) 2.153(4)
d(M-O), Å	-	-	-	2.193(2) (MeOH)	2.228(3) (MeOH) 2.240(3) (DMF)	1.976(7) (MeOH)
d(M-O _{water}), Å	-	2.109(4) 2.357(12)	2.080(5) 2.204(10)	-	-	-
∠ (N _N -M-N _N), °	104.16(19) 104.85(16)	85.3(3) 87.06(18) 92.94(17) 96.4(2) 178.2(3) 179.04(19)	83.3(3) 87.8(2) 92.8(2) 94.89(19) 177.8(2) 178.8(2)	96.59(9)	-	-
∠ (N _N -M-O _{carbonyl}), °	97.56(16) 97.74(16) 99.26(16) 106.0(2) 108.49(18) 112.76(15) 119.52(17) 122.97(16)	87.15(18) 88.00(17) 88.5(2) 88.46(16) 89.02(16) 89.4(2) 89.5(2) 89.7(2) 90.57(17) 91.5(2) 91.94(17)	86.3(2) 87.8(3) 87.97(18) 88.0(2) 88.11(19) 88.48(19) 89.7(3) 89.8(2) 91.43(19) 90.9(2) 91.00(19) 92.6(2)	83.06(8) 85.34(8) 86.88(8) 86.94(8) 91.44(8) 178.68(8)	-	-
∠ (N _N -M-O), °	-	87.30(16) 87.5(4) 90.9(4) 92.64(17) 172.8(4) 176.48(18)	87.3(2) 87.7(6) 92.1(2) 94.2(6) 176.0(3) 177.5(2)	86.82(9) 176.55(9)		
∠ (O _{carbonyl} -M-O _{carbonyl}), °	104.74(13) 133.50(18)	174.41(17) 177.9(2)	173.20(19) 176.8(3)	91.85(8) 95.91(7) 171.82(7)	77.18(10) 82.83(11) 83.55(12) 99.59(10) 111.27(10) 165.89(13)	79.29(14) 100.53(16) 144.3(2)
∠ (O _{carbonyl} -M-O), °	-	88.49(16) 90.3(3) 91.4(3) 96.37(16)	88.9(4) 89.45(19) 93.4(4) 96.2(2)	88.21(8) 93.52(8) 93.89(8)	81.50(12) 84.44(11) 86.78(10) 89.78(11) 90.66(13) 107.20(11) 163.10(10) 163.48(10)	85.8(2) 90.72(17) 91.75(14) 96.2(3) 119.4(4) 168.75(14)
∠ (O-M-O), °	-	-	-	-	87.11(11)	88.5(2)

Graphical Abstract