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Control of dimensionality in Manganese Coordination Polymers using rigid tetrahedral-shaped [1.1.1.1]metacyclophane ligands bearing benzoate coordinating sites: from homochiral 1D to 3D diamond-like structures

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ABSTRACT

Solvothermal synthesis involving tetrasubstituted carboxylic derivatives of [1.1.1.1]metacyclophane (**1-2**) bearing rigid phenyl spacer, that inherently adopt the *1,3*-Alternate conformation, with Manganese salts (acetate and nitrate) led to new 1D and 3D coordination polymers: {**1**₃-Mn₉O₃(CH₃COO)₆(C₅H₅N)₁₂} (**1**₃-Mn₉) and {**2**-Mn₂(C₃H₇NO)₂} (**2**-Mn₂), respectively. The X-ray diffraction analysis revealed that: (i) ligand **1**, containing *meta*-benzoate coordinating sites, forms a 1D chiral helicoidal Coordination Polymer (**1**₃-Mn₉) with trinuclear metallic clusters (Mn^{II}Mn^{III}₂(μ₃-O)) acting as linear connection nodes; (ii) ligand **2**, bearing *para*-benzoate moieties forms, a 3D diamond-like Coordination Polymer (**2**-Mn₂) presenting Mn(II) polymeric chains bridged by tetrahedral-shaped ligand. The obtained Mn-based compounds are the first examples of coordination polymers based on tetrasubstituted [1.1.1.1]metacyclophane ligands bearing carboxylate coordinating groups.

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Design of new molecular materials able to exhibit, in the crystalline phase, specific physical properties, such as magnetism, conduction, luminescence, selective adsorption, catalysis etc., still attracts a growing interest due to their wide potential application in nanotechnologies, for example. The formation of extended metal-organic compounds, so called Coordination Polymers (CP)¹, networks² or MOFs,³ based on organic ligands and bridging metallic ions, can be considered as the key step for the obtention of new polyfunctional molecular systems with desired structure and properties. The control of the molecular self-assembly and recognition processes⁴ can be thus achieved by rational design of the organic ligands both with the appropriated choice of metallic cations.

In this aspect, metacyclophane derivatives such as calix[4]arene,⁵ thiacalix[4]arene⁶ and [1.1.1.1]metacyclophane⁷ displaying a four-membered macrocyclic backbone are of particular interest to act as ligands for building new Coordination Polymers. They can be indefinitely chemically modified, through synthetic functionalization of both lower and/or upper rims. Concerning their geometry, when blocked in *1,3*-Alternate conformation, they may adopt symmetrical tetrahedral shape, which is suitable for the generation of high dimensionality periodic structures when combined with different metallic cations, as already demonstrated for (thia)calix[4]arene.⁸

Compared to calix[4]arene, [1.1.1.1]methacyclophane display a reinforced rigidity of their molecular platform while

adopting a *1,3*-Alternate conformation over a wide range of temperature (60°C to 150°C)⁹ resulting from the repulsion of *ortho*-disposed methyl groups, preventing thus the spontaneous rotation of aryl units around C-C single bonds in solution, as well as in the solid state. Therefore, the [1.1.1.1]metacyclophane backbone represents a very attractive platform and a lot of various functional groups using as terminal coordinating sites (phenol,¹⁰ thiophenol,¹⁰ p-methylthiophenyl,¹⁰ p-methoxyphenyl,¹⁰ methylthio,¹¹ cyano^{10,12} pyridyl,^{10,11,13,14} imidazolyl¹⁵ or pyrazolyl^{16,17} bisquinolinyl¹⁸ diphenylphosphanyl¹¹ or diphenylphosphoryl,¹¹ bipyridyl¹⁸ amino,¹¹ carboxylic^{11,19} groups) have been grafted to metacyclophane platform leading to *V*-shaped or to tetrahedral-shaped (disubstituted or tetrasubstituted compounds, respectively) ligands.

The coordination abilities towards transition metallic cations of some of previously reported [1.1.1.1]methacyclophane derivatives have been investigated in the solid state, which led to the formation 0D-3D coordination compounds.²⁰ It should be mentioned that, up to now, no Coordination Polymers based on [1.1.1.1]metacyclophane bearing O-donor coordinating sites, such as carboxylate groups, have been reported. In order to form robust Coordination Polymers, carboxylate donor ligands satisfy various geometric requirements, which may lead to stable networks presenting various dimensionalities and topologies, when combined with metallic cations.²¹

Along this line, we designed two macrocyclic ligands (**1** and **2**,¹⁹ figure 1) based on [1.1.1.1]metacyclophane tetrasubstituted with acids functional groups, and blocked in *1,3*-Alternate conformation, which are suitable for the formation of high dimensional networks. One can note that both ligands, due to the *1,3*-alternate conformation of the macrocyclic platform, present a tetrahedral shape and are positional isomers. Whereas **1** offers two coordinating sites located on both sides of the macrocyclic platform and composed of two closely disposed carboxylic groups located in *meta* position of the benzoate rings, **2** presents carboxylic groups pointing in *para* position of the benzoate substituents, forming thus a rigid ligand with four divergently orientated binding sites. Thus, the influence of the location of the coordinating groups on the phenyl ring on the dimensionality of the formed coordination compounds will be discussed here below.

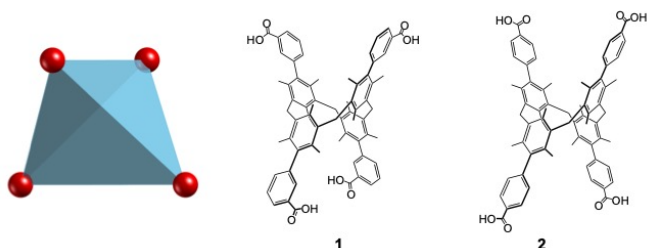


Figure 1: Macrocyclic ligands **1** and **2** derived from [1.1.1.1]metacyclophane blocked in *1,3*-Alternate conformation and the corresponding polyhedral representation.

Tetrasubstituted [1.1.1.1]metacyclophane derivatives (**1** and **2**)¹⁹ containing carboxylic functional groups, were combined with Mn(II) salts in solvothermal conditions leading to the formation of two new Coordination Polymers (**1**₃-Mn₉ and **2**-Mn). In the structural description performed below, the distances found in **1** or **2** are not discussed because they are in accordance with the ones found in the solid-state structures of the previously reported ligands.¹⁹

1₃-Mn₉ results from the combination of Mn(OAc)₂ with **1** under solvothermal conditions, using pyridine as base and solvent for the deprotonation of the carboxylic groups into carboxylate (see experimental conditions in supplementary data). Its crystal was analyzed using X-Ray diffraction which showed that **1**₃-Mn₉ crystallizes in a trigonal *R*32 chiral space group (see the crystallographic table S1) displaying the formula {**1**₃-Mn₉O₃(CH₃COO)₆(C₅H₅N)₁₂}. The obtained coordination compound is composed of Mn cations, fully deprotonated ligand **1**⁴⁻ (according to observed C-O distances, as shown in table S2), one oxide anion O²⁻, that has been generated during solvothermal process, acetate anions and pyridine molecules (free and coordinated to metallic atoms). Taking this into account, the charge balance leads to Manganese cations presenting two different oxidation states, as shown by the formula {**1**₃-Mn^{II}₃Mn^{III}₆O₃(CH₃COO)₆(C₅H₅N)₁₂}. This assumption is also supported by the presence of two crystallographically independent Mn atoms (Mn1 = Mn(III) and Mn2 = Mn(II)) in the network.

Two trinuclear Mn₃O(AcO)₂(C₅H₅N)₃ building units, (figure 2a) are bridged by **1**⁴⁻ ligands, behaving as deformed tetrahedral linkers, leading thus to a one-dimensional Coordination Polymer, as shown in figure 2b, directed along the *c* axis. The formation of similar trinuclear Mn₃O(AcO)₂(C₅H₅N)₃ units has already been observed in other Coordination Polymers.^{22,23} The binding between [1.1.1.1]metacyclophane carboxylate moieties and

trinuclear Mn-cluster nodes leads to a distortion of the linear geometry of the 1D Coordination Polymer, transforming it into an helicoidal structure (Figure 2b). Surprisingly, only one type of helices was found within the homochiral crystal lattice. The crystal packing of **1**₃-Mn₉ results from the parallel stacking of homochiral chains along the *a* and the *c* axes.

The Manganese centres are in a slightly deformed octahedral environment, as shown in figure 2a, with 5 oxygen atoms belonging to O²⁻, bridging acetate ligands and carboxylate ligands from **1**⁴⁻. The sixth coordination site is occupied by a nitrogen atom from a pyridine moiety. The bonds and angles are given in table S2 and the distances are in accordance with the presence of Mn(II) and Mn(III) cations: shorter Mn-O and Mn-N distances are assigned to Mn(III) (Mn1) atoms and a slight distortion for Mn(II) (Mn2) was observed.

In the trinuclear Mn^{II}Mn^{III}₂(μ₃-O) unit, the Mn-Mn distances are equal to 3.386(2), 3.507(3) and 3.508(4)Å, displaying thus a slightly deformed isosceles triangle.

The magnetic properties of such triangular mixed valence systems have already been reported in the literature, displaying antiferromagnetic coupling between the magnetic centres.²⁴

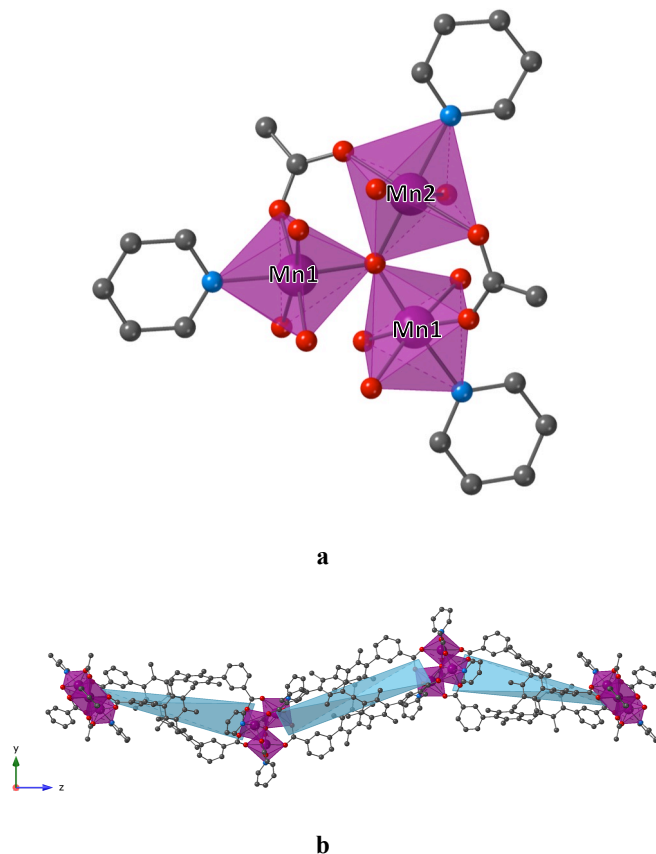


Figure 2: Solid-state structure of **1**₃-Mn₉ showing (a) the environment of the Mn atoms in the trinuclear unit and (b) the resulting helicoidal chain running along the *c* axis. H atoms and solvent molecules are not presented for clarity.

Pyridine solvent molecules are also present in the crystal, with weak π -stacking with aromatic fragments of **1**⁴⁻. Unfortunately, **1**₃-Mn₉ appeared to be unstable in air, and no XRPD diagram could be recorded for the corresponding crystalline powder.

2-Mn_2 is formed by the combination, in DMF, of $\text{Mn}(\text{NO}_3)_2$ with **2** in solvothermal conditions (see experimental conditions in supplementary data). Suitable crystals of formula $\{2\text{-Mn}_2(\text{C}_3\text{H}_7\text{NO})_2\}$ (2-Mn_2) were formed and analyzed. It was established that 2-Mn_2 crystallizes in a monoclinic $C2/c$ space group, as shown in the crystallographic table S1. Its crystal is composed of Mn(II) cations, fully deprotonated ligand 1^+ (as shown by the C-O distances, table S2) and DMF molecules coordinated to the metallic cations. The structure was refined by applying the squeeze command.²⁵ In contrast to 1_3-Mn_9 , 2-Mn_2 presents a 3D structure, where the Mn(II) atoms form polymeric chains, which are interconnected by 1^+ , acting as tetrahedral connectors (Figure 3a). Two crystallographically independent Mn(II) atoms are located alternatively in the chain (figure 3a); they both present a deformed octahedral environment composed of 6 O atoms (see bonds and angles in table S2). Mn1 is surrounded by 2 O atoms belonging to DMF ligand, located in *trans* position, and 4 O atoms from carboxylate groups belonging to 4 different ligands. Each carboxylate group acts a monodentate coordinating group to Mn1 cations and bridging Mn1 with Mn2 atoms with a Mn-Mn distance equal to 3.788(5)Å. Mn2 is also surrounded by 6O atoms from 4 carboxylate groups of 4 different macrocycles. Contrary to Mn1, for Mn2 two of the four coordinating carboxylate fragments act as bidentate binding group, the other are bridging. The formation of chains involving O bridged Mn(II) species with short distances between the magnetic centers has been extensively reported in the field of molecular magnetism, with coupling ranging from antiferromagnetic to ferromagnetic depending on the structural parameters.²⁶

The structure is resulting from the connection between 1^+ and Mn(II) cations, where 1^+ behave as deformed tetrahedral-shaped organic linkers,²⁷ leading to a 3D diamond-like structure, as shown in figures 3b and c. The three-dimensional coordination compound displays channels aligned along z axis, with cavity size about 13×8 Å.

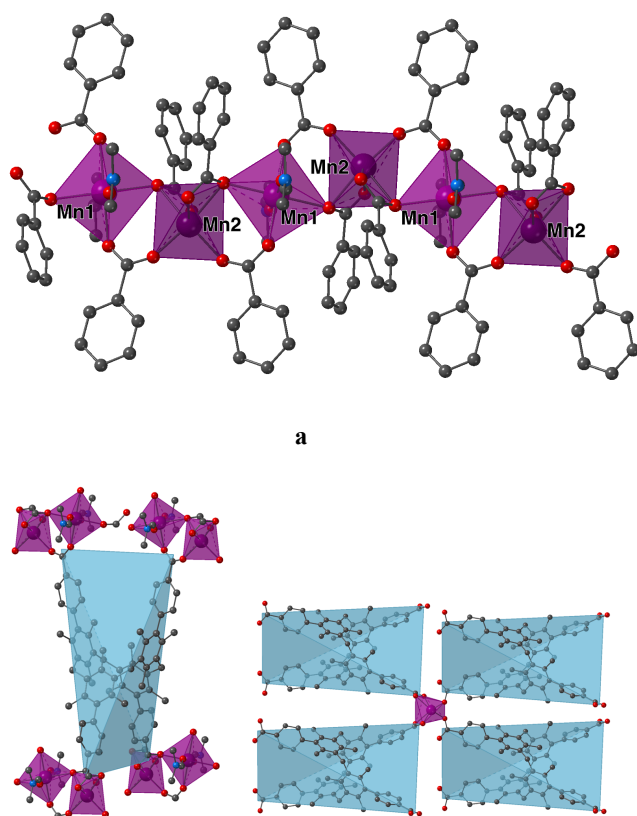


Figure 3: Solid-state structure of 2-Mn_2 showing (a) the environment of the Mn atoms in the chain, (b) environment of the ligands and of one of the Mn atoms, and (c) the overall diamond-like structure, resulting from the recognition of tetrahedra. H atoms are not presented for clarity.

The XRPD analysis of microcrystalline samples of 2-Mn_2 revealed a good match between simulated and observed diagrams implying the presence of one single crystalline phase (Figure S1).

In conclusion, we have investigated the coordination abilities of two carboxylic/ate-based tetrasubstituted ligands, (**1** and **2**) derived from the [1.1.1.1]metacyclophane blocked in *1,3*-Alternate conformation. As expected, the ligands, that differ by the position of the carboxylate coordinating groups (*meta* or *para*) on their benzoate substituents, display a different coordination behavior while building Coordination Polymers with Manganese (II) cations. A 1D chiral helicoidal Coordination Polymer (1_3-Mn_9) was formed with **1**, which accounts for the “inner” coordination mode resulting from the *meta* position of the carboxylate groups on the phenyl substituent. This low dimensionality is the consequence of great geometrical constraints for **1**. In contrast, ligand **2**, bearing carboxylate coordinating groups in *para* position of the phenyl spacer, is well suited for *exo* coordination with metallic cations, and leads to a 3D diamondoid-like Coordination Polymer (2-Mn_2).

The study of the coordination abilities of **1** and **2** with other metals is still under investigations.

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Supplementary Data

Table for X-ray diffraction studies of 1_3-Mn_9 and 2-Mn_2 , relevant bonds and angles for 1_3-Mn_9 and 2-Mn_2 , XRPD diagram for 2-Mn_2 and complete experimental part.

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