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## ARTICLE

# Nuclearity control in calix[4]arene based zinc (II) coordination complexes

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Three zinc based coordination complexes were selectively generated in the crystalline phase using new flexible molecular “tweezers” calix[4]arene derivative ligand decorated with two appended carboxylic moieties and benzyl spacers ((**3-4H**)). Through the control of the metal/ligand ratio and the synthetic conditions, the coordination sphere around the zinc cations was found to be different, which influenced the nuclearity of the obtained complexes. The mononuclear complex (**3-3H**)<sub>2</sub>-Zn(DMF)<sub>2</sub> was obtained while two partially deprotonated ligands (**3-3H**)<sup>-</sup> cap the metallic cation, leading to non tubular “8”-shaped structure with metal/ligand ratio equal to 1/2. The dinuclear (**3-2H**)<sub>2</sub>-Zn<sub>2</sub>py<sub>4</sub> complex displays a tubular structure with metal/ligand ratio equal to 1/1 where two zinc cations act as linear metal linker between two (**3-2H**)<sup>2-</sup> species which adopts a cone conformation. Finally, the third trinuclear coordination complex (**3-2H**)<sub>4</sub>-Zn<sub>3</sub>(OH)<sub>2</sub> was obtained using (**3-4H**) and the highly coordinating sulfonylcalix[4]arene (**4-4H**), exhibiting 3/1/1 metal/**3/4** ratio. Thus, it has been demonstrated that under self-assembly conditions, the nuclearity of the new complexes based on zinc cations and calix[4]arene dicarboxylate (**3-4H**) can be tuned, using different synthetic conditions (nature of solvent, crystallization method, use of a highly coordinating ligand (**4-4H**)).

## Introduction

In the field of supramolecular chemistry, controlling and designing molecular building blocks for the formation of metal-organic superstructures by self-assembly is highly challenging. The resulting large nanometre scale assemblies, such as mono- and polynuclear species, are formed with greater frequency due to the elucidation of supramolecular motives and recognition patterns formed between organic ligands and metallic cations or clusters, displaying different topologies and nuclearities. For building these species, a large variety of ligands may be used: from simple organic ligands to sophisticated macrocyclic structures. Calixarenes<sup>1</sup> are macrocyclic molecules that have been well studied for this purpose, due to the possibility to control the nature of the coordinating sites *via* synthetic tools as well as their molecular conformation. This family of macrocycles has been used for the formation of a large variety

of coordination compounds in the crystalline phase, as well as in solution, because of the rich coordination abilities and their relatively rigid scaffold. Calix[4]arene derivatives have been successfully involved in coordination with d/f metal cations leading to formation of extended coordination compounds demonstrating various dimensionalities (1D-3D), and topologies,<sup>2</sup> displaying smart physical properties such as luminescence, single-molecular magnet behaviour or gas storage / separation.<sup>3,4</sup>

On the other hand, when adopting a *cone* conformation, (**1-4H**) calix[4]arene,<sup>5</sup> (**2-4H**) thiocalix[4]arene<sup>6</sup> and (**4-4H**) tetrasulfonylcalix[4]arenes<sup>7,8</sup> (Figure 1), have shown a high ability to generate discrete polynuclear metal complexes (0D), due to formation of at least four pre-organized coordination cavities composed of two O-phenolate moieties and one S- or SO<sub>2</sub>-bridging group of macrocyclic backbone.

In the last years, several examples of high nuclearity coordination complexes based on the cone conformer of (**1-4H**)<sup>9,10,11,12</sup> and (**2-4H**)<sup>13,14,15</sup> including large oxoclusters<sup>16,17,18,19,20</sup> have been reported. In some cases, giant high nuclear spheres comprising up to 48 metal atoms were obtained using (**2-4H**).<sup>21,22</sup> The use of (**4-4H**), offering four additional SO<sub>2</sub>-binding sites, was the occasion to obtain complexes of different nuclearities<sup>23,24</sup> and cluster capsules as well.<sup>25,26</sup> Moreover, it was found that these macrocyclic ligands enable to discover

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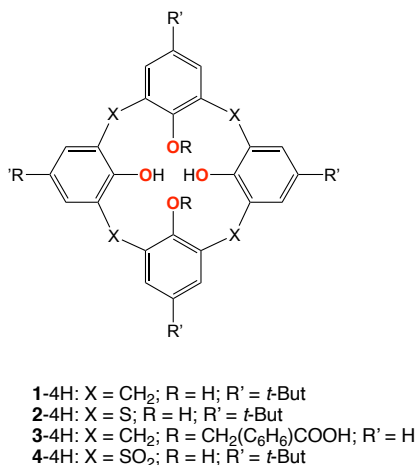
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recently this new and fascinating world of calixarene based high nuclearities complexes.<sup>27</sup> Nanocages spheres<sup>28</sup> of different size with smart potential applications, are a natural extension of this approach.



**Figure 1.** Classical *p*-*tert*-butylcalix[4]arene (1-4H), thiacalix[4]arene (2-4H), the targeted macrocyclic ligand (3-4H) and Tetrasulfonylcalix[4]arene (4-4H)

It is important to note, that such macrocyclic calixarene-based complexes, presenting a hollow metal-organic structure, can sometimes also be considered as Metalla(macro)cycles<sup>29,30,31</sup> adopting different sizes and nuclearities. Due to the presence of confined metal centers metalla(macro)cycles represent very attractive supramolecules able to be used as catalysts, magnetic, luminescent and redox materials. It was shown that one of the possible ways to generate these type of hybrid species is to combine [1.1.1.1]-metacyclophanes derivatives, a subclass of calix[4]arene compounds, bearing two or four terminal coordinating binding sites with metallic cations like Co(II), Cu(II), Zn(II), Hg(II) and Ag(I).<sup>32,33,34,35</sup> In a recent work, we investigated the propensity of (4-4H) to form calixarene based metallomacrocycles: the first example of non-symmetrical trinuclear species build from two different types of calixarenes has been reported.<sup>36</sup> For this purpose, we designed a *tert*-butylcalixarene (with a shape analogue to the one of (3-4H), Figure 1) presenting a cone conformation combined with a tweezer shape, while appending two coordinating groups on the lower rim of the macrocyclic species leading to realisation of chelate coordination mode well adopted for high nuclearity complexes formation. Some of related coordination compounds involving a tweezer based calixarene dicarboxylic ligand, analogous to (3-4H), have already been reported,<sup>37</sup> including also extended systems.<sup>38</sup>

In this work, we intend to understand the coordination abilities of the calixarene new ligand (3-4H), Figure 1, that has been designed for the formation of OD coordination compounds, and presenting a tweezers shape with benzoic/ate appending coordinating group. This ligand has been combined with Zinc nitrate salt, and, depending on the synthetic conditions, a variety of complexes of different nuclearities has been obtained. The structure of three new calixarene based symmetrical complexes is presented here below, evidencing the

formation of a mononuclear ML<sub>2</sub> and dinuclear M<sub>2</sub>L<sub>2</sub> compounds. Furthermore, using two different calixarene ligands *i.e.* (3-4H) and the highly coordinating (4-4H), a trimetallic metallamacrocyclic was obtained.

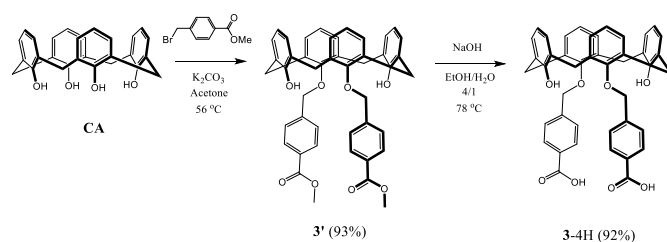
## Results and discussion

### Synthesis of (3-4H)

Ligand (3-4H) has been designed as a tweezer for binding the zinc cations and presents a disubstituted calix[4]arene derivative bearing two carboxylic groups connected to macrocyclic platform *via* benzyl moieties. The synthesis of (3-4H) was achieved in high yield following a slightly modified procedure described for preparation of its *p*-*tert*-butyl analogue<sup>39,40</sup> following a two steps procedure (Figure 2). Firstly, two appended substituents containing ester junction have been successfully grafted to the macrocyclic platform using nucleophilic substitution reaction between *p*-*H*-calix[4]arene (CA)<sup>41</sup> and methyl 4-(bromomethyl)benzoate in the presence of potassium carbonate acting as a base, leading to 3'. Finally, a targeted dicarboxylic acid derivative (3-4H) was generated by hydrolysis of the obtained intermediate diester derivative 3' in the basic media using sodium hydroxide.

The structure of compound (3-4H) was established and characterized in solution using both <sup>1</sup>H-/<sup>13</sup>C-NMR spectroscopies and MALDI TOF-mass spectrometry which confirmed the appearance of two grafted benzyl carboxylic moieties in the distal substituted macrocyclic backbone (see Experimental section) adopted in cone conformation.

The structure was also confirmed in the solid state, while crystallized from a DMSO solution.



**Figure 2.** Synthetic pathway for the formation of (3-4H)

### Structure of (3-4H)

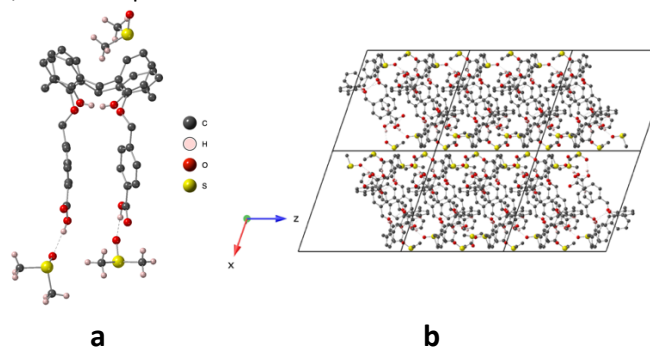
The structure of the new ligand (3-4H) has been determined using X-ray diffraction on single crystals which revealed that (3-4H) crystallizes in a monoclinic *P*2<sub>1</sub>/*c* space group (see crystallographic Table 1) forming a solvate with three DMSO molecules giving rise to formula (3-4H) • 3(DMSO). As indicated by the C-O distances (Table 2), the carboxyl moieties remain fully protonated in the (3-4H) compound. As expected, in the crystalline phase, (3-4H) displays a cone conformation

demonstrating a molecular tweezer shape decorated by two pendant arms equipped with carboxylic coordinating sites (Figure 3). In the crystal, two of three DMSO molecules are connected to calix[4]arene molecule due to formation of H-bonds with carboxylic groups displaying O...O distances of 2.588(4) and 2.608(4) Å, as shown in Figure 3a. The bonds and distances in the macrocyclic ring are in accordance with what is usually observed for parent calix[4]arene compound.<sup>42</sup> The oppositely disposed aryl rings of the macrocyclic platform are not parallel and form a dihedral angle equal to 40.66° and 81.51° leading to pinched cone conformation of calix[4]arene backbone stabilized by intramolecular H-bonding between OH-phenolic moieties and O-ether junctions belonging to neighbouring aryl groups with O...O distances in the range of 2.749(2)- 2.895(2) Å (Table 3) which is typical for lower rim disubstituted calix[4]arene compounds.<sup>43,44,45,46,47</sup>

**Table 3.** Observed intramolecular H-bonds distances in the crystal structure of (3-4H) determined by X-ray diffraction on single crystals.

D-H...A	d <sub>O...O</sub> , (Å)
O2...O1	2.665(2)
O4...O3	2.749(2)
O4...O1	2.895(2)
O2...O1	2.665(2)

The aromatic rings of appended carboxyphenyl substituents are found not parallelly aligned demonstrating a tilt angle of 23.94° and a distance between two phenyl rings of 4.637(5) Å which shows a very weak  $\pi$ -interaction between two pendant arms. In the crystal, the DMSO molecules form columns running along the Oz axis, as shown in Figure 3b. The DMSO molecules are lying between planes formed by alternately disposed ligands without any specific interactions. There is a DMSO molecule included in the cone cavity of the calixarene, as shown in Figure 3a, with T shape C-H- $\pi$  interactions of 3.342 Å.



**Figure 3.** The structure of (3-4H) obtained by X-Ray diffraction on single crystals: a) the protonated calixarene based ligand, together with H-bonding interactions with 2 DMSO solvent molecules, and one included in the cavity of calixarene and b) the packing of the ligands in the xOz plane. H atoms which are not involved in H-bonding are omitted for clarity. For bond distances and angles see the text and Tables 2 and 3

### Synthesis of zinc (II) complexes

The obtained new ligand (3-4H) was combined with zinc (II) nitrate (always in stoichiometric excess) in order to investigate its propensity to form, in the crystalline phase, new supramolecular complexes with controlled nuclearities.

Whereas two coordination compounds, (3-3H)<sub>2</sub>-Zn(DMF)<sub>2</sub> and (3-2H)<sub>4</sub>-Zn<sub>3</sub>(OH)<sub>2</sub>, were obtained when (3-4H) and zinc (II) nitrate were mixed in DMF/MeOH solution under hard solvothermal conditions followed by slow evaporation of the mother liquor at room temperature under air (see experimental section), crystals of (3-2H)-Zn<sub>2</sub>py<sub>4</sub> were formed upon slow liquid diffusion.

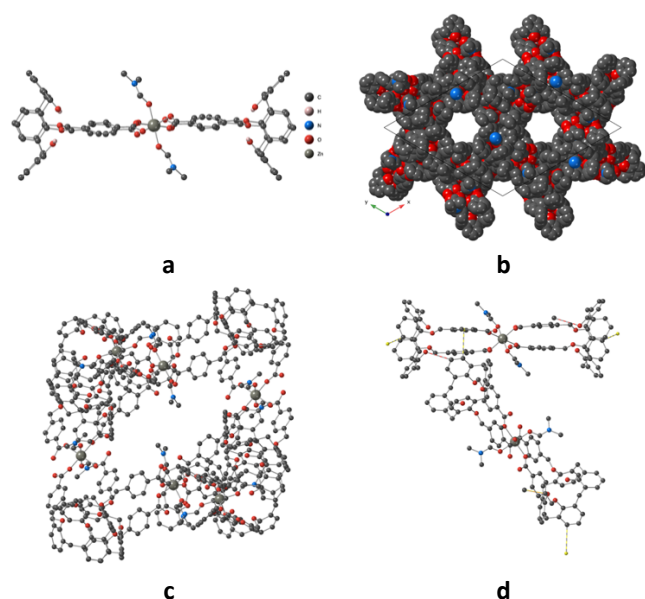
The structures of the obtained coordination compounds were established using X-Ray diffraction on single crystals. The synthesis of all the complexes reproducibly produces single crystals that were suitable for X-ray diffraction and the purity of the obtained polycrystalline powders was checked using X-ray powder diffraction, when possible.

### Structural description of zinc (II) complexes

All structural characteristics (bonds distances and angles) belonging to the macrocyclic calix[4]arene backbone supporting the formation of supramolecular complexes will be shortly described since they correspond well with those observed for earlier reported species. It was shown that in all formed coordination complexes, macrocyclic (3-2H)<sup>2-</sup> and (3-3H)<sup>-</sup> molecular tweezers as well as 4<sup>-</sup> ligand adopt a cone conformation, that will not be further discussed.

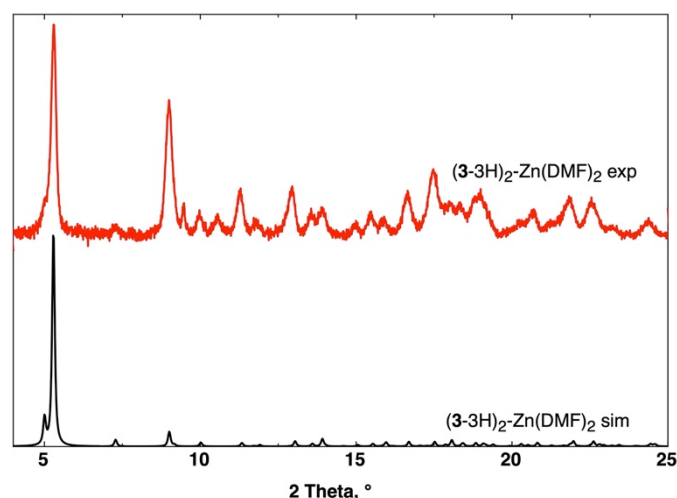
#### (3-3H)<sub>2</sub>-Zn(DMF)<sub>2</sub>

Solvothermal synthesis in DMF/MeOH solution (1/1) between (3-4H) and Zn<sup>II</sup>(NO<sub>3</sub>)<sub>2</sub> • 6H<sub>2</sub>O in 2-fold excess of metallic salts, followed by the slow evaporation of the mother liquor, produced colourless single crystals suitable for X-ray diffraction. The analysis revealed the formation of a symmetrical complex presenting the following formula: (3-3H)<sub>2</sub>-Zn(DMF)<sub>2</sub>. The obtained coordination compound crystallizes in the trigonal system, space group  $R\bar{3}$ , as shown in the crystallographic Table 1. No solvent molecules are present in the crystal lattice. Crystals of (3-3H)<sub>2</sub>-Zn(DMF)<sub>2</sub> are composed of two partially deprotonated ligands (3-4H) into (3-3H)<sup>-</sup>, a Zn<sup>2+</sup> cation and two coordinated DMF molecules. The analysis of the CO distances in the carboxylic/ate moiety (Table 2) together with the charge balance in the complex, reveals a partial deprotonation of (3-4H) into the (3-3H)<sup>-</sup> moiety, with a disorder of the protonation. The formed complexes are symmetrical (see Figure 4a), and the obtained “capsules” are non tubular. As expected, the environment around the Zn<sup>2+</sup> cations is a deformed octahedron, as shown by the bonds and distances, provided in Table 2. In the unit cell, the metallic complexes are displaying hexagonal channels of a diameter of ca 9.5 Å, with hexagons parallelly stacked along the *a* and *b* axes, as shown in Figure 4b. This arrangement is ensured by T shape C-H- $\pi$  interactions of 3.345 Å and weak C-H...O interactions of 3.268 Å, as shown in Figure 4d. This network is formed through noncovalent forces and van der Waals interactions leading to a crystalline structure presenting hexagonal 1D channels. The formation of similar honeycomb-like columns in calix[4]arene based structures has been already documented in the literature.<sup>48,49,50,51,52,53</sup> In some cases, the adsorption properties of such systems involving purely organic calixarene based compounds reveal to be highly selective.<sup>54,55,56,57</sup>



**Figure 4.** The structure of  $(3-3H)_2-Zn(DMF)_2$  obtained by X-Ray diffraction on single crystals: a) the mononuclear complex, and b) the packing of the ligands in the xOz plane and c) the formed hexagons and d) details of C-H $\cdots$ O interactions. H atoms are omitted for clarity (except those located on the phenol moieties). For bond distances and angles see the text and Table 2.

The purity of  $(3-3H)_2-Zn(DMF)_2$  polycrystalline samples was investigated by PXRD on microcrystalline powders (see Figure 5). A good match between the observed and calculated patterns from the XRD data was observed, attesting a crystalline phase for the  $(3-3H)_2-Zn$  obtained complex in the solid state.



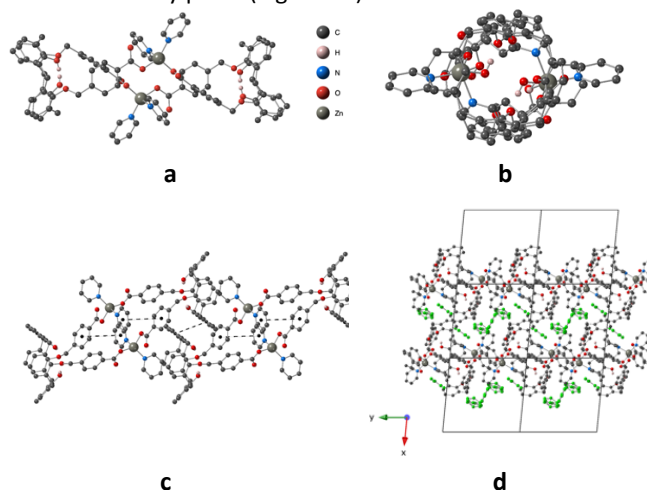
**Figure 5.** For  $(3-3H)_2-Zn(DMF)_2$ , comparison of the simulated (sim, black) and experimental (exp, red) powder X-Ray diffraction studies (PXRD) diagrams.

### $(3-2H)_2-Zn_2Py_4$

In contrast to  $(3-3H)_2-Zn(DMF)_2$ , the crystals of  $(3-2H)_2-Zn_2Py_4$  were obtained using mild conditions upon liquid diffusion of pyridine solution of  $(3-4H)$  into MeOH solution containing 2-fold excess of  $Zn^{II}(NO_3)_2 \cdot 6(H_2O)$ . The X-ray diffraction analysis revealed the formation of a symmetric complex presenting the following formula  $(3-2H)_2Zn_2(Py)_4 \cdot 5(py)$  ( $(3-2H)_2-Zn_2Py_4$ ). The compound crystallizes in the monoclinic system, space group

$P\bar{1}$ , as shown in the crystallographic Table 1. Crystals of  $(3-2H)_2-Zn_2Py_4$  are composed of two di-deprotonated ligands  $(3-2H)^{2-}$  (confirmed by the C-O distances, see Table 2), two  $Zn^{2+}$  cations, four coordinated pyridine molecules and five uncoordinated pyridine molecules, as free solvent in the unit cell (see figure 6a). The formed metallamacrocycles are symmetrical with an inversion centre located between the metallic cations, and the formed capsules reveal to present a tubular shape as shown in figure 6b. The environment around the  $Zn^{2+}$  cations is a deformed tetrahedron, as shown by the bonds and distances, provided in Table 2. There is a long Zn-O distance of *ca* 3 Å, so that the environment of  $Zn^{2+}$  cations cannot be considered as octahedral.

In the unit cell, the metallic complexes are interacting through very weak  $\pi$ - $\pi$  interactions, (phenyl ring of the macrocycle but also pyridine molecules) as shown in Figure 6c, with distances of 4.265 and 4.598 Å. The uncoordinated pyridine molecules are located between the planes formed by the assembly of ligands, located in the xOy plane (Figure 6d).



**Figure 6.** The structure of  $(3-2H)_2-Zn_2Py_4$  obtained by X-Ray diffraction on single crystals: a) the dinuclear complex, and b) the tubular formed capsule, c) the supramolecular interactions between two dinuclear complexes and d) the packing of the network in the xOy plane. H atoms are omitted for clarity (except those located on the phenol moieties). For bond distances and angles see the text and Table 2.

Unfortunately, as checked by the unsuccessful PXRD experiments, the crystalline phase of  $(3-2H)_2-Zn_2Py_4$  was found to be unstable when exposed to the air, probably due to easy loss of solvated molecules.

### $(3-2H)_4-Zn_3(OH_2)$

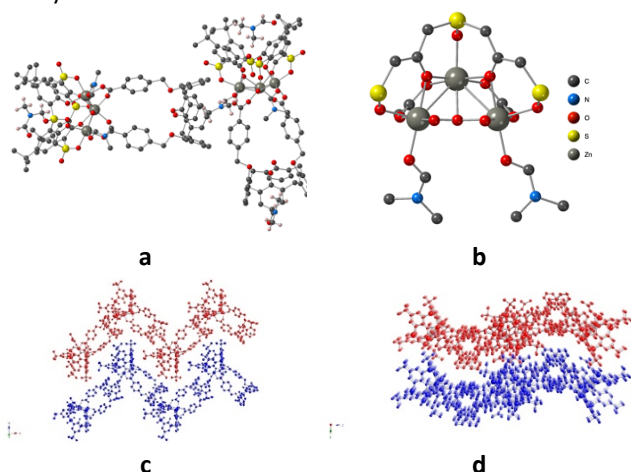
Solvothermal synthesis in DMF/MeOH solution (1/1) between  $(3-4H)$ ,  $(4-4H)$  and  $Zn^{II}(NO_3)_2 \cdot 6(H_2O)$  with the following ratio: 1/1/4, followed by the slow evaporation of the mother liquor, produced colorless single crystals suitable for X-ray diffraction. The analysis revealed the formation of a symmetric complex presenting the following formula  $Zn_3(OH_2)(DMF)_2(3-2H)(4-2H) \cdot DMF$  ( $(3-2H)_4-Zn_3(OH_2)$ ). The compound crystallizes in the orthorhombic system, space group  $Pbca$ , as shown in the crystallographic Table 1. Crystals of  $(3-2H)_4-Zn_3(OH_2)$  are composed of one di-deprotonated ligand  $(3-2H)^{2-}$  (confirmed by the CO distances, see Table 2),  $4^+$ , three  $Zn^{2+}$  cations including



also a  $\mu_3$ -coordinated water molecule, and four uncoordinated disordered DMF molecules, as shown in Figure 7a.

Three crystallographically independent  $\text{Zn}^{2+}$  cations are all in a deformed octahedral O6 environment, as shown in Figures 7b and in Bonds and angles given in Table 2. Two  $\text{Zn}^{2+}$  cations are surrounded by six O-atoms: three belong to  $\mathbf{4}^{4-}$  (two O-atoms come from phenolate groups, with one O-atom coming from sulfonyl moieties), one oxygen atom from a bridging carboxylate moiety of  $(\mathbf{3-2H})^{2-}$ , one oxygen from a coordinated DMF molecule and one  $\mu_3$ -O-atom from a coordinated water molecule located in the middle of the triangle. The third  $\text{Zn}^{2+}$  cation is surrounded by three atoms from  $\mathbf{4}^{4-}$  (two O-atoms from phenolate moieties, one O-atom from sulfonyl moieties), two O-atoms from the bridging carboxylate moieties of  $(\mathbf{3-2H})^{2-}$  and one  $\mu_3$ -O atom from the coordinated water molecule. The Zn-O distances are in the 2.013(2) to 2.172(3) Å range (see Table 2). For the triangles formed by the trimetallic units, there are two short Zn-Zn distances (3.0093(8) and 3.0178(7) Å) and one long Zn-Zn distance of 3.7894 (10) Å (see Table 2), which confirms the presence of a water molecule in the middle of the non-isosceles triangle.

It is important to note that the metallic triangles, resulting from the association of two short and one long M-M bonds, are maintained by a  $\mu_3$ -O atom from a coordinated water molecule and are reproducibly obtained. This triangular feature has already been observed in the literature.<sup>36,58</sup>



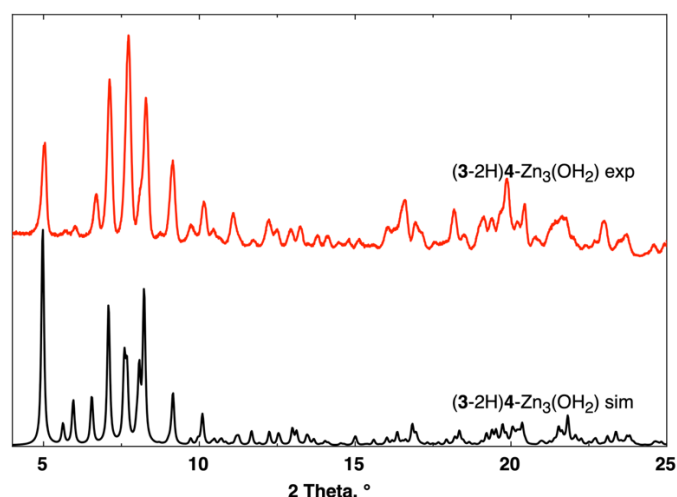
**Figure 7.** The structure of  $(\mathbf{3-2H})_4\text{-Zn}_3(\text{OH}_2)$  obtained by X-Ray diffraction on single crystals: a) two trinuclear complexes hosting a free DMF molecule in the  $\mathbf{4}$  cavity and hosting a coordinated DMF molecule in the  $(\mathbf{3-2H})^{2-}$  cavity, b) the surrounding of the metallic cations in the trinuclear unit, c) the packing of the complexes along the xOz plane showing the formation of 1D supramolecular chains, d) 3D crystal packing. H atoms and uncoordinated DMF molecules are omitted for clarity. For bond distances and angles see the text and Table 2.

In the crystal cell, the molecules of metallamacrocyle are found to be hetero-orientated and form the angle of  $79.08^\circ$  between the planes formed by triangular metallic units which indicates the crucial influence of weak intermolecular interactions on the crystal packing of obtained complex. In particular, the molecules of metallamacrocyle acting as pseudo V-shaped building units form the 1D supramolecular zigzag chains along Ox axis which ensured by C-H... $\pi$  interaction between the Zn-coordinated DMF

molecule belonging to one  $(\mathbf{3-2H})_4\text{-Zn}_3(\text{OH}_2)$  molecule included in the hydrophobic cavity of  $(\mathbf{3-2H})^{2-}$  belonging to neighboring  $(\mathbf{3-2H})_4\text{-Zn}_3(\text{OH}_2)$  complex with C-H...  $\text{C}_{\text{Ar6}}(\text{centroid})$  distances equal to 3.397 and 3.468 Å (Figure 7c). In addition, one free DMF molecule is included in the hydrophobic cavity of  $\mathbf{4}$  with C-H... $\pi$  interaction, as shown in Figure 7a. In crystal, the 1D chains are stacked in antiparallel fashion along Ox and Oy axes, thus completing the 3D packing (Figure 7d).

Furthermore, DMF molecules in the crystal lattice interact with aromatic cavity of  $\mathbf{4}^{4-}$  forming the inclusion complex with the 1/1 ratio and participate in H-bonding with the  $\text{Zn}_3(\mu_3\text{-OH}_2)$  node leading to O...O distance of 2.746 (5) Å. The remained solvate molecules are lying in the interstices between the complexes without any specific interactions with the discrete trinuclear species.

The purity of  $(\mathbf{3-2H})_4\text{-Zn}_3(\text{OH}_2)$  polycrystalline samples was investigated by PXRD on microcrystalline powders (see Figure 8). A good match between the observed and calculated patterns from the XRD data was observed, attesting a pure crystalline phase for the  $(\mathbf{3-2H})_4\text{-Zn}_3(\text{OH}_2)$  obtained complex in the solid state.



**Figure 8.** For  $(\mathbf{3-2H})_4\text{-Zn}_3(\text{OH}_2)$ , comparison of the simulated (sim, black) and experimental (exp, red) powder X-Ray diffraction studies (PXRD) diagrams.

## Discussion

The use of new designed “tweezer-like” organic ligand  $(\mathbf{3-4H})$  has successfully produced three new discrete supramolecular complexes when combined with zinc (II) cations, in stoichiometric excess.

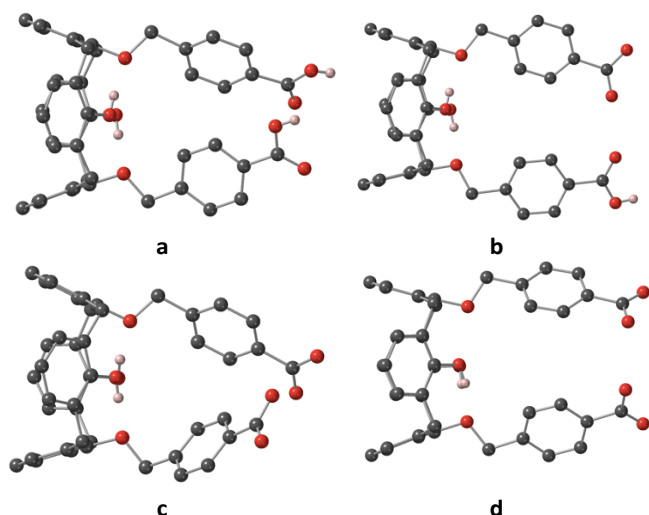
It was found that the number of metallic cations within the obtained coordination complexes (from 1 to 3) can be controlled by synthetic conditions: nature of the used solvents, slow diffusion technique at RT or solvothermal conditions, as well as the involvement of highly coordinating sulfonylcalix[4]arene ( $\mathbf{4-4H}$ ).

It should be noted that in the crystal structure of  $(\mathbf{3-3H})_2\text{-Zn}(\text{DMF})_2$  mononuclear complex Zn cation adopts an octahedral coordination sphere composed of six “hard” O-atoms coming from four carboxylate moieties belonging to two adjacent monodeprotonated  $(\mathbf{3-3H})^-$  species and two DMF solvent

molecules. For the dinuclear  $(\mathbf{3-2H})_2\text{-Zn}_2\text{py}_4$  complex, the involvement of pyridine, used as solvent, offering soft N-atom for coordination with Zn cations leads to the observation of the tetrahedral coordination sphere of metal center, with  $\text{N}_2\text{O}_2$  environment.

Thus, it is important to note that  $\text{Zn}^{2+}$  cations when being tetracoordinated allow to transform the “8”-like supramolecular motif of the metallamacrocycle, which was observed for  $(\mathbf{3-3H})_2\text{-Zn}(\text{DMF})_2$  into a hollow tubular like structure for  $(\mathbf{3-2H})_2\text{-Zn}_2\text{py}_4$  with the M/L ratio equal to 1/1. Moreover, changing the solvent molecules significantly influences on arrangement of the obtained supramolecular complexes in the crystal: whereas  $(\mathbf{3-3H})_2\text{-Zn}(\text{DMF})_2$  is not solvated and, within the crystal, it presents a porous structure displaying a formation of hexagonal honeycomb-like channels due to C-H... $\pi$  interactions between the macrocyclic aromatic rings, the appearance of pyridine solvate molecules in the interstices between  $(\mathbf{3-2H})_2\text{-Zn}_2\text{py}_4$  blocks the intermolecular C-H... $\pi$  bonding between the complexes and leads to aligned stacking of metallamacrocycles in crystal without any pores formation.

In the solid-state, the tweezer-like shape of the ligand was observed for all compounds. Figure 9 are represented the shape of ligand  $(\mathbf{3-nH})^m$  for the four obtained compounds. One can observe, that due to the rotation around the C-O-C and also C-C bonds, the tweezer-like shape is adapting to the environment of the metal to which the carboxylate groups are coordinated. In all compounds, the phenyl rings of the arms are not parallel.



**Figure 9.** Representations of the tweezer-like shape of ligands  $(\mathbf{3-nH})^m$  involved in the formation of coordination complexes: for  $(\mathbf{3-4H})$  (a),  $(\mathbf{3-3H})_2\text{-Zn}(\text{DMF})_2$  (b),  $(\mathbf{3-2H})_2\text{-Zn}_2\text{py}_4$  (c) and  $(\mathbf{3-2H})_4\text{-Zn}_3(\text{OH}_2)$  (d).

Finally, the increasing of nuclearity of Zn complexes and generation of trinuclear coordination species  $(\mathbf{3-2H})_4\text{-Zn}_3(\text{OH}_2)$  was achieved by using a combination of  $(\mathbf{3-4H})$  with the highly coordinating polydentate co-ligand  $(\mathbf{4-4H})$ . In this case, the obtained metal-organic system can be considered as a supramolecular assembly of two calix[4]arenes displaying

different coordination mode with the trinuclear metallic node held in between. The most attractive feature of obtained crystal structure is related with the observation of C-H... $\pi$  bonded 1D zigzag chain formation within the crystal. It turned to be possible due to self-inclusion event between the metallamacrocycles performed by interaction of Zn-coordinated DMF-molecule with the hydrophobic cavity of calix[4]arene  $(\mathbf{3-2H})^2$ . This phenomenon was not observed earlier for analogous compounds where the role of dicarboxylate ligand was played by the calix[4]arene derivative bearing two O-(4-carboxy)propoxy moieties and four bulky *tert*-butyl groups. It confirms that the absence of bulky *tert*-butyl groups in case of macrocycle  $(\mathbf{3-4H})$  plays the crucial role in the formation of 1D supramolecular chains in the crystal of  $(\mathbf{3-2H})_4\text{-Zn}_3(\text{OH}_2)$ .

## Experimental

### Characterization techniques

$^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra were recorded at room temperature on a Bruker 300 MHz and 500 MHz. FT-IR spectra were recorded on a Perkin Elmer ATR spectrometer. Mass spectra (MS (ES+)) were recorded on a Bruker Micro-TOF spectrometer. The IR spectra of the polycrystalline samples were recorded on a Bruker Tensor 27 spectrometer (Bruker Optic GmbH, Germany) in KBr pellets. Elemental analysis was performed by the Analysis Service of the Faculty of Chemistry. Elemental analysis was performed on a Vario Macro CHN Analyzer (Elementar Analysensysteme GmbH, Langenselbold, Germany).

### Synthesis

**General:** All reagents and solvents were of analytical grade and purchased from commercial sources and were used without further purification. The synthesis of  $(\mathbf{4-4H})$  was adapted from previously reported procedures.<sup>39,40</sup>

#### Synthesis of $(\mathbf{3-4H})$

The synthesis of  $\mathbf{3-4H}$  was achieved in two steps starting from *p*-*H*-calix[4]arene<sup>41</sup> as initial compound.

**3'**  
A mixture of *p*-*H*-calix[4]arene (**CA**) (1 g, 2.3 mmol), potassium carbonate (0.68 g, 4.9 mmol) and methyl 4-(bromomethyl)benzoate (1.6 g, 7 mmol) in acetone (50 mL) was refluxed during 20 h. After cooling the solvent was evaporated to dryness, the residue was treated by 1M HCl (100 ml) and extracted by  $\text{CH}_2\text{Cl}_2$  (2x50 ml). Organic layer was collected and washed once by dist.  $\text{H}_2\text{O}$  (100 ml). After separation the organic phase was dried over  $\text{MgSO}_4$  and filtrated. Organic solvent was evaporated under reduced pressure. The product was crystallized by adding of methanol to residue (150 ml) affording to pure methyl ester of (**3'**) (1.55 g) as white solid (93%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 7.99 (2H, d,  $J=8.5$  Hz, Ar-H), 7.78 (2H, d,  $J=10.9$  Hz, Ar-H), 7.06 (2H, d,  $J=7.5$  Hz, m-H), 6.91 (2H, d,  $J=7.5$  Hz, m-H), 6.78 (1H, t,  $J=7.5$  Hz, p-H), 6.67 (1H, t,  $J=7.5$  Hz, p-H),

5.14 (2H, d,  $J=7.5$  Hz,  $\text{OCH}_2$ ), 4.29 (2H, d,  $J=13.2$  Hz,  $\text{CH}_2_{\text{endo}}$ ), 3.93 (3H, s,  $\text{COOCH}_3$ ), 3.37 (2H, d,  $J=13.2$  Hz,  $\text{CH}_2_{\text{exo}}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 166.9, 153.3, 151.8, 141.9, 133.2, 130.2, 129.9, 129.3, 128.7, 127.9, 127.0, 125.9, 119.3, 77.7, 52.2, 31.5; MS ( $\text{ESI}^+$ ,  $m/z$ ) 743.2 [ $\text{M}+\text{Na}$ ] $^+$ .

(**3-4H**): (0.8 g, 1.1 mmol) was mixed with sodium hydroxide (0.29 g, 6.6 mmol) of in EtOH/ $\text{H}_2\text{O}$  mixture (30 mL, v/v, 4:1) and refluxed during 16h. After cooling a solution of 1M HCl (5 mL) was added affording to precipitation of white solid which was filtrated and washed by water (2x50 mL). Recrystallisation of obtained solid from MeOH afforded to a pure targeted product (**3-4H**) (0.7g, 92%).  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ , 300 MHz)  $\delta$ : 12.92 (1H, s,  $\text{COOH}$ ), 8.17 (1H, s, OH), 7.96 (4H, d,  $J=8.0$  Hz, Ar-H), 7.82 (4H, d,  $J=8.0$  Hz, Ar-H), 7.14 (2H, d,  $J=7.5$  Hz, m-H), 7.05 (2H, d,  $J=7.5$  Hz, m-H), 6.82 (1H, t,  $J=7.5$  Hz, p-H), 6.59 (1H, t,  $J=7.5$  Hz, p-H), 5.19 (2H, s,  $\text{OCH}_2$ ), 4.15 (2H, d,  $J=12.9$  Hz,  $\text{CH}_2_{\text{endo}}$ ), 3.39 (2H, d,  $J=12.9$  Hz,  $\text{CH}_2_{\text{exo}}$ );  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ , 500 MHz)  $\delta$ : 167.0, 152.6, 151.8, 141.5, 133.6, 130.6, 129.6, 129.1, 128.7, 127.6, 126.8, 125.6, 119.3, 77.5, 40.4, 40.1, 30.7; MS ( $\text{ESI}^+$ ,  $m/z$ ) 691.2 [ $\text{M}-\text{H}$ ] $^-$ . Formula:  $\text{C}_{44}\text{H}_{36}\text{O}_8$ , Anal. Calcd.: C, 76.29 %; H, 5.24 %. Found: C, 76.55 %; H, 5.36 %. IR ( $\text{cm}^{-1}$ ): 3392; 3022; 2926; 2861; 1715; 1696; 1614; 1466; 1219; 1090; 1016; 756.

### Crystallization conditions

(**3-4H**): (**3-4H**) (5 mg, 0.007 mmol) was dissolved in DMSO (2 mL). Slow evaporation of obtained solution afforded to formation of single crystals suitable for X-ray analysis in few days. Formula:  $\text{C}_{50}\text{H}_{54}\text{O}_{11}\text{S}_3$ , Anal. Calcd.: C, 64.77%; H, 5.87 %; Found: C, 65.13 %; H, 5.63 %.

(**3-3H**) $_2\text{-Zn}(\text{DMF})_2$ : (**3-4H**) (5 mg, 0.007 mmol) and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (4.1 mg, 0.014 mmol) were dissolved in DMF/MeOH mixture (2 mL, v/v, 1:1) in the Pyrex vial (5 mL) equipped with a screw cap. A few drops of 0.1M HCl were added to prepared solution. The obtained mixture was heated under solvothermal conditions at 80 °C during 3 days. Slow evaporation of resulting solution at room temperature produced colorless crystals (3.5 mg, 61%) suitable for X-ray diffraction analysis in 6 days Formula:  $\text{C}_{94}\text{H}_{82}\text{N}_2\text{O}_{18}\text{Zn}$ , Anal. Calcd.: C, 70.87 %; H, 5.19 %; N, 1.76 %; Found: C, 70.85 %; H, 5.25 %; N, 1.82 %. IR ( $\text{cm}^{-1}$ ): 3401; 3021; 2929; 2860; 1715; 1654; 1614; 1465; 1384; 1250; 1016; 762.

(**3-2H**) $_2\text{-Zn}_2\text{py}_4$ : In a crystallization tube (length 20 cm, diameter 4 mm), a pyridine solution (0.5 mL) of (**3-4H**) (5 mg, 0.007 mmol) was carefully layered with a pyridine/MeOH mixture (1 mL, 1/1). Then a MeOH solution (1 mL) containing  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (4.1 mg, 0.014 mmol) was added. Slow diffusion at room temperature afforded to formation of colorless crystals (4.5 mg, 56%) suitable for X-ray diffraction analysis after 7 days. Formula:  $\text{C}_{133}\text{H}_{115}\text{N}_9\text{O}_{16}\text{Zn}_2$ , Anal. Calcd.: C, 71.76%; H, 5.21 %; N, 5.66 %; Found: C, 72.14 %; H, 5.11 %; N, 5.73 %. IR ( $\text{cm}^{-1}$ ): 3394; 3061;

2925; 2861; 1608; 1563; 1466; 1450; 1363; 1218; 1195; 1015; 773; 700.

(**3-2H**)**4**- $\text{Zn}_3(\text{OH})_2$ : Compounds (**3-4H**) (20 mg, 0.029 mmol), (**4-4H**) (24 mg, 0.029 mmol) together with  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (34.4 mg, 0.115 mmol) were dissolved in DMF/MeOH mixture (1/1, 5 mL) and put into a Pyrex crystallization reactor equipped with a screw cap. Then, the solution was heated under MW irradiation conditions (100 W) and stirred for 3 hours. After cooling and filtration, colorless single crystals suitable for X-ray diffraction analysis were obtained upon slow evaporation of the mother liquor at room temperature in 7 days. Total yield: 45 mg (71%). Formula:  $\text{C}_{102}\text{H}_{120}\text{N}_6\text{O}_{27}\text{Zn}_3$ , Anal. Calcd.: C, 56.03%; H, 5.53 %; N, 3.84; Found: C, 56.21 %; H, 5.72 %; N, 3.93 %. IR ( $\text{cm}^{-1}$ ): 3403; 3065; 2961; 2869; 1712; 1668; 1609; 1561; 1496; 1464; 1411; 1264; 1220; 1082; 998; 799; 753; 623; 579; 558.

### Single-Crystal X-ray diffraction

The single-crystals X-ray diffraction data for (**3-4H**), (**3-3H**) $_2\text{-Zn}(\text{DMF})_2$ , (**3-2H**) $_2\text{-Zn}_2\text{py}_4$  and (**3-2H**)**4**- $\text{Zn}_3(\text{OH})_2$  were collected on the 'Belok' beamline of Kurchatov Synchrotron Radiation Source (National Research Center 'Kurchatov Institute', Moscow, Russian Federation) using a Rayonix SX165 CCD detector at  $\lambda = 0.793127$  Å. The frames were collected using an oscillation range of 1.0° and  $\phi$  scan mode. The data were indexed and integrated using the utility iMOSFLM from the CCP4 program suite<sup>59</sup> and then scaled and corrected for absorption using the Scala program<sup>60</sup>. Structures were solved using Olex2 software<sup>61</sup> by direct methods with SHELXT<sup>62</sup> refined by the full-matrix least-squares on  $F^2$  using SHELXL<sup>63</sup>. Non-hydrogen atoms were refined anisotropically. The crystallographic data are available for free of charge downloading from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/datarequest/cif](http://www.ccdc.cam.ac.uk/datarequest/cif). CCDC: (**3-4H**): 2016288; (**3-3H**) $_2\text{-Zn}(\text{DMF})_2$ : 2016287; (**3-2H**) $_2\text{-Zn}_2\text{py}_4$ : 2016285 and (**3-2H**)**4**- $\text{Zn}_3(\text{OH})_2$ : 2016286.

### X-ray diffraction on powder

Powder diffraction studies (PXRD) diagrams were collected on polycrystalline samples, on a Bruker D8 diffractometer using monochromatic  $\text{Cu-K}\alpha$  radiation with a scanning range between 3.8° and 40° at a scan step size of 2°  $\text{min}^{-1}$ . As already demonstrated and currently admitted, for all compounds, discrepancies in intensity between the observed and simulated patterns are due to preferential orientations of the microcrystalline powders.

### Conclusions

A design of three new Zn (II) based complexes have been performed based on a tweezer-like calix[4]arene based ligand (**3-4H**) bearing two rigid O-benzoic/ate coordinating centers. It was shown that the flexible "tweezer" shape of the ligand allows



the formation of mono-, di- and trinuclear supramolecular complexes which topology and crystal structure can be controlled by changing (i) the nature of the used solvents (pyridine or DMF), (ii) the synthetic method, as well as (iii) the use of the polydentate co-ligand (**4-4H**). This powerful approach enables the control of the nuclearity for the obtained systems. It was established that mononuclear species displaying “8”-like structure ( $M/L=1/2$ ) were formed when Zn cations adopts octahedral coordination sphere composed of six “hard” O-atoms (in presence of DMF molecules). At the meanwhile, a combination of (**3-4H**) with zinc cations and pyridine molecules led to formation of dinuclear complex of tubular type ( $M/L=1/1$ ). The third complex, based on two macrocycles of different nature were generated when the formation of  $Zn_3$ -triangular metallic node was observed. In terms of crystal packing it was demonstrated a crucial role played by weak intermolecular interaction such as C-H... $\pi$  bonding for the formation of hexagonal channels and 1D supramolecular chains in the case of mononuclear and trinuclear species crystal arrangement.

The investigation of coordination ability of obtained molecular tweezers towards d/f elements in order to obtain new

functional coordination compounds of higher nuclearities is currently in progress.

## Conflicts of interest

There are no conflicts to declare.

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**Table 1.** Crystallographic data for (3-4H), (3-3H)<sub>2</sub>-Zn(DMF)<sub>2</sub>, (3-2H)<sub>2</sub>-Zn<sub>2</sub>py<sub>4</sub> and (3-2H)<sub>4</sub>-Zn<sub>3</sub>(OH)<sub>2</sub>

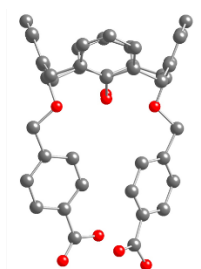
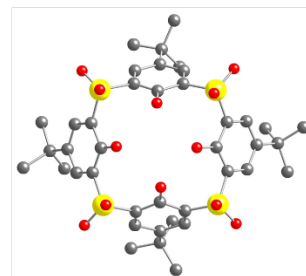
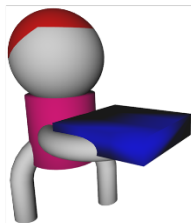
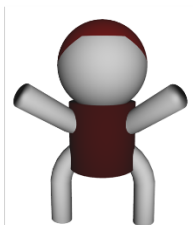
	(3-4H)	(3-3H) <sub>2</sub> -Zn(DMF) <sub>2</sub>	(3-2H) <sub>2</sub> -Zn <sub>2</sub> py <sub>4</sub>	(3-2H) <sub>4</sub> -Zn <sub>3</sub> (OH) <sub>2</sub>
Empirical formula	C <sub>50</sub> H <sub>54</sub> O <sub>11</sub> S <sub>3</sub>	C <sub>94</sub> H <sub>82</sub> N <sub>2</sub> O <sub>18</sub> Zn	C <sub>133</sub> H <sub>115</sub> N <sub>9</sub> O <sub>16</sub> Zn <sub>2</sub>	C <sub>102</sub> H <sub>120</sub> N <sub>6</sub> O <sub>27</sub> S <sub>4</sub> Zn <sub>3</sub>
Formula weight	927.11	1592.98	2226.07	2186.38
Crystal system	monoclinic	trigonal	triclinic	orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>R</i> -3	<i>P</i> -1	<i>Pbca</i>
<i>a</i> /Å	16.713(3)	33.388(5)	14.070(3)	26.971(5)
<i>b</i> /Å	17.962(4)	33.388(5)	14.720(3)	23.006(5)
<i>c</i> /Å	16.109(3)	22.267(4)	15.430(3)	35.506(7)
$\alpha$ /°	90	90	66.56(3)	90
$\beta$ /°	108.93(3)	90	67.55(3)	90
$\gamma$ /°	90	120	76.46(3)	90
Volume/Å <sup>3</sup>	4574.4(18)	21497(7)	2697.1(13)	22031(8)
<i>Z</i>	4	9	1	8
$\rho_{\text{calc}}$ /cm <sup>3</sup>	1.346	1.107	1.371	1.318
$\mu$ /mm <sup>-1</sup>	0.302	0.425	0.694	1.071
<i>F</i> (000)	1960.0	7506.0	1164.0	9152.0
Color	Colorless	Colorless	Colorless	Colorless
Crystal size/mm <sup>3</sup>	0.3 × 0.2 × 0.2	0.2 × 0.2 × 0.1	0.2 × 0.2 × 0.2	0.1 × 0.1 × 0.1
Wavelength (Å)	$\lambda$ = 0.79313 (synchrotron)	$\lambda$ = 0.79313 (synchrotron)	$\lambda$ = 0.79313 (synchrotron)	$\lambda$ = 0.79313 (synchrotron)
2 $\theta$ range for data collection/°	2.874 to 61.896	2.576 to 61.946	3.382 to 61.91	2.894 to 61.95
Index ranges	-20 ≤ <i>h</i> ≤ 21, -23 ≤ <i>k</i> ≤ 23, -20 ≤ <i>l</i> ≤ 20	-38 ≤ <i>h</i> ≤ 43, -43 ≤ <i>k</i> ≤ 41, -28 ≤ <i>l</i> ≤ 28	-18 ≤ <i>h</i> ≤ 18, -19 ≤ <i>k</i> ≤ 19, -19 ≤ <i>l</i> ≤ 19	-32 ≤ <i>h</i> ≤ 34, -29 ≤ <i>k</i> ≤ 29, -45 ≤ <i>l</i> ≤ 45
Reflections collected	41425	51481	56420	179422
Independent reflections	10408 [ <i>R</i> <sub>int</sub> = 0.0496, <i>R</i> <sub>sigma</sub> = 0.0399]	10874 [ <i>R</i> <sub>int</sub> = 0.0416, <i>R</i> <sub>sigma</sub> = 0.0301]	12169 [ <i>R</i> <sub>int</sub> = 0.0347, <i>R</i> <sub>sigma</sub> = 0.0270]	25095 [ <i>R</i> <sub>int</sub> = 0.0799, <i>R</i> <sub>sigma</sub> = 0.0417]
Data/restraints/parameters	10408/0/588	10874/0/524	12169/0/750	25095/0/1317
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.027	1.047	1.072	1.044
Final <i>R</i> indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0462, <i>wR</i> <sub>2</sub> = 0.1098	<i>R</i> <sub>1</sub> = 0.0705, <i>wR</i> <sub>2</sub> = 0.2099	<i>R</i> <sub>1</sub> = 0.0434, <i>wR</i> <sub>2</sub> = 0.1160	<i>R</i> <sub>1</sub> = 0.0626, <i>wR</i> <sub>2</sub> = 0.1734
Final <i>R</i> indexes [all data]	<i>R</i> <sub>1</sub> = 0.0701, <i>wR</i> <sub>2</sub> = 0.1227	<i>R</i> <sub>1</sub> = 0.0885, <i>wR</i> <sub>2</sub> = 0.2266	<i>R</i> <sub>1</sub> = 0.0493, <i>wR</i> <sub>2</sub> = 0.1203	<i>R</i> <sub>1</sub> = 0.0943, <i>wR</i> <sub>2</sub> = 0.1961
Largest diff. peak/hole / e Å <sup>-3</sup>	0.38/-0.40	0.52/-1.39	0.80/-0.68	1.49/-0.67
CCDC number	2016288	2016287	2016285	2016286



**Table 2.** Characteristic bond distances and angles see for (3-4H), (3-3H)<sub>2</sub>-Zn(DMF)<sub>2</sub>, (3-2H)<sub>2</sub>-Zn<sub>2</sub>py<sub>4</sub> and (3-2H)4-Zn<sub>3</sub>(OH)<sub>2</sub> determined using X-Ray diffraction on single crystals.

	3-4H	(3-3H) <sub>2</sub> -Zn(DMF) <sub>2</sub>	(3-2H) <sub>2</sub> -Zn <sub>2</sub> py <sub>4</sub>	(3-2H)4-Zn <sub>3</sub> (OH) <sub>2</sub>		
Zn-O				2.025(3)		
				2.036(3)	2.029(3) <sub>w</sub>	2.013(2) <sub>w</sub>
		2.140(2)	1.9433(15) 1.9596(15)	2.085(3) <sub>w</sub>	2.039(2)	2.056(3)
		2.147(2)		2.106(3)	2.098(3)	2.107(3)
				2.141(2)	2.106(3)	2.131(3)
Zn-N				2.142(3)	2.172(3)	2.172(3)
			2.0283(17)			
Zn-O <sub>DMF</sub>			2.0792(17)			
		2.073(2)	+		2.033(3)	
Zn-Zn		2.074(2)			2.046(3)	
					3.0093(8)	
OZnO(N) Angle (°)					3.0178(7)	
					3.7894 (10)	
				81.08(10)	83.44(11)	82.37(10)
				81.11(10)	83.50(10)	83.62(10)
				83.60(10)	84.04(10)	84.55(10)
				84.71(10)	85.37(10)	85.06(10)
		88.88(8)	97.59(7)	87.55(11)	88.08(12)	88.12(11)
		89.45(9)	103.16(7)	88.77(11)	90.86(10)	88.95(11)
		90.55(9)	103.78(7)	89.96(10)	90.93(12)	91.31(11)
		91.12(8)	110.93(7)	93.51(11)	91.60(12)	91.69(10)
		91.11(8)	113.29(6)	95.26(11)	92.36(10)	93.14(10)
		180	123.66(7)	95.92(11)	92.73(10)	94.34(10)
				97.93(10)100.	96.58(11)	95.58(11)
				93(11)	99.97(12)	100.52(11)165.
				159.07(10)17	168.63(10)	86(10)
				4.52(11)	174.08(12)17	171.69(10)173.
				176.92(11)	4.88(11)	94(10)
C-O (carboxylate) in (3-nH)	1.215(3) + 1.328(3)	1.228(4) + 1.267(4)	1.235(2) + 1.295(2)		1.250(5) + 1.272(5)	
	1.215(2) + 1.324(3)	1.229(4) + 1.293(4)	1.239(2) + 1.291(2)		1.258(5) + 1.262(5)	

## Graphical Abstract

**3-4H****4-4H**

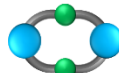
- molecular "pincer"



- ligand with exposed high coordinating cavity



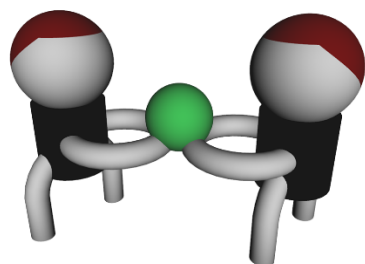
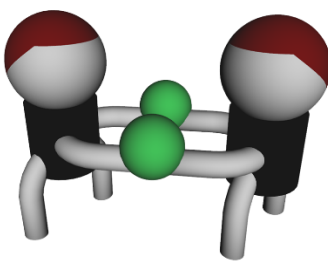
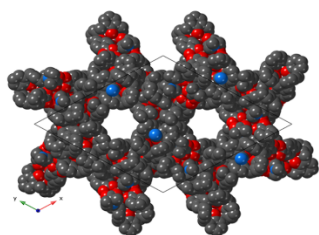
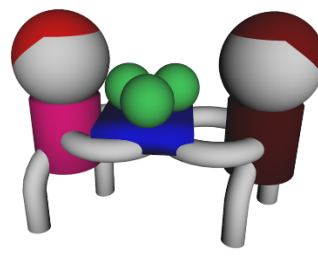
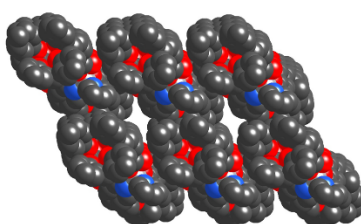
M/L=1/2



M/L=1/1



M/L=3/1

**(3-3H)<sub>2</sub>-Zn(DMF)<sub>2</sub>****(3-2H)<sub>2</sub>-Zn<sub>2</sub>py<sub>4</sub>****(3-2H)<sub>4</sub>-Zn<sub>3</sub>(OH<sub>2</sub>)**