Constructing Robust Channel Structures by Packing Metallacalixarenes: Reversible Single-Crystal-to-Single-Crystal Dehydration

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Metal-directed self-assembly processes that form well-defined architectures represent an important chapter in supramolecular chemistry.[1] The leading-role actors in such processes are the metal ions, through their stereochemical preferences, and the ligands, through the relative position of the donor atoms.[2] Racks, ladders, grids, helicates, and boxes are examples of inorganic superstructures that are obtained through spontaneous and correct sequential interactions between highly instructed components.[2] Other discrete nanostructures resulting from self-assembly processes involving metal ions are the metallacalixarenes.[3] These are structural analogues of calixarenes that are obtained by assembling metal ions having two available coordination sites with organic ligands providing 120° bond angles (for example, pyrimidine or 4,7-phenanthroline derivatives).[4] The bridging CH_2 groups in classical calixarenes are replaced by the metal ions. Appropriate assembling cations are monochelated square-planar or tetrahedral metal ions, the two other coordination sites being occupied by labile ligands.[4]

The particular shape of calixarenes and calixarene-like compounds raises the following question: is it possible to construct channels by stacking these molecules in the crystal on top of each other? An important condition to be fulfilled in the case of metallacalixarenes is to avoid the presence of counterions in the crystal, which occupy the void space and cannot be removed without changing the chemical nature of the material. This is possible by employing appropriate anionic organic ligands that generate neutral crown-like complexes. Such ligands can be dianionic species resulting from deprotonation of 5-substituted derivatives of 1,3-benzenedicarboxylic acid (with predisposed carboxylic groups at 120°, as requested for the construction of metallacalixarenes). As the assembling cation, we chose a copper(II) complex species with two cis positions blocked by N,N,N',N'-tetramethylethylenediamine (tmen).

The reaction between [Cu(acac)(tmen)]ClO_4 and trimesic acid (H_3trim) in the presence of triethylamine in a molar ratio of 3:2:6 in 10:5:1:1 (v/v) MeOH/MeCN/H_2O/DMF, followed by slow evaporation, leads to single crystals of [Cu_4(tmen)$_4$(Htrim)$_4$]·nH_2O (1·nH_2O). Our synthetic approach was based on the observation that mixed-ligand (acetylacetonato–polyamine) copper(II) complexes react with carboxylate ions by losing the acetylacetonato (acac) ligand.[5]

Three different hydrates, 1·2H_2O, 1·8H_2O, and 1·12H_2O, were obtained within the same or different batches, all of them being isomorphous (see the Supporting Information). Apart from the indicated number of water molecules, each type of crystal contains some other strongly disordered water molecules that were not assigned.
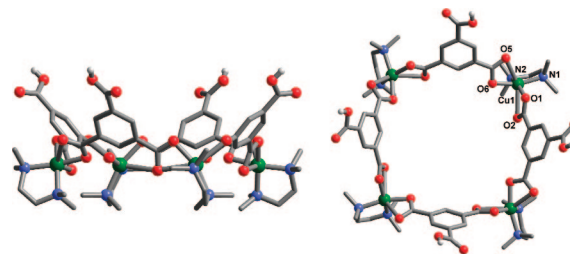

Figure 1. Side and top views of the metallacalixarene 1.

The crystallographic investigation of crystals 1·nH_2O revealed the formation of a calixarene-like structure (Figure 1) made up of tetranuclear complexes, with the copper ions connected through Htrim^{2-} bridges (one of the carboxylic groups in H_3trim is not deprotonated). The metallacalixarene exhibits a cone conformation, with the –COOH groups oriented outward. Each copper(II) ion is hexacoordinated by the two tmen nitrogen atoms [Cu1–N1 = 2.024(4) Å, Cu1–N2 = 2.014(5) Å] and four oxygens from two chelating carboxylato groups, with two short and two long Cu–O distances [Cu1–O1 = 2.007(3) Å, Cu1–O6 = 1.975(3) Å, Cu1–O2 = 2.519(3) Å, Cu1–O5^{ii} = 2.451(3) Å, ^{ii} = 1 − x, 1 + y, z] (Figure 1). The distance between the copper ions is 9.41 Å. These data refer to 1·2H_2O; data for the other compounds are given in Table S2 in the Supporting Information.

The most interesting features of the crystal structure are revealed by the analysis of the packing diagram. The tetranuclear rings are disposed in the crystal in parallel ABABAB... stacking layers (Figure S1 in the Supporting Information). The superposition of the rings belonging to A, A′, A″... (or B, B′, B″...) layers generates channels running along the crystallographic c axis (Figure 2). We also note that compound 1 crystallizes in a noncentrosymmetric space group (P4nc) with all of the molecules oriented in the same direction.

The crystallization water molecules are accommodated in the channels, their arrangement differing from one crystallohydrate to another. For example, in 1·2H_2O, the two water molecules are located on C_4 axes, but in 1·8H_2O, only one of the water molecules is on a C_4 axis while the others are on general positions. The dodecahydrate will be described below.

The presence of water molecules in the channels prompted us to investigate whether it is possible to remove them without destroying the architecture of the crystal.

Thermogravimetric analysis (TGA) of 1·nH_2O shows that at 240 °C the water molecules are completely removed (Figure S2). There are no well-defined steps in the dehydration process, most probably because of the presence of different crystallohydrates. By heating single crystals of 1·nH_2O at 170 °C under vacuum, we succeeded

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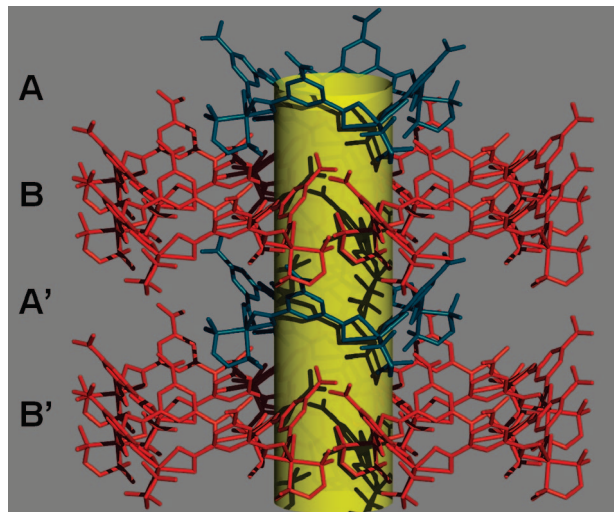‡ Université d'Angers.

Figure 2. Packing diagram for crystalline **1**, showing one channel (water molecules have been omitted).

in removing the water molecules, and the crystals retained their shapes. This suggests that a single-crystal-to-single-crystal transformation occurred. The dehydrated crystals, **1-DEHYDR**, were covered with mineral oil, embedded in Araldite glue under nitrogen, and then investigated by X-ray diffraction. The crystal structure of **1-DEHYDR** shows that the water molecules were removed, the channels being empty. We also found that this process is reversible: upon exposure of the crystals to moisture, the single crystals are again preserved. We isolated two different crystallohydrates: **1-REHYDR**·2H$_2$O and **1-REHYDR**·12H$_2$O (see the Supporting Information).

The infrared spectra of **1**·nH$_2$O were investigated in situ at different temperatures by heating the crystals up to 170 °C under a flow of nitrogen (Figure S3). The only change we observed was the progressive diminution of the band located at 3460 cm^{-1}, which is due to the water molecules. The other bands remained unchanged, indicating that the molecular architecture was preserved. The stability of the crystals was also proved by XRD measurements recorded between 30 and 250 °C on microcrystalline samples of **1**. At 210 °C the crystals are still stable (Figure S4). During the preparation of this report, a similar reversible dehydration process for a tubelike coordination polymer was described by Sun and co-workers.[6]

The morphology of water clusters is a subject of current interest in chemistry and biology.[7] Since the water molecule, as both a donor and an acceptor in hydrogen bonding, can act as a supramolecular tetrahedral synthon, the topologies of cyclic octameric water clusters can follow the conformations of cyclooctane (crown, boat, boat−chair), which are also constructed from tetrahedral synthons. Another possible topology is the cagelike one, with the water molecules disposed at the corners of the cube. The very first crystallographically characterized octameric water cluster exhibits this last topology.[8] Another (H$_2$O)$_8$ cluster, observed by Atwood et al.,[9] shows a cyclooctane-like boat conformation. We took a closer look at the aggregation of the water molecules in the dodecahydrates **1**·12H$_2$O and **1-REHYDR**·12H$_2$O, which are grouped into an octamer and a tetramer. In our case, the octamer water molecules describe a crown with D_{4d} symmetry (Figure 3); the distances between the water molecules are O11w···O12w =
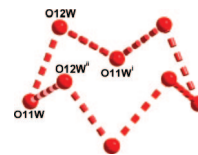

Figure 3. Octameric water cluster in **1**·12H$_2$O and **1-REHYDR**·12H$_2$O. Symmetry codes: (i) −1 + x, 1 − y, z; (ii) 1 − x, 1 + y, z.

2.571 and O12w···O11w^i = 2.830 Å. In the tetrameric cluster, the water molecules form a square with O···O distances of 3.116 Å. The (H$_2$O)$_8$ clusters are trapped inside each metallacalixarene, being anchored by hydrogen bonds to the oxygen atoms of the chelating carboxylato groups (Figure S5). The tetrameric clusters alternate with the octameric ones and are located between the A and B layers (Figure S6).

Aiming to prove that the self-assembly process involving {Cu(tmen)}$^{2+}$ and other 5-substituted benzene-1,3-dicarboxylato anions is general and thus leads to similar metallacalixarenes, we employed 5-hydroxybenzene-1,3-dicarboxylic acid and obtained a second metallacalixarene, **2** (Figure S7).

The magnetic properties of **1** were investigated over the temperature range 2−300 K (Figure S8). No exchange interaction between the copper(II) ions was detected.

In conclusion, we have shown that a new family of metallacalixarenes can be obtained by employing 5-substituted benzene-1,3-dicarboxylato anions and {Cu(tmen)}$^{2+}$ assembling cations. The packing of these rings generates channel structures. We have also shown that the crystalline materials are quite robust, undergoing a reversible single-crystal-to-single-crystal dehydration process. The robustness of the structure arises from strong hydrogen bonds established between the COOH groups from one layer and the coordinated COO$^-$ groups from another one (Figure S9). Further work on this family of compounds is in progress.

References

(1) Constable, E. C. *Pure Appl. Chem.* **1996**, *68*, 253.
(2) (a) Lehn, J.-M. *Science* **1993**, *260*, 1762. (b) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853.
(3) Pecoraro, V. L.; Stemmler, A. L.; Gibney, B. R.; Bodwin, J. J.; Wang, H.; Kampf, J. W.; Barwinski, A. *Prog. Inorg. Chem.* **1997**, *45*, 83.
(4) See, for example: (a) Barea, E.; Navarro, J. A. R.; Salas, J. M.; Quirós, M.; Willermann, M.; Lippert, B. *Chem.—Eur. J.* **2003**, *9*, 4414. (b) Maekawa, M.; Konoka, H.; Minematsu, T.; Kuroda-Sowa, T.; Munakata, M.; Kitagawa, S. *Chem. Commun.* **2007**, 5179. (c) Bardají, E. G.; Freisinger, E.; Costisella, B.; Schalley, C. A.; Brünig, W.; Sabat, M.; Lippert, B. *Chem.—Eur. J.* **2007**, *13*, 6019. (d) Armentano, D.; Mastropietro, T. F.; Julve, M.; Rossi, R.; Rossi, P.; De Munno, G. *J. Am. Chem. Soc.* **2007**, *129*, 2740.
(5) Ene, C. D.; Tuna, F.; Fabelo, O.; Ruiz-Pérez, C.; Madalan, A. M.; Roesky, H. W.; Andruh, M. *Polyhedron* **2008**, *27*, 574.
(6) Dai, F.; He, H.; Sun, D. *J. Am. Chem. Soc.* **2008**, *130*, 14064.
(7) (a) Joannopoulos, J. D. *Nature* **2001**, *414*, 257. (b) Bartoli, S.; Bazzicalupi, C.; Biagini, S.; Borsari, L.; Bencini, A.; Faggi, E.; Giorgi, C.; Sangregario, C.; Valtancoli, B. *Dalton Trans.* **2009**, 1223.
(8) Blanton, W. B.; Gordon-Wylie, S. W.; Clark, G. R.; Jordan, K. D.; Wood, J. T.; Geiser, U.; Collins, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 3551.
(9) Atwood, J. L.; Barbour, L. J.; Ness, T. J.; Raston, C. L.; Raston, P. L. *J. Am. Chem. Soc.* **2001**, *123*, 7192.

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