

# Tetrapyridoxycalix[4]arene and its copper(II) complex: an ionic crystal engineering tecton for self-inclusion polymers

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Received: 15 December 2008 / Accepted: 30 January 2009 / Published online: 19 February 2009  
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**Abstract** The crystal structures of a tetradentate pyridylcalix[4]arene ligand and its first copper(II) complex are discussed. The metal free ligand is mainly self-assembled by dipole–dipole interactions and a combination of CH–N bonds and CH– $\pi$  interactions. The corresponding copper(II) perchlorate complex exhibits a self-inclusion behaviour to supramolecular zig-zag polymers.

**Keywords** Self-Assembly · Calixarenes · Copper · N-Ligands · X-ray Diffraction

## Introduction

The prediction of a structure-crystal packing relationship is a major goal in crystal engineering and crystal design [1]. The importance of understanding weak supramolecular forces in the solid state is of high relevance to create tailor made crystalline materials with certain characteristics and properties [2, 3]. This is for instance exploited in the synthesis of reticular porous coordination frameworks, the so called MOFs (metal organic frameworks) [4, 5], which have exceptional physical properties and are potential

materials for future industrial applications [5] e.g. gas storage, purification of compounds, heterogenous catalysis etc. The well-understood interactions of ligands and corresponding metal centers, or metal clusters are the basis for the rational design of such materials. However, weaker supramolecular interactions such as CH– $\pi$  or dipole–dipole interactions of course interfere, making the prediction of packing motifs in the crystalline state from the molecular information of precursors even more difficult [2, 3]. Nevertheless, by careful investigation of crystal structure databases typical supramolecular synthons for those weak forces have been identified [3].

By combining these weak intermolecular forces with the propensity of macrocyclic compounds to bind guests in their interior, supramolecular tectons for self-inclusion complexes such as oligomers and polymers can be rationalized. Especially macrocyclic compounds such as cyclodextrins [6] or calixarenes [7–10] were introduced for self-inclusion purposes.

During our ongoing studies within this field we synthesized a set of lower-rim functionalized pyridoxycalix[4]arenes [11–14] as ligands for the complexation of various transition metals. We found some fascinating self-aggregation behaviour in the presence of palladium(II) chloride to hexameric supracycles [11] or zig-zag self-inclusion polymers [14]. In all cases the palladium center has two effects. 1st: Fixing the pyridyl moieties perpendicular to the  $\pi$ -plane of the connected macrocyclic phenol-unit. 2nd: Diminishing the electron-density on the pyridyl-rings and therefore activating them as  $\pi$ -acceptors to form supramolecular synthons in the crystalline state where the pyridyl-moiety is accommodated in the  $\pi$ -electron rich cavity. This is verified mainly via examination by single crystal X-ray diffraction. Other examples of calix[4]arene self-inclusion polymers are rare [7–10], especially with  $\pi$ – $\pi$ -interactions enhanced by transition metals.

**Electronic supplementary material** The online version of this article (doi:10.1007/s10847-009-9548-3) contains supplementary material, which is available to authorized users.

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Here we introduce the first ionic pyridoxycalix[4]arene self-inclusion complex, potentially allowing us to study the influence of the counter-ion on the self-inclusion properties.

## Experimental section

Calixarene 1 was synthesized as described before [11]. Suitable single-crystals of 1 were grown by slow diffusion of toluene into a saturated dichloromethane solution of 1.

Crystal data for 1: (C<sub>24</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>), *M<sub>r</sub>* = 366.40 g/mol; colorless, 0.25 × 0.20 × 0.17 mm<sup>3</sup>, monoclinic, *C2/c*, *a* = 18.885(3) Å, *b* = 9.8490(17) Å, *c* = 20.559(4) Å, β = 103.424(4)°, *V* = 3726.8(12) Å<sup>3</sup>, *Z* = 8, ρ<sub>calc</sub> = 1.306 g/cm<sup>3</sup>, θ<sub>max</sub> = 25.05°, λ(Mo K<sub>α</sub>) = 0.71073 Å, *T* = 213(2) K, 3277 independent reflections, 3277 [*I* > 2σ(*I*)], *R* = 0.0403, *wR* = 0.1029, (*R* = 0.0531, *wR* = 0.1110 for all data), GOF = 1.034.

Synthesis and crystal growth of the copper(II) complex 2: A suspension of 1 (24 mg, 33 μmol) and copper(II) perchlorate (9 mg, 34 μmol) in absolute acetonitrile (7 mL) was heated 14 h under reflux. The red-purple solution was cooled to room temperature. Insoluble material was filtered off and solvent was removed by rotary evaporation to give 30 mg (91%) of 2 as a deep purple glassy solid. The solid was dissolved in dichloromethane (2 mL) and slowly diluted with methanol (2 mL) to give after 3 days purple single-crystals (m. p. >300 °C) suitable for X-ray diffraction.

Crystal data for 2: (C<sub>50.50</sub>H<sub>42</sub>Cl<sub>5</sub>CuN<sub>4</sub>O<sub>12.50</sub>), *M<sub>r</sub>* = 1145.67 g/mol; purple, 0.175 × 0.097 × 0.020 mm<sup>3</sup>, monoclinic, *P2<sub>1</sub>/n*, *a* = 16.530(2) Å, *b* = 16.768(1) Å, *c* = 17.437(2) Å, β = 94.477(7)°, *V* = 4818.2(7) Å<sup>3</sup>, *Z* = 4, ρ<sub>calc</sub> = 1.579 g/cm<sup>3</sup>, θ<sub>max</sub> = 25.25°, λ(Mo K<sub>α</sub>) = 0.71073 Å, *T* = 105(2) K, 8672 independent reflections, 4421 [*I* > 2σ(*I*)], *R* = 0.0644, *wR* = 0.1205, (*R* = 0.1448, *wR* = 0.1474 for all data), GOF = 0.941.

Intensity data were collected on a Bruker AXS-SMART 1000 (1) and on an Oxford Xcalibur2 (2) using monochromatic Mo-K<sub>α</sub> radiation (λ = 0.71073 Å). The data were corrected for Lorentz polarization and absorption effects. Both structures were solved by direct methods and refined by full-matrix least squares using SHELXTL-97 [15]. All non-hydrogen atoms were refined using

anisotropic thermal parameters. All hydrogen atoms were placed at geometrically estimated positions. CCDC-710799 (1), and CCDC-710800 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## Results and discussion

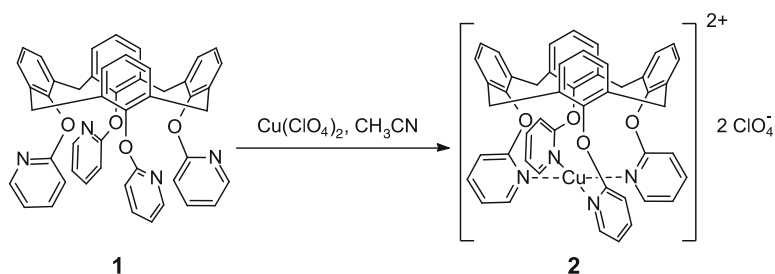
In the following contribution we discuss the X-ray single crystal structures of the tetrapyridoxycalix[4]arene 1 and its copper(II) perchlorate complex 2 forming self-inclusion polymers.

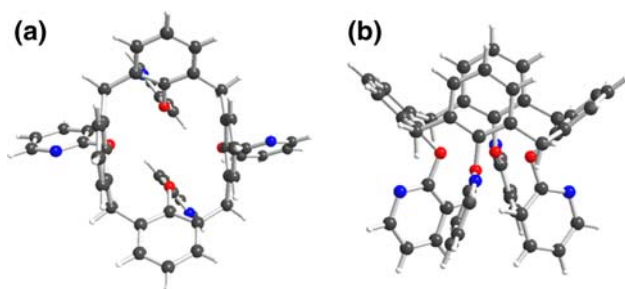
Calixarene 1 was synthesized as described earlier [11], and was reacted with copper(II) perchlorate in hot acetonitrile to give the complex 2 in 91% yield (Scheme 1).

Single crystals of the ligand 1 of sufficient quality for X-ray diffraction were grown by slow dilution of a saturated dichloromethane solution of 1 with toluene. 1 crystallizes in the monoclinic space group *C2/c* with eight calixarenes in the unit cell. Each molecule shows a pinched cone conformation with dihedral angles of 2.4(1)° and 95.7(1)° of the distal phenolic π-planes (Fig. 1). The pyridyl substituents are oriented almost orthogonal to the aromatic phenol units with the nitrogen atoms directed exo to the center of the molecules.

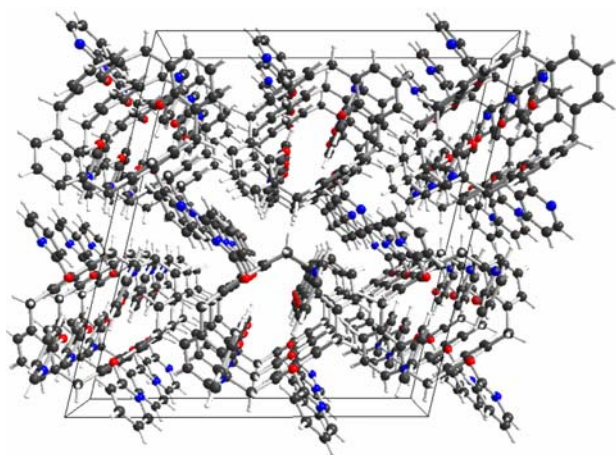
No solvent molecules are included in the crystal. The molecules are stacked to columnar rows along the crystallographic *b*-axis (Fig. 2) where the calixarenes are head-to-tail oriented by dipole–dipole interactions of the more electron-rich cavity (head) and the somewhat electron-poor pyridyl moieties at the lower rim (tail). The rows themselves are directed in layers of opposite orientation. However, two adjacent calixarenes of two different stacks additionally interact via a) very weak CH...N bonds [16–18] of pyridylsubstituents and b) CH...π interactions of the pyridylic CHs and the phenolic π-plane (Fig. 3) [19]. This was confirmed by a distance of *d*(N...H) = 2.74(1) Å (dashed yellow line in Fig. 3) and an N–H–C angle of 130.9° between two adjacent pyridine-rings laying almost in the same virtual plane (distance between planes = 0.28 Å). These values are very similar to the metrics

**Scheme 1** Synthesis of the copper(II) complex 2

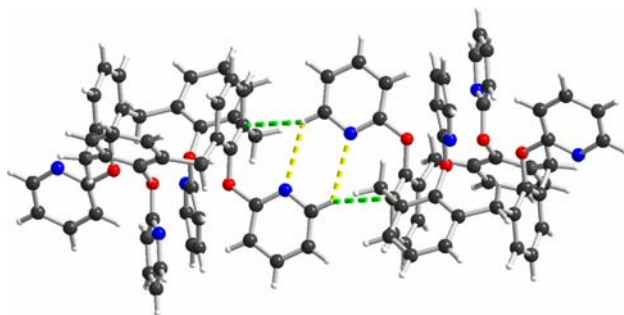




**Fig. 1** X-ray crystal structure of ligand 1 showing one calixarene molecule. Black: carbon, white: hydrogen, blue: nitrogen, red: oxygen. a top view, b side view



**Fig. 2** Crystal packing of 1 along the crystallographic b-axis showing the columnar stacks. For the color code see Fig. 1



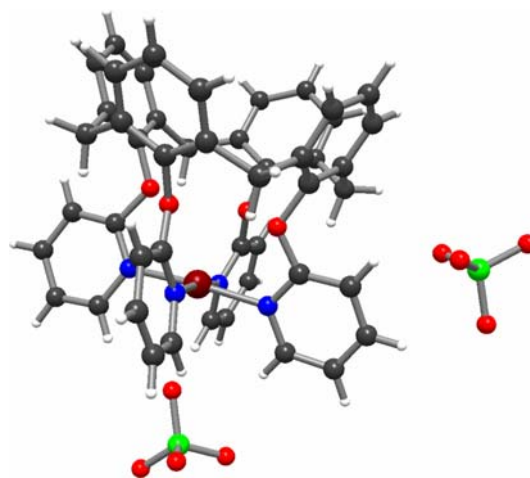
**Fig. 3** Section of the crystal structure of 1 depicting the weak CH...N interactions (dashed yellow lines) and the CH... $\pi$  interactions (dashed green lines) show the shortest atom-atom contacts between the pyridyl-6-H and the adjacent phenolic  $\pi$ -planes). For the color code see Fig. 1

of a pyridine derivative that Boese and coworkers have investigated in the crystalline state (in their case:  $d(\text{N}\cdots\text{H}) = 2.73 \text{ \AA}$  and  $\text{N-H-C}$  angle of  $134.7^\circ$ ) [17]. The closest orthogonal distance of the pyridylic H-6 to the phenolic  $\pi$ -plane is  $2.41(1) \text{ \AA}$  (the dashed green line in Fig. 3 shows the closest  $\text{H}\cdots\text{C}$  contact ( $d = 2.79(4) \text{ \AA}$  of this interaction). This is in the typical range of  $\text{CH}\cdots\pi$

interactions [19]. Additionally, intermolecular  $\text{CH}\cdots\text{N}$  interactions are assumed by short contact distances of the 6-positioned hydrogens to the 6-positioned carbon centers of nearby pyridyl moieties ( $d = 2.86(4) \text{ \AA}$ ) and of the phenolic hydrogen atoms to the pyridyl nitrogen atoms ( $d(\text{H}\cdots\text{N}) = 2.71(3) \text{ \AA}$ ).

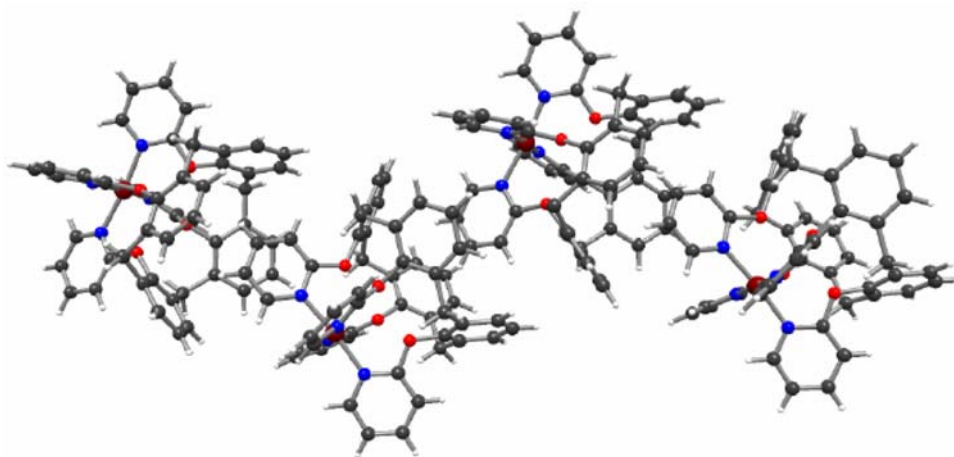
Suitable single crystals of 2 were grown by slow dilution of a saturated dichloromethane solution of 2 with methanol. The compound crystallizes in the monoclinic spacegroup  $P2_1/n$  and contains four calixarenes besides molecules of dichloromethane and four molecules of methanol in the unit cell. The single calixarene scaffolds are forced into an almost  $\text{C}_{4v}$ -symmetric cone conformation by the complexation of the copper(II) ion (Fig. 4). This can be assigned by the dihedral angles of the opposite phenolic  $\pi$ -planes of  $61.7^\circ$  and  $62.4^\circ$ . This widens the cavity for including potential guest molecules. The copper(II) center is square planar surrounded by the four pyridine nitrogen atoms ( $d(\text{Cu-N}) = 2.01(5), 2.01(5), 2.02(5)$  and  $2.02(5) \text{ \AA}$ ). The in plane angles ( $\text{N-Cu-N}$ ) are in the range of  $88.4(2)$ – $93.1(21)^\circ$ , whereas the out of plane angles of opposite nitrogen atoms and the copper center are ( $\text{N-Cu-N}$ )  $174.7(19)^\circ$  and  $173.7(19)^\circ$ . One of the perchlorate counter ions is oriented to the copper center where one oxygen atom is placed approximately on the tip of a square planar pyramid. Although the distance  $d(\text{Cu-O}) = 2.96(5) \text{ \AA}$  is larger than the sum of the van-der-Waals radii a small contribution is expected by a Jahn–Teller-effect. The  $\text{N-Cu-O}_{\text{perchlorate}}$  angles are in the range of  $85.7(16)^\circ$  and  $88.3(16)^\circ$ , again a hint for the interaction of one perchlorate anion with the copper cation [20]. The other perchlorate anion is embedded in the voids of the self-inclusion zig-zag chains (see below).

The calixarenes themselves self-assemble to zig-zag-chains where one pyridyl moiety of one calixarene is



**Fig. 4** Section of the x-ray crystal structure of the copper-complex 2. Black: carbon, white: hydrogen, red: oxygen, blue: nitrogen, green: chlorine. The inclathrated dichloromethane and methanol molecules are omitted for clarity

**Fig. 5** Self-inclusion zig-zag-chain formed by the calixarene-copper complex 2. Four accommodated molecules are shown. Inclathrated solvent molecules and perchlorate anions are omitted for clarity. For the color code see Fig. 4



accommodated into the cavity of another (Fig. 5). We conclude that the copper(II) cation has a comparable effect as the palladium(II) in the dipyridylcalix[4]arene complexes: [11, 14] fixation of pyridyl-moieties perpendicular to the phenolic  $\pi$ -planes of the same calixarene molecule and diminishing the electron-density on the pyridyl rings and therefore activating them for the self-inclusion process. The Cu–Cu distance is 10.992 Å and in comparison with the calixarene-Pd zig-zag-chains about 1 Å longer [11, 14]. This is probably due to the sterically more demanding lower rim of 2, with four orthogonally fixed pyridyl moieties instead of just two. The Cu–Cu–Cu angle is 100.28° and much closer to the ideal value of the Pd-centers in our hexameric supracycle [11] (103.5°) than to the corresponding zig-zag chains (120.7 and 133.5°) [14].

## Conclusions

Within our research on self-assembled calixarene transition metal complexes we introduced the first ionic congener of a self-inclusion polymer forming a zig-zag chain with a metal-metal-metal angle close to our hexameric supracycle system. The fact that the anions are weakly interacting with the cationic center or even been incorporated in the lattice voids allows us to fine tune this system by exchanging the counter anions of the copper(II) salt applied, thus varying the size and chemical nature of the anions. With this opportunity we will elaborate the influence of the counteranions on the self-inclusion behaviour and try to understand anion-packing-relationships.

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