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Coordination Polymer Chains of Dimeric Pyrogallol[4]arene Capsules

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S Supporting Information

ABSTRACT: Copper seamed dimeric metal−organic pyrogallol[4]arene capsules have been synthesized and engineered into coordination polymer chains, either by direct coordination or with additional bridging ligands. The formation of this copper capsule also demonstrates selective formation of either hexameric or dimeric metal−organic capsules.

Since the initial discovery of a hydrogen-bonded hexameric capsule more than a decade ago, numerous studies have demonstrated that *C*-alkylpyrogallol[4]arenes (PgCs) exhibit a wide variety of superstructures in both solution and the solid state.[1] The presence of 12 hydroxyl groups per macrocycle assists in the formation of self-assembled entities through an impressive scaffold of hydrogen bonds. Studies in recent years have also highlighted the significance of PgCs as multidentate ligands for metal ions. Metal-hydroxyl coordination imparts additional stability to the framework and may impart additional functionality to the capsules.[2−5] Such superstructures can potentially function as stable carriers for a cadre of guest molecules, such as pharmaceuticals, or as catalytic “nanobeads” for industrial processes. Any practical implementation, however, is hindered by a lack of synthetic control over the system. Both hexameric copper[3] and dimeric zinc[5] metallo-PgC capsules have been reported, but it is highly desirable to develop a standard protocol by which assemblies of a desired size can be fabricated regardless of metal identity. Herein we report the synthesis and structure of a dimeric capsule comprising eight Cu^{II} centers and two *C*-methyl pyrogallol[4]arenes (PgC1), representing the first example of a metal displaying the versatility to form both hexameric and dimeric metallo-PgC capsules.

The previously reported dimeric Zn^{II}−PgC capsule was synthesized through the direct complexation of *C*-propyl pyrogallol[4]arene (PgC3) and eight Zn^{II} ions in pyridine (Py) to afford **1** (Figure 1A,B).[5a] Synthesis of the dimeric Cu^{II}−PgC capsule reported here was achieved through the complexation of PgC1 and cupric acetate in hot dimethyl sulfoxide (DMSO) to afford crystalline **2** upon cooling. Notably, this synthesis differs markedly from that of the hexameric Cu^{II} analog, which is formed using copper nitrate in wet methanol.[3] In addition, the disparate preparative methods for the Zn^{II}− and Cu^{II}−PgC dimeric capsules result in the encapsulation and ligation of different solvent species, the latter of which can be seen in Figure 1B and 1D.

Although the overall structures of **1** and **2** are comparable, the substitution of Cu^{II} for Zn^{II} leads to minor, although not insignificant, changes in coordination geometry. Because both complexes can be regarded as distorted five-coordinate systems with respect to the metal (M) ions, τ_5 values were calculated for each structure to qualitatively compare M geometries. This parameter, introduced by Addison et al.,[6] evaluates the trigonality of distorted five-coordinate systems, with a τ_5 value of 1 indicating a perfect trigonal bipyramid and a value of 0 indicating a perfect square pyramid. An analog of **1** (**1***), in which all Py ligands are displaced by DMSO, was used in these calculations.[5b] Average τ_5 values of 0.417 and 0.331 were determined for **1*** and **2** respectively (Supporting Information (SI)). The tendency toward greater square pyramidal geometry in **2** has an overall contractive effect on the octametallic belt, resulting in a mean adjacent Cu−Cu distance of 3.645 Å in **2**, as compared to 3.786 Å for Zn−Zn in **1***. This result is of direct relevance toward future studies concerning host−guest interactions in dimeric M^{II}−PgC capsules, as the implementation of Cu^{II} over Zn^{II} allows specific tuning of interior volume and geometry.

Previous reports regarding the dimeric Zn^{II}−PgC capsule showed that exoligand exchange could be accomplished without compromising the overall dimer framework.[5b] Thus, we decided to investigate the effects that other ligands would have on the packing of the dimeric copper capsules, with specific emphasis on intercapsule linking. Examples of linking discrete molecular capsules are sparse, and to our knowledge only one prior example of linking in PgC capsules has been reported. Atwood and coworkers described the synthesis and structure of a copper-seamed hexamer employing *C*-propan-3-olpyrogallol[4]arene (PgC3OH).[3] This capsule displays linking through coordination bonds from hydroxyl groups of PgC3OH tails to Cu^{II} centers from adjacent hexamers. Also of interest are examples of molecular capsules made up of calixarenes displaying intercapsule linking; however, such reports are rare.[7] Due to its application as a unidirectional charge transfer ligand in metal−organic frameworks,[8] 4,4′-bipyridine (4,4′-bipy) was a logical choice of linking unit. Crystalline **2** was dissolved in a hot DMSO solution containing 4,4′-bipy, and small crystals of a 1-D coordination polymer (CP), **3**, were formed upon cooling (Figure 2). This 1-D CP of linked dimeric Cu^{II}−PgC1 capsules is an unprecedented example of intercapsule tethering. In **3**, N-donor atoms from 4,4′-bipy molecules displace DMSO ligands on five of eight Cu^{II}

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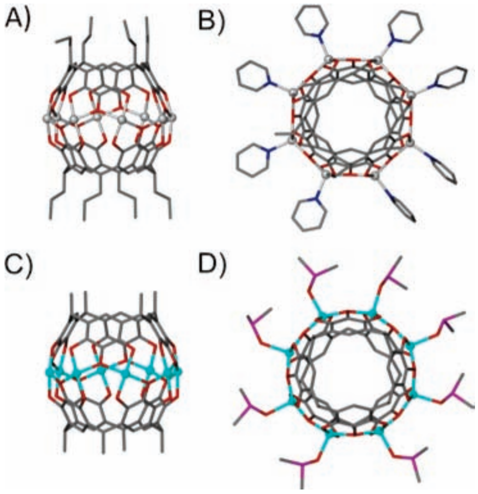

Figure 1. Crystal structures of **1**[5a] and **2**. (A) Side view of **1**, H atoms and ligated/guest Py omitted for clarity. (B) Orthogonal view of **1** showing Zn^{II} Py ligands. (C) Side view of **2**, H atoms and ligated/guest DMSO omitted for clarity. (D) Orthogonal view of **2** showing Cu^{II} DMSO ligands.

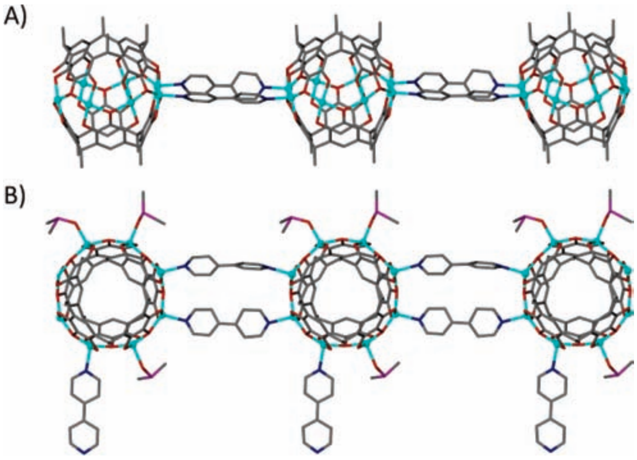

Figure 2. Crystal structure of **3**. (a) Side view showing the 1-D CP. (b) Top view showing additional 4,4′-bipy ligands. Axial ligands (in A) and hydrogen atoms (in A and B) omitted for clarity.

centers. Of these five 4,4′-bipy ligands, four act as tethers on opposite sides of a given capsule to form the 1-D CP (Figure 2). The remaining 4,4′-bipy is projected between layers of bridging 4,4′-bipys of adjacent CP strands.

To determine if linking had any influence on the coordination geometry within the capsule, an average τ_5 value was calculated for all Cu centers in this structure (SI). The resulting value of 0.332 shows that the displacement of DMSO ligands by 4,4′-bipy does not have a significant effect on the overall Cu^{II} coordination geometry. Indeed, individual τ_5 values for specific Cu centers did not show any logical trend that would indicate a difference between DMSO and 4,4′-bipy ligands. This consistency supports the notion that, at least in this case, ligand exchange does not alter the overall dimeric Cu^{II}−PgC capsule framework, allowing for the use of these moieties as flexible building blocks in the potential formation of larger and more complex assemblies; one can readily envision obtaining a 2-D CP through appropriate modification of experimental conditions.

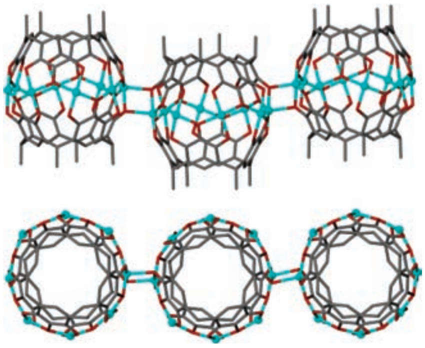

Figure 3. Orthogonal views of the crystal structure of compound **4**. Hydrogen atoms and axial ligands omitted for clarity.

In our second example of capsule linking, binding occurs from one octametallic belt directly to another, rather than through a bridging ligand as in the previous case. The synthesis of **4** occurred somewhat serendipitously from an attempt to synthesize a dimeric Cu^{II}−PgC capsule with axial Py ligands for comparison with the previously reported zinc analog. Unexpectedly, each dimeric Cu^{II}−PgC capsule binds to two neighboring capsules through four Cu−O bonds, to form the 1-D coordination polymer **4** (Figure 3). The intercapsule linking Cu−O bonds have an average length of 2.27 Å and are, as expected, longer than the intracapsule bonds (average length 1.97 Å).

As in the previous example of capsule linking, τ_5 values were calculated to determine if the linking had any effect on the Cu coordination geometry. Due to the sterically induced absence of an axial ligand on Cu4, mean τ_5 values were computed both including (wherein Cu4 was treated as if five-coordinate) and excluding Cu4, giving values of 0.322 and 0.367 respectively. As the Cu4 center had a τ_5 value of 0.008, indicating near-perfect square pyramidal, or more likely square planar, geometry, it is understandable why the difference between the two former τ_5 values is so large. The increased tendency toward trigonality in all other Cu centers, however, is an interesting finding and may be due to some degree of autocompensation to minimize the change in Cu−O bond distances caused by the flattening around Cu4. This compensation, however, is unlikely to have been caused by linking, per se, but rather by steric factors.

The synthesis of a dimeric Cu^{II}−PgC capsule marks an important first step toward facile control over self-assembly in these systems. Relatively simple synthetic routes for the controlled production of either hexameric or dimeric Cu^{II}−PgC capsules have now been realized, rendering both moieties readily accessible targets for further study. Capsule linking via bridging ligands represents another significant advancement in the chemistry of these materials, as it demonstrates that ligand exchange can be readily implemented to impart specialized functionality to the individual building blocks. Direct capsule linking provides yet another unique pathway toward directed structural design and unlocks the imagination with respect to more unconventional possibilities with these molecular capsules.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental details for **2**−**4**, calculation of τ_5 values, large versions of Figures 1−3, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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