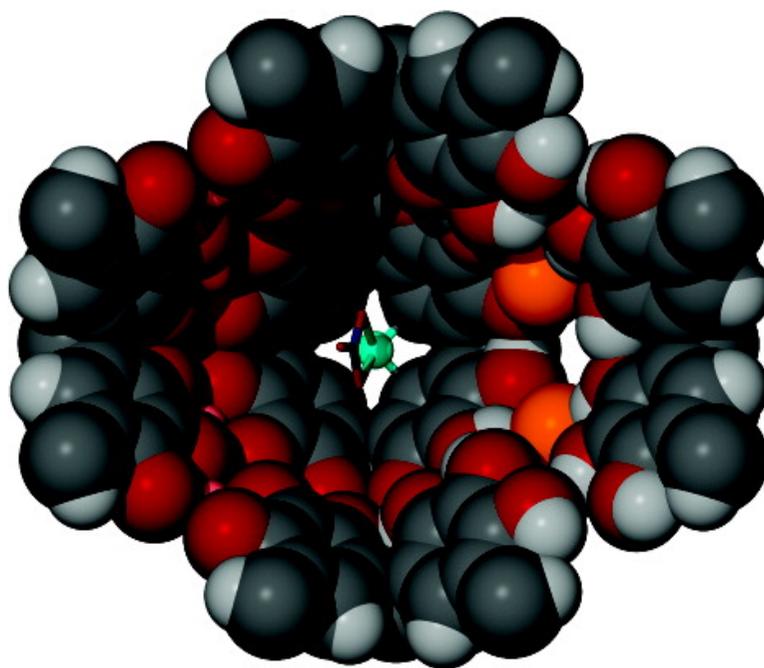


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## Ion Transport to the Interior of Metal–Organic Pyrogallol[4]arene Nanocapsules

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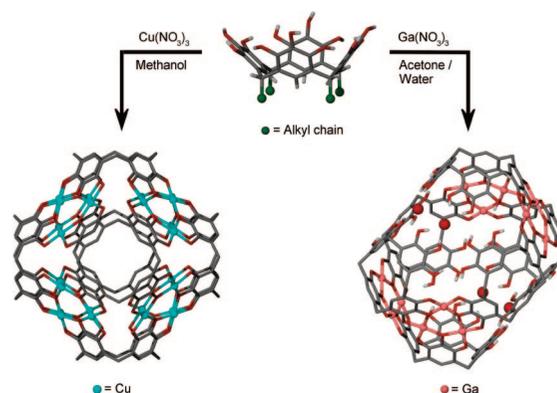
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The formation of nanometer scale capsule (or capsule-like) assemblies continues to attract interest because of the potential application of such architectures as encapsulation tools or delivery vehicles, gas sequestration agents, and catalytic media for example.<sup>1,2</sup> Both *C*-alkylresorcin[4]arenes and the related pyrogallol[4]arenes have been shown to assemble into voluminous hexameric hydrogen-bonded assemblies in both solution and the solid state,<sup>2</sup> with molecular encapsulation being studied by various methods. In a number of our recent studies, we have shown that addition of copper(II) or gallium(III) nitrate hydrates results in the formation of hexameric metal–organic nanocapsules (MONCs) via metal center insertion, a process that involves concomitant elimination of protons from pyrogallol[4]arene hydroxyl groups (Figure 1).<sup>3–5</sup> For Cu(II), 24 metal centers insert with elimination of 48 H<sup>+</sup> to afford a spherical capsule that is near identical in diameter to the hydrogen-bonded analogue.<sup>3</sup> For Ga(III), 12 metal centers insert with elimination of 36 H<sup>+</sup>, resulting in distortion to the capsule and adoption of a “rugby-ball”-like shape (Figure 1).<sup>4</sup> This distortion in the Ga-MONCs results in the incorporation of water molecules into what we have termed structural “gates” (Figure 1). Copper addition to gallium MONCs resulted in the formation of mixed metal assemblies,<sup>5</sup> and although we are continuing to investigate the formation of such species, we wished to investigate the possibility of metal centers (or other molecular material) passing through the structural gates to reside in the capsule interior.

With the abovementioned goal in mind, we selected cesium and silver as starting points for these experiments. Both metal centers are well-known to interact with aromatic  $\pi$ -systems, and there are various examples of Cs or Ag interaction with calixarenes in general; those cited here being structures in which the host molecules are in a cone conformation.<sup>6,7</sup> Cesium hydroxide and silver nitrate solutions (in methanol and acetonitrile, respectively) were added to acetone solutions of preformed *C*-butylpyrogallol[4]arene (PgC4) Ga-MONCs (Figure 1). In each case, standing with slow evaporation over a number of days afforded single crystals of assemblies **1** (Cs) and **2** (Ag) that were analyzed using X-ray diffraction. In both cases, the PgC4 Ga-MONCs are found to act as a host to both types of metal center and counterion (for Ag at least).<sup>8</sup>

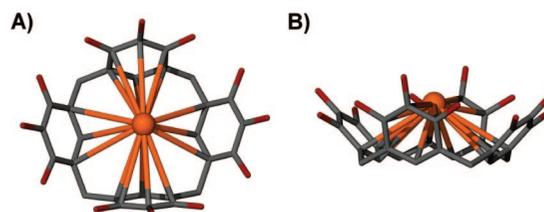
Crystals of assembly **1** were weakly diffracting, required synchrotron radiation, and are in a monoclinic cell with structural solution performed in the space group  $P2_1/n$ . The asymmetric unit was found to contain half of the PgC4 Ga-MONC framework, and following structure refinement, a large peak was observed deep within the cavity of one PgC4 molecule. This was assigned as cesium, was allowed to freely refine to an occupancy of 46%, and has subsequently been modeled as such. In this position, the cesium

is bound to two entire aromatic rings of the PgC4 and three of the atoms in each of the remaining two aromatic rings (18 Cs–C distances in the range of 3.566–3.872 Å, Figure 2). In addition there are a number of badly disordered aquo ligands that have been refined with partial occupancies.



**Figure 1.** The assembly of *C*-alkylpyrogallol[4]arenes into metal–organic nanocapsules (MONCs) via metal center insertion and proton elimination. Copper insertion affords a near spherical nanocapsule while gallium insertion results in the incorporation of structural water molecules in gates to the interior of the assembly. Figures not to scale. Hydrogen atoms, solvent molecules, metal ligands, and pyrogallol[4]arene lower rim alkyl chains omitted for clarity.

Our previous studies examining the binding of cesium with pyrogallol[4]arenes found the metal to form ionic dimeric capsules.<sup>6f</sup> In those studies, the metal centers are located near the upper rims of the host molecules while also coordinating to guest acetonitrile solvent molecules. In assembly **1**, the cesium centers have not coordinated in the gates of the MONC, but have rather fully entered the nanocapsule, forming a larger number of polyhaptoaromatic interactions compared to previous studies (Figure 2B). This is likely due to the conformational distortion imparted by the gallium centers, the presence of the structural water molecules, and the aforementioned propensity of the metal to form such interactions with calixarenes.<sup>6</sup>



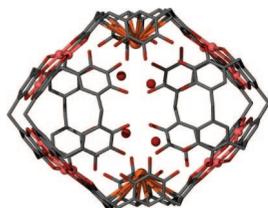
**Figure 2.** Top (A) and side on (B) views of part of the structure of assembly **1** showing the cesium binding within the PgC4 cavity. Hydrogen atoms, solvent molecules, disordered cesium aquo ligands, and PgC4 lower rim alkyl chains omitted for clarity.

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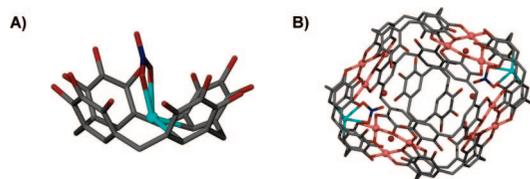
<sup>§</sup> Advanced Light Source.

Symmetry expansion of the asymmetric unit affords the entire nanocapsule arrangement with a total of 0.92 cesium centers disordered over the two positions within the overall assembly (Figure 3). As a result of poor diffraction, even with synchrotron radiation, disordered solvent molecules both on the interior and exterior of the nanocapsule were only resolved to a limited extent.



**Figure 3.** The symmetry expanded MONC in assembly **1** showing the cesium binding within PgC4 molecules. Structural water molecules, acting as gates are shown as red spheres. Hydrogen atoms, solvent molecules, cesium aquo ligands and PgC4 lower rim alkyl chains omitted for clarity.

Crystals of assembly **2** are in a triclinic cell and structural solution was performed in the space group  $P\bar{1}$ . The asymmetric unit contains half of the PgC4 Ga-MONC, and in a similar manner to assembly **1**, the presence of the heterometal center was not clear in the initial structure solution. Refinement showed a large peak corresponding to a partial occupancy silver center (refined and subsequently modeled with occupancy of 50%) with a chelating nitrate anion (Figure 4A). The silver center also resides very deep within the PgC4 cavity and forms polyhaptoaromatic interactions with two aromatic rings with Ag–C distances of 2.663 and 2.695 Å. These values are consistent with previously reported examples of silver-calixarene interactions.<sup>7</sup> The quality of diffraction data allowed for relatively good resolution of the disordered solvent molecules and symmetry expansion shows a nanocapsule arrangement containing a total of one silver nitrate ion pair disordered over the two positions. Comparison between assemblies **1** and **2** shows the metal centers to reside in different pyrogallol[4]arenes relative to the aqueous structural gates. The presence of particular anions may direct metal center placement within these nanocapsules and is a feature we are currently exploring.



**Figure 4.** Views of assembly **2** showing (A) part of the asymmetric unit emphasizing the silver coordination to the aromatic rings and the presence of the nitrate anion and (B) the expanded structure showing overall MONC structure and silver center placement.

With respect to the mode of transport, our hypothesis requires the PgC4 Ga-MONCs to remain intact during ion (or ion pair) passage through the aqueous gates. We believe the likelihood of PgC4 dissociation from the assembly (that would result in very large portals) to be low. This assumption is based on studies of lability within somewhat related self-assembled  $M_4L_6$  Ga/catechol cages by Raymond and co-workers.<sup>9</sup> Those studies demonstrated that for guest exchange purposes, partial metal–ligand dissociation involving the breaking of only two Ga–O bonds does not occur and that guest exchange takes place solely via cage deformation (even with very large guest molecules). Furthermore, such a process would remove high degrees of selectivity that are frequently observed within that system type. Dissociation of one PgC4 from

the Ga assembly would require the breaking of eight Ga–O bonds from the related Ga/pyrogallol moieties. On the basis of the aforementioned precedent we believe this to be unlikely.

In conclusion, our experiments show that metal ions and ion pairs can move through aqueous structural gates to the interior of pyrogallol[4]arene metal-organic nanocapsules. Kim and co-workers very recently reported the action of metal-organic polyhedra as synthetic ion channels that can transport alkali metal ions across lipid membranes.<sup>10</sup> Although this particular goal was not the primary thrust of the research described here, the ready modification to the lower rim of the pyrogallol[4]arene framework lends itself to such potential application. Research continues on these new and interesting metal–organic nanocapsules, ion transport phenomena, and associated host–guest chemistry.

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**Supporting Information Available:** Experimental details; crystallographic details for assemblies **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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