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A Coordination Cage with an Adaptable Cavity Size

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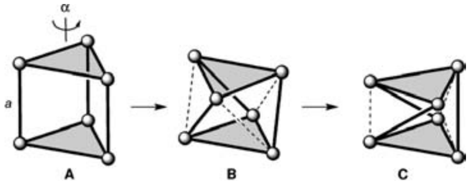
Abstract: A hexanuclear coordination cage can increase the size of its cavity from nearly zero to more than 500 Å^3, which allows the encapsulation of two coronene molecules.

Coordination cages (CCs) are obtained by combining metal complexes having available coordination sites with polytopic ligands.[1] The size and symmetry of CCs are appealing aspects, but they may also display fascinating host−guest chemistry. Recent highlights include the utilization of CCs as nanoreactors[2] or transport vehicles for cytotoxic compounds[3] and the stabilization of reactive molecules such as white phosphorus,[4] a coordinatively unsaturated Mn complex,[5] and cyclic trimers of siloxanes.[6]

The basic design principles of CCs are well-established.[1] Key to success is the utilization of metal complexes and ligands with appropriate symmetry. In addition, the building blocks must be rather rigid to circumvent formation of entropically favored small aggregates and/or dynamic mixtures of complexes. As a consequence, the final cages tend to be rigid as well. The lack of flexibility of CCs is in contrast to what is found for many biological receptors, for which "induced fit" and "conformational selection" phenomena are frequently observed.[7] Therefore, it appears interesting to investigate strategies that would allow the synthesis of adaptable CCs.

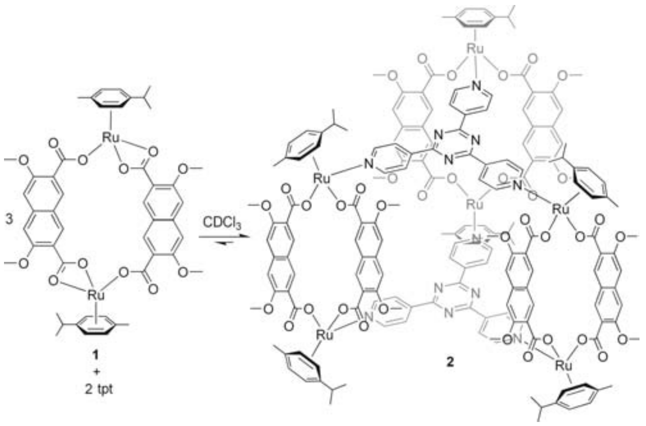
Scheme 1 shows the distortion of a trigonal prism along its threefold symmetry axis. The rotation of one trigonal plane with respect to the other leads to a reduction in the height of the polygon (the distance between the trigonal planes) if the lengths of the edges *a* are not altered.[8] A similar distortion might be realized with a trigonal prismatic CC by using coordinative bonds with sufficient conformational freedom. It should be noted that the ligands themselves can be rigid, as the distances of the metal centers with direct connections would not change. Below we describe an implementation of this concept. It is shown that a hexanuclear Ru cage can vary the size of its cavity from nearly zero to more than 500 Å^3, which is large enough to accommodate two coronene molecules.

Scheme 1. Distortion of a Trigonal Prism **A** along Its Threefold Symmetry Axis Results in Polyhedra with Reduced Height (**B** and **C**)



The dinuclear complex **1** (Scheme 2) was chosen as the starting material. Its synthesis was achieved by reaction of 3,6-dimethoxynaphthalene-2,7-dicarboxylic acid with the acetate complex [(p-cymene)Ru(OAc)$_2$]. The latter was obtained in situ by reaction of the chloro-bridged dimer [(p-cymene)RuCl$_2$]$_2$ with 4 equiv of AgOAc. Complex **1** was characterized by NMR spectroscopy and elemental analysis, and its solid-state structure was determined by single-crystal X-ray diffraction [see the Supporting Information (SI)]. Each (p-cymene)Ru center is coordinated to two carboxylate groups, one of which is bound as an O,O′-chelate. The Ru atoms in complex **1** are 10.9 Å apart.

Scheme 2. Synthesis of Cage **2**



It was expected that the four-membered chelate ring of the carboxylate could be opened with neutral donor ligands.[9] Reaction of complex **1** with a tritopic ligand could thus lead to the formation of a hexanuclear Ru cage.[10] Such a cage should display reasonable conformational freedom at the metal centers because the connecting ligands are all monodentate. The carboxylate ligands are particularly useful in this context, as they are known to have a flexible coordination geometry.[11]

The commonly used ligand 2,4,6-tris(pyridin-4-yl)-1,3,5-triazine (tpt) was employed as a tritopic N-donor ligand. The putative formation of a cage was first examined by NMR spectroscopy. Complex **1** (3 equiv, $[\mathbf{1}]_{\text{final}} = 5.7$ mM) was mixed with tpt (2 equiv) in CDCl$_3$. The ^{1}H NMR spectrum of the mixture showed minor signals for the starting materials **1** and tpt along with signals for the new complex **2** (Figure S2c in the SI). The fact that small signals for both starting materials were present suggested that complex **2** was in equilibrium with its constituent components **1** and tpt. The spectrum recorded 10 min after mixing was identical to one recorded after 1 h, indicating that the system equilibrates rapidly. There have been several reports about trigonal prismatic CCs that are able to encapsulate polyaromatic compounds.[1,10,12] ^{1}H NMR spectroscopy showed that **2** is able to bind two molecules of coronene. Upon addition of increasing amounts of the guest, signals of a new complex grew in intensity along with a

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signal at 5.83 ppm that can be attributed to encapsulated coronene. The complete conversion into the new species was achieved with 2 equiv of coronene with respect to **2** (Figure S2a); further addition of coronene resulted in an increased intensity of the "free" coronene signal at 8.90 ppm. The complexation of the two guest molecules appears to be a cooperative process: the addition of 1 equiv of coronene with respect to **2** gave ~50% of the host−guest complex (**2** × 2 coronene) along with "free" **2**. It is also evident that coronene stabilizes the host, as the signals of the starting materials **1** and **2** disappeared upon addition of coronene.

Very similar results were obtained when perylene was used as the guest instead of coronene: the addition of 2 equiv of perylene with respect to **2** resulted in the clean formation of (**2** × 2 perylene). However, the thermodynamic stability of the perylene adduct was found to be lower than that of the coronene adduct: when 2 equiv of coronene was added to a solution of (**2** × 2 perylene), a fast (<1 min) and quantitative transformation to (**2** × 2 coronene) was observed (Figure S3).

Since complex **2** is in a dynamic equilibrium with the starting materials **1** and tpt, it was difficult to isolate **2** in pure form. Small amounts of crystalline **2** were finally obtained from dichlorobenzene, and single crystals of the host−guest complex (**2** × 2 coronene) were obtained from chloroform. X-ray diffraction analyses of both complexes were performed, and graphic representations of the solid-state structures are shown in Figure 1.

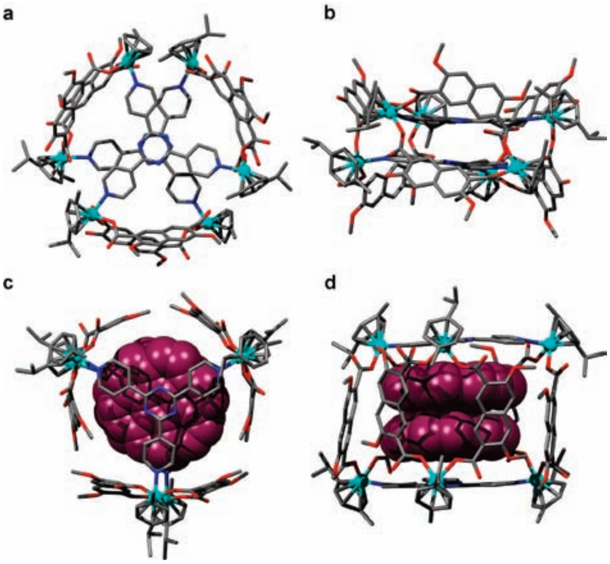

Figure 1. Molecular structures of cage **2** [(a) top view; (b) side view] and its coronene adduct (**2** × 2 coronene) [(c) top view; (d) side view] in the solid state. Color coding: C, gray or purple; O, red; N, blue; Ru, cyan. Hydrogen atoms and cocrystallized solvent molecules have been omitted for clarity.

The crystallographic analyses confirmed that the pyridyl N-donor atoms of the triazine ligand **2** coordinate to the Ru centers to form a hexanuclear complex. The connectivity found for complex **2** is the same as in the host−guest complex (**2** × 2 coronene): all six (*p*-cymene)Ru complexes are bound to two carboxylate groups and one pyridyl group. Striking differences, however, are observed for the overall geometry of the two complexes. In complex **2**, the triazine ligands are stacked on top of each other, whereas two coronene molecules are inserted between the triazine ligands in the host−guest complex (Figure 1b,d).[13] As a result, the distance between the central C_3N_3 rings is increased from 3.4 to 10.9 Å. The average distance between Ru atoms that are directly connected by the dicarboxylate ligands is similar in **2** (10.6 ± 0.1 Å) and the coronene adduct (10.5 ± 0.2 Å). Modulation of the cavity size is therefore not achieved by distortion of the ligands but rather by the mechanism outlined in Scheme 1. Accordingly, the triazine ligands show an eclipsed conformation in the adduct (**2** × 2 coronene) and a more staggered conformation in **2** with $\alpha \approx 80°$ (Figure 1a,c). The twisting of the triazine ligands renders complex **2** chiral. The chirality of solid **2** is not manifested in the NMR spectra of complex **2** in solution, suggesting that the solvent $CDCl_3$ leads to a cavity expansion similar to that observed for coronene (see the SI for a more detailed discussion).

In summary, we have described a hexanuclear coordination cage that can adopt two distinct structures: a compressed structure without an internal cavity and an elongated structure that is able to accommodate two coronene molecules ($V \approx 500$ Å^3). Importantly, the modulation of cavity size is not achieved by a guest-induced constitutional rearrangement but rather by a conformational change that is enabled by the use of flexible connections between the metal atoms and the ligands. The results demonstrate that it is possible to construct highly adaptive CCs with appropriately designed building blocks.

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Supporting Information Available: Experimental procedures and crystallographic data for **1**, **2**, and (**2** × 2 coronene) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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