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A Novel Cascade Supramolecular Complex with a Reversible Nanosized 18-Component H-Bonded $\{(C_6H_6)_6(SbF_6)_{12}\}^{12-}$ Cage Unit Templated by a Chiral Metal–Organic Complex

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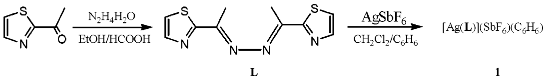
A novel cascade supramolecular complex $[Ag(\mathbf{L})](SbF_6)\cdot C_6H_6$ with a reversible nanosized $\{(C_6H_6)_6(SbF_6)_{12}\}^{12-}$ H-bonded cage unit was reported.

Because of their important application in biology and chemistry, interest in the design and synthesis of molecular nanocontainers involving H bonding or metal coordination has grown rapidly.[1] During past decades, numerous beautiful synthetic host−guest systems based on metal-coordination interactions with potential utility as selective capsules for molecular recognition and separation have come into being.[2,3] As for the H-bonded molecular cages, to date, most efforts have been directed toward the formation of nanocontainers using a few large presynthesized tailored organic molecules capped by H-bonding sites.[4,5] In contrast, nanocapsules constructed from a large number of small-sized components templated by complicated species, especially chiral metal−organic complexes, have received much less attention. This is probably due to the inherent difficulties in harmonizing the subtle relationship between the "self-assembly" and the "templation of guest moieties" in the synthetic systems. On the other hand, although numerous open-framework materials that are able to reversibly absorb and desorb guest molecules have been reported, reversible host frameworks templated by metal−organic complexes in the solid state have, to the best of our knowledge, never been described. In this contribution, we report a novel cascade[6] supramolecular complex $[Ag(\mathbf{L})](SbF_6)\cdot(C_6H_6)$ (**1**) featuring *reversible formation* of the H-bonded benzene−SbF_6^- 3D framework composed of an 18-component nanocontainer unit (ca. 1.7 nm^3) that encapsulates a chiral metal−organic $\{Ag_3\mathbf{L}_3\}^{3+}$ crown guest containing SbF_6^- anions.

Scheme 1. Synthesis of Schiff-Base Ligand **L** and Complex **1**



As shown in Scheme 1, when $AgSbF_6$ was treated with **L** in a methylene chloride/benzene mixed-solvent system, compound **1** was obtained as light-yellow crystals in 91% yield (Scheme 1). X-ray crystal structural analysis revealed that **1** crystallizes in the chiral rhombohedral space group *R*3 and features a "second-sphere" supramolecular system. Each Ag atom in **1** lies in a distorted tetrahedral coordination environment (Figure S1 in the Supporting Information). The ligand itself is tetradentate and provides two pairs of chelating donors in the middle. Three 3-fold symmetry-related Ag(I) centers are crosswise linked together by three twisted **L** ligands (the dihedral angle between the two terminal thiazole planes is ca. 90°) through the middle chelating N donors,

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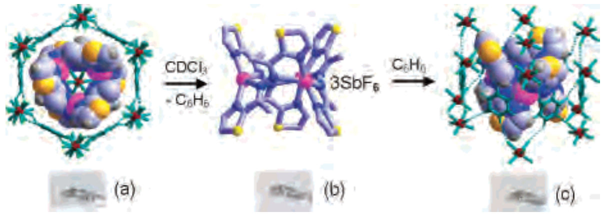

Figure 1. (a) Top view of the individual $(SbF_6)_2{-}Ag_3\mathbf{L}_3{-}(C_6H_6)_6(SbF_6)_{12}$ cascade structure of **1**. (b) Side views of the $SbF_6{-}Ag_3\mathbf{L}_3$ crownlike moiety. (c) Side view of the individual $(SbF_6)_2{-}Ag_3\mathbf{L}_3{-}(C_6H_6)_6(SbF_6)_{12}$ cascade structure of **1′**. The crystal pictures shown herein were taken on the same crystal.

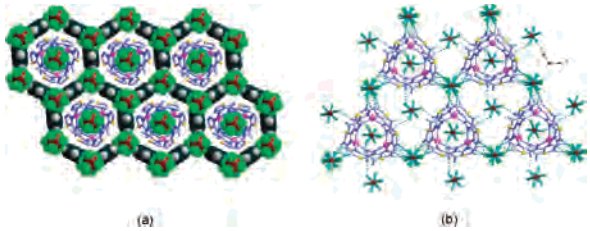

Figure 2. (a) Top view of the 2D single layer formed by anion−benzene (the SbF_6^-−benzene system and crown guest are shown as space-filling and stick-ball models, respectively). (b) Top view of the single 2D layer formed by anions and helicates. The benzene guests are omitted for clarity.

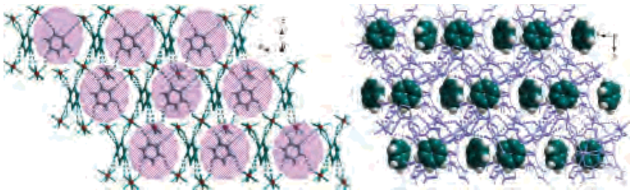

Figure 3. Side view of the 3D anion−benzene host (left; the $\{Ag_3\mathbf{L}_3\}^{3+}$ crown guest is shown as the ellipsoid in purple) and the 3D anion−helicates host (right) driven by the weak C−H···F interactions.

affording a chiral triple-helical trinuclear crownlike cationic complex $\{Ag_3\mathbf{L}_3\}^{3+}$ (Figure S1 in the Supporting Information). It is well-known that the zigzag −RC═N−N═CR− bridging spacers with d^{10} metal ions favor the formation of helical sub-building blocks because of the ligand twisting enforced by the substitutents at the imino C atoms.[7,8] In the cationic complex $\{Ag_3\mathbf{L}_3\}^{3+}$, three Ag(I) atoms form an equilateral triangle with a Ag···Ag distance of 5.3 Å. The two uncoordinated SbF_6^- anions arrange on both sides of the Ag_3 plane and fill in the bowl-like space surrounded by three **L** ligands.

The remarkable feature of **1** is its cascade structure: the inclusion of the SbF_6^- anions in a $\{Ag_3\mathbf{L}_3\}^{3+}$ crown host, which itself is further encapsulated in a larger nanosized $\{(C_6H_6)_6(SbF_6)_{12}\}^{12-}$ cagelike unit driven by weak C−H···F interactions (Figure 1). This unit is formed by 6 benzene molecules and 12 SbF_6^- anions through weak C−H···F interactions (Figure S2 in the Supporting Information).[9] In this cagelike unit, the dihedral angle between adjacent benzene molecules is ca. 120°. A total of 12 SbF_6^- anions are located above and below the benzene cylinder, respectively, and stitch 6 benzene molecules together through 24 sets of weak C−H···F interactions to generate this novel regular hexagonal cage unit. The volume of the individual cage is ca. 1.7 nm^3. In general, nanosized molecular containers driven by weak C−H···X interactions are obtained from the self-assembly of a few presynthesized tailored large organic molecules capped by H-bonding sites, such as cavitand-based monomers.[10] To our knowledge, the ordered nanosized cagelike unit consisting of a large number of small pieces of fragments, such as the 18-component $\{(C_6H_6)_6(SbF_6)_{12}\}^{12-}$ anion herein, is quite rare. The top view of **1** shows how the C_6-symmetric $\{(C_6H_6)_6(SbF_6)_{12}\}^{12-}$ host cage traps the C_3-symmetric $\{Ag_3\mathbf{L}_3\}^{3+}$ crown guest, which further encapsulates two SbF_6^- counterions (Figure 2a). The embedded $\{Ag_3\mathbf{L}_3\}^{3+}$ crown is fixed in the $\{(C_6H_6)_6(SbF_6)_{12}\}^{12-}$ host by 15 sets of inter-guest−host C−H···F hydrogen interactions (Figure S3 in the Supporting Information). Such an arrangement is comparable to Russian Matroshka (nesting) dolls.[6] As indicated in Figure 2a, the individual H-bonded nanocages align in the solid state to form a 2D honeycomb layer extending in the crystallographic *ab* plane, in which each cage shares six benzene edges with its neighbors. Furthermore, the 2D layers are stacked offset along the crystallographic *c* axis and join together through interlayer C−H···F interactions to generate a 3D H-bonded framework (Figure 3 and Figure S4 in the Supporting Information). The $\{Ag_3\mathbf{L}_3\}^{3+}$ crowns are located in each individual $\{(C_6H_6)_6(SbF_6)_{12}\}^{12-}$ cage. From another point of view, this system can also be regarded as a 3D host framework sustained by weak C−H···F interactions between SbF_6^- anions and the $\{Ag_3\mathbf{L}_3\}^{3+}$ helicates. As shown in Figure 2b, the $\{Ag_3\mathbf{L}_3\}^{3+}$ crowns are connected to each other into 2D layers in the crystallographic *ab* plane through C−H···F interactions formed by SbF_6^- and thiazole protons. These layers are further linked together into a 3D framework through interlayer C−H···F interactions along the crystallographic *c* axis. The benzene molecules are fixed in the cavities of such a framework (Figure 3).

The crystals of **1** are air-stable and not soluble in common organic solvents. The thermogravimetric analysis (TGA) revealed that the H-bonded benzene−SbF_6^- framework and the $\{Ag_3\mathbf{L}_3\}^{3+}$ core are stable up to 125 and 250 °C, respectively (Figure S5 in the Supporting Information). Particularly interesting is that the formation of an H-bonded $\{(C_6H_6)_6$-

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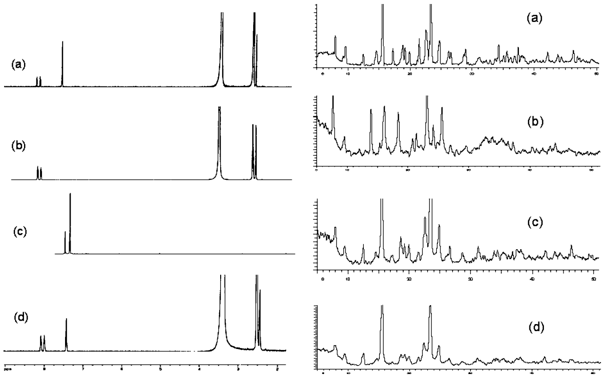

Figure 4. **4** (left) and **5** (right). **4**: (a) ^{1}H NMR spectrum of as-synthesized **1** in DMSO-d_6; (b)^{1}H NMR spectrum in DMSO-d_6 after immersion of the product from part a in $CDCl_3$ for 2 h; (c) ^{1}H NMR spectrum of the $CDCl_3$ filtrate; (d) ^{1}H NMR spectrum in DMSO-d_6 after immersion of the product from part b in benzene for 24 h. All ^{1}H NMR spectra were recorded at room temperature. **5**: X-ray powder diffraction patterns; (a) original crystals of **1**; (b) **1** extracted by $CDCl_3$; (c) sample obtained by exposure of the product from part b to the benzene vapor for 24 h at room temperature and drying at room temperature for 1 day; (d) **1** was heated to 160 °C and then exposed to benzene vapor or immersion in benzene for 24 h.

$(SbF_6)_{12}\}^{12-}$ cage around the triple-helical trinuclear complex $\{Ag_3\mathbf{L}_3\}^{3+}$ is reversible in the solid state. When the crystals of **1** were immersed in $CDCl_3$ at room temperature for 2 h, light-yellow crystalline solids were obtained by filtering and drying in air for 24 h. The ^{1}H NMR spectrum was recorded on these crystals in DMSO-d_6, As shown in Figure 4b, the benzene proton resonance disappeared. The ^{1}H NMR spectrum of the $CDCl_3$ filtrate indicated that benzene molecules were successfully extracted (Figure 4c). As shown in Figure 1, the change in the quality of the single crystals after loss of the benzene molecules is difficult to see by the microscope-aided eye, but the degradation of the crystal quality prevented us from establishing such changes through a X-ray single-crystal analysis definitively. Elemental analysis results indicated that the chemical composition of these crystals without benzene molecules is in good agreement with the formula $[Ag\mathbf{L}](SbF_6)$. Anal. Calcd for $C_{10}H_{10}N_4S_2AgSbF_6$: C, 20.20; H, 1.68; N, 9.43. Found: C, 20.32; H, 1.78; N, 9.53. Moreover, the TGA trace shows the $[Ag\mathbf{L}](SbF_6)$ crownlike core decomposed at ca. 250 °C, which is very consistent with that of **1** (Figure S6 in the Supporting Information). Upon exposure of the desolvated sample of **1** to benzene vapor for 24 h at room temperature, the ^{1}H NMR spectrum was recorded in DMSO-d_6 at room temperature again. As shown in Figure 4d, the benzene molecules came back. Fortunately, the crystallinity of the samples recovered during the process, which enabled us to determine its structure by X-ray single-crystal structural analysis. The crystal structure of the benzene-regenerated sample is identical with that of as-synthesized **1**, which means that its initial form was regenerated. This reversible process is further confirmed by the X-ray powder diffraction on a bulk sample of **1′** (Figure S5 in the Supporting Information). In addition, the TGA traces of the regenerated sample **1′** and as-synthesized sample **1** exhibit the same thermal behavior (Figure S6 in the Supporting Information). On the other hand, the H-bonded frame−benzene molecules could also be moved by heating as-synthesized **1** to 160 °C in air but with loss of crystallinity. When the desolvated sample was exposed to benzene vapor or immersed in benzene for 24 h, the powder X-ray diffraction spectrum (Figure S5 in the Supporting Information) of the sample indicated that the benzene molecules had returned along with the H-bonded cages. Thus, formation of the H-bonded $\{(C_6H_6)_6(SbF_6)_{12}\}^{12-}$ nanocage is reversible. In other words, this 3D anion−benzene framework consisting of the 18-component H-bonded nanocage units could be synthesized by a chiral $\{Ag_3\mathbf{L}_3\}^{3+}$ template-driven reaction. There is no doubt that the crownlike $\{Ag_3\mathbf{L}_3\}^{3+}$ guest template is the dominant effect in the formation of the H-bonded $\{(C_6H_6)_6(SbF_6)_{12}\}^{12-}$ cage. Previously, most studies of reversible guest inclusion have been performed on more robust framework materials. In contrast, studies of reversible hosts based upon inclusive, stable guest templates are unprecedented. Compound **1** herein provides a clue to the design and synthesis of complicated H-bonded host frameworks based on presynthesized complicated metal−organic guest templates.

H-bonding and coordinative interactions can be considered the most important driving forces in the construction of host−guest assemblies. To date, various molecular containers driven by H-bonding or/and coordinative interactions, such as glycoluril, cyclophane, calixarene, tetrahedral metal cluster, and multiangular heterocyclic organic spacers, have been built,[1−5] and various organic and inorganic species have been entrained as guests based on matching of the size, shape, and chemical surface with the microenvironment offered by the host. Compared to single-inclusion host−guest complexes, double-inclusion host−guest systems are a rare phenomenon, limited by current synthetic ability and by the understanding of self-assembly. To the best of our knowledge, complex **1** is the first example of a double-inclusion cascade supramolecular complex with a reversible H-bonded benzene−anion host in the solid state.

In summary, we have synthesized an unusual cascade supramolecular complex with a reversible H-bonded host framework in the solid state. More importantly, this work demonstrates a new synthetic strategy to modular host frameworks that utilize complicated metal−organic species as the template. The increasing availability of larger ordered H-bonded cages resulting from a large number of small pieces of molecular panelings will permit the construction and understanding of more elaborate architectures based on the weak interactions that approach the size, complexity, and mechanism of biological systems.

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Supporting Information Available: Crystallographic data of **1** and **1′** (CIF) and synthesis and characterization of **L** and **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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