Host–Guest Systems

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Capsules and Star-Burst Polyhedra: An [Ag_2L_2] Capsule and a Tetrahedral [Ag_4L_4] Metallosupramolecular Prism with Cyclotriveratrylene-Type Ligands**

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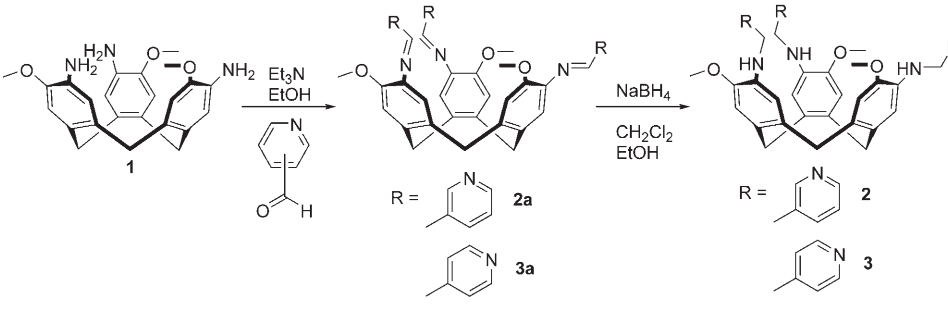
Cyclotriveratrylene (CTV) is a macrocyclic host molecule that strongly favors a crown conformation, which gives it a bowl shape with a shallow molecular cavity.[1] Indeed, despite CTV being known for over 40 years, the alternative saddle conformation has only recently been isolated by the rapid quenching of a hot solution or melt,[2] or within a novel CTV-based cryptophane.[3] The bowl-shaped CTV is a cyclic trimer which has a distinctly spiked, pyramidal aspect. We wish to exploit this characteristic to create self-assembled capsules and polyhedra through the formation of metallosupramolecular assemblies. These would likewise have a spiked aspect that allows for significantly more internal space than could be afforded from a similar flat or flexible ligand. A range of spectacular polyhedral structures have been reported from the self-assembly of metal salts with multifunctional ligands.[4] CTV itself is not a good molecular component for such assemblies as it lacks predictable coordination sites for transition metals, hence we have synthesized a number of CTV analogues with pyridyl groups at the upper rim for use as ligands for these types of assemblies as well as coordination networks.[5] Notably, a number of crystalline hydrogen-bonded assemblies feature tetrahedral clusters of CTV hosts arranged in a back-to-back fashion,[6] which excludes the possibility of forming an assembly with internal space. Likewise a 3D coordination polymer with a C_3-substituted CTV derivative also shows this back-to-back stacking.[7] Self-assembled complexes of CTV-related host molecules that do show an internal space would result from the head-to-head association of host molecules. Examples are currently restricted to a dimeric [Pd_3L_2] capsule that has been characterized in solution by Shinkai and co-workers.[8] This capsule results from the assembly of a trisubstituted CTV derivative possessing rigid pyridyl arms with *cis*-protected Pd salts. Covalently linked cryptophanes, where two CTV fragments are linked in a head-to-head fashion by organic spacers, are well established.[9]

Other bowl-shaped host molecules have been shown to form both capsule assemblies and more complicated polyhedral structures. Capsule structures assembled from hydrogen bonds or coordination chemistry are known with calixarenes and calixresorcinarenes.[10] Considerably more complicated assemblies such as a cyclic trimer,[11] cyclic hexamers,[12] a tetrahedron,[11b] a snub cube,[13] icosahedron,[14] and a cuboctahedron[15] have also been reported from similar tetrameric molecular hosts.

We report herein a new type of [M_2L_2] dimeric capsule with a CTV-related host molecule in the complex [Ag_2(tris(3-pyridylmethylamino)cyclotriguaiacylene)$_2$(CH_3CN)$_2$]·2PF_6·4CH_3CN, along with the first example of a discrete polyhedral cluster larger than a dimeric capsule assembled with a CTV-related host molecule. This latter complex [Ag_4(tris(4-pyridylmethylamino)cyclotriguaiacylene)$_4$(CH_3CN)$_4$]·4BF_4·7CH_3CN·2.8H_2O features a tetrahedral metallosupramolecular prism with a novel stellated "star-burst" aspect to the assembly.

The precursor 3,8,13-triamino-2,7,12-trimethoxy-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (**1**) has been previously reported,[16] and can be converted into the tris(pyridylmethylamino)cyclotriguaiacylenes **2** and **3** in good yields by reaction with the appropriate pyridinecarboxaldehyde, followed by reduction with sodium borohydride (Scheme 1).



Scheme 1.

Reaction of ligand **2** dissolved in acetone with $AgPF_6$ in CH_3CN gives the crystalline complex [Ag_2(**2**)$_2$(CH_3CN)$_2$]·2PF_6·4CH_3CN (**4**), whose structure was determined by X-ray crystallography.[17] The metal complex [Ag_2(**2**)$_2$(CH_3CN)$_2$]$^{2+}$ is a dinuclear, dimeric species with a capsulelike structure (Figure 1). The centrosymmetric capsule forms through the head-to-head coordination of two ligands to two Ag^I centers to give an [M_2L_2] capsule rather than the [M_3L_2] capsule reported by Shinkai and co-workers. The Ag^I center is coordinated by a terminal acetonitrile ligand at an Ag–N distance of 2.347(3) Å, and three pyridyl groups at Ag–N distances of 2.322(3), 2.346(2), and 2.247(2) Å in a distorted tetrahedral geometry.

The conformation and directionality of twist of the pyridyl arms of ligand **2** are all similar, and directed above the

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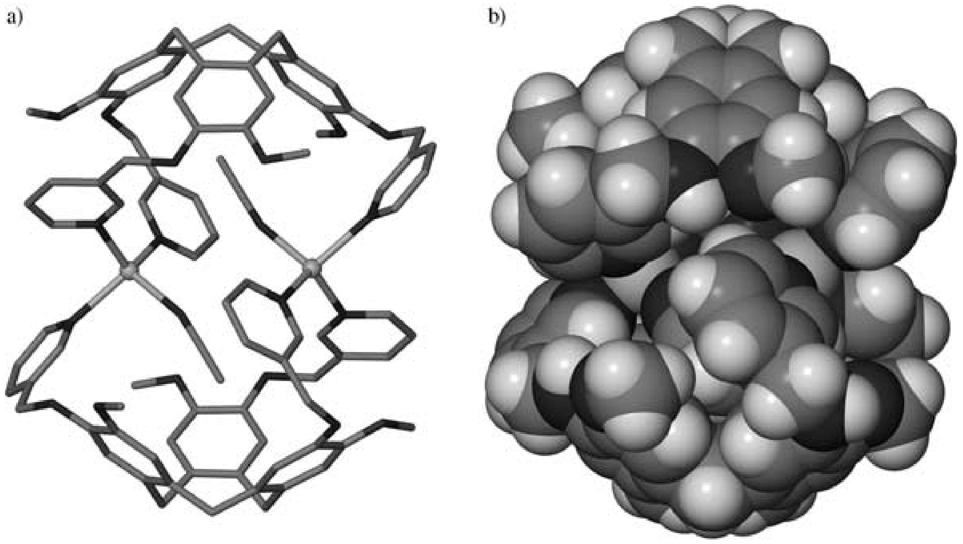

Figure 1. The capsule structure of $[Ag_2(\mathbf{2})_2(CH_3CN)_2]^{2+}$ from the crystal structure of **4**. a) Stick representation, b) space-filling representation.

molecular cavity of the ligand. This arrangement means that the Ag^I centers are likewise located above the molecular cavity which results in the capsule having an equatorial region that is pinched inwards. Each coordinated acetonitrile ligand is directed into the cavity of a molecular host. Such host–guest associations between a host and coordinated acetonitrile have been previously observed for silver–CTV complexes.[18] The two specific host–guest interactions observed in this structure may be a factor favoring the formation of an $[M_2L_2]$ capsule over the $[M_3L_2]$ species.

^{1}H NMR spectroscopic analysis of the dimeric capsule suggests a species related to the solid-state structure may be present in solution. Addition of one equivalent of a silver salt to a solution of **2** results in subtle, but significant, changes to the ^{1}H NMR spectrum: in particular, the splitting of the signal for the methylene spacer of the pyridyl arms of **2** into two doublets and the considerable upfield shift of the H2 proton of the pyridyl ring. The former change is likely to originate because of restricted rotation of the pyridyl arm of **2** upon coordination, while the latter may result from internalization of the pyridyl H2 within a capsule or related species. However, the $[Ag_2(\mathbf{2})_2(CH_3CN)_2]^{2+}$ capsule characterized by X-ray crystallography has C_2 symmetry but in solution the ligand (**2**) possesses C_3 symmetry—that is, only one set of signals are observed. Thus, either a fluxional process which is fast on the NMR timescale is simplifying the expected spectrum for the $[Ag_2(\mathbf{2})_2(CH_3CN)_2]^{2+}$ capsule, or another species such as an $[Ag_3(\mathbf{2})_2]^{3+}$ cage or an $[Ag(\mathbf{2})]^+$ complex where the ligand is a tripodal tridentate donor is present in solution. Rapid crystallization (ca. 20 min) of the $[Ag_2(\mathbf{2})_2(CH_3CN)_2]^{2+}$ capsule occurs from acetonitrile solution when the silver salt used is silver(I) cobalt(III) bis(dicarbollide) ($Ag[Co(C_2B_9H_{11})_2]$) which indicates there is some form of preorganization of the structure in solution.

Titration of **2** with $Ag[Co(C_2B_9H_{11})_2]$ leads to a significant upfield shift of the pyridyl H2 signal when up to one equivalent of the silver salt is added. The upfield movement of the resonance then stabilizes before undergoing a downfield shift as more than 1.5 equivalents of $Ag[Co(C_2B_9H_{11})_2]$ are added. The pyridyl H6 proton signal mimics this behavior, but undergoes a significantly less-pronounced upfield shift, while the signals for the more remote pyridyl H4 and H5 move progressively downfield throughout the titration. In an additional set of experiments, crystals of **4** prepared in acetonitrile were redissolved in [D$_6$]acetone or CD_3NO_2, but signals for the incarcerated acetonitrile, disappointingly, could not be observed. These results suggest that while a related $[Ag_2(\mathbf{2})_2]^{2+}$ capsule may be present in solution, other species, including the originally anticipated $[Ag_3(\mathbf{2})_2]^{3+}$ capsule, and possibly a 1:1 complex, are also likely solution structures. ES-MS results demonstrate the presence of a 1:1 complex in solution, thus suggesting that the ligand may in fact act as a tripodal tridentate donor in solution. This 1:1 complex then dimerizes upon crystallization to generate the $[M_2L_2]$ capsule. Further solution studies will be discussed in a future full paper that demonstrates the generality of this capsule-related topology with other tetrahedral transition-metal ions.

Use of the 4-substituted ligand **3** in place of the 3-substituted ligand **2** has a profound effect on the type of metallosupramolecular prism isolated. Reaction of **3** with one equivalent of $AgBF_4$ in CH_3CN gives the crystalline complex $[Ag_4(\mathbf{3})_4(CH_3CN)_4]\cdot 4BF_4\cdot 7CH_3CN\cdot 2.8H_2O$ (**5**). The crystal structure of **5** was determined by single-crystal techniques.[17] Complex **5** contains a $[Ag_4(\mathbf{3})_4(CH_3CN)_4]^{4+}$ metallosupramolecular prism in which the Ag^I centers form the vertices of a slightly distorted tetrahedral prism, with Ag···Ag separations along the tetrahedron edges ranging from 8.29 to 10.33 Å. Four tris(4-pyridylmethylamino)cyclotriguaiacylene ligands form the faces of the $[M_4L_4]$ tetrahedral prism (Figure 2).

There are four independent ligands within complex **5**, and each shows a noncrystallographic C_3 symmetry. The conformation of each ligand is similar, with the plane of each pyridyl arm at approximately 90° to the plane of the core arene group to which it is attached. All pyridyl arms are directed inwards in relation to the ligand core. This conformation allows for formation of a convergent, discrete structure, rather than a polymeric structure which would result from an *exo* pyridyl arm conformation. Each molecule of **3** bridges between three Ag^I centers. There are four crystallographically independent Ag^I centers, and each is coordinated by pyridyl groups from three different molecules of **3** and an acetonitrile ligand. The $Ag{-}N_{py}$ and Ag–NCMe interatomic distances range from 2.216(13) to 2.328(13) and 2.390(18) to 2.60(3) Å, respectively, and the metal geometries are distorted tetrahedral, distorted trigonal pyramidal, or have a geometry in-between these extremes. Three of the four Ag^I centers have their terminal acetonitrile ligand directed *exo* from the tetrahedral

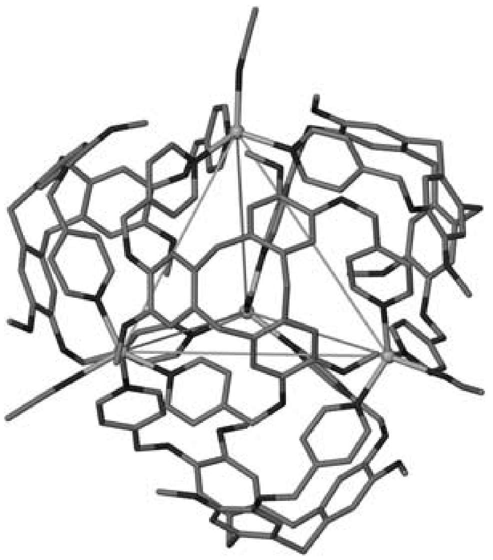

Figure 2. Tetrahedral metallosupramolecular prism $[Ag_4(\mathbf{3})_4(CH_3CN)_4]^{4+}$ from the X-ray crystal structure of **5**. Thin lines highlight the tetrahedral prism formed by the Ag^I centers (shown as spheres).

prism, and one, Ag(3), has the terminal acetonitrile molecule directed into the prism. The geometry of Ag(3) is closest to trigonal pyramidal with the acetonitrile ligand forming a long bond (Ag–N: 2.60(3) Å) in the capping position.

Tetrahedral metallosupramolecular prisms have been reported by a number of researchers, with most examples having an $[M_4L_6]$ stoichiometry where the six ligands define the edges of the tetrahedron.[19] There have been fewer examples of tetrahedral metallosupramolecular assemblies where the ligand defines a face of the tetrahedron. These are a $[M_8L_4]$ distorted tetrahedron from Fujita and co-workers,[20] a distorted $[M_{12}L_4]$ tetrahedron reported by Robson and co-workers,[21] a handful of $[M_4L_4]$ tetrahedra with triscatecholate ligands,[22,23] an $[M_4L_4]$ tetrahedron formed from a disk-shaped tridentate ligand,[24] and an $[M_4L_4]$ tetrahedron with a podand borate ligand.[25] Additionally, a flattened tetrahedral structure, in which the calixresorcinarene ligands act as the vertices of a metallosupramolecular tetrahedron, has been reported by Beer and co-workers.[11b] Aside from the final two examples, these tetrahedra feature ligands with a flat trigonal core. Where the structure of **5** differs from these examples is in having a pyramidal ligand defining the triangular faces of the tetrahedron, which gives the assembly a spiked starlike aspect, somewhat akin to stellations of a prism.[26] Figure 3a highlights this "star-burst" aspect of **5** and shows the tetrahedron of Ag^I ions and the centers of the lower rim -$(CH_2)_3$- plane of the ligands. This "star-burst" topology engenders the structure with a greater internal volume than a tetrahedron of equivalent dimensions formed with a planar trigonal ligand.

Overall, the $[Ag_4(\mathbf{3})_4(CH_3CN)_4]^{4+}$ prism is a molecular host for five molecules of acetonitrile. Four of these acetonitrile guests form host–guest interactions, each with an individual ligand, in which the hydrophobic methyl group is directed into the molecular cavity. Distances between the methyl carbon atom of the guest and the lower rim -$(CH_2)_3$- plane of the host ligand range between 3.74 and 3.86 Å. The fifth acetonitrile molecule is disordered across two positions with 65% occupancy as the *endo* CH_3CN molecule coordinated to Ag(3) and 35% occupancy as a guest in the middle of the assembly (Figure 3b).

The tetrahedral prisms pack together in the crystal lattice with various π-stacking interactions apparent. These include face-to-face interactions between core arene groups at centroid separations of 3.56 Å and edge-to-face interactions between pyridyl CH groups and core arene groups at C–H···centroid separations of 2.40 Å (C···centroid distance 3.3 Å). The additional solvent molecules and BF_4^- counterions fill spaces created by the packing of the prisms. These sites are approximations of the tetrahedral and octahedral interstitial holes displayed by close-packing spheres, which are created as $[Ag_4(\mathbf{3})_4(CH_3CN)_4]^{4+}$ has a roughly spherical surface. Note that $[Ag_4(\mathbf{3})_4(CH_3CN)_4]^{4+}$ does not genuinely close pack as it is not truly spherical; distortions are such that each $[Ag_4(\mathbf{3})_4(CH_3CN)_4]^{4+}$ unit is in proximity to 11 others rather than the 12 expected of a genuinely close-packed array.

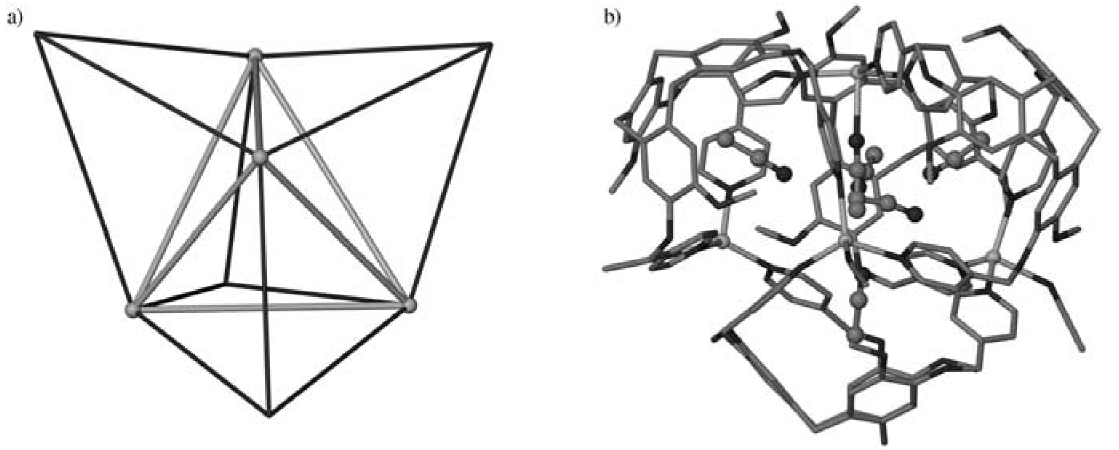

Figure 3. a) Star-burst aspect of $[Ag_4(\mathbf{3})_4(CH_3CN)_4]^{4+}$ with Ag^I centers shown as spheres and the centers of the ligand's lower rim -$(CH_2)_3$- plane shown as 3-connecting points. b) Host–guest associations within prism $[Ag_4(\mathbf{3})_4(CH_3CN)_4]^{4+}$ with guest CH_3CN molecules inside the prism shown in ball-and-stick representation.

We have reported herein the first structural characterizations of metallosupramolecular cages incorporating ligands derived from the molecular host CTV. In the first case, the additional flexibility engineered into our ligand system over that reported by Shinkai and co-workers, coupled with the geometrically more accommodating silver centers have resulted in the isolation and structural characterization of a more compact [M_2L_2] molecular capsule which incarcerates two coordinated CH_3CN guests. The utilization of the more-divergent 4-pyridyl ligand **3** led to the formation of a significantly expanded stellated tetrahedron with an internal space capable of accomodating five CH_3CN guest molecules. This dichotomy of structures observed presents the intriguing possibility that by tailoring the size of the guest we can control the formation of various metallosupramolecular cages with this ligand system.

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