Supramolecular Chemistry

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Star-Burst Prisms with Cyclotriveratrylene-Type Ligands: A $[Pd_6L_8]^{12+}$ Stella Octangular Structure**

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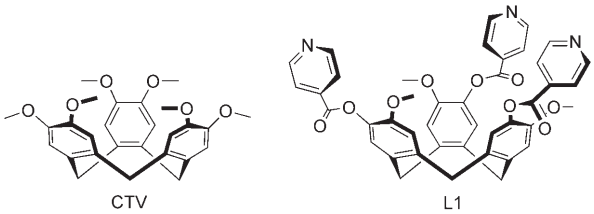
Cyclotriveratrylene (CTV) is a macrocyclic host molecule with a shallow molecular cavity and a distinctly spiked, pyramidal shape. CTV and/or its derivatives have application as molecular hosts,[1] as precursors to cryptophanes and extended-arm cavitands,[1,2] as components in hydrogen-bonded or coordination networks,[3,4] and as ligands within 3D capsular or prismatic metallo-supramolecular assemblies.[4–6] In this last area the bowl shape of a CTV derivative provides a convergent binding mode and such ligands can form assemblies with greater internal volumes than could a corresponding planar analogue. Furthermore, the CTV-type ligands impart embedded molecular recognition sites within the assemblies, and it has been shown that simple host–guest interactions at these sites can have a directing influence on the overall self-assembly process.[4] The self-assembly of 3D metallo-supramolecular species from transition-metal ions and multifunctional ligands is well established, and a spectacular range of cagelike polyhedral/prismatic structures have been reported.[7] The use of cavitand or host molecules within these structures is still under-developed, and most reported examples utilize cavitands with fourfold symmetry. The majority of the examples involve dimeric capsule structures,[8] with only rare examples of higher structures known.[9] Metal-based structures incorporating threefold symmetric cyclotriveratrylene ligands are particularly unusual and only three types have been previously reported: capsule-like $[M_3L_2]$ complexes by Shinkai and co-workers,[10] our own $[Ag_2L_2]^{2+}$ capsules,[4,5] and $[Ag_4L_4]^{4+}$ "star-burst" tetrahedra.[4–6] The star-burst aspect to these structures comes from the rigid pyramidal shape of the CTV-related ligands.

Herein we report a new star-burst metallo-supramolecular assembly with a stella octangular structure that was characterized by single-crystal and solution studies. The stella octangular structure was obtained from the self-assembly of "naked" Pd^{II} ions with the CTV-related ligand tris(isonicotinoyl)cyclotriguaiacylene. Like all symmetrical tris-substituted CTV derivatives, this is a chiral ligand, and the $[Pd_6(L1)_8]^{12+}$ complexes produced are likewise chiral. Tris(isonicotinoyl)-cyclotriguaiacylene has previously been shown to form 1D coordination chains with Ag^I ions.[3b] "Naked" Pd^{II} ions form square-planar complexes with highly labile ligands such as NO_3^- ions, and its use with multifunctional ligands has led to the formation of several large 3D metallo-supramolecular structures.[11]



A solution containing a mixture of tris(isonicotinoyl)cyclotriguaiacylene and $Pd(NO_3)_2$ in a 3:4 metal/ligand ratio and an excess of *o*-carborane in dimethylsulfoxide (DMSO) gave two types of single crystals on diffusion of acetone vapor. CTV is known to form host–guest complexes with *o*-carborane, hence its inclusion as a potential bulky guest molecule.[12] Crystals of $[Pd_6\{tris(isonicotinoyl)cyclotriguaiacylene\}_8]\cdot 12(NO_3)\cdot n(DMSO)\cdot m(H_2O)$ (**1**) could be isolated from the solution but rapidly decompose when removed from their mother liquor. The single-crystal X-ray structure of **1** reveals that eight tris(isonicotinoyl)cyclotriguaiacylene molecules and six $Pd(NO_3)_2$ ligands self-assemble into a $[Pd_6[L1)_8]\cdot 12(NO_3)$ cage structure with octahedral symmetry (Scheme 1).

Complex **1** crystallizes in a tetragonal unit cell[13] and the asymmetric unit consists of two different Pd environments: while one Pd atom is coordinated to two ligands, two Pd atoms are sited on fourfold axes. Both crystallographically distinct ligands approximate C_3 molecular symmetry, with the isonictinoyl arms pointing way from the host's cavity. For both types of ligand, each isonictinoyl group coordinates to three different Pd sites. Each Pd site has approximately square-planar geometry, coordinated by isonictinoyl groups of four ligands with Pd–N bond lengths ranging from 1.878(10) to 2.046(7) Å. Overall a discrete $[Pd_6(L1)_8]^{12+}$ metallo-supramolecular assembly is formed (Figure 1). The Pd centers are arranged in an octahedron with respect to one another, with Pd···Pd separations along the edges of the octahedron ranging from 16.583 to 16.647 Å, and with the longest separations between the vertices being 23.539 Å. The ligands occupy the eight faces of the octahedron, with their molecular cavities all facing into the center of the overall complex. Hence the ligands sit well above the octahedral faces, with distances of either 8.913 or 8.718 Å between the center of the Pd_3 face and

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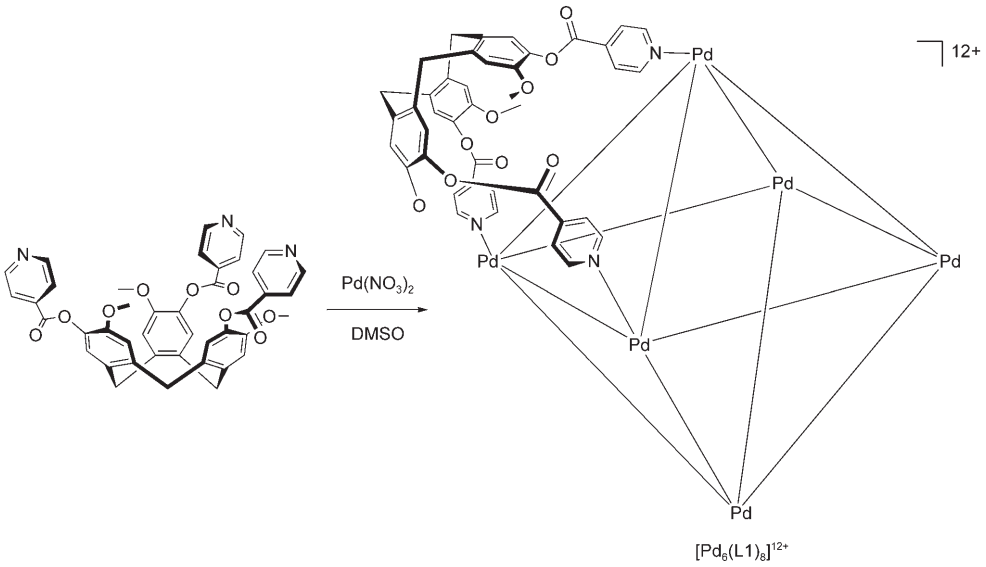

Scheme 1. Self-assembly of the $[Pd_6(L1)_8]^{12+}$ cage.

the outer edge of the ligand (distance taken to the centroid of the basal hydrogen atoms of the ligand's -$(CH_2)_3$- plane). Notably each $[Pd_6(L1)_8]^{12+}$ species self-assembles with eight ligand molecules of the same chirality, hence complex **1** is chiral, but exists as a racemate, with both enantiomers being present.

The orientation of the rigid pyramidal ligand frameworks gives the $[Pd_6(L1)_8]^{12+}$ structure in **1** a star-burst aspect so that it does not resemble a simple octahedron, but rather a stella octangular structure. A stella octangular structure is a stellation of an octahedron that occurs when the edges of the octahedron are extended until they intersect at points to produce a starlike prism (Figure 2); it can also be regarded as the intersection of two tetrahedra. Molecular entities with stellated structures have rarely been identified; and the only self-assembled example is a pentanuclear silver complex reported by Constable et al.[14]

The overall size of the assembly in complex **1** is roughly 3.1 nm, as measured from the centers of the basal hydrogen atoms of the -$(CH_2)_3$- planes for diametrically opposed ligands. The surface of the structure is not fully enclosed, and there are eight windows (Figure 1b), although access through these windows is partially blocked by the methoxy groups of the ligand. The well-ordered $[Pd_6(L1)_8]^{12+}$ complex only accounts for around 40% of the crystal volume. The high degree of disorder of solvent and counterions and the subsequent low quality of the X-ray data mean that the full details of the complex could not be structurally determined, although some NO_3^- ions, DMSO, and water positions could be located. There was no evidence of the incorporation of *o*-carborane.

Metallo-supramolecular structures based on $[M_6L_8]^{n+}$ where the metal ions form the vertices of an octahedron have been reported for a handful of other tripodal ligands.[15–19] In all these cases the ligands are achiral and based on a 1,3,5-tris-substituted benzene core, which leads to structures of considerably less spiked aspect than seen in the $[Pd_6(L1)_8]^{12+}$ structure of **1**, and have either truncated octahedral or octahedral geometry. The largest of these structures, of around 3 nm in size, is formed with a variety of divalent transition-metal ions and a disclike ligand with a hexaphenylenebenzene core, but does not contain any significant windows.[19]

The crystalline sample is not a single phase, and contains lower symmetry monoclinic crystals whose structure could not be reliably determined.[20] Crystallization in the absence of *o*-carborane repeatedly yielded crystals with a similar tetragonal cell, but, again, X-ray data were too weak to allow for determination of the structure.[20]

^{1}H NMR spectroscopy and ESI mass spectrometry (ESI-MS) studies demonstrate that the self-assembly of the $[Pd_6(L1)_8]^{12+}$ stella octangular structure also occurs in solution. The ESI-MS of **1** shows a series of signals at m/z 2328.1, 1730.8, and 1372.6, which can be assigned to $[\{Pd_6(L1)_8\}(NO_3)_{(12-x)}]^{x+}$ ($x = 3, 4, 5$) which arise from the octahedral core but with different numbers of anions. ESI-MS studies in the

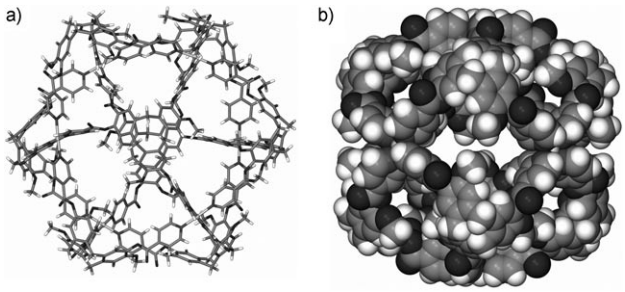

Figure 1. Two views of the $[Pd_6(L1)_8]^{12+}$ metallo-supramolecular assembly from the X-ray crystal structure of **1**: a) stick model b) space-filling model.

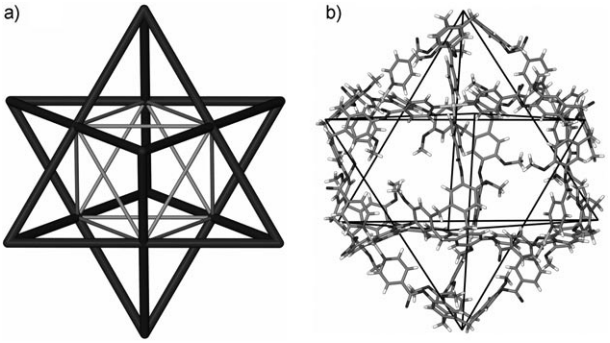

Figure 2. a) A stella octangular structure, with the thin gray lines showing the octahedron that is stellated to form the overall structure; b) structure of $[Pd_6(L1)_8]^{12+}$ with black lines joining the cavitand apexes to highlight the stella octangular nature of the structure.

presence of *o*-carborane did not show inclusion of this potential guest.

A number of recent studies have used diffusion ordered NMR spectroscopy (DOSY) to characterize large supramolecular structures in solution.[8b,21,22] DOSY NMR studies of a 4:3 mixture of L1 and $Pd(NO_3)_2$ in $[D_6]$DMSO showed a signal for the major solution component, with a diffusion coefficient of $0.555 \times 10^{-10}\ m^2 s^{-1}$. A diffusion coefficient of $1.284 \times 10^{-10}\ m^2 s^{-1}$ was obtained for a solution of ligand L1 alone in $[D_6]$DMSO, which gives a $D_{complex}/D_{ligand}$ ratio of 0.43:1. This value is significantly less than the ratio of 0.68:1 observed for the previously studied $[Ag_4L_4]^{4+}$ coordination cage with a related cyclotriguaiacylene-based ligand,[4] and is consistent with a very large species being present in solution. A spherical radius can be estimated from the Stokes–Einstein relationship,[22] which in this case gives a hydrodynamic radius of 19.4 Å. As expected, this is marginally larger than the static radius determined by X-ray crystallography and is consistent with the $[Pd_6(L1)_8]^{12+}$ structure existing in solution.

In summary we have demonstrated the self-assembly of a $[Pd_6(L1)_8]^{12+}$ stella octangular structure from tris(isonicotinoyl)cyclotriguaiacylene and "naked" palladium ions. The formation of large cagelike structures from components that are themselves molecular hosts gives structures with significant internal space as well as internal binding sites, and points to their potential for use as nanoscale vessels.

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[13] Crystal data for **1**: $C_{372}H_{400}N_{32}O_{128}Pd_6S_{18}$, $M_r = 8582.72$, tetragonal, $P4/n$, $a = 32.5130(6)$, $c = 31.5740(13)$ Å, $V = 33376.7(16)$ Å^3, $Z = 2$, $\rho_{calcd} = 0.854\ Mg\,m^{-3}$, $\mu = 0.270\ mm^{-1}$, $F(000) = 8888$, colorless block, $0.50 \times 0.40 \times 0.20\ mm^3$, $2\theta_{max} = 46°$, $T = 120(2)$ K, 371119 reflections, 23252 unique (100% completeness), $R_{int} = 0.1295$, 1172 parameters, GOF = 1.148, $wR_2 = 0.3602$ for all data, $R_1 = 0.1225$ for data with $I > 2\sigma(I)$. CCDC 658314 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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