

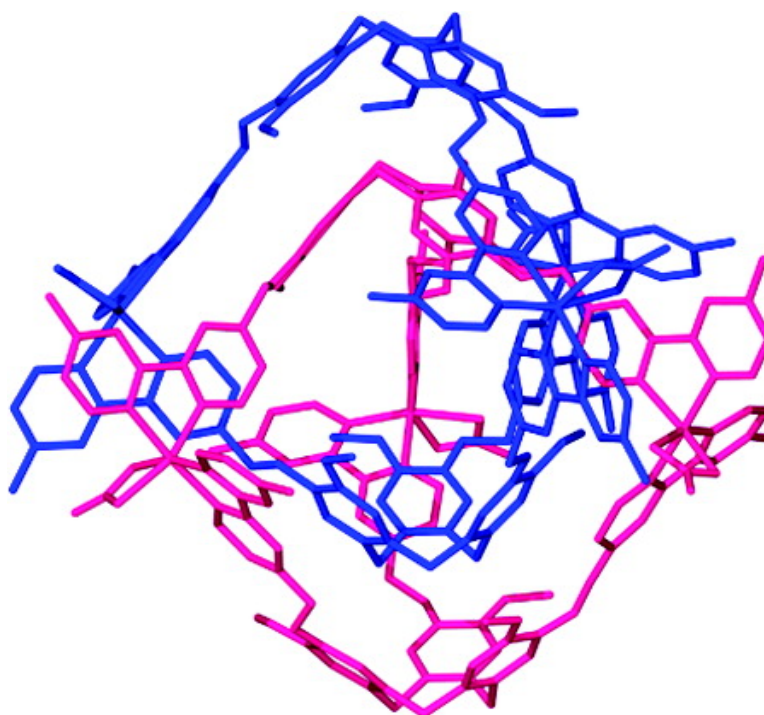
Communication

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Self-Assembly of a 3-D Triply Interlocked Chiral [2]Catenane

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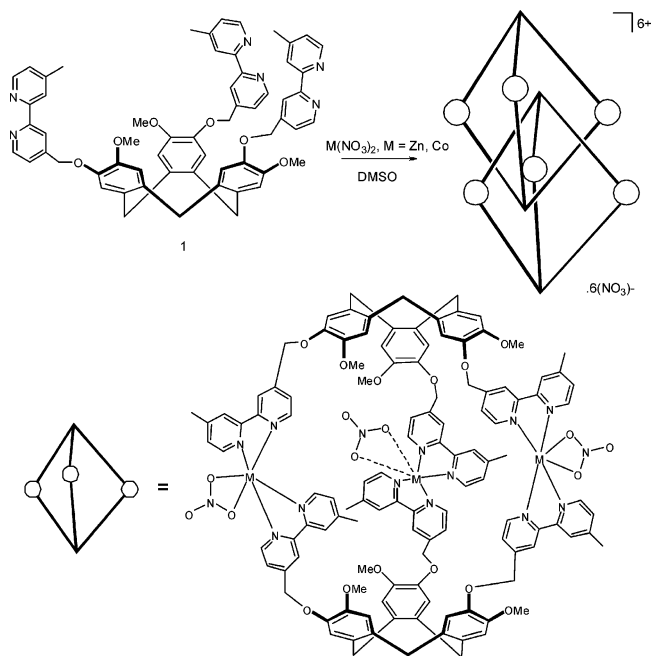
Threaded molecules such as catenanes and rotaxanes have garnered much attention in recent years,¹ and concurrent with this has been the development of 3-D metallo-supramolecular assemblies that can be formed with a variety of prismatic and polyhedral structures.² Threaded metallo-supramolecular assemblies have been largely restricted to catenanes of 2-D metalla-cycles,^{3,4} and include examples of doubly braided [2]catenanes.⁴ To the best of our knowledge, the only example of an interlocking 3-D metallo-supramolecular assembly is the [2]catenane reported by Fujita and co-workers.⁵ In this assembly two asymmetric trigonal bipyramidal $[M_3(L_1)(L_2)]^{6+}$ cages interlock and the formation of the catenane is driven by π - π stacking interactions between the two types of ligand. Despite this assembly being known for the best part of a decade, a second system displaying the same interlocking motif has yet to be reported. We report the second such system herein. This occurs with the cyclotrimeratrylene-related molecular host (\pm)-2,7,12-trimethoxy-3,8,13-tris(4-[4'-methyl-2,2'-bipyridyl]benzyloxy)-10,15-dihydro-5H-tribenzo[*a,d,g*]cyclononene **1** in the complexes $[M_3(\mathbf{1})_2(\text{NO}_3)_3]_2^{6+}$ where $M = \text{Zn(II)}$ or Co(II) . Cyclotrimeratrylene (CTV) has a relatively rigid bowl-shape, and a small number of single cage 3-D metallo-supramolecular assemblies with cyclotrimeratrylene-based ligands have been previously reported.^{6,7}

Ligand **1** was synthesized in 64% yield from reaction of 4-bromomethyl-4'-methyl-2,2'-bipyridine with cyclotriguaiacylene in dry dimethylformamide in the presence of NaH. Two different cyclotrimeratrylene-based ligands with appended 2,2'-bipyridine moieties have been previously reported.⁸ Ligand **1** self-assembles with $\text{Zn}(\text{NO}_3)_2$ or $\text{Co}(\text{NO}_3)_2$ in dimethylsulfoxide (DMSO) to form $[M_3(\mathbf{1})_2(\text{NO}_3)_3]_2^{6+}$ where $M = \text{Zn(II)}$ or Co(II) . Cyclotrimeratrylene (CTV) has a relatively rigid bowl-shape, and a small number of single cage 3-D metallo-supramolecular assemblies with cyclotrimeratrylene-based ligands have been previously reported.^{6,7}

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Scheme 1. Self-Assembly of [2]Catenane Species



cages are known for a number of systems,^{5,9} including single cage examples with CTV-based ligands from Shinkai et al.⁶

A trigonal bipyramidal cage contains three windows and in complex **2** two such cages interlock through all three windows to form a [2]catenane; see Scheme 1 and Figure 1. The molecular bowls of the host ligands of different cages stack on top of one another in a slightly misaligned manner. There are no face-to-face π - π stacking interactions evident between these molecular bowls, given a separation of 4.77 Å between the centers of the aromatic rings. Within the inner part of the [2]catenane two ligand **1** molecular bowls are facing one another creating an inner binding core. There is significant space within this inner core estimated at $\sim 200 \text{ \AA}^3$.

The two cages of the catenane do not interlock in a centered fashion. This is due to two types of weak hydrogen bonding interaction that occur between the catenating cages. The closest interaction is between a CH of the bpy of one cage and the OMe groups of the internal ligands of the second cage at C-H...O distance 2.37 Å (corresponding C...O separation 3.17 Å). There is also C-H...O hydrogen bonding between the unbound O of the nitrate ligand and the pendant methyl group on the bpy moieties of one of the two types of ligand, at C-H...O distance 2.46 Å and C...O separation 3.37 Å. Both types of hydrogen bond occur at six positions in the core or around the periphery of the [2]catenane respectively, Figure 1.

A single $[Zn_3(\mathbf{1})_2(\text{NO}_3)_3]^{3+}$ cage contains both enantiomers of the ligand; however, within each [2]catenane all six tris-chelated

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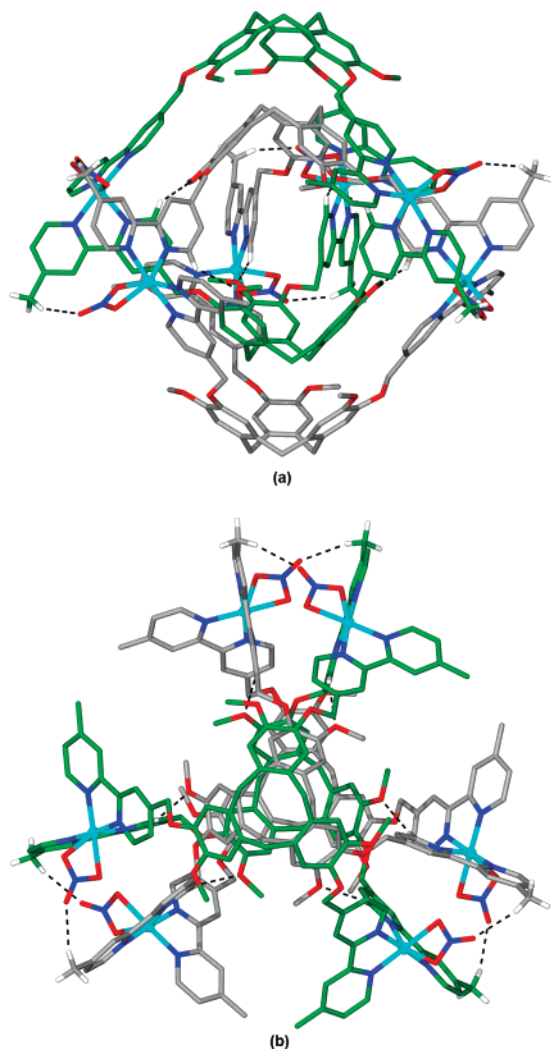


Figure 1. From the crystal structure of $[\text{Zn}_3(\mathbf{1})_2(\text{NO}_3)_3]_2 \cdot 6(\text{NO}_3) \cdot 10(\text{DMSO}) \mathbf{2}$, giving two views of the [2]catenane. Hydrogen atoms not involved in hydrogen bonding are excluded for clarity. The two catenating cages have different colors.

Zn(II) centers have the same hand and hence the [2]catenane is chiral. Overall, the complex crystallizes as a racemic mixture. There are extensive face-to-face $\pi-\pi$ stacking interactions between [2]catenane assemblies in the crystal lattice at an aryl ring centroid separation of 3.56 Å. Each $[\text{Zn}_3(\mathbf{1})_2(\text{NO}_3)_3]^{3+}$ forms $\pi-\pi$ interactions with six others to give an octahedral network of the [2]catenanes.

1-D ^1H NMR experiments were carried out on d_6 -DMSO solutions of $\mathbf{1}$ and $\text{Zn}(\text{NO}_3)_2$ in 2:3 and 1:3 proportions at various concentrations and temperatures but in all cases the spectra were too broad to assign. 2-D diffusion ordered (DOSY) NMR gave a molecular mass for the main component in solution consistent with a single $[\text{Zn}_3(\mathbf{1})_2(\text{NO}_3)_3]^{3+}$ cage. Electrospray mass spectrometry (ES-MS) studies also show the presence of the single cage along with the [2]catenane through an overlapping doubly and singly charged peak at m/z 2416.55 which corresponds to $\{[\text{Zn}_3(\mathbf{1})_2(\text{NO}_3)_3]_2 \cdot (\text{NO}_3)_4\}^{2+}$ and $\{[\text{Zn}_3(\mathbf{1})_2(\text{NO}_3)_3] \cdot (\text{NO}_3)_2\}^+$ (calcd 2416.68). Additional peaks were present for species $\{[\text{Zn}_2(\mathbf{1})(\text{NO}_3)_2] \cdot (\text{NO}_3)\}^+$,

$\{[\text{Zn}(\mathbf{1})(\text{NO}_3)]\}^+$, and $\{[\text{Zn}(\mathbf{1}-\text{C}_{12}\text{H}_{11}\text{N}_2)(\text{NO}_3)]\}^+$. ES-MS studies of the Co(II)-system show the presence of the [2]catenane much more clearly with a triply charged peak at m/z 1573.04 corresponding to $\{[\text{Co}_3(\mathbf{1})_2(\text{NO}_3)_3]_2 \cdot (\text{NO}_3)_3\}^{3+}$ (calcd 1575.33). Additional peaks were assigned to the 1:1 Co:1 species $\{[\text{Co}(\mathbf{1})(\text{NO}_3)]\}^+$ and $\{[\text{Co}(\mathbf{1}-\text{C}_{12}\text{H}_{11}\text{N}_2)(\text{NO}_3)]\}^+$ and there was no indication of a single cage species. The observed loss of a methyl-bipyridine arm in species $\{[\text{Zn}(\mathbf{1}-\text{C}_{12}\text{H}_{11}\text{N}_2)(\text{NO}_3)]\}^+$ and $\{[\text{Co}(\mathbf{1}-\text{C}_{12}\text{H}_{11}\text{N}_2)(\text{NO}_3)]\}^+$ indicate that the assemblies are fragmenting in the mass spectrometer. It is also notable that, as might be expected for a [2]catenane, there are only $[\text{M}_3\text{L}_2]_2$, $[\text{M}_3\text{L}_2]$, or smaller species observed.

The self-assembly of the $[\text{M}_3(\mathbf{1})_2(\text{NO}_3)_3]_2 \cdot 6(\text{NO}_3)$ [2]catenanes demonstrates that the triply interlocking [2]catenane motif is accessible for chemical systems other than Fujita's original example. Furthermore, it can be formed by symmetrical 3-D metallo-supramolecular assemblies where the ligands do not show extensive $\pi-\pi$ stacking between them. Homomeric or "self-stacking" motifs as seen in complex $\mathbf{2}$ are common with CTV and its derivatives^{7c,10} and may provide clues as to how this complicated topological motif occurs in this instance.

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Supporting Information Available: Full experimental details; mass spectra; additional structure diagrams; crystal information in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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