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COMMUNICATION

M_3L_2 metallo-cryptophanes: [2]catenane and simple cages†‡

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Crystalline M_3L_2 complexes with either single cage or triply interlocking [2]catenane chiral structures are formed the self-assembly of host-like ligands with transition metals.

Cryptophanes are molecular 3D cage-like hosts where two cyclotriveratrylene (CTV) fragments are linked together *via* organic functional groups.[1] Metallo-cryptophanes are analogous species where the CTV moieties are linked *via* metal–ligand coordination, and there have been few reported examples.[2–4] Our recently reported complex $[M_3(L)_2(NO_3)_3]_2^{6+}$ where M = Zn(II) or Co(II) and L = tris(4′-methyl-2-2′-bipyridine-4-methyl)cyclotriguaiacylene is a highly unusual metallo-cryptophane where two cages form a triply interlocked [2]catenane.[4]

In catenanes and other interlocked molecular species the threading of one component through another, or coming together of precursors in specific arrangements, are critical steps in their formation. Templation and structure directing supramolecular interactions such as π–π stacking or hydrogen bonding are important strategies to induce molecular threading or close association of components.[5] Most catenanes are essentially 2D. A handful of examples of [2]catenane structures involving interlocked 3D cages have been reported,[4,6–9] and a 3D coordination polymer comprised of catenated adamantane cages has recently been reported by Lu.[10] Beer, for example, reports an anion templated assembly of a triply interlocked organic cage;[6] while examples of triply and quadruply interlocked metallo-cages where aromatic π–π stacking interactions are observed between individual cage species have been reported by Fujita,[7] and Kuroda respectively.[8] Cooper and coworkers have recently reported a triply interlocked organic cage where there is no template nor obvious structure-directing supramolecular interactions between the components.[9]

We report herein M_3L_2 metallo-crytophanes involving CTV-type ligands with monodentate pyridyl or pyrimidine groups with the N-donor in a 3-position. One such complex affords the second example of a triply interlocked [2]-catenane based on metallo-cryptophanes. Different types of larger CTV-based metallo-cages have also been reported.[11]

Tris(3-pyridylmethyl)cyclotriguaiacylene **1** and tris-[4-(5-pyrimidyl)benzoyl]cyclotriguaiacylene **2** were synthesised as racemic mixtures in 44% and 81% yields respectively from the CTV-analogue cyclotriguaiacylene (CTG), Scheme 1.‡ Reaction of **1** with $Ag(ClO_4)$ in dimethylformamide (DMF) gave a triply interlocked [2]catenane metallocryptophane $\{[Ag_3(\mathbf{1})_2]\}_2.(ClO_4)_6.(solvent)_n$, as revealed by X-ray crystallography.§ Crystals with similar unit cell parameters were obtained by use of $Ag(BF_4)$ or $Ag(SbF_6)$ in place of $Ag(ClO_4)$. Reaction of **2** with $[Ag(CH_3CN)_4]BF_4$ in DMSO or with $Cu(NO_3)_2$ in DMF yields single-cage $[M_3(\mathbf{2})]_2]^{n+}$ metallo-cryptophanes in the solid state.

The crystal structure of the complex $\{[Ag_3(\mathbf{1})_2]\}_2.(ClO_4)_6\cdot(DMF)_3$ has an asymmetric unit comprising two interlocked $[Ag_3(\mathbf{1})_2]^{3+}$ units, six perchlorate anions disordered across seven molecular positions, and three DMF molecules. Ag(I) cations have approximately linear coordination and are coordinated by pyridyl groups from two different **1** ligands. Ag–N distances range from 2.107(6) to 2.311(10) Å, and N–Ag–N angles from 165.1(4) to 176.9(4)°. One Ag also shows a long contact to a DMF at Ag–O separation 2.580(13) Å.

One $[Ag_3(\mathbf{1})_2]^{3+}$ metallo-cryptophane cage of the [2]catenane is shown in Fig. 1a. The cage is composed of two **1** ligands, both of the same enantiomer. Hence this metallo-cryptophane is analogous to the chiral *anti* isomer cryptophanes.[1] This is in contrast with the previously reported $[Zn_3(L)_2(NO_3)_3]_2^{6+}$ [2]catenane structure where a *syn*-type isomer containing both enantiomers of the ligand was formed. The second $[Ag_3(\mathbf{1})_2]^{3+}$ cage, while crystallographically distinct, is structurally very similar to the first. It is oriented such that the host ligands of the two cages form a bowl-in-bowl arrangement, and the two form a triply interlocked [2]catenane, Fig. 1b. The [2]catenane is chiral as all **1** ligands are the same enantiomer, although each crystal is a racemate.

There are no significant intermolecular interactions between the two cages of the [2]catenane. Despite the bowl-in-bowl arrangement of the ligands, there are no π–π stacking interactions between them, as indicated by the long aromatic ring centroid separations ranging from 4.64 to 4.98 Å. Furthermore, there are no Ag…Ag interactions (all separations > 5.2 Å). While the Ag centres of one cage are positioned above the

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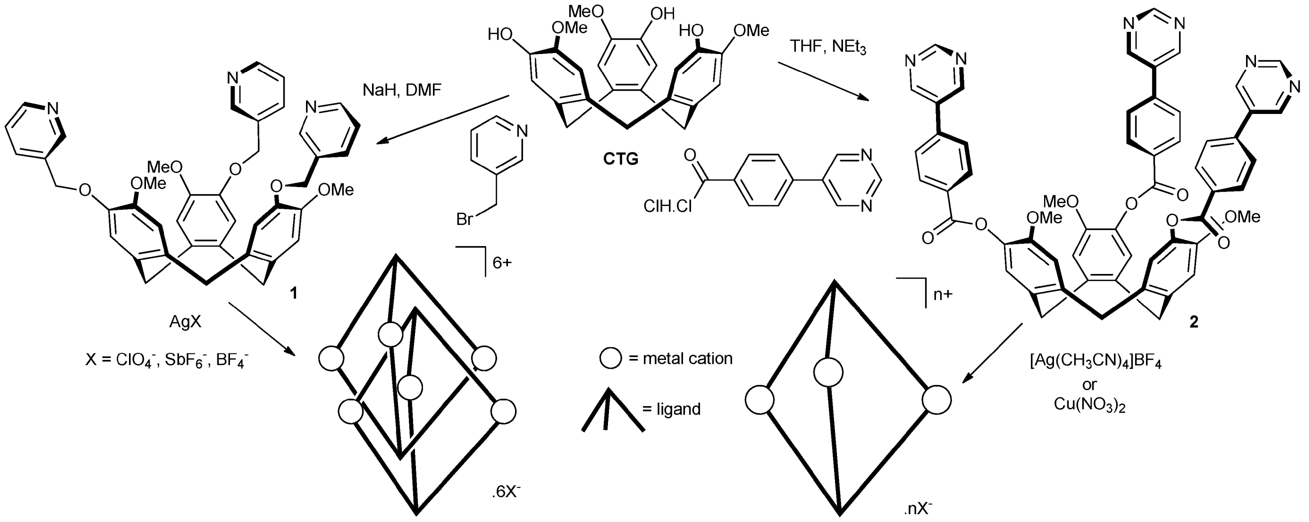

Scheme 1 Synthesis of ligands **1** and **2**, and cartoon schematic of [2]catenane and single cage formation.

ether groups of the ligands of the other cage, the Ag…O separations (average 3.13, closest 2.91 Å) are considerably greater than the sum of the ionic and van der Waals radii (2.66 Å).[12] Hence the [2]catenane has formed without a template and in the absence of any evident strong structure-directing interactions that are maintained in the final complex.

The solution-phase assembly of the [2]catenane was investigated by NMR and electrospray mass spectrometry. The ^{1}H NMR spectrum of a mixture of Ag(ClO$_4$) and **1** in d_7-DMF showed considerable broadening and changes to the chemical shifts of the ligand, consistent with coordination occurring in solution.‡ The ESI-MS gives excellent evidence for the formation of the [2]catenane, in particular through *m*/*z* peaks attributable to species with four ligands: $\{[Ag_5(\mathbf{1})_4](ClO_4)_4\}^+$, $\{[Ag_4(\mathbf{1})_4](ClO_4)_3\}^+$. Other peaks in the spectrum are assigned to species $\{[Ag_4(\mathbf{1})_3](ClO_4)_3\}^+$, $\{[Ag_3(\mathbf{1})_3](ClO_4)_2\}^+$, $\{[Ag_3(\mathbf{1})_2](ClO_4)_2\}^+$, and $[Ag(\mathbf{1})]^+$.

The crystalline complexes $[Ag_3(\mathbf{2})_2](BF_4)_3.(solvent)_n$ and $[Cu_3(\mathbf{2})_2(H_2O)_6(NO_3)_3](NO_3)_3.(solvent)_n$ are isomorphic,§ and only the $[Cu_3(\mathbf{2})_2(H_2O)_6](NO_3)_6.(solvent)_n$ complex will be discussed in detail (see supplementary information for Ag(I) complex‡). The Cu(II) centres of $[Cu_3(\mathbf{2})_2(H_2O)_6(NO_3)_3](NO_3)_3$ have distorted square pyramidal coordination with two pyrimidine groups in a *trans* arrangement at Cu–N distance 2.054(3) Å and N–Cu–N angle 177.26(16)°; disordered *trans* aquo ligands (Cu–O 2.020(10) and 2.105(10) Å); and a long contact to a disordered nitrate (Cu–O 2.446 Å). Only one of the nitrogen atoms of each pyrimidine group binds to the metal. The $[Cu_3(\mathbf{2})_2(H_2O)_6(NO_3)_3]^{3+}$ complex forms an *anti*-metallocryptophane, Fig. 2a, of *ca.* 2 nm size and with significant internal space.

The metallo-cryptophane can also be described as a trigonal bipyramidal cage with the three metals forming the equatorial plane. Viewed down the axial direction, the metallated side-arms extend outwards. Flat layers of interdigitated $[Cu_3(\mathbf{2})_2(H_2O)_6(NO_3)_3]^{3+}$ cations are formed with each metallo-cryptophane surrounded by six others, Fig. 2b. Each metallated arm of a cage projects into a window of an adjacent cage, forming triangular interstitial cavities within the layer, Fig. 2c. In the crystal lattice, these layers pack such that a CTV fragment of a cage of another layer sits above this cavity. Hence the packing of the metallo-cryptophanes is reminiscent of simple close packing of spheres but with six layers in the repeat unit accounting for the very long *c* unit cell dimension of *ca.* 105 Å.

The solution properties of $[Ag_3(\mathbf{2})_2](BF_4)_3$ and $[Cu_3(\mathbf{2})_2(H_2O)_6](NO_3)_6$ were also investigated by NMR and electrospray MS, however no evidence was seen for their formation in solution. The ^{1}H NMR spectrum of a 3 : 2 mixture of $[Ag(MeCN)_4])BF_4$ and **2** in d_6-DMSO shows no shifts compared to the spectrum of the free ligand. This is further confirmed with the electrospray MS of a similar solution which shows peaks at *m*/*z* 1063.2, 2017.5 and 2973.8 for the small fragments$\{Ag(\mathbf{2})\}^+$, $\{Ag(\mathbf{2})_2\}^+$ and $\{Ag(\mathbf{2})_3\}^+$. Likewise the electrospray MS of a DMF solution of Cu(NO$_3$)$_2$ and **2** shows dominant peaks for the fragments $\{Cu(\mathbf{2})(NO_3)\}^+$, $\{Cu(\mathbf{2})_2(NO_3)\}^+$, $\{Cu(\mathbf{2})_3(NO_3)\}^+$ and at *m*/*z* 1079.2 and 2035.5 and 2989.8 respectively.

In both the [2]catenane and single cage metallocryptophanes reported here, the *anti*-isomer was obtained. This is in contrast to similar previously reported metallocryptophanes where a mixture of isomers[2] or the *syn*-isomer[4] were obtained. Here, formation of the *anti*-isomer is likely to be predetermined by the nature of the ligand. Both **1** and **2** have coordinating N-atoms in (effectively) the 3-position, and, with the metal acting as a linear linker, only the *anti*-isomer can form on steric grounds.

The second example of a non-templated [2]catenane metallo-cryptophane reported here, together with other recently reported 3D and non-templated catenanes, indicated that such catenation of cage-like molecules may be more general, and points to complex self-assembly processes.

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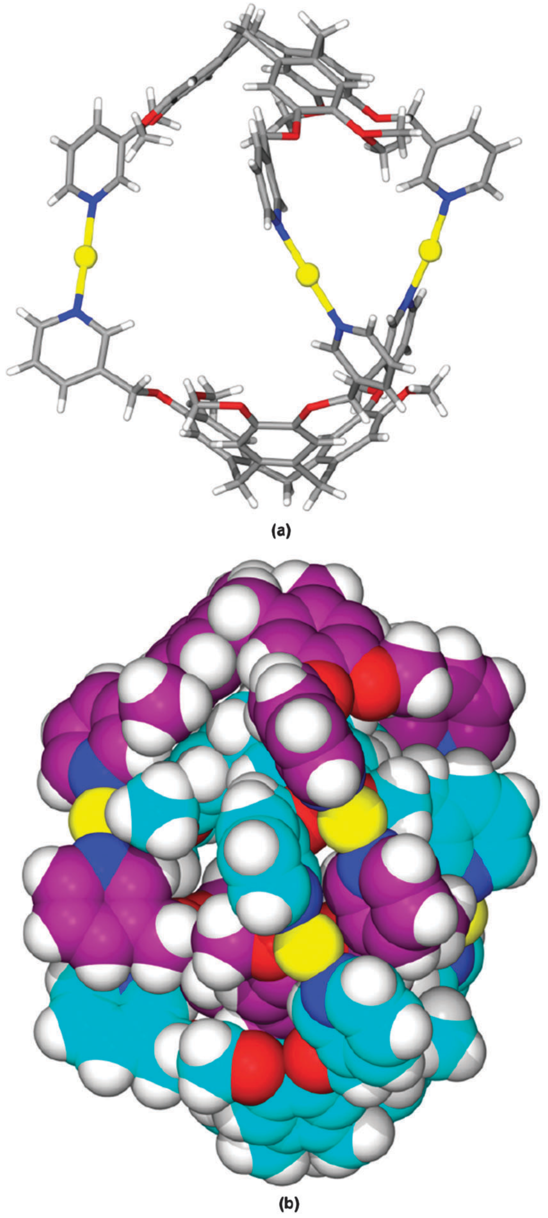

Fig. 1 From the crystal structure of $\{[Ag_3(\mathbf{1})_2]\}_2.(ClO_4)_6\cdot(DMF)_3$. (a) A single $[Ag_3(\mathbf{1})_2]^{3+}$ metallo-cryptophane; (b) two metallocryptophanes (shown in different colours) interlocking to form a [2]catenane.

Notes and references

§ The SQUEEZE routine of PLATON[13] was employed on all structures.

Crystal data. $\{[Ag_3(\mathbf{1})_2]\}_2.(ClO_4)_6\cdot(DMF)_3.(solvent)_n$: $C_{177}H_{177}Ag_6Cl_6N_{15}O_{51}$, Mr = 4190.26, monoclinic, a = 33.352(3), b = 19.288(2), c = 40.328(3) Å, β = 104.583(4), V = 25107(4) Å^3, space group Cc, Z = 4, θ_{max} = 22.50°, T = 150(1) K, 1774 parameters, 124 restraints, R_1 = 0.1037 (for 15793 data $I > 2\sigma(I)$), wR_2 = 0.2617 (all 27816 data). CCDC 812990.

$[Cu_3(\mathbf{2})_2(H_2O)_6](NO_3)_6.(solvent)_n$: $C_{114}H_{96}Cu_3N_{18}O_{45}$, Mr = 2628.71, trigonal, a = 16.6949(7), c = 105.524(9) Å, V = 25471(3) Å^3, space group $R\bar{3}c$, Z = 6, θ_{max} = 25.99°, 245 parameters, R_1 = 0.0927 (for 4514 data $I > 2\sigma(I)$), wR_2 = 0.3215 (all 5563 data). CCDC 812988.

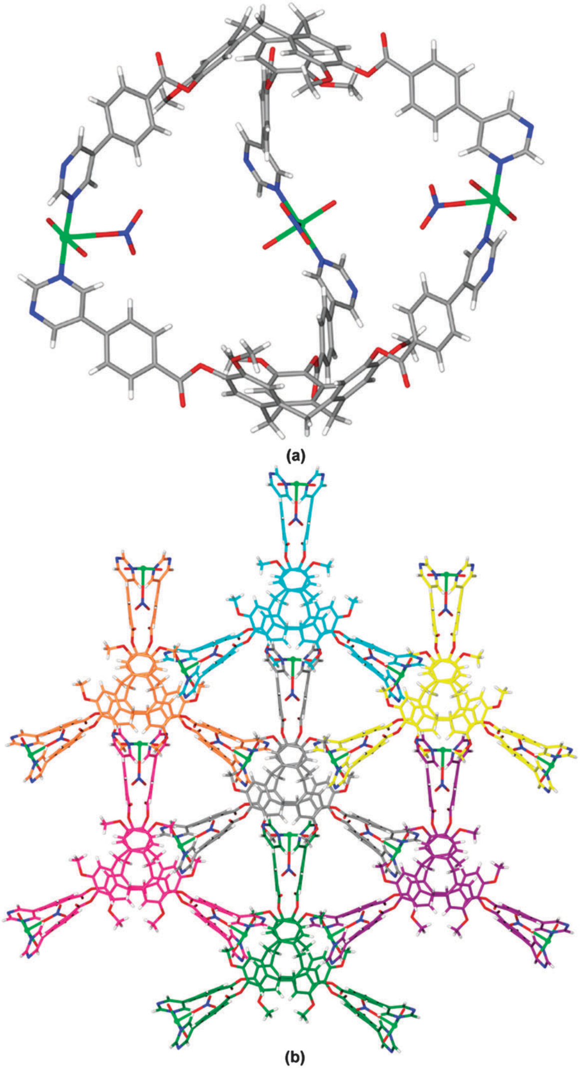

Fig. 2 From the crystal structure of $[Cu_3(\mathbf{2})_2(H_2O)_6](NO_3)_6$.n(solvent). (a) the metallo-cryptophane; (b) packing in layers in the *ab* plane. Disordered aquo and nitrate ligands are shown in a single averaged position.

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