

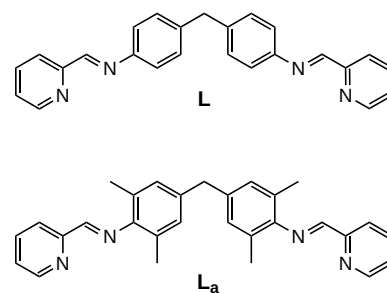
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Assembly of a Nanoscale Chiral Ball through Supramolecular Aggregation of Bowl-Shaped Triangular Helicates**

Laura J. Childs, Nathaniel W. Alcock, and Michael J. Hannon*

Biological systems provide many intricate and elegant examples of the use of self-assembly through noncovalent recognition events to generate large functional arrays. Chemists have also been attempting to mimic this approach by using supramolecular interactions to construct a wide range of arrays of defined size and architecture (albeit on a smaller size scale).^[1] Metallo-supramolecular chemistry in particular has been a popular and effective tool.^[2] However, in common with other supramolecular systems synthesis of building blocks (in this case of the ligands) by the formation of *covalent* bonds places restrictions on the size of the architectures that have been generated. This situation represents a potential barrier to progress in this field. One approach to address this problem is to use multiple recognition events in sequence. Thus, an initial event generates a supramolecular structure which is then aggregated into a larger array in a second supramolecular event.^[3–6] As in the assembly of “simple” supramolecular structures, a challenge is to control the aggregation such that a discrete array (rather than a polymeric array) is obtained. We have been exploring the use of shape to control such aggregation and we recently reported the use of imine-based ligands to form arc-shaped double-helicates which aggregate into a discrete circular array as a result of their curved topography.^[4] We have been investigating whether the same approach can be applied to form three dimensional (rather than planar) structures and herein we report the assembly of a supramolecular ball from commercially available components by this approach.

We have shown that the reaction of ligand **L** with metal ions capable of tetrahedral coordination leads to a solution equilibrium of two dimeric isomers; a helicate (*rac* isomer)



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and a metallo-cyclophane (*meso* isomer).^[7] In an attempt to perturb this equilibrium, we designed ligand **L_a** in which methyl groups are introduced into the spacer with the goal of (sterically) twisting the phenyl rings out of planarity with the pyridylimine units and thus disfavoring the *meso* isomer.^[8] While the methyl groups do indeed bring about this effect, their presence also has other dramatic consequences.

Ligand **L_a** was prepared in 81% yield by mixing two equivalents of 2-pyridinecarboxaldehyde and one equivalent of 4,4'-methylenebis(2,6-dimethylaniline) in methanol. Reaction of **L_a** with [Cu(MeCN)₄][PF₆] in methanol yielded a red solution from which a deep red solid precipitated on cooling. The color ($\lambda = 470$ nm in MeCN) arises from a metal-to-ligand charge transfer (MLCT) and is characteristic of copper(I) in a bispyridylimine environment^[7]. The same compound can be prepared in a one-pot reaction simply by mixing the aldehyde with the diamine, then adding the copper salt. The compound can also be prepared in a solvent-free reaction by grinding the three reactants together.^[9] The electrospray mass spectrum shows peaks corresponding to a dimeric species and a trimer. The ¹H NMR spectra of the compound have been recorded in both CD₂Cl₂ and CD₃CN solution. In acetonitrile at room temperature, a single set of resonance signals is observed. However, in CD₂Cl₂ at room temperature, a second set of resonance signals is observed consistent with the presence of two solution species. The CH₂ region of the ¹H NMR spectrum is particularly informative (Figure 1): two singlets are observed and there is no evidence (even at low temper-

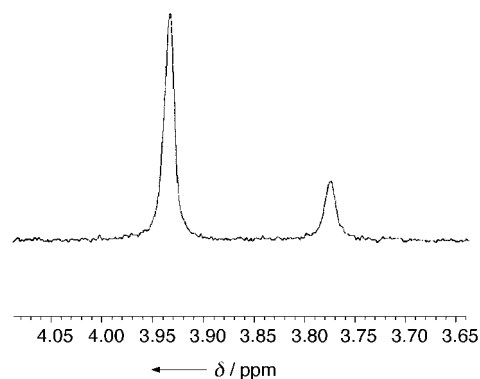


Figure 1. The CH₂ resonance signals in the ¹H NMR spectrum of the copper(I) complex of **L_a** in CD₂Cl₂ at 273 K.

ature) of the pair of doublets which is characteristic of the CH₂ group in the cyclophane architecture^[7]. This result implies that, as envisaged, the introduction of the methyl group has sterically disfavored the formation of the *meso* isomer. The NMR spectroscopic data, coupled with the ESIMS data, leads us to conclude that the solution species must be a dimeric helix [Cu₂(**L_a**)₂]²⁺ and a trinuclear circular helicate [Cu₃(**L_a**)₃]³⁺.^[10]

The results of NMR diffusion experiments in CD₂Cl₂ are consistent with the presence of two species of different volumes and indicate that the major component is the smaller (i.e. dimeric) species.

Diffusion of diethyl ether into a nitromethane solution of the compound afforded X-ray quality crystals, the solid-state

structure of which reveals a chiral trinuclear circular helicate [Cu₃(**L_a**)₃]³⁺ (Figure 2).^[11]

Each copper(I) center, as expected, is four coordinate, in a pseudo-tetrahedral coordination environment bound to two

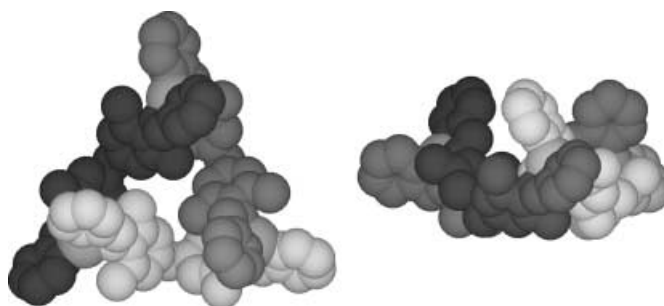


Figure 2. Molecular structure of the [Cu₃(**L_a**)₃]³⁺ ion a) top view and b) side view; to emphasize the helical nature each ligand is shown in a different shading. Hydrogen atoms are omitted for clarity.

pyridylimine units from two different ligands. These metal ions prescribe the three vertices of the triangle. Each ligand wraps “over and under” the plane formed by the three metal ions leading to a trinuclear, triangular, circular helicate.^[12] The structure reveals why the methyl groups have favored a trimeric species (which is not observed with ligand **L**). There are six CH–π interactions (CH–centroid 2.9–3.0 Å) within the triangle which occur between the methyl groups of one ligand and the phenyl rings of an adjacent ligand and presumably these factors contribute to the energetic stability.

The side view of the [Cu₃(**L_a**)₃]³⁺ ion (Figure 2b) reveals that the triangle is not planar, but slightly bent to give a bowl-shaped motif. This bowl-shaped distortion arises to accommodate the CH–π interactions and the constraints of the ligand connectivity. Three pyridyl rings (one from each ligand) point towards the cavity of the bowl and are arranged like the blades of a propeller. These “blades”, together with the bowl-shaped topography, have dramatic consequences for the solid-state aggregation of the [Cu₃(**L_a**)₃]³⁺ triangular circular helicates (Figure 3).^[13,14] Four of the bowl-shaped triangular units assemble in a tetrahedral fashion through CH–π interactions to form a tetrameric ball-shaped aggre-

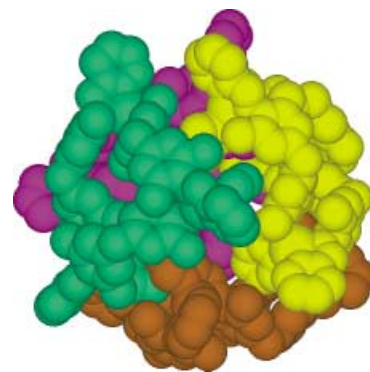


Figure 3. Molecular structure of the ball shaped array resulting from the aggregation of four [Cu₃(**L_a**)₃]³⁺ circular helicates; each circular helicate is shown in a different color. Hydrogen atoms are omitted for clarity.

gate. The blades of each triangle point into the cavity of the ball and a total of 12 CH– π interactions (CH–centroid 2.9 Å) are formed between the pyridyl rings of the triangles with the phenylene spacers of adjacent triangles. Each triangle in the ball is of identical chirality so that the overall ball-shaped structure is also chiral. This chiral recognition is a consequence of the propeller-type twist arrangement of the pyridyl blades of each triangle. The four sets of blades lock together and the propeller twisting of the triangles needs to be in the same direction to allow the triangles to fit together.^[15] The diameter of the resulting ball is approximately 2.5 nm (C...C). Four PF₆[−] counterions are located in the internal cavity and form short F...H contacts (2.35–2.88 Å).^[16] Each of these anions is located above a triangular face and makes three contacts with that triangle and four additional contacts to each of the other three triangles (15 contacts per anion in total). These contacts may contribute to the stabilization of the structure.

The resulting nanoscale structure^[17] is quite remarkable, it is a supramolecular assembly of 12 copper(I) ions and 12 ligands. It is striking as it can be assembled in a one-pot reaction simply by mixing inexpensive commercial reagents: 24 aldehydes, 12 diamines, and 12 copper(I) hexafluorophosphate units. While the structure described does not yet approach the complexity of assembly and level of sophistication seen in biological systems, it does indicate that with judicious (and/or fortuitous) design, large, complex architectures of nanoscale dimensions may be assembled from simple and small molecular components through controlled aggregation using multiple recognition events.

Experimental Section

L_a: 2-pyridinecarboxyaldehyde (0.829 g, 6.84 mmol) was dissolved in methanol (90 mL) and stirred under a nitrogen atmosphere. A solution of 4,4'-methylenebis(2,6-dimethylaniline) (0.678 g, 3.42 mmol) in methanol was added and the mixture stirred at room temperature for 24 h. The yellow solution was then concentrated by rotary evaporation to produce a yellow solid (1.125 g, 81 %). IR (KBr): $\tilde{\nu}$ = 2996w, 2905m, 2846w, 1638s, 1583m, 1476s, 1433s, 1385s, 1318w, 1283w, 1200s, 1141m, 1089w, 1042w, 987m, 876m, 837m, 774s, 742m, 695w, 647w, 616w cm^{−1}; MS (EI/CI): *m/z* 433 [*M*+H]⁺; ¹H NMR (CDCl₃): δ = 8.72 (d, *J* = 4.6 Hz, 1H; H₆), 8.35 (s, 1H; H_i), 8.28 (d, *J* = 7.7 Hz, 1H; H₃), 7.84 (t, *J* = 7.7 Hz, 1H; H_{4/5}), 7.40 (dd, *J* = 7.5, 7.7, 4.6 Hz, 1H; H_{4/5}), 6.94 (s, 2H; Ph), 3.85 (s, 1H; CH₂), 2.15 ppm (s, 6H; CH₃).

[Cu₃(L_a)₃][PF₆]₃: Ligand L_a (0.084 g, 0.019 mmol) was dissolved in methanol and treated with [Cu(MeCN)₄][PF₆] (0.072 g, 0.19 mmol) under nitrogen to give a dark red solution. The solution was heated at reflux overnight then cooled to room temperature affording a very deep red precipitate on standing. This solid was collected by filtration and washed with diethyl ether (0.173 g, 71 % yield). IR (KBr): $\tilde{\nu}$ = 2902w, 1586m, 1474m, 1440m, 1380m, 1303w, 1200m, 1140w, 900w, 836s, 772m, 742w, 558m cm^{−1}; MS (ESI in MeCN): *m/z* 1135 {Cu₂(L_a)₂(PF₆)⁺}, 927 {Cu(L_a)₂}⁺, 816 {Cu₃(L_a)₃(PF₆)₃}²⁺, 495 {Cu₂(L_a)₂}²⁺, {Cu(L_a)₂}⁺; ¹H NMR: (CD₂Cl₂, 273 K): δ = 8.67 (d, *J* = 5.0 Hz, 4H; H₆ helix), 8.65 (d, *J* = 4.8 Hz, 1H; H₆ trimer), 8.49 (s, 4H; H_i helix), 8.39 (s, 1H; H_i trimer), 8.21 (td, *J* = 7.8, 1.6 Hz, 4H; H_{4/5} helix), 8.13 (td, *J* = 7.7, 1.5 Hz, 1H; H_{4/5} trimer), 8.00 (m, 5H; H₃ helix and trimer), 7.85 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 4H; H_{4/5} helix), 7.76 (ddd, *J* = 7.7, 5.1, 1.1 Hz, 1H; H_{4/5} trimer), 6.99 (s, 4H; Ph helix), 6.95 (s, 1H; Ph trimer), 6.84 (s, 1H; Ph trimer), 6.65 (s, 4H; Ph helix), 3.92 (s, 4H; CH₂ helix), 3.75 (s, 1H; CH₂ trimer), 2.16 (s, 12H; CH₃ helix), 2.02 (s, 3H; CH₃ trimer), 1.27 ppm (s, 15H; CH₃ helix and trimer); UV/Vis (MeCN): 470 (ϵ = 12000), 334 (ϵ = 28000), 328 (ϵ = 75000) nm.

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- a) Crystal-structure data for C_{29.25}H₂₉N₄O_{0.25}CuPF₆, *M_r* = 649.07, cubic, space group *P*4₃2, *a* = 27.5381(2), *b* = 27.5381(2), *c* = 27.5381(2) Å, α = 90, β = 90, γ = 90°, *V* = 20883.4(3) Å³, *T* = 180(2) K, λ = 0.71073, *Z* = 24, ρ_{calcd} = 1.239 Mg m^{−3}, *F*(000) = 2232, μ (MoK α) = 0.729 mm^{−1}, crystal: red plates, crystal dimensions = 0.4 × 0.02 × 0.01 mm, data collected with a Siemens SMART three-circle system with CCD area detector. The crystal was held at 180(2) K with an Oxford Cryosystem Cryostream Cooler; θ_{max} = 22.48°. A total of 88425 reflections were measured, 4550 unique [*R_{int}* = 0.1737]. Absorption correction by Psi-scan. Weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0383 P)]$, where $P = (F_o^2 + 2F_c^2)/3$. GOF on *F*² was 1.499, *R*1 [for 10956 reflections with *I* > 2 σ (*I*)] = 0.0830, *wR*2 = 0.2037. Data/restraints/parameters 22935/0/1317. Largest difference Fourier peak and hole 0.502 and −0.459 e Å^{−3}. Refinement used SHELXL 97 (G. M. Sheldrick, **1997**); b) CCDC-187879 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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