Selective Anion Binding Drives the Formation of Ag\textsubscript{1,8}L\textsubscript{6} and Ag\textsubscript{1,12}L\textsubscript{6} Six-Stranded Helicates

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Here we describe the formation of an unexpected and unique family of hollow six-stranded helicates. The formation of these structures depends on the coordinative flexibility of silver and the 2-formyl-1,8-naphthyridine subcomponent. Crystal structures show that these assemblies are held together by Ag\textsubscript{4}L, Ag\textsubscript{4}Br, or Ag\textsubscript{6} (SO\textsubscript{4})\textsubscript{2} clusters, where the templating anion plays an integral structure-defining role. Prior to the addition of the anionic template, no six-stranded helicate was observed to form, with the system instead consisting of a dynamic mixture of triple helicate and tetrahedron. Six-stranded helicate formation was highly sensitive to the structure of the ligand, with minor modifications inhibiting its formation. This work provides an unusual example of mutual stabilization between metal clusters and a self-assembled metal–organic cage. The selective preparation of this anisotropic host demonstrates new modes of guiding selective self-assembly using silver(I), whose many stable coordination geometries render design difficult.

Self-assembly can produce complex metal–organic architectures from simple starting materials.\textsuperscript{1–3} Such structures have been the subject of intense recent exploration, with applications spanning guest binding, stabilization of reactive species, biomolecular interactions, and chemical purification.\textsuperscript{4–8} These applications often depend on binding a target in the plesiospherical cavity of a metal–organic cage. These isotropic cavities can bind roughly spherical guests or guest agglomerates\textsuperscript{10–13} but are ill-adapted to bind asymmetric and anisotropic guests. The introduction of flexible organic ligands,\textsuperscript{4–6} or metal coordination spheres\textsuperscript{7,14} has led to the formation of new metal–organic cages, with nonspherical internal cavities, partially alleviating these limitations.\textsuperscript{21–25}

Silver(I), in combination with dipyrrol peptidic linkers, has recently been shown to generate a wealth of complex knotted architectures via self-assembly.\textsuperscript{26–28} The strategy of incorporating a guest of interest into the architecture formed, as a template\textsuperscript{29–31} or other structural elements,\textsuperscript{32,33} can enhance selectivity and sensitivity in guest binding.\textsuperscript{34–36} Furthermore, if the guest is anionic,\textsuperscript{37–39} the diverse coordination chemistry of anions can be used to effect the selective recognition\textsuperscript{40–42} of targeted anions.\textsuperscript{33}

We hypothesized that the flexible coordination sphere of silver(I) ions\textsuperscript{44–49} in combination with organic ligands that assemble in situ around these metal-ion templates, would provide access to new structure types that bind anions as structural elements. Zhao and co-workers have previously shown that nitrogen containing macrocycles can stabilize atomically precise silver clusters with defined geometries, supporting this hypothesis.\textsuperscript{50,51}

Here we describe the formation of a family of complex six-stranded silver helicates upon the addition of three anions: iodide, bromide, and sulfate. This family comprises two novel structure types, with sulfate generating a structure distinct from those templated by halides. Key structural elements within these architectures are unique silver(I)-anion clusters,\textsuperscript{50,51} whose geometries are molded by the central anions, which in turn are held in an unusual, polarized, environment.

Building on the discovery that silver(I) assembles with 2-formyl-1,8-naphthyridine,\textsuperscript{1} a tritopic subcomponent, and anionic templates to form a trigonal prism with disilver vertices,\textsuperscript{17} we investigated the use of linear ditopic anilines in place of triangular ones. Initial experiments, involving the mixture of benzidine (2) together with 1, various silver salts, and prospective guests in acetonitrile (Figure 1a), gave in all cases an intractable gel (SI Section 8).

Reasoning that increasing steric hindrance and widening the torsion angle between the phenylene groups of the dianiline could lead to a different outcome,\textsuperscript{52} we explored the self-assembly of 2,2′-dimethyl-[1,1′-biphenyl]-4,4′-diamine (3) with 1 in acetonitrile, and observed the formation of discrete species with various silver(I) salts (Figure 1b). With silver perchlorate, we observed a 1:1 ratio of integrals between two species (Figure 1c). Diffusion ordered spectroscopy (DOSY) NMR revealed that one had a significantly larger diffusion coefficient (Figure 1c). Mass spectrometry indicated that the smaller species had Ag\textsubscript{4}L\textsubscript{3} composition, with the larger species corresponding to Ag\textsubscript{6}L\textsubscript{6} (Figures S72 and S75). Approximately 400 attempts to grow crystals of these species failed.

The observation of well-defined bands of peaks in the DOSY spectrum is consistent with the formation of discrete species, as opposed to poorly defined oligomers in solution.\textsuperscript{53,55} We...
Two 1H NMR signals observed for each proton environment in 
Furthermore, a twofold desymmetrization was observed, with an Ag₈L₆ tetrahedron and SI Section 10). The presence of 12 uncoordinated nitrogen donors within 9 violates the principle of maximal coordinative saturation, which has often, and successfully, been used to predict the product of metal–organic self-assembly processes. The absence of coordinative stabilization may be a consequence of the nonchelating coordination vectors of 1, which precluded the formation of simple structures. The lack of coordinative saturation is compensated for by the extensive aromatic stacking seen in the crystal structure of 9.

Silver–silver separations were 2.96–3.00 Å between silver atoms bridged by a single naphthyridine moiety, greater than those observed in simpler mononuclear naphthyridine-bridged silver complexes. The iodide ion coordinated to all four Ag ions in the cluster, with Ag–I separations of 2.79–2.88 Å, consistent with previous reports of Ag₁I₄ clusters.

Having determined the structure of 9, we investigated whether alternative anions might lead to the generation of further examples of this new structure type. Addition of tetramethylammonium sulfate to a mixture of Ag₄I₃ and Ag₈L₆(SO₄)₂ stoichiometry, based upon similarities between 1H NMR spectra (SI Section 9). Mass spectrometry indicated that instead a Ag₁₂L₆(SO₄)₄ structure was formed, with Ag₁₂I₆ stoichiometry, based upon similarities between 1H NMR spectra (Figure S9). However, mass spectrometry confirmed that a Ag₁₂L₆(SO₄)₂ architecture had been formed (Figures S69 and S77).

The X-ray crystal structure of 9 revealed its highly unusual six-stranded helicate structure (Figure 3a,b), which is capped at each end by a Ag₄I cluster consisting of a Ag₃ triangle capped by an apical Ag on the outside and iodide on the inside (Figure 3c). The six ligand strands bridge two such Ag₄I clusters, and, to our surprise, no precipitate was observed.

Typical coordination environments for the Ag centers were observed in 9. One arm of each ligand coordinates via all three available nitrogen donors, and the other via only a single inner naphthyridine nitrogen. This differentiation leads to the twofold desymmetrization seen in the 1H NMR spectrum. The six-stranded helicate structure was similar to 9, yet the silver clusters at the ends of both assemblies are dramatically different. Instead of the Ag₄I clusters of 9, the vertices of 10 consist of Ag₆(SO₄)₂ clusters composed of inner and outer Ag₃ triangles. The externally facing sulfate coordinates to the outer triangle of silver ions via a single, triply coordinated, oxygen atom. The coordination of this sulfate is reinforced by nonclassical hydrogen bonding from three naphthyridine nitrogen. This di

FIGURE 1. Self-assembly of Ag₄L₃ and Ag₈L₆ architectures. Conditions: (a) AgNTf₂ (2 equiv), 2 (1 equiv), 1 (2 equiv), d₅-MeCN, 5 min; (b) AgNTf₂ (2 equiv), 3 or 4 (1 equiv), 1 (2 equiv), d₅-MeCN, 5 min. Structures of 5 and 6 are MM3-optimized models. (c) DOSY NMR of 5 and 6.

Modeled potential structures for the Ag₈L₆ architecture and found that a tetrahedral geometry was preferred by 300–400 kcal mol⁻¹ (SI Section 9). Although we cannot definitively assign the product structures without crystallographic data, we infer that the two species are likely to be Ag₄L₃ helicate 5 and Ag₈L₆ tetrahedron 6, consistent with previously reported systems, our modeling studies, and the solution data (SI Section 4.4). Investigations of host–guest behavior showed binding to a range of anionic and organic guests, with some alterations in the 5:6 equilibrium (SI Section 7).

When dianiline 4 was used in place of 3 we observed similar results (Figure 1b and SI Section 10).

Having extensively screened potential guest species, we next turned to the addition of halides to these silver(I) based assemblies. We had initially avoided the use of halides, anticipating precipitation of silver halide species (the solubility product of AgI is 10⁻¹⁴.₃ in acetonitrile). However, upon addition of TBA iodide, a new species, 9, immediately formed and, to our surprise, no precipitate was observed.

Characteristic ¹H NMR signals were observed for 9 at 6 ppm, ca. 1 ppm upfield of any signals of 5 or 6 (Figure 1c). Furthermore, a twofold desymmetrization was observed, with two ¹H NMR signals observed for each proton environment in free ligand (Figure S1). DOSY spectroscopy gave results consistent with the formation of a single species (Figure S8).
Ligand coordination again shows pairwise alternation, here between three and two coordinating nitrogen atoms per ligand arm. The uncoordinated donor atoms were again imine nitrogens.

We next investigated whether other anions could template structures similar to 9 and 10. Among the 38 anions tested (SI Sections 6.7 and 6.8), only bromide proved able to efficiently template a six-stranded helicate (11). The \(^1\)H NMR spectrum of 11 again exhibited a twofold desymmetrization, and a single species was observed by DOSY spectroscopy, with a hydrodynamic radius of 11.9 Å, similar to the cases of 9 and 10 (Figures S8, S15, and S22). Attempts to grow crystals suitable for X-ray diffraction proved unsuccessful. However, we inferred the Ag\(_8\)L\(_6\)Br\(_2\) structure of 11 to be an analogue of 9 by comparing the \(^1\)H NMR, COSY, and HSQC spectra of 9−11. The spectra of 9 and 11 were clearly similar, whereas that of 10 was notably different (Figure 4a and SI Section S).

We then probed further the selectivity of the assembly process. Silver tetrafluoroborate, hexafluorophosphate, perchlorate, and triflate all furnished six-stranded helicates adopting the framework of 9 when combined with 1, 3, and potassium iodide (Figures S38 and S39). Titration of TBA bromide into a mixture of 5 and 6 revealed no intermediate species (i.e., from binding a single bromide). Instead, formation of 11 (containing two bromide anions) was seen immediately, in the continued presence of 5 and 6 (Figures S42 and S46), suggesting that the six-stranded helicate assembled cooperatively (SI Sections 6.3 and 6.6). Using 2 or 4 in place of 3 led to immediate gelation (for 2) or shifts in the equilibrium of 7 and 8 (for 4, Figures S55 and S68).

These results highlight the extent to which the subcomponent self-assembly of metal−organic architectures may depend critically upon subtle variations in subcomponent structure. The lack of methyl groups on 2 favored polymerization over the assembly of discrete structures. The subtle steric and electronic differences between the methyl groups of 3 and the trifluoromethyl groups of 4 disfavored, in the latter case, the formation of six-stranded helicates analogous to 9−11. We hypothesize this sensitivity to be due to the slightly weaker ligand field in the case of ligands incorporating 4, which disfavors structures that incorporate the more highly cationic silver clusters incorporated into the new structure types 9−11.

This work describes the development of a system of novel six-stranded helicates, which assemble around atomically precise silver clusters. Specific anionic templates, in turn, serve to shape these clusters, such that the identity of the anion dictates the architecture observed. The ability of 2-formyl-1,8-napthyridine to bridge silver ions enables these complex structures to form from simple subcomponents. These new assemblies are sensitive to the precise nature of the ligand chosen and are selective for the templates employed, with potential applications in sensing specific analytes.
Figure 3. (a) X-ray crystal structure of 9; (b) schematic view of 9. (c) X-ray crystal structure of 10; (d) schematic view of 10. (e) End-on view of crystal structure of 9 showing cluster geometry. (f) End-on view of crystal structure of 10 showing the silver cluster and nonclassical hydrogen bonds to the exterior sulfate. (g) View from within the crystal structure of 10, showing nonclassical hydrogen bonds to the internal sulfate.

Figure 4. (a) Comparison of $^1$H NMR spectra of 10 (top), 11 (middle), and 9 (bottom), showing the similarity between the spectra of 9 and 11. Simplified (b) schematic and (c) cartoon views of six-stranded helicate 11.
The ability to use atomically precise clusters in place of mono- or dimetallic vertices in metal–organic cages has the potential to generate a vastly increased diversity of architectures, as we continue to uncover the principles underpinning silver–naphthyridine self-assembly. Future work will focus on exploring the photophysical properties of these novel clusters\(^6\) and on expanding the range of architectures formed by the interplay of anion templation, ligand design, and coordinational flexibility to generate increased structural diversity.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge at [https://pubs.acs.org/doi/10.1021/jacs.0c11905](https://pubs.acs.org/doi/10.1021/jacs.0c11905).

Experimental procedure and details; MM3 models and calculated energies; mass spectrometry data; X-ray crystallography data (PDF)

X-ray data for 9 (CCDC 2024152) (CIF)

X-ray data for 10 (CCDC 2024153) (CIF)

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*Notes*

The authors declare no competing financial interest.

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