

Designed Synthesis of Metal Cluster-Centered Pseudo-Rotaxane Supramolecular Architectures

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S Supporting Information

ABSTRACT: The designed synthesis and structural characterization of two metal cluster-centered metallocupramolecular architectures are reported. In complex $[(CF_3SO_3)_2Ag_4(tBuC\equiv C)(Py8)](CF_3SO_3)_2$ (**1**) and $[(CF_3SO_3)_2Ag_4\{C\equiv C-(m-C_6H_4)-C\equiv C-(m-C_6H_4)-C\equiv C-(m-C_6H_4)-C\equiv C\}Ag_4(CF_3SO_3)(Py8)_2](CF_3SO_3)_4$ (**2**), organic acetylide ligands are utilized to induce the formation of polynuclear silver aggregates, which are encapsulated into the central cavity of the neutral macrocyclic compound azacalix[8]pyridine (**Py8**). The tetrasilver cluster centered [2]- and [3]-pseudo-rotaxane structures are obtained and fully characterized by X-ray crystallography, ESI mass spectrometry, and 1H NMR spectroscopy.

The study of metallocupramolecular complexes has emerged as an active research field and attracted intense interest in the past two decades. Such multicomponent complexes have shown a variety of potential applications, acting for example as precursors of electronic,¹ photophysical,² and magnetic materials,³ or used in catalysis,⁴ molecular recognition,⁵ and transport.⁶ Supramolecular coordination assembly based on directional bonding,⁷ symmetry interaction,⁸ and weak linkage⁹ has proven to be an effective approach to achieve well-defined metallocupramolecular architectures, wherein most of them are generally constructed from single metal centers by virtue of their typical octahedral, square planar, or tetrahedral coordination geometries. In contrast, metallocupramolecular structures involving polynuclear metal clusters as centers are rarely reported. Although metal cluster entities have specific physical properties¹⁰ and the incorporation of cluster aggregates into coordination assemblies may endow abundant functions to the resulting metallocupramolecules, however, multivariate coordination geometries of cluster aggregates make the designed synthesis of cluster-centered supramolecular structures a formidable task.

On the other hand, the template-directed approach is often employed to access multinuclear clusters through the induction of anionic inner bonding sites of macrocyclic ligands.¹¹ Inspired by such a cluster-macrocycle model, we envisioned that adscititious anionic ligands can be judiciously used to dictate the assembly of metal cluster aggregates upon a neutral macrocyclic ligand as a template (Scheme 1). Moreover, the peripheral coordination of a macrocyclic ligand is likely to simplify the coordination modes of metal clusters. We herein describe the designed synthesis and structural characterization of two cluster-centered metallocupramolecular complexes, namely $[(CF_3SO_3)_2Ag_4(tBuC\equiv C)(Py8)](CF_3SO_3)_2$ (**1**) and

$[(CF_3SO_3)_2Ag_4\{C\equiv C-(m-C_6H_4)-C\equiv C-(m-C_6H_4)-C\equiv C-(m-C_6H_4)-C\equiv C\}Ag_4(CF_3SO_3)(Py8)_2](CF_3SO_3)_4$ (**2**) (**Py8** = azacalix[8]pyridine), both featuring a pseudorotaxane structure with the encapsulation of an acetylide-tetrasilver aggregate into a neutral polypyridine macrocycle.

Considering the rigid linear geometry of acetylene units and their ready chemical availability via the Pd-catalyzed coupling reactions,¹² we purposefully investigated the assembly of silver acetylide complexes $[AgC\equiv CR]_n$ with the neutral polydentate macrocyclic ligand **Py8**. The polymeric silver acetylide complex $[AgC\equiv C^tBu]_n$ usually has very poor solubility in common solvents as reported previously.¹³ However, treatment of a suspension of $[AgC\equiv C^tBu]_n$ and silver triflate with **Py8** in a mixed solvent of methanol and dichloromethane yielded a clear pale yellow solution. Silver triflate is herein used to increase the silver ion concentration, which is required for the formation of multinuclear silver aggregate.^{13c} Light yellow crystals were subsequently acquired by the diffusion of diethyl ether into the solution. X-ray crystallographic analysis provided the formula of this crystalline complex **1** as $[(CF_3SO_3)_2Ag_4(tBuC\equiv C)(Py8)](CF_3SO_3)_2$.¹⁴ The asymmetrical unit of **1** consists of two independent silver atoms, half **Py8** ligand, half *tert*-butylacetylide anion, and one and a half triflate groups. As shown in Figure 1a, the two silver atoms (Ag1 and Ag2) and their inversion-related ones (Ag1A and Ag2A) constitute a square planar tetranuclear aggregate, which is held together by both σ - and π -bonding of the *tert*-butylacetylide anion in the $\mu_4-\eta^1, \eta^1, \eta^1, \eta^2$ mode. The π -type Ag–C bonding distance at Ag1–C2 = 2.704(16) Å is longer than the σ -type ones in the range 2.130(14)–2.430(19) Å. The triple bond length in $tBuC\equiv C^-$ is 1.195(9) Å, in good agreement with the values observed in other silver *tert*-butylacetylide complexes.¹⁵ Relative to the *tert*-butylacetylide anion, the triflate group S1 is located at the opposite side of the Ag_4 plane and binds the Ag1–Ag2 edge through a simple μ_2-O, O' coordination mode. Every edge of the Ag_4 square (Ag1···Ag2 = 2.941(1) Å; Ag1···Ag2A = 2.997(1) Å) is much shorter than twice the van der Waals radius of the silver atom (3.4 Å), suggesting the existence of argentophilic interaction.¹⁶ This Ag_4 square aggregate is encapsulated by the central cavity of the **Py8** ligand and is stabilized by the coordination of its four alternate pyridyl nitrogen atoms, which are coplanar but make a dihedral angle of 16.3° with the Ag_4 square (Figure 1b). Furthermore, a $[(tBuC\equiv C)Ag_4(CF_3SO_3)]$ moiety with the *tert*-butylacetylide anion and the triflate group attached to the Ag_4 plane on either

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Scheme 1. Structure of Azacalix[8]pyridine (Py8) and Its Role in Protecting the Coordination Sites of a Metal Cluster

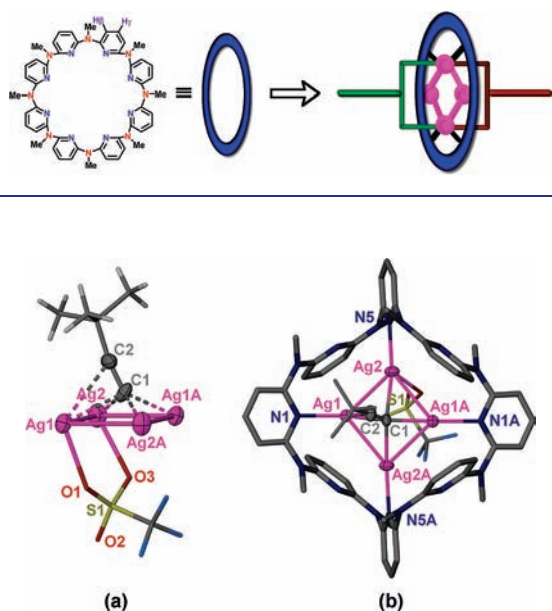


Figure 1. (a) Tetranuclear silver aggregate coordinated by *tert*-butylacetylide and triflate in complex $[(\text{CF}_3\text{SO}_3)_2\text{Ag}_4(\text{tBuC}\equiv\text{C})(\text{Py8})](\text{CF}_3\text{SO}_3)_2$ (**1**) with atom labeling (the thermal ellipsoids set at 50% probability level). The CF_3SO_3^- and $\text{tBuC}\equiv\text{C}^-$ groups are disordered and can be located at either side of the Ag_4 plane. Only one pair of CF_3SO_3^- and $\text{tBuC}\equiv\text{C}^-$ is shown here. (b) Encapsulation of the Ag_4 aggregate into the Py8 macrocyclic ligand in **1**. Hydrogen atoms and two free triflate groups are omitted for clarity. Symmetry code: $A \frac{1}{2}-x, \frac{1}{2}-y, -z$. Selected bond lengths and distances (Å): C1–C2 1.195(9); C1–Ag1 2.130(14), C1–Ag1A 2.407(18); C1–Ag2 2.241(17); C1–Ag2A 2.430(19); C2–Ag1 2.704(16); Ag1–N1 2.245(7); Ag2–N5 2.217(7); Ag1⋯Ag2 2.941(1); Ag1⋯Ag2A 2.997(1).

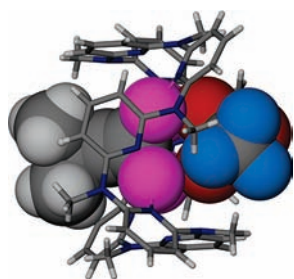


Figure 2. Pseudorotaxane structure in **1** with the $\text{tBuC}\equiv\text{C}$, CF_3SO_3 , and Ag_4 aggregate shown as a space-filling model. Color scheme for atoms: Ag, purple; C, black; H, gray; O, red; N, blue; F, cyan.

side is threaded through the Py8 macrocyclic ring, thus giving rise to a pseudorotaxane structure (Figure 2). To the best of our knowledge, this structure represents the first example of a cluster-centered organometallic rotaxane among the reported organometallic¹⁷ and hybrid organic–inorganic¹⁸ rotaxanes. Moreover, in contrast to the parallelogram 1,3,4,6-alternate conformation of Py8 in its free crystalline state,¹⁹ the Py8 ligand in **1** is folded into a 1,5-planar-2,4,7-alternate configuration, thus affording a cylinder belt (8.86 Å × 8.97 Å) surrounding the $[(\text{tBuC}\equiv\text{C})\text{Ag}_4(\text{CF}_3\text{SO}_3)]$ central chain (Figure 2).

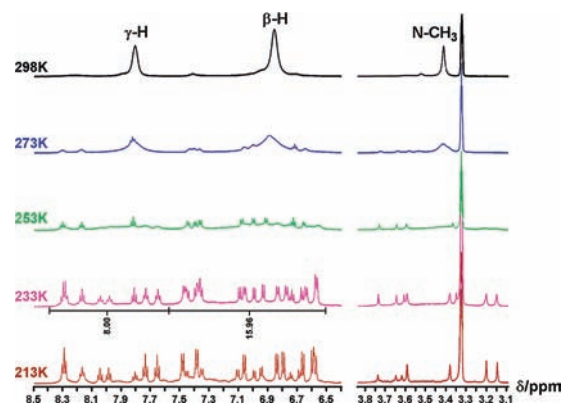


Figure 3. Partial ^1H NMR spectra (600 MHz, methanol- d_4) of the pyridyl and bridging N-Me protons of the Py8 ligand in **1** at different temperatures.

Formation of complex **1** was also confirmed by the electro-spray ionization (ESI) mass spectrometry, which displays two isotopically resolved peaks at $m/z = 1659.55$ and 755.34 corresponding to $[\text{1}-\text{OTf}]^+$ and $[\text{1}-2\text{OTf}]^{2+}$, respectively (Figure S1 in the Supporting Information). The ^1H NMR spectroscopy of **1** at 298 K shows two broad singlets at 6.87 and 7.81 ppm due to the pyridyl β - and γ -proton signals of the Py8 ligand, respectively. Both signals experience significant downfield shifts ($\Delta\delta = 0.16$ and 0.47 ppm, respectively) compared with the chemical shifts of the free Py8 in solution.¹⁹ However, only one set of proton signals for the Py8 ligand in the solution of **1** conflicts with its coordination behavior in the crystalline structure, where in two kinds of pyridine rings, coordinated and uncoordinated, can be clearly discriminated. We subsequently collected the proton NMR of **1** at lower temperatures. As the temperature decreases from 298 to 213 K (Figure 3), the broad pyridyl γ -proton signal at 7.81 ppm is gradually split into seven sharp triplets ranging from 7.6 to 8.3 ppm, and meanwhile the resonance of the pyridyl β -protons exhibits over ten doublet and multiplet peaks in the range 6.5–7.5 ppm. The ratio of the proton signals in the above two regions is close to 1:2, equal to the proportion of γ - to β -protons in Py8. Seven singlets for the methyl groups in the bridging N-Me moieties are observed as well at 213 K. Moreover, the interconversion of several triplet and doublet peaks takes place upon the variation of temperature. For example, the ratio of three triplets at 7.80, 7.75, and 7.65 ppm is approximately 1:1.5:1.5 at 233 K, whereas it is changed to 1:2:2 at 213 K. The NMR studies indicate that the conformation of the Py8 ligand in **1** is fluxional in solution at room temperature relative to the ^1H NMR time scale. The eight pyridyl nitrogen atoms undergo a rapid dissociation–recombination equilibrium to bond to the central Ag_4 aggregate, analogous with the contact between thread and ring in the reported organometallic rotaxane structures.^{17,18}

We next embarked on the employment of a specific angled organic ligand to direct the construction of cluster-centered metallosupramolecular architectures. The extending conjugated ligand 1,3-bis((3-ethynylphenyl)ethynyl)benzene was synthesized, and it reacted with silver nitrate in the presence of triethylamine to generate a new silver acetylide complex $[\text{AgC}\equiv\text{C}-(m\text{-C}_6\text{H}_4)\text{-C}\equiv\text{C}-(m\text{-C}_6\text{H}_4)\text{-C}\equiv\text{C}-(m\text{-C}_6\text{H}_4)\text{-C}\equiv\text{CAg}]_n$ as a white powder (see Supporting Information). A synthetic procedure similar to that of **1** with $[\text{AgC}\equiv\text{C}-(m\text{-C}_6\text{H}_4)\text{-C}\equiv\text{C}-(m\text{-C}_6\text{H}_4)\text{-C}\equiv\text{C}-(m\text{-C}_6\text{H}_4)\text{-C}\equiv\text{CAg}]_n$ in place

X-ray crystallographic data for **1** and **2** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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