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Argentivorous Molecules: Structural Evidence for $Ag^+-\pi$ Interactions in Solution

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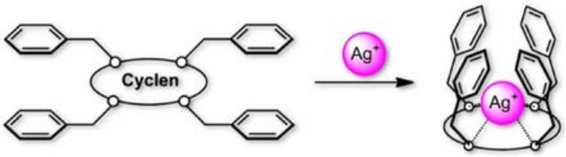
ABSTRACT



Tetra-armed cyclens bearing aromatic side arms were prepared by the reductive amination of cyclen with substituted benzaldehydes. When equimolar amounts of Ag^+ ions were added to the ligands, the aromatic rings covered the Ag^+ ions incorporated in the ligand cavities, as if the aromatic ring "petals" caught the Ag^+ ions in the way an insectivorous plant (Venus flytrap) catches insects. The ligands are called "argentivorous molecules". Evidence of intramolecular $Ag^+-\pi$ interactions in solution and in the solid state is reported.

Metal-cation$-\pi$ interactions have been a topic of much interest in the past decade.[1-5] $Ag^+-\pi$ interactions[6] in particular are one of the most extensively studied topics in the areas of supramolecular chemistry,[7,8] molecular sensors,[9,10] and functional materials.[11] Many studies have reported $Ag^+-\pi$ interactions in the solid state. A few groups have reported the structures of Ag^+ complexes with $Ag^+-\pi$ interactions in solution, using ^1H NMR spectroscopy.[9]

It is well-known that cyclic polyamines such as cyclen and cyclam form stable complexes with heavy-metal ions.[12] When aromatic rings are introduced into the cyclic polyamines, it is possible to make a new type of host compound in which the aromatic side arms can interact with the Ag^+ ions incorporated in the macrocycles by $Ag^+-\pi$ interactions between the Ag^+ ions and the aromatic side arms. Recently, we reported that two aromatic side arms of a tetra-armed cyclam bearing 3′,5′-difluorobenzyl groups (**1**) interact with the Ag^+ ions incorporated in the cyclam moiety in the solid state.[13] In the X-ray structure of the Ag^+ complex with **1**, the Ag^+ ion is buried in the cyclam ring. Gyr et al. reported that[14] an Ag^+ ion incorporated in tetrakis(2-methysulfanylethyl)cyclen is exposed on the surface of the cyclen ring (see Figure S1 in the Supporting Information (SI)). The diameter of the cavity of cyclen, which is a 12-membered ring, is smaller than that of cyclam, which is a 14-membered ring. These results prompted us to focus on tetra-armed cyclens bearing aromatic side arms. We expected that stronger interactions between the Ag^+ ion incorporated in the cyclen unit and the aromatic side arms would be observed in solution and in the solid state. In addition, if our presumption is correct, we would be able to make a supramolecular system with novel functions.

Here we report conformational changes in Ag^+ complexes with tetra-armed cyclens bearing aromatic side arms, which we have named "argentivorous molecules",

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in solution and in the solid state. Tetra-armed cyclens (**2a**–**2b**, **5a**–**5f**, and **6**, Figure 1) bearing benzyl groups were prepared by reductive amination of cyclen with aromatic aldehydes in the presence of $NaBH(OAc)_3$. We also prepared cyclic triamine analogs (**3**) and an armed cyclen bearing 2-phenylethyl groups as side arms (**4**) (see the SI).

Titration experiments using UV–vis spectra were carried out to confirm the Ag^+–π interactions in solution. Figure S4(2a) shows the Ag^+-ion-induced UV–vis spectral changes of **2a**. An increase in the absorbance at λ_{max} (260 nm), without any absorption wavelength shift, was observed upon the addition of Ag^+ ions. An inflection point was observed at 1.0 (= $[Ag^+]/[\mathbf{2a}]$), showing a 1:1 complex. From the UV–vis spectral data, the log K value of the complex was estimated to be ca. 6.8.[15] When Ag^+ ions were added to a mixture of cyclen and *m*-difluorobenzene (= 1/4) (see Figure S4(mix-Ag)), no spectral changes were observed. Similar spectral changes were observed in Ag^+ complexes with calixarene derivatives, reported by Ho[9c] and Prodi.[10b] This result strongly supports Ag^+–π interactions between the aromatic side arms and the Ag^+ ions in solution.

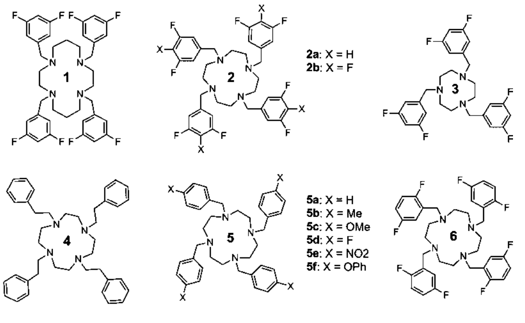

Figure 1. Structures of tetra-armed cyclens and analogs.

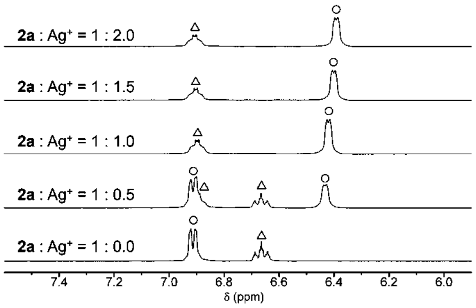

Figure 2. Ag^+-ion-induced ^1H NMR shift changes of **2a** (aromatic region) in a mixture of CD_2Cl_2 and CD_3OD (0.75 mL/0.02 mL). As the intensities of the doublet at δ 6.4 ppm and the triplet at δ 6.9 ppm increase, the intensities of the doublet at δ 6.9 ppm and the triplet at δ 6.65 ppm decrease. The exchange rate of the complex and the metal-free ligand would be slower than the NMR time scale under the conditions used because the cyclen units bind Ag^+ ions strongly.

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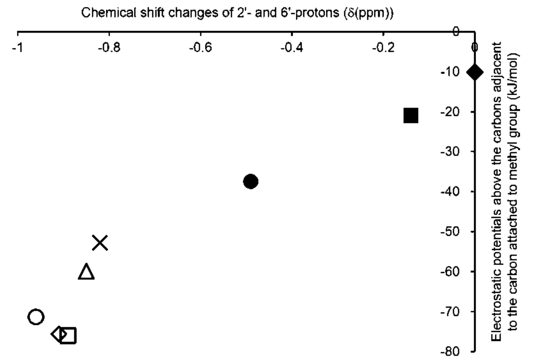

Figure 3. Correlation of Ag^+-ion-induced chemical shift changes of the protons at the 2′- and 6′-positions of the side arms, and the electrostatic potentials of the corresponding substituted benzenes. **2a** (●), **2b** (■), **5a** (○), **5b** (◇), **5c** (□), **5d** (×), **5e** (◆), and **5f** (△).

To examine the structure of the Ag^+ complex with **2a** in solution, titration experiments using ^1H NMR were carried out in a mixture of CD_2Cl_2 and CD_3OD. The signals of the protons at the 2′- and 6′-positions in the aromatic rings appear as a doublet (J_{HF} = 7.0 Hz) coupled with the next F-atom at δ 6.9 ppm. As shown in Figure 2, unusual higher-field shifts (−0.49 ppm) of the protons at the 2′- and 6′-positions were observed upon addition of equimolar amounts of Ag^+ ions. When **2b**, which has 3′,4′,5′-trifluorobenzyl groups, was used as a ligand, the protons at the 2′- and 6′-positions shifted to higher field by ca. −0.14 ppm (see Figure S5(2b-Ag)). The addition of Li^+, Na^+, Mg^{2+}, and Ca^{2+} ions to **2a** did not give significant chemical shift changes of the corresponding protons (see Figures S5-(2a-Li)−S5(2a-Ca)). In the case of Hg^{2+} ions, the protons at the 2′- and 6′-positions were not shifted, although the 4′-position protons of the aromatic rings shifted to lower field (see Figure S5(2a-Hg)). The titration experiments suggest that (i) the stoichiometry between the ligands and Ag^+ ions is 1:1, (ii) the chemical shift changes vary, depending on the number of F-atoms on the aromatic rings, and (iii) the chemical shift changes to higher field of the protons at the 2′- and 6′-positions do not occur in the case of alkali-metal, alkaline-earth-metal, and Hg^{2+} ions. To study the ring-size effect on the Ag^+-ion-induced chemical shift changes, titration experiments were carried out using **1** and **3**. Chemical shift changes to lower field were observed upon the addition of equimolar amounts of Ag^+ ions (see Figures S5(1-Ag) and S5(3-Ag)). In addition, **4**, bearing 2-phenylethyl groups as side arms, also showed chemical shift changes to lower field (see Figure S5(4-Ag)). These results indicate that the significant chemical shift changes of the protons at the 2′- and 6′-positions occur only in the tetra-armed cyclens with benzyl groups as side-arms. Arya,[9a] Choi,[9b] and Kimura[9e] have reported $Ag^+-\pi$ interactions with crown ethers or calixarenes bearing alkynic, aromatic, or alkenic side arms in solution. They reported that the signals from the alkynic, aromatic, and alkenic protons connected to carbons that interacted with Ag^+ ions shifted to lower field. However, in our case, the chemical shifts of the aromatic protons connect to carbons that interacted with Ag^+ ions shifted to higher field.

To see if the substituents on the aromatic side arms affect the chemical shift changes of the protons at the 2′- and 6′-positions, ^1H NMR titration experiments were carried out using **5a**−**5f** (see Figures S5(5a-Ag)−S5(5f-Ag)). Figure 3 shows the correlation between the chemical shift changes of the protons at the 2′- and 6′-positions and the electrostatic potentials of the corresponding substituted benzenes. The electrostatic potential is defined as the energy of interaction of a positive point charge with the nuclei and electrons of a molecule, and the value of the electrostatic potential correlates with the electron densities on the aromatic rings. Figure S7 shows electrostatic potential maps of the side arm components of **2a**, **2b**, and **5a**−**5f**.[16,17] As we expected, when the substituents on the aromatic side arms are electron-donating groups, significant chemical shift changes to higher field (−0.82 to −0.96 ppm) were observed. In contrast, small or no chemical shift changes were observed for the protons at the 2′- and 6′-positions with electron-withdrawing groups. These results indicate that the protons at the 2′- and 6′-positions are

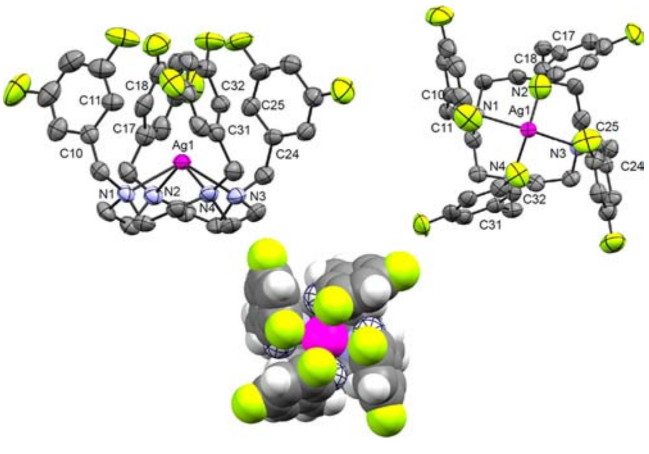

Figure 4. Side view (top left) and top view (top right) of the ORTEP diagrams (hydrogens and anions omitted) and space-filling diagram (bottom) of the X-ray structure of $AgCF_3SO_3$ complex with **2a**. The protons at the 2′-/6′-positions (meshed) are located in the shielded area in the next benzene.[18]

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(15) See SI for the log*K* values of **2a** for Hg^{2+}, Cu^{2+}, and Zn^{2+} ions. Although the log*K* values for these metal ions are higher than that for Ag^+ ion, conformational changes of the side-arms are observed only when Ag^+ ion was added.

located in the shielded area of the next aromatic side arm in solution.

X-ray crystallography was performed on the Ag$^+$ complexes with **2a** and **5a**–**5f** (see Figures S6(2a-Ag)–S6-(5f-Ag)). Figure 4 shows the X-ray structure of the AgCF$_3$SO$_3$ complex with **2a**. The Ag$^+$ ion is four-coordinated by the four ring N-atoms. Interestingly, the four aromatic rings cover the Ag$^+$ ion incorporated in the cyclen moiety, with the aromatic ring "petals" catching the Ag$^+$ ions in the same way as an insectivorous plant (Venus flytrap) catches insects. The N1–Ag1, N2–Ag1, N3–Ag1, and N4–Ag1 bond distances are in the range 2.408–2.497 (average 2.447) Å; the C10–Ag1, C17–Ag1, C24–Ag, and C31–Ag1 distances are in the range 3.499–3.631 (average 3.555) Å; and the C11–Ag1, C18–Ag1, C25–Ag, and C32–Ag1 distances are in the range 3.234–3.574 (average 3.405) Å. The distances are comparable with those of anthracene-cryptand–Ag$^+$ and anthracene-diphosphine–Ag$^+$ systems.[8] The X-ray structure suggests that the Ag$^+$ ions interact with the aromatic side arms with η^2-hapticity. The X-ray structure strongly supports the higher-field shift of the protons at the 2′- and 6′-positions (meshed protons in Figure 4). It is important to note that the 4′-nitrobenzyl side arms of **5e** also cover the Ag$^+$ ions in the solid state (see Figure S6(5e-Ag)), although no chemical shift changes of the protons at the 2′- and 6′-positions were observed in the ^{1}H NMR titration (see Figure S4(5e-Ag)). This means that the Ag$^+$–π interaction occurs even if the electron density on the aromatic rings is very low. Several groups have reported the X-ray structures of Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} complexes with tetra-armed cyclens.[19] Aromatic side arms in the complexes with armed cyclens, however, never cover the metal ions incorporated in the cyclen unit. We named the tetra-armed cyclens bearing aromatic side arms argentivorous molecules.

To visualize the Ag$^+$–π interactions, the isosurfaces of the LUMO of the Ag$^+$ complexes were calculated using the B3LYP/3-21G(*) theoretical level.[16] Figure 5 shows the LUMO of the X-ray structure and the virtual structure of the **5a**/Ag$^+$ complex (see Figure S8 for LUMOs of the Ag$^+$ complexes with **2a** and **5a**–**5f**, and Figure S9 for LUMOs and HOMOs of the Ag$^+$ complexes with **2a** and **5a**–**5f**). In the X-ray structure, the LUMO of the Ag$^+$ ion is distorted by interaction with the HOMOs of the aromatic rings. In contrast, the LUMO of the Ag$^+$ ion in the virtual structure without any interaction with aromatic side arms is a sphere-shaped orbital. These graphics clearly support Ag$^+$–π interactions between the Ag$^+$ ion and the aromatic side arms.

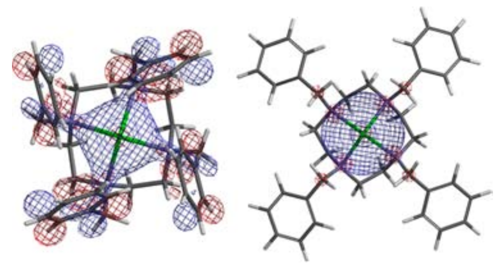

Figure 5. Isosurfaces (at 0.032 au) of the LUMO of the X-ray structure (left) and the virtual structure (right) of **5a** from the B3LYP/3-21G(*) calculation.

In conclusion, we have demonstrated that tetra-armed cyclens with aromatic side arms behave similarly to an insectivorous plant (Venus flytrap) when they form Ag$^+$ complexes. We confirmed that the conformational changes are the result of Ag$^+$–π interactions between the Ag$^+$ ions and the side arms in solution and in the solid state. Investigation of functionalized compounds using the unique conformational changes of the argentivorous molecules is now in progress.

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Supporting Information Available. Experimental procedures and physicochemical properties, titration experiments, X-ray structures, and molecular calculations (PDF). Crystallographic data of ligands and complexes (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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