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Article

Crown Bowl: Metallocyclophane by Self-Assembly of 4′-Pyridylmethyl-Armed 12-Crown-4 Ethers with Ag^+ Ions

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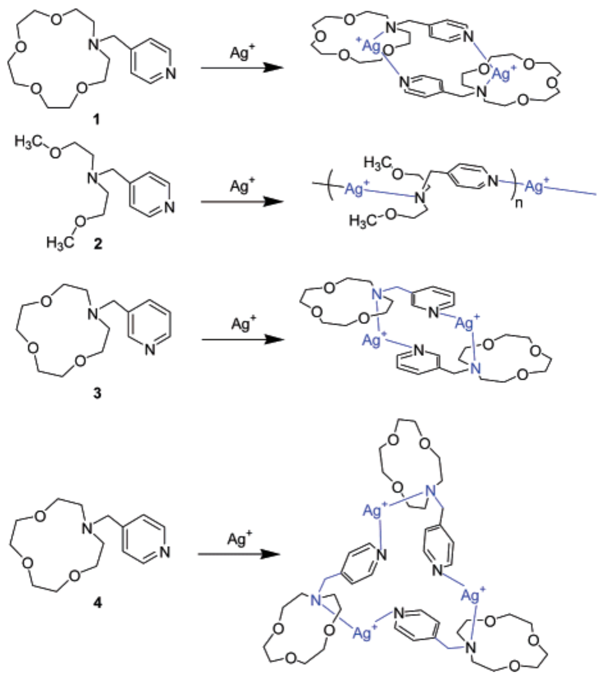
New 3′-pyridylmethyl- and 4′-pyridylmethyl-armed monoaza-12-crown-4 ethers were prepared by the reductive amination of monoaza-12-crown-4 with the appropriate pyridinecarbaldehyde in the presence of $NaBH(OAc)_3$. X-ray crystallography, cold electrospray ionization mass spectrometry, and ^1H NMR titration experiments show that Ag^+ complexes with 3′-pyridylmethyl- and 4′-pyridylmethyl-armed monoaza-12-crown-4 ethers are dimetallo[3.3]-metacyclophane and trimetallo[3.3.3]paracyclophane, respectively (crown bowl). The structure of the metallocyclophanes can be controlled by the positions of the N atoms in the pyridine side arms and the ring size of the crown moiety.

Introduction

Construction of supramolecular networks and discrete systems by treating pyridine-containing flexible ligands with Ag^+ ions has become the focus of intense interest.[1] The goal of this research is to control the shapes and sizes of the formed supramolecular structures as well as their chemical and physical properties. During our research efforts on the development of Ag^+-selective macrocyclic ligands, we have found that a complex of monoaza-15-crown-5 ether having a 4′-pyridylmethyl group (**1**) with Ag^+ formed a [3.3]-paracyclophane-like complex, while an open-chain analogue (**2**) of the ligand formed a coordination polymer with Ag^+ ions.[2] These results indicate that the crown ether moiety is necessary to form the cyclophane structure and that the ring members of the crown ether may affect the structure of the metallocyclophane. Here, we report structures of a dimetallo-[3.3]metacyclophane and trimetallo[3.3.3]paracyclophane (crown bowl) by treating 3′-pyridylmethyl- (**3**) and 4′-pyridylmethyl-armed monoaza-12-crown-4 (**4**) with Ag^+ ions, respectively.



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Experimental Section

Melting points were obtained with a Mel-Temp capillary apparatus and not corrected. Fast atom bombardment mass spectrometry (FAB-MS) was performed using a JEOL 600 H spectrometer. ^{1}H NMR spectra were measured in $CDCl_3$ on a JEOL ECP400 (400 MHz) spectrometer. Cold electrospray ionization mass spectrometry (ESIMS) spectra were recorded on a JEOL JMS-T100CS spectrometer.

Preparation of Pyridylmethylmonoaza-12-crown-4 Ethers. *N*-3′-Pyridylmethylmonoaza-12-crown-4 (3). Sodium borohydride triacetate [$NaBH(OAc)_3$; 0.248 g, 1.09 mmol] was added to a mixture of monoaza-12-crown-4 (0.200 g, 1.0 mmol) and 3-pyridinecarbaldehyde (0.214 g, 2.0 mmol) in 1,2-dichloroethane (25 mL) under an Ar atmosphere. The mixture was stirred for 3 days at room temperature under 1 MPa of pressure (Ar atmosphere). The reaction was quenched by adding aqueous saturated $NaHCO_3$, and the product was extracted with $CHCl_3$ (30 mL × 3). The combined extract was dried ($NaHCO_3$), and the solvent was evaporated under reduced pressure. The residue was purified by gel permeation column chromatography, and the ligand was obtained in 48% as a hygroscopic yellow oil. ^{1}H NMR ($CDCl_3$): δ 8.55 (s, 1H), 8.49 (d, $J = 4.9$ Hz, 1H), 7.75 (d, $J = 3.8$ Hz, 1H), 7.22−7.28 (m, 1H), 3.61−3.74 (m, 14H), 2.74 (t, $J = 4.9$ Hz, 4H). FAB-MS (*m*/*z*) (matrix: *m*-NBA): 266 ([M + 1]$^+$, 100%). Anal. Calcd for $C_{14}H_{22}N_2O_3 \cdot {}^1/_3H_2O$: C, 61.74; H, 8.39; N, 10.29. Found: C, 61.57; H, 8.17; N, 10.03.

***N*-4′-Pyridylmethylmonoaza-12-crown-4 (4).** Sodium borohydride triacetate [$NaBH(OAc)_3$; 0.248 g, 1.09 mmol] was added to a mixture of monoaza-12-crown-4 (0.200 g, 1.0 mmol) and 4-pyridinecarbaldehyde (0.214 g, 2.0 mmol) in 1,2-dichloroethane (25 mL) under an Ar atmosphere. The mixture was stirred for 3 days at room temperature under 1 MPa of pressure (Ar atmosphere). The reaction was quenched by adding aqueous saturated $NaHCO_3$, and the product was extracted with $CHCl_3$ (30 mL × 3). The combined extract was dried ($NaHCO_3$), and the solvent was evaporated under reduced pressure. The residue was purified by gel permeation column chromatography. The main fraction was recrystallized from hexane to give ligand **4** in 36%. Mp: 54.0−55.9 °C. ^{1}H NMR ($CDCl_3$): δ 8.53 (d, $J = 5.9$ Hz, 2H), 7.37 (d, $J = 5.9$ Hz, 2H), 3.64−3.73 (m, 14H), 2.78 (t, $J = 4.8$ Hz, 4H). FAB-MS (*m*/*z*) (matrix: *m*-NBA): 266 ([M + 1]$^+$, 100%). Anal. Calcd for $C_{14}H_{22}N_2O_3$: C, 63.14; H, 8.27; N, 10.52. Found: C, 62.99; H, 8.46; N, 10.43.

Preparation of AgOTf Complexes. Ligand **3** or **4** (0.01 mmol) in acetonitrile (1.0 mL) was treated with AgOTf (0.01 mmol) in methanol (1.0 mL) to give the Ag complexes quantitatively.

3−AgOTf. Mp: >150 °C (dec). Anal. Calcd for $C_{15}H_{22}N_2O_6F_3SAg$: C, 34.43; H, 4.24; N, 5.35. Found: C, 34.44; H, 4.57; N, 5.23.

4−AgOTf. Mp: >165 °C (dec). Anal. Calcd for $C_{15}H_{22}N_2O_6F_3SAg \cdot {}^1/_2H_2O$: C, 33.85; H, 4.36; N, 5.26. Found: C, 33.75; H, 4.42; N, 5.27.

^{1}H NMR Titration Experiments. Titration experiments were carried out at 298 K by the addition of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 3.0, and 5.0 equiv of silver triflate to the armed crown ethers (1.0×10^{-2} mmol) in CD_2Cl_2/CD_3OD (1:1, 0.65 mL).

X-ray Structure Determination. The crystals of AgOTf complexes with **3** and **4** were mounted on the top of a glass fiber. All measurements of **3**−AgOTf were made at 298 K on a Rigaku AFC5S four-circle diffractometer with graphite-monochromated Mo Kα radiation (0.710 69 Å) and a 12-kW rotating-anode generator. Cell contacts and an orientation matrix for data collection were obtained from a least-squares refinement. The data were collected using the $\omega-2\theta$ scan technique to an above maximum 2θ value of 55.0°. All intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SIR 92).[3] The non-hydrogen atoms were refined anisotropically. The coordinates of all hydrogen atoms were calculated at ideal positions and were refined. Neutral atom scattering factors were taken from Cromer and Weber.[4] Anomalous dispersion effects were included in F_c;[5] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[6] The values for the mass attenuation coefficients were those of Creagh and Hubbell.[7] All calculations were made using the TEXSAN crystallographic software package of Molecular Structure Corp.[8] The data collections of **4**−AgOTf were carried out on a Bruker SMART CCD area diffractometer at 90 K. Data were corrected for Lorentz and polarization effects, and absorption corrections were applied with the SADABS program. Structures were solved by direct methods and subsequent difference Fourier syntheses using the program SHELEX. All non-hydrogen atoms were refined anisotropically, and H atoms were placed at calculated positions and thereafter refined with $U_{iso}(H) = 1.2U_{eq}(C)$. The crystallographic refinement parameters of complexes **3**−AgOTf and **4**−AgOTf are summarized in Table 1, while the selective bond distances and angles of these complexes are listed in Tables 2 and 3.

Table 1. Crystal Data and Refinement Parameters for Complexes **3**−AgOTf and **4**−AgOTf

compound	**3**−AgOTf	**4**−AgOTf
formula	$C_{15}H_{22}N_2O_6SF_3Ag$	$C_{92}H_{132}N_{12}O_{43}S_6F_{18}Ag_6$
fw	523.27	3275.74
T/K	298	90
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a/Å	10.731(2)	12.6204(10)
b/Å	11.945(2)	16.1678(13)
c/Å	8.406(2)	18.0139(14)
α/deg	110.32(1)	66.1490(10)
β/deg	103.27(2)	74.902(2)
γ/deg	78.20(2)	72.695(2)
U/Å^3	974.2(3)	70.120(2)
Z	2	2
D_c/(g cm^{-3})	1.784	1.738
μ/mm^{-1}	1.201	1.133
reflns collcd	4707	22045
unique reflns, R_{int}	4467, 0.009	14225, 0.0260
R_F[a]	0.038 [3692; $I > 2\sigma(I)$]	0.0332 [12584; $I > 2\sigma(I)$]
R_F, $R_w(F^2)$ (all data)[a]	0.062, 0.116	0.0389, 0.0996
GOF	1.54	1.089
T_{min}, T_{max}	0.69, −0.47	1.414, −0.579

[a] $R_F = \Sigma||F_o - F_c||/\Sigma|F_o|$. $R_w(F^2) = [\Sigma w|F_o^2 - F_c^2|^2/\Sigma w]F_o^4)]^{1/2}$.

Results and Discussion

New armed monoaza-12-crown-4 ethers were prepared by treating monoaza-12-crown-4 with the appropriate pyridine-

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Table 2. Selective Bond Distances (Å) and Angles (deg) for **3**−AgOTf

Ag1−N1	2.319(3)	N2−Ag1−N1′	153.0(1)
Ag1−N2	2.184(3)	Ag1−N1−C9	110.2(2)
Ag1−O1	2.593 (9)	N1−C9−C10	113.3(3)
Ag1−O2	2.834 (9)	N1−Ag1−N2	153.0(1)
Ag1−O3	2.518(9)		

Table 3. Selective Bond Distances (Å) and Angles (deg) for **4**−AgOTf

Ag1−N6	2.177(2)	N6−Ag1−N1	161.45(9)
Ag1−N1	2.267(2)	N2−Ag2−N3	161.89(8)
Ag2−N2	2.195(2)	N4−Ag3−N5	165.27(9)
Ag2−N3	2.302(2)	C23−N3−Ag2	111.84(16)
Ag3−N4	2.182(2)	C37−N5−Ag3	112.24(17)
Ag3−N5	2.246(2)	C9−N1−Ag1	112.23(16)
Ag1−O1	2.628(2)		
Ag1−O2	2.771(2)		
Ag1−O3	2.553(2)		
Ag2−O4	2.604(2)		
Ag2−O5	2.754(2)		
Ag2−O6	2.5293(19)		
Ag3−O7	2.619(2)		
Ag3−O9	2.623(2)		
Ag3−O8	2.692(2)		

carbaldehydes in the presence of $NaBH(OAc)_3$ in 1,2-dichloroethane under 1 MPa (Ar atmosphere).[9] Ligands **3** and **4** were treated with equimolar amounts of AgOTf in CH_3CN/MeOH to give silver triflate complexes **3**−AgOTf and **4**−AgOTf in quantitative yields, respectively.

The structures of **3**−AgOTf and **4**−AgOTf complexes have been determined by X-ray crystallography. Figure 1 shows the ORTEP diagram of **3**−AgOTf. The **3**−AgOTf complex forms a dimetallo[3.3]metacyclophane structure where two pyridine units are bridged by the C10−N1−Ag1* and C10*−N1*−Ag1 atoms. In this complex, the Ag^+ ion is two-coordinated by the ring N and the pyridine N atoms of the nearest-neighbor molecule. The Ag1*−N1(ring N) and Ag1*−N2*(pyridine N) bond distances are 2.319 and 2.184 Å, respectively. The Ag1*···O1, Ag1*···O2, and Ag1*···O3 distances are 2.518, 2.834, and 2.594 Å, respectively. These distances suggest weak Ag1*···O1 and Ag1*···O3 interactions and no Ag1*···O2 interaction.

On the other hand, the **4**−AgOTf complex forms a trimetallo[3.3.3]paracyclophane structure where three pyridine units are bridged by the Ag1−N1−C10, Ag2−N3−C23, and Ag3−N5−C37 atoms (Figure 2). The Ag(1−3)−ring N(1, 3, and 5) and Ag(1−3)−pyridine N(2, 4, and 6) bond distances are in the ranges of 2.25−2.30 and 2.18−2.20 Å, respectively. The Ag···ring O distances are in the range of 2.53−2.77 Å. These distances suggest weak Ag···ring O interactions as in the **3**−AgOTf complex. The cyclophane has a bowl-shaped cavity (Figure 3)l; therefore, it is expected that the complex can be used for recognition of neutral or ionic guest molecules.

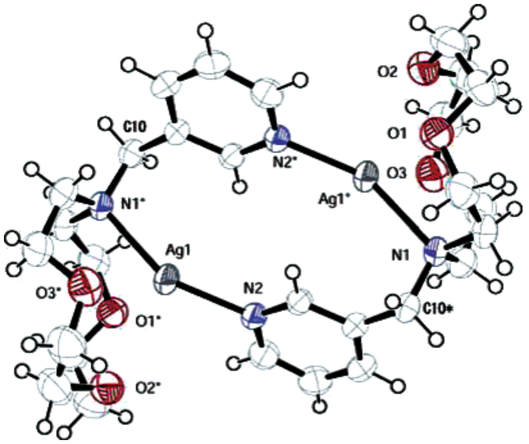

Figure 1. ORTEP diagram of the **3**−AgOTf complex. Triflate anions are omitted.

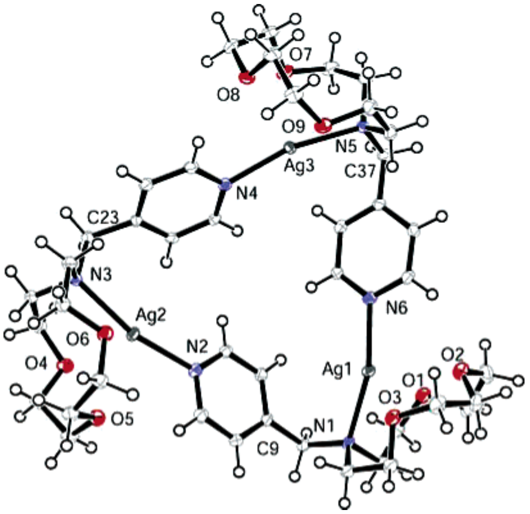

Figure 2. ORTEP diagram of the **4**−AgOTf complex. Triflate anions are omitted.

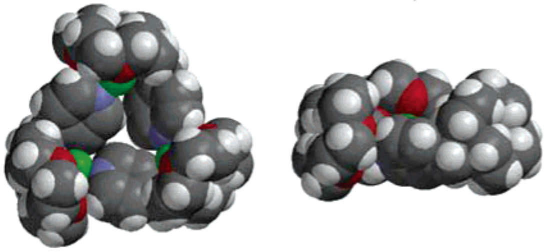

Figure 3. Side and top views of the **4**−AgOTf complex.

Stoichiometry of the interaction of Ag^+ with both ligands was investigated by cold ESIMS. Figure 4 shows observed ion peaks of **3**−AgOTf (a) and **4**−AgOTf (b) complexes (0.001 mol/L in methanol; nitrogen as a nebulizer gas; nebulizer gas temperature = −30 °C) and the theoretical ion distributions (c). In the cold ESIMS spectral data of the **3**−AgOTf complex, which forms a dimer, ion peaks for [**3** + Ag−H]$^+$, [**3** + 2Ag + CF_3SO_3 − H]$^+$, [2**3** + Ag−H]$^+$, [2**3** + 2Ag + CF_3SO_3 − 2H]$^+$, and [2**3** + 4Ag + 3CF_3SO_3 − 3H]$^+$ were observed with the correct theoretical ion distributions (parts a and c of Figure 4), while ion peaks for [3**3** + 3Ag + 2CF_3SO_3 − 3H]$^+$ were not observed. On the other hand, ion peaks for [**4** + Ag − H]$^+$, [**4** + 2Ag + CF_3SO_3 − H]$^+$, [2**4** + Ag − H]$^+$, [2**4** + 2Ag + CF_3SO_3 − 2H]$^+$, [2**4** + 4Ag + 3CF_3SO_3 − 3H]$^+$, and [3**3** + 3Ag + 2CF_3SO_3 − 3H]$^+$ were observed in the **4**−AgOTf complex, which forms a trimer (parts b and c of Figure 4), and those ion peak patterns agree with the theoretical ion distributions. These cold ESIMS data support the fact that ligands **3** and **4** form 2:2 and 3:3 complexes, respectively.

To obtain solution structural information, an Ag^+-induced ^1H NMR titration experiment was carried out in CD_2Cl_2/

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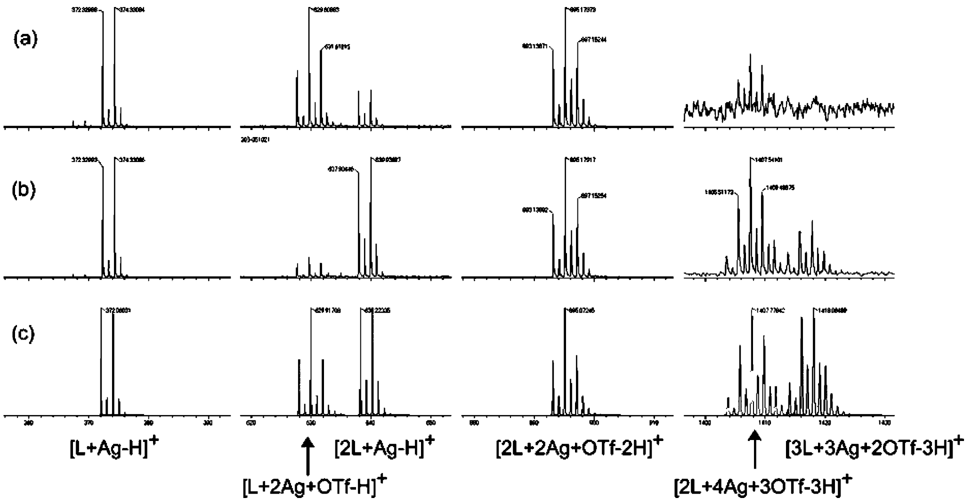

Figure 4. Observed ion peaks of the **3**−AgOTf (a) and **4**−AgOTf (b) complexes and the theoretical ion distributions (c).

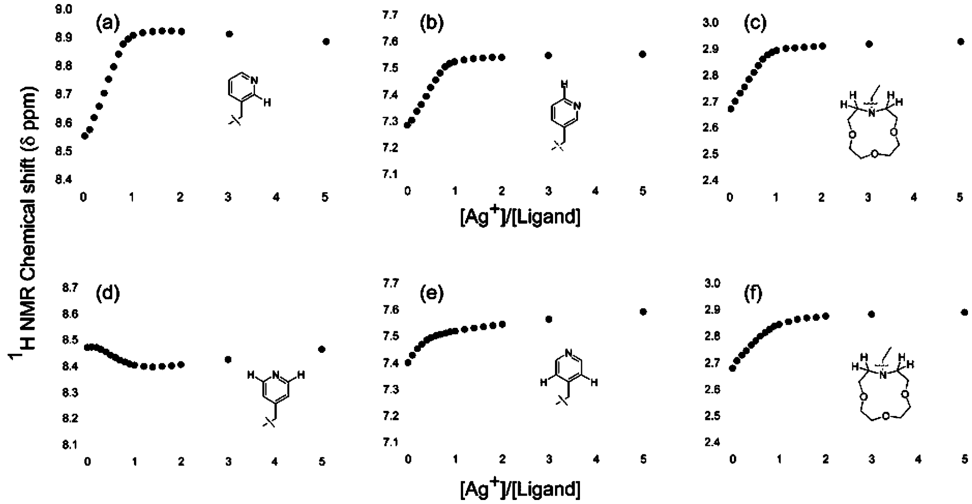

Figure 5. Ag^+-induced ^1H NMR spectral changes of ligands **3** (a−c) and **4** (d−f).

CD_3OD (1:1). Parts a−f of Figure 5 show the Ag^+-induced ^1H NMR shift changes of the pyridine and crown ring protons in ligands **3** (parts a−c of Figure 5) and **4** (parts d−f of Figure 5). These titration curves, except the pyridine protons at positions 3′ and 5′ of ligand **4**, have an inflection point at $[Ag^+]/[ligand] = 1.0$, indicating that the stoichiometry of the interaction of Ag^+ and both ligands is 1:1 in CD_2Cl_2/CD_3OD (1:1). The crystallographic data of **3**−AgOTf (Figure 1) indicate that the signal for the proton at the 2′ position of the pyridine ring would shift to a lower field in the ^1H NMR spectrum because of ring current effects of the pyridine ring on the side arm. As expected, the signals for the protons at the 2′ and 6′ positions in ligand **3** shifted to lower field by about 0.35 and 0.1 ppm, respectively, when 1.0 equiv of AgOTf was added (parts a and b of Figure 5). The signal for the crown ring protons next to the N atoms shifted to lower field by 0.22 ppm (Figure 5c). On the other hand, the signal for the pyridine protons at positions 2′ and 6′ (Figure 5d) and 3′ and 5′ (Figure 5e) of ligand **4** shifted to lower and higher fields by about 0.1 ppm, respectively. The crown ring protons next to the N atoms shifted to lower fields by about 0.17 ppm (Figure 5f). The crystallographic data of **4**−AgOTf (Figures 2 and 3) showed that the three pyridine rings form a bowl-like structure and the pyridine rings are separated from each other. Therefore, the ring currents of the pyridine rings have little effect on chemical shift changes. In addition, the pyridine protons of the **4**−AgOTf system showed complicated curves: (i) the signals at positions 2′ and 6′ shift to higher field by about 0.07 ppm until 1:1 ($[Ag^+]/[ligand]$) and then shift to lower field (Figure 5d) and (ii) the titration curve of the pyridine protons at positions 3′ and 5′ has an inflection point at $[Ag^+]/[ligand] = 0.5$ (Figure 5e). When **4**−AgOTf forms a trimer, the complex has a bowl-like cavity as described above. Therefore, it is reasonable to assume that some interactions between the pyridine rings and excess Ag^+ ions and/or triflate anions would affect the chemical shift of the pyridine protons to give the complicated titration curves. The considerable difference in chemical shift changes lends support that **3**−AgOTf and **4**−AgOTf complexes form a dimer and trimer in CD_2Cl_2/CD_3OD (1:1), respectively.

In conclusion, we have demonstrated that Ag^+ complexes with **3** and **4** form dimetallo[3.3]metacyclophane and trimetallo[3.3.3]paracyclophane structures, respectively. These results indicate that the structure of the metallocyclophanes formed by treating pyridylmethyl-armed monoazacrown ethers with Ag^+ ions can be controlled by both the positions of the N atoms in the pyridine side arms and the ring size of the crown ether. Molecular recognition studies by these metallocyclophanes are now in progress.

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Supporting Information Available: X-ray data (CIF format) of **3**−AgOTf and **4**−AgOTf. This material is available free of charge via the Internet at http://pubs.acs.org.

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