DALTON COMMUNICATION

A [3.3]paracyclophane-like silver complex with 4′-pyridylmethyl-armed monoaza 15-crown-5 ether

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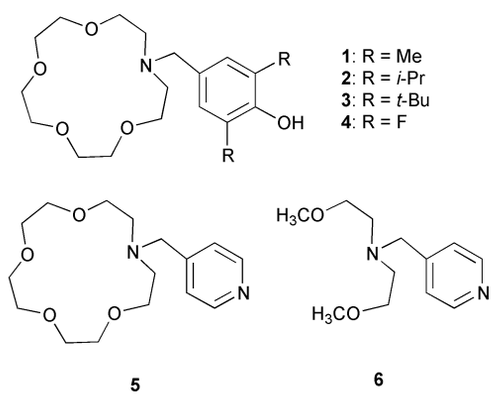
4′-Pyridylmethyl-armed monoaza-15-crown-5 ether forms a [3.3]paracyclophane-like 2 : 2 complex with AgOTf both in the solid state and in solution, while bis(2-methoxyethyl)-4′-pyridylmethylamine forms a linear polymer with AgOTf.

Increasing attention has been focused on the polymer-like complexes of ligand–Ag^+ systems.[1–6] Since Ag^+ has various coordination modes, the ligand–Ag^+ complexes have supramolecular structures with one-, two- or three-dimensional polymeric frameworks. We have reported the molecular structure of alkali metal complexes with armed-monoaza-crown ethers, **1**–**4** (see Scheme 1), having 3′,5′-disubstituted-4′-



Scheme 1

hydroxybenzyl groups (alkyl = Me, *i*-Pr, *t*-Bu and F).[7] To further investigate the effects of metal cations on the structures of polymer-like complexes, the preparation of Ag^+ complexes with these ligands has been attempted. However, the phenol moiety in those ligands decomposed when mixed with Ag^+, and no crystals could be obtained. Since the pyridine N atom has a great affinity toward Ag^+,[8] we have prepared a new armed-azacrown ether having a 4′-pyridylmethyl group in the side arm (**5**). We expected that ligand **5** would form not only polymer-like complexes with alkali metal cations,† but would also form a new type of complex with heavy metal cations. Here, we report a [3.3]paracyclophane-like 2 : 2 complex of ligand **5** with Ag^+ ions.

The new pyridine armed-azacrown ether **5**‡ was prepared by the reductive amination of monoaza-15-crown-5 with 4-pyridinecarbaldehyde in the presence of sodium borohydridetriacetate in 1,2-dichloroethane by the method previously reported.[9] A silver triflate complex of ligand **5**, **5**–AgOTf, was obtained (host : guest ratio = 1 : 1) as dark brown crystals.§ The structure of **5**–AgOTf has been determined by single crystal X-ray analysis.¶ As shown in Fig. 1, the Ag^+ cation in **5**–AgOTf is three-coordinated by the ring N atom (N1), the ring O atom (O4), and the pyridine N atom (N2*) of the nearest-neighbor molecule. The triflate anion does not coordinate to Ag^+. The Ag1–N1, Ag1–N2*, and Ag1–O4 bond lengths

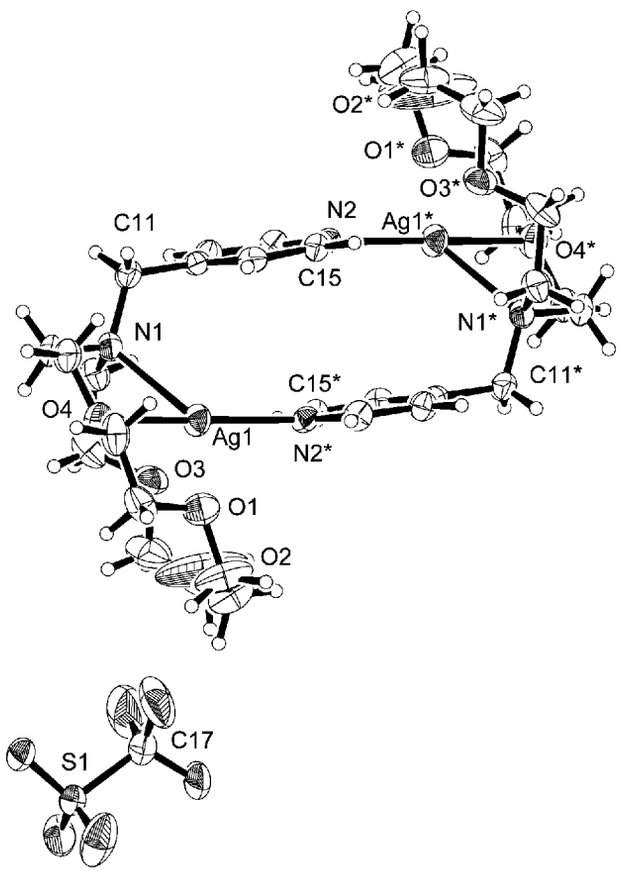


Fig. 1 An ORTEP diagram of the **5**–AgOTf complex.

are 2.507(4), 2.238(4), and 2.435(4) Å, respectively. The Ag–N(1 and 2*) and Ag–O4 bond lengths are comparable with those of the Ag^+ complexes of the pyridine-containing ligands and the lariat monoaza-15-crown-5 ethers.[1–3] The Ag1···O1, Ag1···O2, and Ag1···O3 distances are 2.623(4), 2.975(6), and 2.797(4) Å, respectively. These distances suggest weak Ag1···O1 and Ag1···O3 interaction and no Ag1···O2 interaction. The big thermal ellipsoid for the O2 atom also suggests that this ring oxygen does not coordinate to the Ag^+ cation. Interestingly, the complex is a 2 : 2 complex with the two pyridine units bridged by the Ag1–N1–C11 and Ag1*–N1*–C11* atoms. Fig. 1 also suggests that the pyridine rings are slightly overlapped at the C15 carbon. The two pyridine rings are parallel, and the distance between them is about 3.32 Å (C15–C15*). This value is similar to that obtained for Hartshorn and Steel's dimetalloparacyclophane.[10] Thus, the partial structure of the **5**–AgOTf complex is in the form of a [3.3]paracyclophane-like structure.

In order to investigate the role of the crown ether ring in the paracyclophane structure, ligand **6**‖ was prepared by reductive

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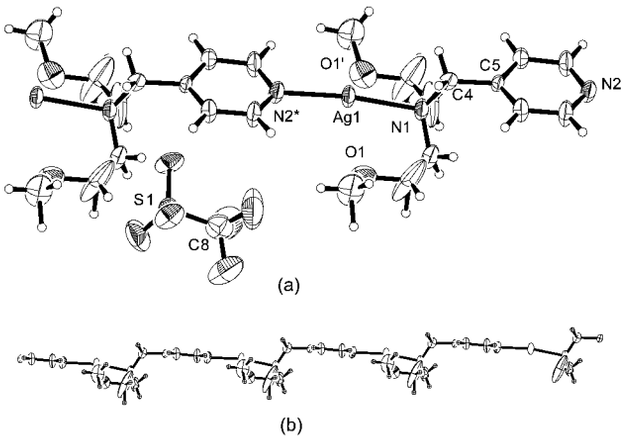

Fig. 2 ORTEP diagrams of the **6**–AgOTf complex (a) and a view along the *b* axis (b).

amination of bis(2-methoxyethyl)amine with 4-pyridinecarbaldehyde. Ligand **6** is a compound where a $–CH_2OCH_2$-$CH_2OCH_2–$ unit has been removed from the monoazacrown ether ring portion of the cyclic ligand **5**. It is well known that Ag^+ favors a linear two-coordinate system when associated with monodentate ligands, while it is hard to form two-coordinate complexes when chelating ligands are used.[11] We expected that ligand **6**, which is a chelating ligand, would form a [3.3]-paracyclophane-like complex such as **5**–AgOTf. However, ligand **6** formed a linear polymer-like complex with AgOTf. Figs. 2a and 2b show the ORTEP[12] diagram of the **6**–AgOTf complex.§ Ag^+ is two-coordinated by the aliphatic nitrogen atom (N1) and the pyridine nitrogen atom (N2*) in the side arm of the nearest-neighbor molecule to give a linear polymer-like complex (Fig. 2b). The Ag1–N1 and Ag1–N2* (or Ag1*–N2) bond lengths are 2.29(1) and 2.20(1) Å, respectively. The Ag1 · · · O1 distance is 2.633(9) Å, and suggests a weak interaction between Ag1 and O1 (O1′) atoms. The Ag^+ cation, the ligand and also the anion lie on planes of symmetry in the crystal. The crystal structure shows that the $–CH_2OCH_2$-$CH_2OCH_2–$ unit of the crown ether ring acts as an obstacle to the formation of a linear polymer and also as a coordination site for the complexation of Ag^+. Therefore, the crown ether ring is important for the formation of the paracyclophane structure.

An Ag^+ induced ^{1}H NMR titration experiment was carried out in CD_3CN to obtain solution structural information on the **5**–AgOTf complex. From the single crystal X-ray structure it was expected that the chemical shifts for the protons at the 3′ and 5′ positions of the pyridine ring of ligand **5** would shift to higher field due to ring current effects of the pyridine ring on the side arm (Fig. 1) when the ligand forms the [3.3]paracyclophane-like complex with Ag^+ in solution. Fig. 3 shows the Ag^+ induced ^{1}H NMR shift changes of the pyridine protons in ligands **5** and **6**. These titration curves have an inflection point at $[Ag^+]/[ligand] = 1.0$. Therefore, the stoichiometry of the interaction of Ag^+ and both ligands is 1 : 1 in CD_3CN solution. The NMR signal for the pyridine protons at positions 3′ and 5′ of ligand **5** was shifted to higher field by about 0.33 ppm when 1.0 equiv. of AgOTf was added. This value is much greater than the 0.03 ppm shift observed on addition of 1.0 equiv. of AgOTf to a CD_3CN solution of ligand **6**. On the other hand, the signal for the pyridine protons at positions 2′ and 6′ of ligands **5** and **6** shifted to lower field by about 0.08 and 0.13 ppm, respectively. If the higher field shift change for the protons at positions 3′ and 5′ of ligand **5** is due to the magnetic anisotropy by Ag^+, the chemical shift change for the protons at positions 3′ and 5′ of ligand **6** should be much greater than that of ligand **5** because the distance between the Ag^+ cation and the pyridine N atoms of ligand **6** (2.20 Å) is less than that in ligand **5** (2.238 Å), in the solid state. Thus, these chemical shift changes strongly suggest that ligand **5** forms a [3.3]paracyclophane-like complex in CD_3CN solution. In addition, the signal for the methylene protons next to the nitrogen atom, NCH_2CH_2O in ligand **5**

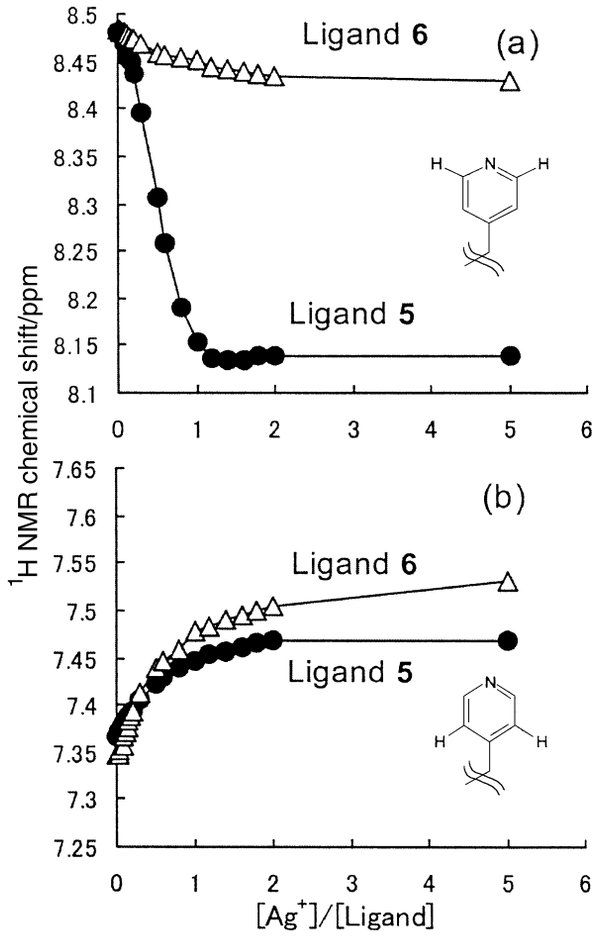

Fig. 3 The Ag^+ induced ^{1}H NMR spectral changes of ligands **5** (●) and **6** (△). (a) 3′ and 5′ protons. (b) 2′ and 6′ protons.

exhibited a greater shift (0.21 ppm) than for the methylene protons next to the oxygen atom, NCH_2CH_2O (0.12 ppm), upon the addition of 1.0 equiv. of AgOTf. These chemical shift changes suggest that the nitrogen atoms coordinate more strongly than the oxygen atoms which agrees with the single crystal X-ray structure.

In conclusion, we have demonstrated that ligand **5** forms a [3.3]paracyclophane-like complex with Ag^+ both in the solid state and in solution. When the crown ether ring is replaced by a non-cyclic ligand, a linear polymer-like complex is formed. The crown ether ring acts as an obstacle to the formation of a linear-type polymer, and therefore a [3.3]paracyclophane-like complex forms. Further studies of the new armed-azacrown ethers having a pyridine unit side arm are in progress.

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Notes and references

† A polymer-like complex of KSCN with ligand **5** was prepared and the structure was determined by single crystal X-ray crystallography. The polymer-like material is composed of a 2 : 2 complex of ligand **5** with K^+ bridged by two SCN^- anions, and the 2 : 2 complex unit is polymerized through the pyridine N atom to give a $\{[\mathbf{5} : KSCN]_2\}_n$ type complex. This result will be published elsewhere.

‡ Sodium borohydridetriacetate [$NaBH(OAc)_3$, 0.33 g, 1.56 mmol] was added to a mixture of 1,4,7,10-tetraoxa-15-azacyclopentadecane (0.23 g, 1.05 mmol) and 4-pyridinecarbaldehyde (0.12 g, 1.14 mmol) in 1,2-dichloroethane (20 mL) under an Ar atmosphere. The mixture was stirred at room temperature for 24 h. The reaction was quenched by adding aqueous saturated $NaHCO_3$, and the product was extracted with $CHCl_3$ (20 mL × 3). The combined extract was dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The residue was

purified by gel-permeation column chromatography. Ligand **5** (0.264 g, 83%) was isolated as a yellow oil. ^{1}H NMR ($CDCl_3$): d 2.79 (4H, t, J = 5.8 Hz), 3.62–3.73 (20H, m), 7.30 (2H, d, J = 5.8 Hz), 8.54 (2H, d, J = 5.8 Hz). EI-MS: m/z 311 (M^+ + 1, 36%). Anal. calc. for $C_{16}H_{26}N_2O_4$: C, 61.91; H, 8.44. Found: C, 61.90; H, 8.64%.

§ Ligand **5** or **6** (0.01 mmol) in acetonitrile (1 mL) was treated with AgOTf (0.01 mmol) in methanol (1 mL). After the solvent had evaporated, the crystals were recrystallized from acetonitrile. The crystals were dried with an Abderhalden's dryer (40 °C, 0.5 Torr). **5**–AgOTf: mp decompose >99 °C. Anal. calc. for $C_{17}H_{26}N_2O_7SAgF_3 \cdot 1/4CH_3CN$: C, 36.39; H, 4.67. Found: C, 36.69; H, 4.74%. **6**–AgOTf: mp decompose >140 °C. Anal. calc. for $C_{13}H_{20}N_2O_5SAgF_3 \cdot CH_3CN$: C, 34.50; H, 4.44. Found: C, 34.67; H, 4.38%. The single crystal used for X-ray analysis was obtained by recrystallization from MeOH.

¶ Crystal data for $C_{17}H_{26}N_2O_7SAgF_3$, **5**–AgOTf: M = 567.32, monoclinic, a = 12.00(1), b = 14.988(5), c = 13.697(6) Å, β = 113.61(3), U = 2257(1) Å^3, T = 298 K, space group $P2_1/n$ (no. 14), Z = 4, μ(Mo-Kα) = 10.47 cm^{-1}, 5629 reflections measured, 5171 unique (R_{int} = 0.017) which were used in all calculations. $R1$ = 0.053 [$I > 2\sigma(I)$], R = 0.084 and Rw = 0.151 (all data).

Crystal data for $C_{13}H_{22}N_2O_5SF_3Ag$, **6**–AgOTf: M = 483.25, orthorhombic, a = 9.50(1), b = 10.901(10), c = 17.79(1) Å, U = 1842(4) Å^3, T = 298 K, space group $Pnma$ (no. 62), Z = 4, μ(Mo-Kα) = 12.59 cm^{-1}, 2184 reflections measured, 1987 unique (R_{int} = 0.000) which were used in all calculations. $R1$ = 0.065 [$I > 2\sigma(I)$], R = 0.182 and Rw = 0.178 (all data). CCDC reference numbers 154473 and 154474. See http://www.rsc.org/suppdata/dt/b1/b101391m/ for crystallographic data in CIF or other electronic format.

‖ Ligand **6** (yellow oil, 0.794 g, 44%) was prepared as for **5** from bis(2-methoxyethyl)amine (1.07 g, 8.03 mmol), $NaBH(OAc)_3$ (1.59 g, 7.50 mmol) and 4-pyridinecarbaldehyde (0.83 g, 7.75 mmol) in 1,2-dichloroethane (50 mL). ^{1}H NMR ($CDCl_3$): δ 2.75 (4H, t, J = 5.8 Hz), 3.30 (6 H, s), 3.47 (4H, t, J = 5.8 Hz), 3.74 (2H, s), 7.29 (2H, d, J = 5.8 Hz), 8.51 (2H, d, J = 5.8 Hz); MS: m/z 225 (M^+, 100%). This compound is a hygroscopic oil. Anal. calc. for $C_{12}H_{20}N_2O_2 \cdot 1/4H_2O$: C, 62.99; H, 9.03. Found: C, 62.88; H, 8.85%.

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