

Molecular Structure of the Silver(I) Triflate Complex with *N,N',N'',N'''*-tetrakis(3',5'-difluorobenzyl)-1,4,8,11-tetraazacyclotetradecane

YOICHI HABATA* and SACHIKO YAMADA

Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274-8510, Japan

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Abstract

The structure of the silver(I) triflate complex with *N,N',N'',N'''*-tetrakis(3',5'-difluorobenzyl)-1,4,8,11-tetraazacyclotetradecane is reported. The $\text{Ag}^+ - \pi$ interaction between the Ag^+ ion incorporated in the cyclam moiety and the aromatic side-arm was observed in solid and solution by X-ray crystallography and UV–VIS titration experiments, respectively. It is also revealed that the Ag^+ complex is stable in gas phase from the FAB-MS. The energy of the $\text{Ag}^+ - \pi$ interaction was estimated as about 30 kJ/mol by Hartree–Fock/3-21G(*) and DFT (B3LYP/3-21G(**)) calculations. The NBO analysis indicated that s donation is the main contribution to the $\text{Ag}^+ - \text{aromatic ring}$ interaction.

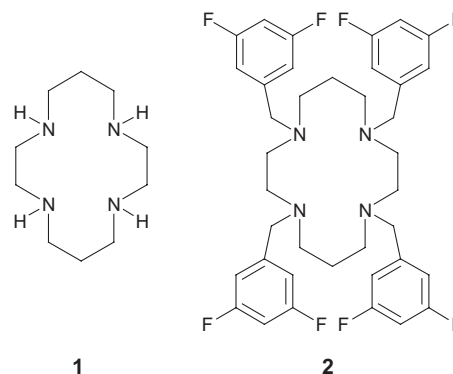
Introduction

Cyclam, 1,4,8,11-tetraazacyclotetradecane, **1**, is a 14-membered macrocyclic compound having four nitrogen atoms in the cyclic skeleton. Although the structure of many silver complexes with cyclam and its derivatives have been reported, almost all of them are cyclam- Ag^{2+} complexes [1], because the Ag^+ ion reacts with cyclam to form the $[\mathbf{1}-\text{Ag}]^{2+}$ complex and **Ag** [2]. Pickardt and Shen, and Wang *et al.* reported a $[\text{Ag}(\text{SCN})\text{cyclam}_{1/2}]$ complex [3] and a mixed-valent silver(I, II) complex using *N,N',N'',N'''*-tetramethylcyclam [4], respectively, but the Ag^+ ions in those complexes are not incorporated in the cyclam cavity. During our research efforts on armed-macrocycles [5], we found the first example for an armed cyclam- Ag^+ complex. Here we report the structure of the complex in solid, solution, and gas phases.

Results and discussions

New armed-cyclam **2** [6] was prepared by the reductive amination of cyclam with 3,5-difluorobenzaldehyde in the presence of $\text{NaBH}(\text{OAc})_3$ in 1,2-dichloroethane by the method previously reported [5c]. A silver triflate complex of armed-cyclam **2**, **2-AgOTf**, was obtained (host:guest = 1:1) as colorless crystals [7]. The structure of **2-AgOTf** has been determined by single crystal X-ray

analysis [8]. As shown in Figure 1, the silver ion is four coordinated by the ring N atoms (N1, N2, N3 and N4). The triflate anion does not coordinate to the silver ion. The Ag1–N1, Ag1–N2, Ag1–N3 and Ag1–N4 bond lengths are 2.36, 2.45, 2.39, and 2.47 Å, respectively, and the average Ag–N length is 2.42 Å. Usually, the Ag–N bond lengths in the cyclam- Ag^{2+} complexes are in the range 2.06–2.21 Å [1]. The Ag1–N bond lengths in **2-AgOTf** are longer than those of the cyclam- Ag^{2+} complexes. These bond lengths suggest that the charge of the silver ion is +1. In addition, two aromatic rings (A and B in Figure 1) cover the Ag^+ cation incorporated in the cyclam. The shortest aromatic carbon- Ag^+ distances are 3.31 Å (C24–Ag1) and 3.06 Å (C34–Ag1) in the rings A and B, respectively. These distances are longer than those of usual $\text{Ag}^+ - \text{aromatic ring}$ distances (in the range 2.4–2.9 Å) [9a], but they are comparable with those of an anthraceno cryptand- Ag^+ (3.15 and



* Author for correspondence. E-mail: habata@chem.sci.toho-u.ac.jp

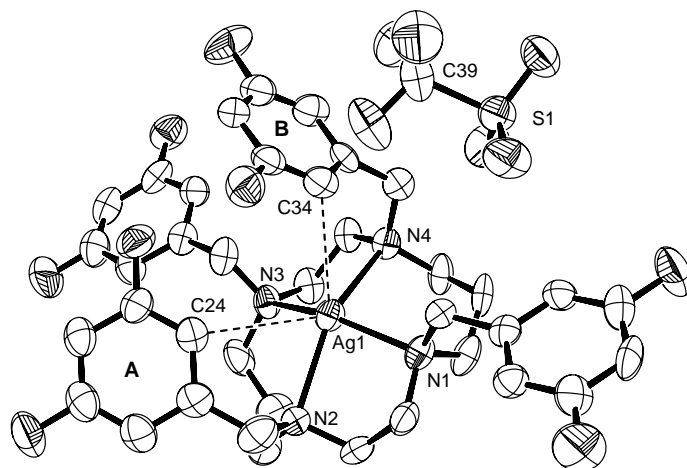


Figure 1. The ORTEP diagram of the 2-AgOTf complex (50% probability level).

3.28 Å) [9b] and anthraceno diphosphine-Ag⁺ (3.05–3.157 Å) systems [9c]. The X-ray result suggests that the Ag⁺ ion interacts with the aromatic side arms in the 2-AgOTf system.

In order to investigate the Ag⁺- π interaction in solution, an Ag⁺ induced UV-VIS titration experiment was carried out in CH₃CN. Figure 2 shows the Ag⁺ induced UV-VIS spectral changes. The absorbance of **2** at λ_{\max} (260 nm) arising from the π - π^* B band increased about 1.3 times when 1.0 equiv. of AgOTf was added. No increase of absorbance at λ_{\max} was observed when Ag⁺ was added to a CH₃CN solution of 3,5-difluorobenzene under the same conditions. The titration experiments indicate that the aromatic rings of the side arms interact with Ag⁺ cations incorporated in the cyclam moiety in solution. From the UV-VIS titration experiment, the log *K* value for the interaction between **2** and Ag⁺ in CH₃CN at 298 K was estimated as >8.

Information on the structure in the gas phase was obtained by FAB-MS. Figure 3 shows the FAB-MS of 2-AgOTf in an NBA matrix. Parent ion peaks arising

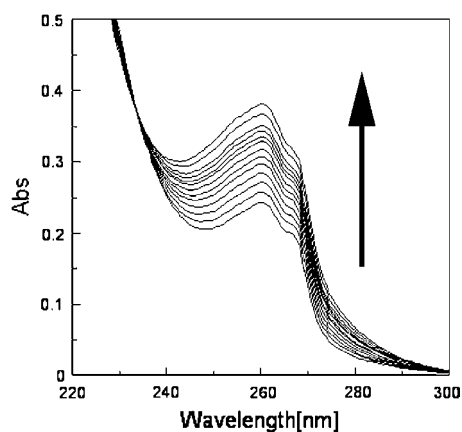


Figure 2. The AgOTf induced UV-VIS spectral changes of **2**. The titration experiment was carried out by addition of 0.2, 0.4, 0.6, 0.8, 0.9, 1.0, 1.2, 1.4, 1.6, 1.8 and 2.0 equiv. of AgOTf to **2** (1.0×10^{-4} mol/L in CH₃CN).

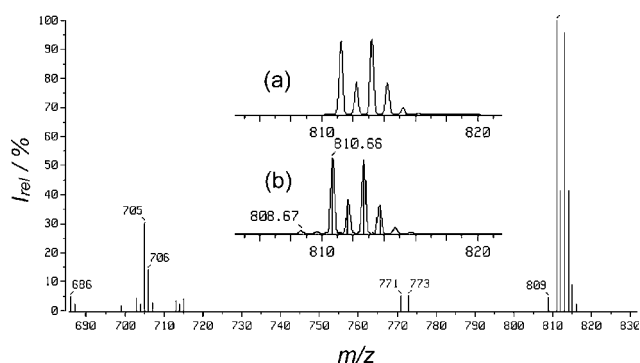


Figure 3. The FAB-MS of the 2-AgOTf complex. The theoretical ion distribution (a) and observed ion peaks (b) are shown.

from **[2 + Ag]⁺** were observed at *m/z* 811 (100%) and 813 (91%), and the observed ion peaks (Figure 3a) agree with the theoretical ion distribution (Figure 3b). Intensity of the ion peak at *m/z* 705 arising from **[2 + H]⁺** was 33%. It is important to note that the intensity of the mass of **[2 + Ag]⁺** is 3 times greater than that of **[2 + H]⁺**. The FAB-MS data shows that ligand **2** forms a stable complex with Ag⁺ in the gas phase.

In order to estimate the energy of the Ag⁺- π interactions, the single point energy calculations for the X-ray structure (Figure 4a) and a virtual structure

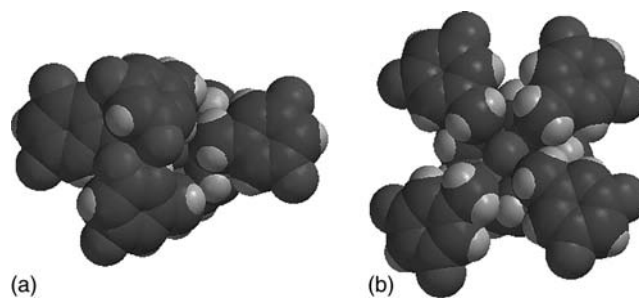


Figure 4. The X-ray structure (a) and a virtual stable structure (b) of the 2-AgOTf complex.

Table 1. Energies of the 2-Ag⁺ complexes

	E (ligand)/au	E (Ag ⁺)/au	E (complex)/au	ΔE_{cf}^a /au	$\Delta E_{cf}/\text{kJ/mol}^b$
HF/3-21G(*)					
X-ray structure	-2461.4198796	-5173.6005918	-7635.2028969	-0.1824265	-479.0
Virtual structure	-2461.4787330	-5173.6005908	-7635.2525548	-0.1732310	-454.8
		$\Delta\Delta E_{HF}$	$(\Delta E_{cf_X} - \Delta E_{cf_V})$	-0.0091955	-24.2
B3LYP/3-21G(*)					
X-ray structure	-2475.6665620	-5176.0103164	-7651.9134968	-0.2366184	-621.2
Virtual structure	-2475.7572195	-5176.0103164	-7651.9901292	-0.2225933	-584.4
		$\Delta\Delta E_{B3LYP}$	$(\Delta E_{cf_X} - \Delta E_{cf_V})$	-0.0140251	-36.8

^a $\Delta E_{cf} = E(\text{complex}) - E(\text{ligand}) - E(\text{Ag}^+)$. ΔE_{cf_X} and ΔE_{cf_V} are ΔE_{cf} for X-ray structure and virtual structure, respectively.

^b 1 au = 2625.5 kJ/mol.

Table 2. Results of the NBO analysis of Ag⁺ in the X-ray and virtual structures of the 2-Ag⁺ complex at the HF/3-21G(*) theoretical level

	4d Orbitals (10)	5s Orbital (0)	Net change
X-ray structure	9.9461 (-0.0539)	0.1133 (+0.1133)	+0.0594
Virtual structure	9.9480 (-0.0520)	0.1073 (+0.1073)	+0.0553

(Figure 4b) were carried out by Hartree–Fock (HF/3-21G(*) and DFT (B3LYP/3-21G(*) methods [10]. As shown in Table 1, the Ag⁺– π interaction energies, $\Delta\Delta E_{HF}$ and $\Delta\Delta E_{B3LYP}$, were estimated as –24.2 and –36.8 kJ/mol by HF and DFT calculations, respectively. Saarenketo *et al.* reported that Ag⁺– π interactions between [2.2.2]cyclophanes having three phenyl groups and Ag⁺ ions are in the range –327 to –259 kJ/mol and –424 to –370 kJ/mol in HF/3-21G(*) and B3LYP/3-21G(*) calculations [11], and an energy for one aromatic ring–Ag⁺ interaction is calculated as about –100 kJ/mol (HF). Therefore, the HF and DFT calculations indicate that the Ag⁺– π interaction in 2-Ag is a weak Ag⁺–aromatic ring interaction. The result agrees with the X-ray data for 2-AgOTf, because the Ag⁺–aromatic ring distances are longer than those of cyclophane–Ag⁺ complexes. The bonding scheme was investigated by the NBO analysis [11] (Table 2). The population of the silver-5s orbital (valence s-orbital) in the X-ray structure is slightly greater than that of the virtual structure with no Ag⁺– π interactions, while the population of 4d orbitals decreased as previously reported by Saarenketo *et al.* [12]. The NBO analysis indicates that s donation is the main contribution to the Ag⁺–aromatic ring bonding as reported by Taylor [13] and Saarenketo [12].

Conclusions

In conclusion, we have demonstrated that ligand 2 forms a stable complex with Ag⁺ ion and that the aromatic side-arms in ligand 2 interact with the Ag⁺ ion incorporated in the cyclam moiety. The X-ray analysis and UV–VIS titration experiments suggested that the structure of the Ag⁺ complex with ligand 2 is the same in solid and solution, namely that of Ag⁺ interacting

with the cyclam moiety. The Ag⁺– π interaction energy between the Ag⁺ ion incorporated in the cyclam moiety and the aromatic rings was also estimated by HF and DFT calculations.

Acknowledgements

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References

1. K.B. Mertes: *Inorg. Chem.* **17**, 49–52 (1978); T. Ito, H. Ito, and K. Toriumi, *Chem. Lett.* 1101–1104 (1981); H.N. Po, E. Brinkman, and R.J. Doedens: *Acta Cryst.* **C47**, 2310–2312 (1991); H.N. Po, S. Shen, and R.J. Doedens: *Acta Cryst.* **49**, 1914–1916 (1993); Q. Wang and T.C.W. Mak: *J. Chem. Soc. Chem. Commun.* 807–808 (2001); M. Munakata, J.C. Zhong, I. Ino, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, and N. Oiji: *Inorg. Chim. Acta* **317**, 268–275 (2001).
2. M.O. Kestner and A.L. Allred: *J. Am. Chem. Soc.* **94**, 7189–7189 (1972); E.K. Barefield and M.T. Mocella: *Inorg. Chem.* **12**, 2829–2832 (1973); I.J. Clark and M.B. Harrowfield: *Inorg. Chem.* **23**, 3470–3745 (1989); R.G. Swisher, D.J. Stuehr, J. Knox, B.M. Fox, and E.L. Blinn: *J. Coord. Chem.* **20**, 101–107 (1989).
3. J. Pickardt and J. Shen: *Z. Naturforsch. Teil B* **49**, 211–214 (1994).
4. Q. Wang, H.K. Lee, and T.C.W. Mak: *New J. Chem.* **26**, 513–515 (2002).
5. (a) Y. Habata, S. Akabori, X.X. Zhang, R.M. Izatt, and J.S. Bradshaw: *J. Heterocyclic Chem.* **38**, 1329–1340 (2001); (b) Y. Habata, A. Watanabe, and S. Akabori: *Supramol. Chem.* **13**, 539–543 (2001); (c) Y. Habata, Y. Yamashita, and S. Akabori: *J. Chem. Soc. Dalton Trans.* 966–968 (2001); (d) Y. Habata and S. Akabori: *J. Heterocyclic Chem.* **38**, 471–474 (2001); (e) Y. Habata, T. Saeki, S. Akabori, X.X. Zhang, and J.S. Bradshaw: *J. Heterocyclic Chem.* **38**, 253–258 (2001); (f) Y. Habata, T. Saeki, S. Akabori, X.X. Zhang, and J.S. Bradshaw: *J. Chem. Soc. Chem. Commun.* 1469–1470 (2000).
6. After a mixture of 1,4,7,10-tetraazacyclododecane (5.0 mmol), 3,5-difluoro-benzaldehydes (35 mmol), and NaBH(OAc)₃ (40 mmol) in 1,2-dichloroethane (40 mL) was stirred for 7 days at rt under

- atmospheric pressure (Ar atmosphere), saturated aqueous NaHCO₃ was added. The organic layer was separated, and the aqueous layer was extracted with CHCl₃ (20 mL × 3). The combined organic layer was washed with water, dried over Na₂SO₄, and concentrated. The residual solid was recrystallized from CH₃CN to give **2** in 61%; **2**: m.p. 125.0–125.5 °C; ¹H NMR (400 MHz, CD₂Cl₂, 25 °C, TMS) δ = 6.88 (d, 8H, ³J(H,F) = 8.4 Hz), 6.66 (t, 4H, ³J(H,F) = 8.4 Hz), 3.39 (s, 8H), 2.58 (s, 8H), 2.46 (t, 8H, ³J(H,H) = 6.9 Hz), 1.74 (quintet, 2H, ³J(H,H) = 6.9 Hz); FAB MS: *m/z* (%) 706 (100) [M + H]⁺; elemental analysis calcd (%) for C₃₈H₄₀N₄F₈: C 64.76, H 5.71; N 7.95; found: C 64.81, H 5.81, N 8.12.
7. AgOTf (0.03 mmol) in CH₃OH (1 mL) was treated with compound **2** in CHCl₃ solution (1 mL). After the solvent had evaporated, the crystals were recrystallized from CH₃OH to give **2**-AgOTf complex quantitatively; **2**-AgOTf: m.p. 148.0–149.0 °C (decomposed); elemental analysis calcd. (%) for C₃₉H₄₀N₄O₃SF₁₁Ag: C 48.71, H 4.19; N 5.83; found: C 48.43, H 4.18, N 5.65.
8. Crystal data for C₃₉H₄₀N₄O₃SF₁₁Ag, **2**-AgOTf: *M* = 961.68, monoclinic, *a* = 8.236(5), *b* = 26.414(8), *c* = 18.279(6) Å, β = 101.82(4), *V* = 3891(2) Å³, *T* = 298 K, space group Cc (no. 9), *Z* = 4, μ(MoK_α) = 6.67 cm⁻¹, 3784 reflections measured, 3440 unique (*R*_{int} = 0.043) which were used in all calculations. *R*₁ = 0.042 [*I* > 2σ(*I*)], *R* = 0.077 and *R*_w = 0.113 [all data].
9. (a) M. Munakata, L.P. Wu, and G.L. Ning: *Coord. Chem. Rev.* **198**, 171–203 (2000) and references cited therein; (b) H. Andrianatoandro, Y. Barrans, P. Marsau, J.P. Desvergne, F. Fages, and H. Bouas-Laurent: *Act Cryst.* **B51**, 293–300 (1995); (c) F. Xu, L. Weng, L. Sun and Z. Zhang: *Organometallics* **19**, 2658–2660 (2000).
10. Spartan 02TM was used as the computer molecular modeling software. The virtual structure was built using the X-ray structure as a template. In the virtual structure, rings A and B (Figure 1) turned out of the cyclam. Structures of ligands in Table 1 were built by eliminating the Ag atoms from the X-ray and virtual structures. The Ag⁺-π interaction energies were estimated as follows; (i) complexing energies for X-ray and virtual structures, Δ*E*_{cf_X} and Δ*E*_{cf_V}, respectively, were calculated by the energies, *E* (complex), *E* (Ag⁺) and *E* (ligand), and then (ii) the Ag⁺-π interaction energies (ΔΔ*E*_{HF} and ΔΔ*E*_{B3LYP}) were calculated using the both complexing energies (Δ*E*_{cf_X} - Δ*E*_{cf_V}). NBO analysis was also carried out for the complexes by Spartan 02TM software.
11. A.E. Reed, R.B. Weinstock, and F. Weinhold: *J. Chem. Phys.* **83**, 735–746 (1985); A.E. Reed, L.A. Curtiss, and F. Weinhold: *Chem. Rev.* **88**, 899–826 (1988).
12. P. Saarenketo, R. Suontamo, T. Jodicke, and K. Rissanen: *Organometallics* **19**, 2346–2353 (2000).
13. I.F. Taylor Jr., E.A. Hall, and E.L. Amma: *J. Am. Chem. Soc.* **91**, 5745–5749 (1969).