A Unique Double Strand Consisting of Siloxane-Type Macrocycles

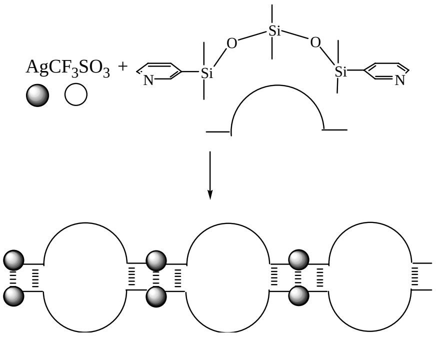
Ok-Sang Jung,* Young-A Lee, and Yun Ju Kim
Materials Chemistry Laboratory, Korea Institute of Science and Technology, Seoul 136-791, Korea

(Received July 29, 2002; CL-020632)

Reaction of $AgCF_3SO_3$ with 1,5-bis(3-pyridyl)hexamethyltrisiloxane produces a unique double strand consisting of siloxane macrocycles that is sustained by both the π–π stackings of pyridine rings and the strong Ag(I)–Ag(I) interactions.

The rational design and synthesis of microporous or channelled supramolecular materials is a challenging and fruitful area owing to various applications in petrochemicals industry, separation science, and harmful materials adsorption.[1–5] To date silicas and aluminosilicates have been used as functional microporous materials because of their thermal robustness and the malleability of the framework size.[6] Recent landmark works have shown that more versatile frameworks are constructed by the use of metal-linker coordinations. Design of ligands with carefully placed binding site offers potentials for the synthesis of tailor-made porous materials. Appropriate angles and flexible components of multidentate ligands play important roles in the self-assembly via coordination.[7–9] We have demonstrated recently that n-Py_2X ($n = 3, 4$; X=O, S) linkers are tectonics for various interesting skeletons.[10–14] Among various bipyridyl ligands, the exploitation of siloxane-containing pyridine-based units has not been explored. We report a unique double strand consisting of siloxane-based crown ether macrocycles of Ag(I) with 1,5-bis(3-pyridyl)hexamethyltrisiloxane (L) along with its related properties. L is a new ligand that may possess a noninnocent angle (O–Si–O), conformational nonrigidity, and a long bipyridyl length. Ag(I) ion has been employed as linear or T-shaped directional units.[12,15]

The L was smoothly prepared by the reaction of 1,5-dichlorohexamethyltrisloxane with m-bromopyridine.[16] The reaction of $AgCF_3SO_3$ (**1**) with L affords colorless crystals of $[Ag(L)](CF_3SO_3)$ (**2**)[17] as shown in Scheme 1. **2** is air-stable and insoluble in water and in common organic solvents. The structure of **2** was established by X-ray characterization[18] (Figure 1). Each L connects two Ag(I) ions (Ag–N = 2.152(5) Å) to give a single strand. The two strands interact significantly via both the face-to-face (π–π) stackings of pyridine rings ($\approx$3.5 Å) and the strong Ag(I)–Ag(I) interactions (3.001(1) Å) to form a unique double strand. The argentophilic interaction is much stronger than that of $[Ag_3(NO_3)_3(Py_2S)_2 \cdot 2H_2O]$ (3.436(2) Å),[12] presumably owing to the electronic effect of the siloxane group. The bent N–Ag–N angle (167.2(3)°) supports the presence of the strong Ag(I)–Ag(I) interactions. The weak coordinating $CF_3SO_3^-$ acts as a simple counteranion around the silver ion ($Ag \cdots O = 2.83$ Å). The most salient feature is that the unique double strand is consisted of siloxane-type 24-membered macrocycles (the longest intracyclic $Si \cdots Si = 9.80$ Å). The macrocycle can be described as a new type of crown ether. Each macrocycle has suitable space for small molecule as visualized by the space-filling view. Thus, the calculated density of the crystal (1.508 g/cm^3) is lower than that of general Ag(I)–bipyridyl compounds ($\approx$2.0 g/cm^3).[10]



Scheme 1.

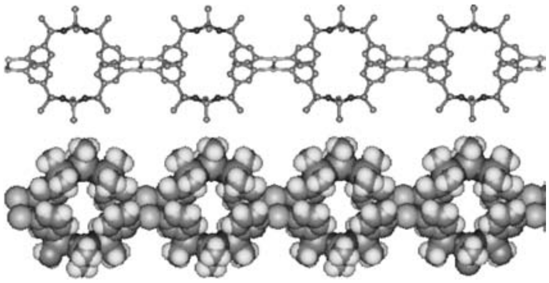


Figure 1. Ball-and-stick view (top) and space-filling (bottom) of infinite **2**. Anion $CF_3SO_3^-$ is omitted for clarity. Selected bond lengths and angles: Ag–N = 2.152(5) Å, Si–O = 1.577(6) ~ 1.585(6) Å, Si–C = 1.810(10) ~ 1.894(7) Å, Ag–Ag = 3.001(1) Å, N–Ag–N = 167.2(3)°, N–Ag–Ag = 96.0(1)°.

The thermal analyses (TGA and DSC) show that **2** melts sharply at 196 °C. This fact indicates that the double-strand structure is unstable in the molten state, presumably because of the strain energy of the double-strand in the molten state. The melting point was also identified on a melting point apparatus. The compound is stable for several days at pH 3.5–10.0 aqueous solution. However, the typical anion exchange[19] is smoothly achieved since the present $CF_3SO_3^-$ anion has been known as a weak coordinating anion and hence as a good leaving group. The anion exchange of **2** with ClO_4^- was monitored by the characteristic IR bands (1095 cm^{-1}; 626 cm^{-1}) of anions. According to the IR spectra (Supporting Information) and elemental analysis,[20] after 24 h, the $CF_3SO_3^-$ anions are completely exchanged with ClO_4^- anions. The other peaks of the spectrum remain virtually unchanged, suggesting the preservation of the skeletal structure during the anion exchange process. Though all experiments including the preparation and the anion exchange are carried out either in aqueous solutions or in water-containing solutions, the infinite skeleton with open framework contains no solvate water molecules. This fact implies that the crown ether-type macrocycle exhibits hydrophobic properties.

In conclusion, the unique double strand demonstrates that the new siloxane-based pyridine may be a useful hemicircle tectonic. The double strand is hydrophobic open framework materials that may contribute to the development of new conceptual cyclic molecules or host-guest sensors for small organic molecules.

References and Notes

1 D. Venkataraman, G. B. Gardner, S. Lee, and J. S. Moore, *J. Am. Chem.* Soc., **117**, 11600 (1995).

2 P. J. Langley and J. Hullinger, *Chem. Soc. Rev.*, **28**, 279 (1999).

3 D. M. L. Goodgame, D. A. Grachvogel, and D. J. Williams, *Angew. Chem., Int. Ed.*, **38**, 153 (1999).

4 S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, and I. D. Williams, *Science*, **283**, 148 (1999).

5 S. Kitagawa and M. Kondo, *Bul1. Chem. Soc. Jpn.*, **71**, 1739 (1998).

6 J. W. Steed and J. L. Atwood, “Supramolecular Chemistry,” John Wiley & Sons, New York (2000), p 258.

7 P. J. Hagraman, D. Hagrman, and J. Zubieta, *Angew. Chem., Int. Ed.*, **38**, 2638 (1999).

8 H. Li, M. Eddaoudi, M. O’Keeffe, and O. M. Yaghi, *Science*, **402**, 276 (1999).

9 E. C. Constable, *Tetrahedron*, **48**, 10013 (1992).

10 O.-S. Jung, Y. J. Kim, Y.-A Lee, J. K. Park, and H. K. Chae, *J. Am. Chem. Soc.*, **122**, 9921 (2000).

11 O.-S. Jung, S. H. Park, D. C. Kim, and K. M. Kim, *Inorg. Chem.*, **37**, 610 (1998).

12 O.-S. Jung, S. H. Park, C. H. Park, and J. K. Park, *Chem. Lett.*, **1999**, 923.

13 O.-S. Jung, S. H. Park, Y.-A Lee, and U. Lee, *Chem. Lett.*, **2000**, 1012.

14 O.-S. Jung, Y. J. Kim, Y.-A Lee, H. K. Chae, H. G. Jang, and J. Hong, *Inorg. Chem.*, **40**, 2105 (2001).

15 M. Munakata, L. P. Wu, and T. Kuroda-Sowa, *Adv. Inorg. Chem.*, **46**, 173 (1999).

16 L: This linker was prepared according to reference M. Schmitz, S. Leninger, J. Fan, A. M. Arif, and P. J. Stang, *Organometallics*, **18**, 4817 (1999); Viscous liquid. 80% yield. Anal. Calcd for $C_{16}H_{26}N_2O_2Si_3$: C, 52.99; H, 7.22; N, 7.72. Found: C, 52.10; H, 7.11; N, 7.80. ^{1}H NMR ($CDCl_3$, $SiMe_4$): δ 0.05 (s, 6H), 0.34 (s, 12H), 7.22 (dd, 2H, $J_1 = 5$ Hz, J_2, 2 Hz), 7.75 (dt, 2H, $J_1 = 9$ Hz, J_2, 2 Hz), 8.54 (dd, 2H, $J_1 = 5$ Hz, J_2, 2 Hz), 8.66 (s, 2H). ^{13}C NMR ($CDCl_3$, $SiMe_4$): δ 153.75, 150.56, 141.02, 134.55, 123,50, 1.55, 0.90. EIMS (80 eV): *m/z*: M^+ 362 .

17 **2**: A methanolic solution (10 mL) of L (109 mg, 0.3 mmol) was slowly diffused into an aqueous solution (10 mL) of **1** (77 mg, 0.3 mmol). Colorless crystals of **2** formed at the interface, and were obtained in 3 days in 80% yield. IR (KBr, cm^{-1}): $\nu(SO_3$, s), 1254 (s); ν(SiO, s), 1048 (s). Anal. Found: C, 32.60; H, 4.19; N, 4.60. Calcd for $C_{17}H_{26}N_2F_3O_5SAg$: C, 32.96; H, 4.23; N, 4.52.

18 Crystal data for **2**: fw = 309.80, monoclinic, $a = 17.3310(4)$ Å, $b = 14.9980(4)$ Å, $c = 13.1890(4)$ Å, $\beta = 127.230(2)^\circ$, $V = 2729.6(1)$ Å^3, $T = 293(2)$ K, space group $C2/m$, $Z = 8$, $D_{\text{calcd}} = 1.508$ g/cm^3, $\mu(\text{Mo K}\alpha) = 0.995$ mm^{-1}, 3219 unique reflections in all calculations. $R1 = 0.0845$ ($wR2 = 0.2682$), $GOF = 1.277$ for 157 parameters.

19 O.-S. Jung, Y. J. Kim, K. M. Kim, and Y.-A Lee, *J. Am. Chem. Soc.*, **124**, 7906 (2002).

20 Anal. found: C, 33.50; H, 4.80; N, 4.70%. Calcd for $C_{16}H_{26}N_2O_6ClSi_3Ag$: C, 33.72; H, 4.60; N, 4.91%.