

A Unique Tub-Metallacycle: Synthesis and Structural Properties of AgPF₆ Bearing 1,3-Bis(3-pyridyl)tetramethyldisiloxane

Byung Il Park, Yun Ju Kim, Young-A Lee,[†] Ki-Min Park,[‡] and Ok-Sang Jung^{*}

Department of Chemistry and Center for Plastic Information System, Pusan National University, Pusan 609-735, Korea

[†]Department of Chemistry, Chonbuk National University, Jeonju 561-756, Korea

[‡]Basic Science Institute, Gyeongsang National University, Jinju 660-701, Korea

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The rational design and synthesis of macrometallacyclic materials is a challenging and fruitful field since the cyclic molecules have various potential applications such as separation science, harmful materials adsorption, molecular containers, ion exchangers, and luminescent sensing.¹⁻⁴ New framework metallacycles have been constructed by the coordination reaction of metal ions with linkers.⁵⁻⁹ Appropriate angles, lengths, and flexible components of multi-dentate N-donor linkers play key important roles in the construction of the tailor-made macrometallacyclic molecules, and thus the synthesis of new linkers is one of significant works in the field. Recently, we have demonstrated that various silicon-containing pyridyl linkers are useful tectonics for desirable functional skeletons.¹⁰⁻¹³ According to our previous works, the reaction of Ag(I) with 1,5-bis(3-pyridyl)hexamethyltrisiloxane (L1) produced an unprecedented double strand consisting of siloxane-macrocycles¹⁴ whereas the similar reaction of Ag(I) with 1,3-bis(4-pyridyl)tetramethyldisiloxane (L2) gave a molecular rectangle with tunable argentophilic interaction.¹⁵

In an effort to expand the coordination chemistry of siloxane-containing pyridyl linkers, the reaction of AgPF₆ with new 1,3-bis(3-pyridyl)tetramethyldisiloxane (L) was carried out. We report a unique tub-metallacyclic dimer prepared by the reaction along with its related structural properties. L is a new linker that possesses a non-innocent angle (O-Si-O), various stable conformers *via* non-rigidity, and potential N-donor bidentate. Ag(I) ion has been

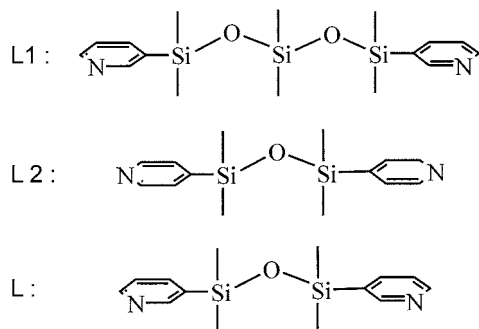
employed as various directional units such as linear or T-shaped geometry.¹⁶⁻¹⁸

Experimental Section

Materials and Measurements. AgPF₆ was purchased from Aldrich, and was used without further purification. Elemental microanalyses (C, H, N) were performed on crystalline samples by the Advanced Analysis Center at KIST using a Perkin Elmer 2400 CHN analyzer. Thermal analyses were carried out under a dinitrogen atmosphere at a scan rate of 10 °C/min using a Stanton Red Croft TG 100. Infrared spectra were obtained on a Perkin Elmer 16F PC FTIR spectrophotometer with samples prepared as KBr pellets. ¹H NMR spectra were recorded on a Varian Gemini 300 instrument. The chemical shifts are reported relative to internal Me₄Si.

Preparation of 1,3-Bis(3-pyridyl)tetramethyldisiloxane (L). To a solution of 3-bromopyridine (7 mmol) in dry ethyl ether (20 mL) under nitrogen gas was added dropwise *n*-butyllithium (7.2 mmol, 2.5 M solution in hexane) at -78 °C. The resulting mixture was stirred at the temperature for 1 h. 1,3-Dichlorotetramethylsiloxane (3.2 mmol) was slowly added to the yellow suspension for 1 h at room temperature. Distilled water (20 mL) was added into the reaction solution, and the organic solution layer was separated. The organic solution was washed with water (2 × 10 mL), and then was dried over MgSO₄. The crude product was purified by column chromatography on silica gel with ethyl acetate. The solvent was evaporated to obtain viscous liquid in 42% yield. Anal. Calcd for C₁₄H₂₀N₂OSi₂: C, 58.29; H, 6.99; N, 9.71. Found: C, 58.20; H, 6.88; N, 9.80. ¹H NMR (300.00 MHz, CDCl₃, SiMe₄): 0.38 (s, 6H), 7.26 (m, 2H), 7.76 (dt, *J* = 2.0 Hz, *J* = 6.0 Hz, 2H), 8.58 (dd, *J* = 2.0 Hz, *J* = 4.0 Hz, 2H), 8.68 (s, 2H). ¹³C NMR (125.76 MHz, CDCl₃, Me₄Si): δ = 0.90, 123.50, 134.25, 140.93, 150.50, 153.52.

Preparation of [AgL]₂(PF₆)₂. A methanol solution (15 mL) of L (58 mg, 0.2 mmol) was slowly diffused into an aqueous solution (15 mL) of AgPF₆ (50 mg, 0.2 mmol). Colorless crystals of [AgL]₂(PF₆)₂ formed at the interface, and were obtained in 6 days in 70% yield. mp. 140 °C (dec). IR (KBr, cm⁻¹): ν (PF₆), 832 (s); ν (Si-O), 1064 (s). Anal. Calcd for C₁₄H₂₀N₂F₆OPSi₂Ag: C, 31.06; H, 3.72; N, 5.17.



^{*}To whom correspondence should be addressed. Phone: -82-51-510-2591; Fax: -82-51-516-7421; e-mail: oksjung@pusan.ac.kr

Table 1. Crystallographic Data for $[\text{AgL}]_2(\text{PF}_6)_2$

formula	$\text{C}_{28}\text{H}_{40}\text{N}_4\text{F}_{12}\text{O}_2\text{P}_2\text{Si}_4\text{Ag}_2$
f.w.	1082.68
space group	$C2/c$
a , Å	29.14(1)
b , Å	8.751(4)
c , Å	16.501(7)
β , deg	92.469(9)
V , Å ³	4204(3)
Z	4
d_{calc} , gcm ⁻³	1.711
μ , mm ⁻¹	1.207
$R \{I > 2\sigma(I)\}$	$R1 = 0.0558$
	$wR2 = 0.1488$

$$R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \quad wR2 = \frac{\sum w(F_o^2 - F_c^2)^2}{\sum wF_o^2}^{1/2}$$

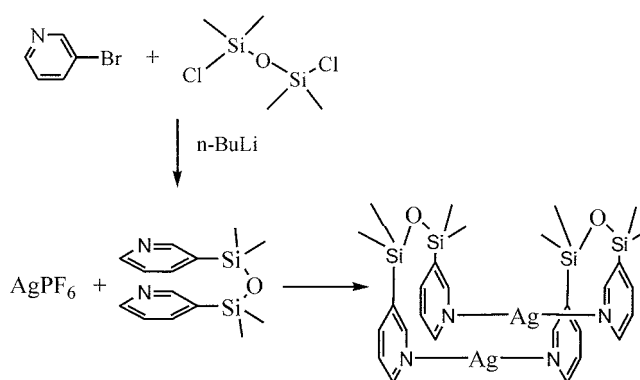
Found: C, 31.40; H, 3.70; N, 5.16.

X-ray Crystallography. All X-ray data were collected on a Bruker SMART automatic diffractometer with a graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) and a CCD detector at ambient temperature. The 45 frames of two dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The data were corrected for Lorentz and polarization effects. The structure was solved by the Patterson method (SHELXS 97) and refined by full-matrix least square techniques (SHELXL 97).¹⁹ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. Crystal parameters and procedural information corresponding to data collection and structure refinement are given in Table 1.

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-252481). The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/perl:catreq/catreq.cgi> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1233 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Synthesis. New ligand, 1,3-bis(3-pyridyl)tetramethyldisiloxane (L), was smoothly prepared by the reaction of 1,3-dichlorotetramethyldisiloxane with 3-bromopyridine according to the literature method.¹⁰ The slow diffusion of AgPF_6 with L afforded single crystals consisting of discrete cyclic dimers (Scheme 1) in contrast to double strand 1D polymers prepared by the reaction Ag(I) with 1,5-bis(3-pyridyl)hexamethyltrisiloxane.¹⁴ The formation of the cyclic dimer was not significantly affected by the change of reactant mole ratios, solvents, and the concentrations, implying that the macrocycle is very favorable species. The product is remarkable in that there is no evidence for usual coordination-polymerization even in the relatively high concentration. The colorless crystalline product is air-stable, and is insoluble in water and common organic solvents. However,

**Scheme 1**

the product is easily dissociated in dimethyl sulfoxide, *N,N*-dimethyl formamide, or acetonitrile.

Crystal Structure. X-ray characterization on a single crystal has provided a macrocyclic dimer of $[\text{AgL}]_2\text{X}_2$ (Figure 1), and its relevant bond lengths and angles are listed in Table 2. The L is used as an unusual horse-shoe tectonic, and connects two Ag(I) ions ($\text{Ag-N} = 2.114(4)$ Å; $2.123(4)$ Å) to form a 20-membered metallacyclic dimer. The angle around the Ag(I) ion ($\text{N-Ag-N} = 175.6(2)^\circ$) is slightly deviated from an ideal linear geometry. The most salient feature is that the conformation of the 20-membered ring is a unique tub to sustain the intraligand face-to-face (π - π) stacking (~ 3.6 Å). However, two interligand pyridine rings

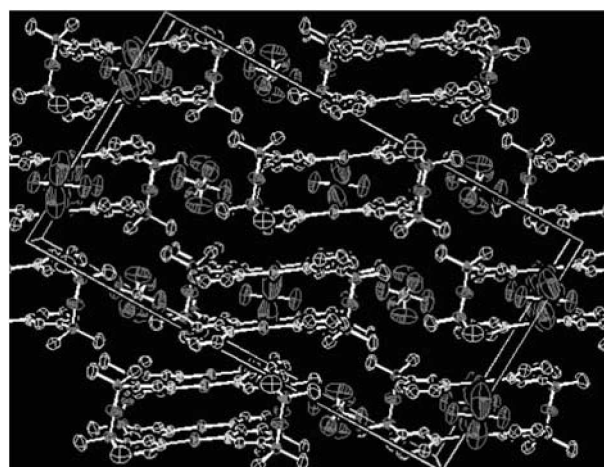
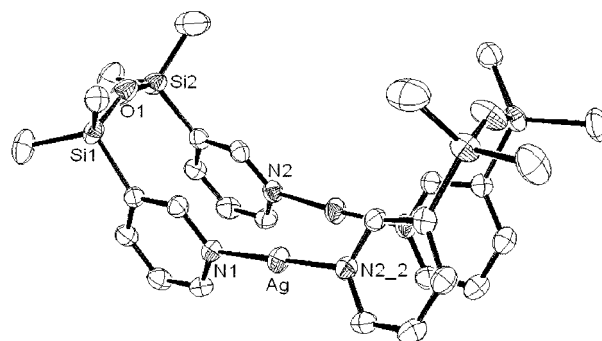


Figure 1. ORTEP drawing (up) and molecular packing (down) of $[\text{AgL}]_2(\text{PF}_6)_2$. For ORTEP drawing, the anions and hydrogen atoms were omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [AgL]₂(PF₆)₂

Ag-N(1)	2.114(4)
Ag-N(2)#1	2.123(4)
Si(1)-O(1)	1.644(4)
Si(1)-C(12)	1.843(6)
Si(1)-C(11)	1.845(6)
Si(1)-C(2)	1.896(5)
Si(2)-O(1)	1.623(4)
Si(2)-C(13)	1.829(8)
Si(2)-C(14)	1.834(7)
Si(2)-C(7)	1.878(6)
N(1)-C(5)	1.348(7)
N(1)-C(1)	1.352(6)
N(2)-C(6)	1.349(6)
N(2)-C(10)	1.351(6)
N(1)-Ag-N(2)#1	175.6(2)
O(1)-Si(1)-C(12)	108.1(3)
O(1)-Si(1)-C(11)	111.7(3)
C(12)-Si(1)-C(11)	112.2(3)
O(1)-Si(1)-C(2)	105.7(2)
C(12)-Si(1)-C(2)	109.6(3)
C(11)-Si(1)-C(2)	109.3(3)
O(1)-Si(2)-C(13)	107.5(4)
O(1)-Si(2)-C(14)	111.6(3)
C(13)-Si(2)-C(14)	110.3(4)
O(1)-Si(2)-C(7)	108.5(2)
C(13)-Si(2)-C(7)	108.9(3)
C(14)-Si(2)-C(7)	109.9(3)
Si(2)-O(1)-Si(1)	151.7(3)
C(5)-N(1)-C(1)	117.5(4)
C(5)-N(1)-Ag	124.2(3)
C(1)-N(1)-Ag	118.2(4)
C(6)-N(2)-C(10)	117.7(4)
C(6)-N(2)-Ag#1	121.6(3)
C(10)-N(2)-Ag#1	120.8(4)

Symmetry transformations used to generate equivalent atoms: #1 -x+1, y, -z+1/2 #2 -x+1/2, -y-1/2, -z-1

around Ag(I) ion has a dihedral angle of 20°. Thus, the intraligand π - π interactions still exist even though the two ligands in the cyclic compound are skewed. That is, the cyclic dimer is an "intraligand-parallel but interligand-skewed" conformer. The Si-O-Si angle (151.7(3)°) of the present compound is a median value between O(SiMe₃)₂ (148.8(2)°)²⁰ and [AgL₂]₂(PF₆)₂ (154.5(8)°).¹⁵ To date, the R₃Si-O-SiR₃ angle is very sensitive to R groups, and has a wide range of 142.2(3)°-180.0°.²¹ The Ag...Ag distance is shorter than the π - π stacking distance, indicating that weak intramolecular Ag...Ag interaction (3.411(1) Å) exist in the solid state. Such a distance is similar to the corresponding value of the known weak Ag...Ag interaction.¹⁶ The 20-membered tub-conformation may be partly stabilized *via* both the face-to-face (π - π) stackings and weak Ag...Ag interactions. The hexafluorophosphate anion is positioned as

a simple counteranion rather than a ligand (Ag...F > 3.5 Å).

Construction Principle. The discrete tub-metallacyclic skeleton was favorably formed irrespective of solvents, mole ratios. Why is the unique 20-membered tub-form so effectively constructed? Of course, a suitable combination of the appropriate length and non-rigid conformation of L and the potential linear geometry of N-Ag(I)-N may contribute to a driving force for the formation of the metallamacrocycle. That is, the Ag-N bonds are indispensable to the 20-membered ring, and the formation of the tub-conformer may be attributed to both the π - π and the weak Ag...Ag interactions. The Si-O-Si angle (151.7(3)°) seems to play an important role in the formation of discrete cyclic molecules instead of infinite linear polymers. The same reaction with a longer similar linker, 1,5-bis(3-pyridyl)hexamethyltrisiloxane, gave infinite double strands, presumably owing to the different stable conformation.¹⁴ For 1,3-bis(4-pyridyl)tetramethyldisiloxane, the similar reaction produced a symmetric molecular rectangle.¹⁵ Thus, delicate difference of the linker results in the formation of significantly different products. To date, the structures of the known silver(I) compounds with siloxane-containing pyridyl linkers have been greatly affected by π - π and Ag...Ag interactions.^{14,15} Such results may be attributed to the electronic effects of siloxane group.

In conclusion, 1,3-bis(3-pyridyl)tetramethyldisiloxane is a new horse-shoe tectonic suitable for tub-metallamacrocyclodimeric molecules. Our works are a good example to show that the conformation be controlled *via* the π - π and Ag...Ag interaction. When we use these siloxane-containing pyridyl ligands in the molecular construction, such a π - π interaction should be carefully considered. The molecular metallamacrocycles may contribute to the development of bond tunable-based materials such as sensor, recognition materials, or molecular switch.

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