

A Unique Zigzag Strand of Silver Perchlorate with Bis(3-pyridyl)cyclotetramethylenesilane

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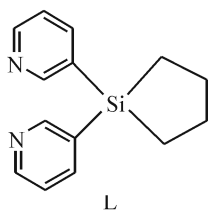
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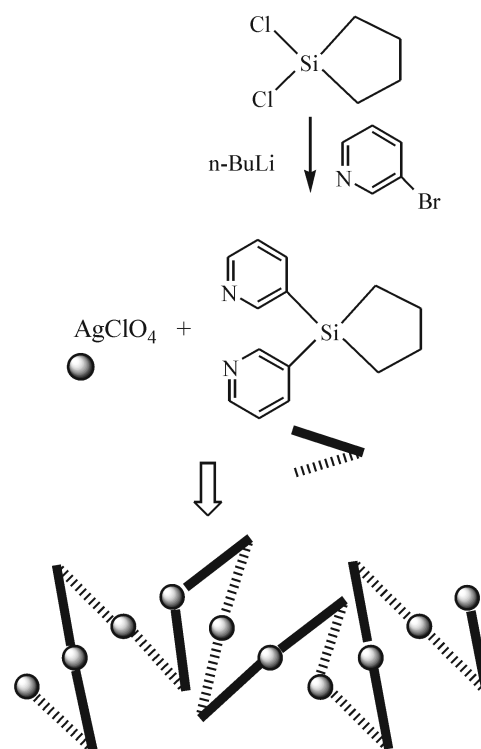
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Metal-based coordination polymers with specific motifs have been attracted due to both aesthetic facet and potential applicability such as electrical conductivity, molecular magnet, host-guest chemistry, crystal bending effect, and catalysis.¹⁻⁹ New motifs can be designed by selecting the coordination geometry of central metals, the structure of spacer ligands, the kinds of counterions, and reaction conditions.¹⁰⁻¹⁴ Among diverse elegant efforts to find key factors in the development of rational molecular structures, the use of new organic tectonics that can bridge two or more metal centers is of current interest. The appropriate angle and flexible components of the tectonics play important roles in establishing a rational design strategy.¹⁵⁻¹⁹ In this context, recently, silicone-containing bipyridyl tectonics have been developed and explored for a fascinating class of materials containing diverse architectures and functions.²⁰⁻²⁴ In order to explore the effects of angle constraint of the spacer ligand on the coordination polymerization, we report a unique structure and related properties of [AgL]ClO₄ prepared by the reaction of AgClO₄ with bis(3-pyridyl)-cyclotetramethylenesilane (L). L is a new tectonic ligand that possesses a rigid cyclotetramethylene moiety, confor-



mational nonrigidity of pyridyl group, and a potential bridged bidentate donor. The new ligand L was prepared according to the Stang's procedure.²⁰ The ligand is a stable crystalline solid which is soluble in common organic solvents. The slow diffusion of AgClO₄ with L affords colorless crystals of [AgL]ClO₄ as shown in Scheme 1. The silver complex is air-stable and is hardly soluble in water and in organic solvents. Its structure was established by X-ray characterization. The crystallographic unit and infinite



Scheme 1

structure are depicted in Figure 1, and relevant bond distances and angles are listed in Table 2. L connects two Ag(I) ions to give a unique molecular strand. The Ag-N bonds are in the range of 2.139(6)-2.176(5) Å. The local geometry of the silver(I) ion approximates to a linear arrangement (N-Ag-N = 173.6(2)^o, 176.8(3)^o). The perchlorate anion hardly interacts with the silver(I) ion, and thus, exists as a counteranion. (the shortest distance of Ag...O(1) = 2.95 Å, 3.04 Å). The most striking feature is that the skeletal strand is severely bent. Thus, the 81.48 Å strand per a c-axis unit (25.27 Å) is included in the unit cell. To our knowledge, this is the highest value of strand-length/unit.

The bent structure seems to be induced by a rigid C-Si-C angle (108.1(2)^o, 113.1(4)^o) of the 5-membered sillcycle. Two kinds of the intrastrand shortest distance Ag(I)...Ag(I) exist as 5.51 Å (parallel) and 6.82 Å (cross). Thus, the shape of this strand is very different according to the point of view (see Fig. 1). The top view including counteranions looks like

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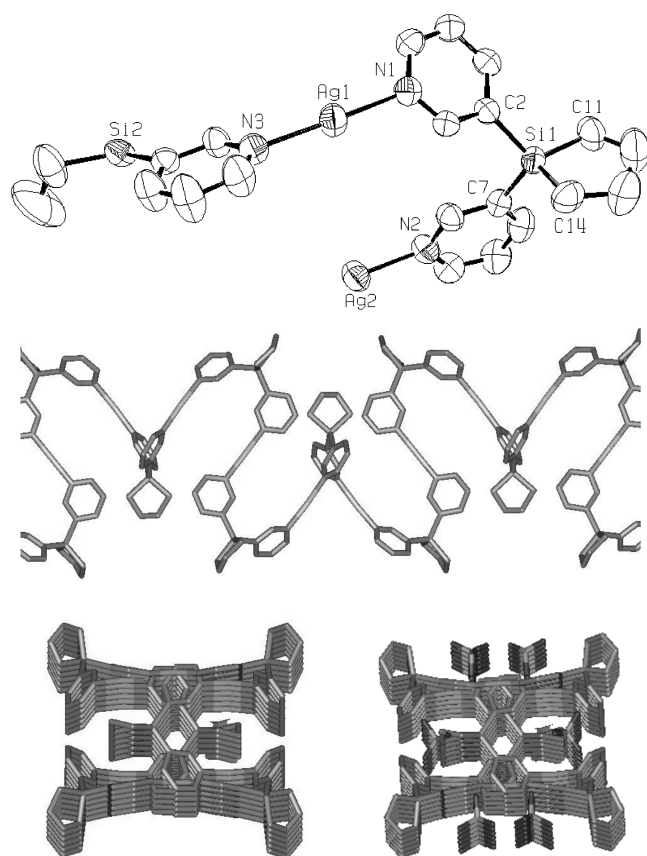


Figure 1. ORTEP view (top), infinite side view (middle), infinite top view (bottom left), and infinite top view including perchlorate anions (bottom right) of $[\text{AgL}]\text{ClO}_4$. For each structure, hydrogen atoms are omitted for clarity.

Table 1. Crystallographic Data for $[\text{AgL}]\text{ClO}_4$

formula	$\text{C}_{42}\text{H}_{48}\text{N}_6\text{O}_{12}\text{Cl}_3\text{Si}_3\text{Ag}_3$
f.w.	1343.09
space group	$C222_1$
a , Å	11.7286(3)
b , Å	17.4235(3)
c , Å	25.2688(6)
V , Å ³	5163.8(2)
Z	4
d_{cal} , gcm ⁻³	1.728
μ , mm ⁻¹	1.415
Crystal size (mm ³)	0.3 × 0.4 × 0.3
Completeness to theta = 27.46	98.3%
Data/restraints/parameters	5663 / 0 / 314
$R \{I > 2\sigma(I)\}$	$R_1 = 0.0553$ $wR_2 = 0.1390$

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad wR_2 = \frac{\sum w(F_o^2 - F_c^2)^2}{\sum wF_o^4}^{1/2}$$

a nano-pillar (11.7 Å × 17.4 Å). The angle and rigidity around the Si atom seems to play a key role in the construction of the unique 1D structure. Thus, delicate tuning and design of Si-containing spacer ligand is in progress in our laboratory.

In order to investigate the behavior of ClO_4^- anion, the IR spectra of the product were measured in various media. The

anion band measured in KBr pellet lies at 1088 cm^{-1} . The band in nujol mull appears at 1089 cm^{-1} . Moreover, the band in ionic liquid (1-*n*-butyl-imidazolium hexafluorophosphate)²⁵ absorbs at 1092 cm^{-1} . Thus, the anion band appears at a similar position irrespective of media, indicating that the perchlorate exists as a counteranion rather than a ligand in the solid structure, which is coincident with the X-ray structure. If the anion strongly interacted with the cationic skeletal structure, the band in ionic media significantly would shift in contrast to the band in neutral nujol media. Though the perchlorate is a counteranion, the anion exchange in aqueous suspension was hardly achieved in contrast to other silver complexes with simple pyridyl ligands.²⁶ The water-repellant properties of the silicon-containing ligand may be attributed to the non-exchangeability. Packing mode of anions may be in part responsible for the non-exchangeability. The TGA and DSC curve shows a drastic collapse at 247 °C.

The present system is significant as a rare example of nano-pillar consisting of the most severely bent strand. Further synthesis of analogues using the new ligands and pervasive applications including anion exchangeability are in progress, and will provide more detailed information on the development of the molecular networks that exhibit desirable properties.

Experimental Section

Bis(3-pyridyl)cyclotetramethylenesilane (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 40 min. Dichlorocyclotetramethylenesilane (3.2 mmol) was slowly added to the yellow suspension. 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 MgSO_4 . The crude product was purified by column chromatography on silica gel with ethyl acetate. The solvent was evaporated to obtain colorless crystals in 62% yield. mp 81 °C. Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{Si}$: C, 69.95; H, 6.71; N, 11.65. Found: C, 69.10; H, 6.58; N, 11.44. ¹H NMR (300 MHz, CDCl_3 , Me_4Si): δ = 1.18 (t, 2H, J = 7.2 Hz), 1.84 (m, 2H), 7.28 (m, 1H), 7.79 (dt, 1H, J = 2.0 Hz, J = 6.0 Hz), 8.64 (dd, 1H, J = 2.0 Hz, J = 4.0 Hz), 8.72 (s, 1H). ¹³C NMR (125.76 MHz, CDCl_3 , Me_4Si): δ = 12.2, 28.0, 123.9, 131.3, 142.8, 151.1, 155.3. EI-MS (80 eV): 240.0 [M^+]. IR (KBr, cm^{-1}): 2942 (s), 1572 (s), 1558 (s), 1394 (s), 1124 (s), 1080 (s), 1020 (s), 794 (s), 716 (s), 682 (s), 628 (s), 506 (s).

Preparation of $[\text{AgL}]\text{ClO}_4$. A methanol solution (6 mL) of L (48 mg, 0.2 mmol) was slowly diffused into an aqueous solution (6 mL) of AgClO_4 (41 mg, 0.2 mmol). Colorless crystals formed at the interface, and were obtained in 1 week in 74% yield. Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{AgClO}_4\text{Si}$: C, 37.56; H, 3.60; N, 6.20. Found: C, 37.50; H, 3.67; N, 6.14. IR (KBr, cm^{-1}): ν (ClO_4), 1088 (s). mp. 247 °C (dec). Using acetone

Table 2. Relevant Bond Distances (Å) and Angles (°) of [AgL]ClO₄

Ag(1)-N(3)	2.169(5)	Ag(1)-N(1)	2.176(5)
Ag(2)-N(2)#1	2.139(6)	Ag(2)-N(2)	2.139(6)
Si(1)-C(14)	1.881(8)	Si(1)-C(7)	1.883(6)
Si(1)-C(11)	1.890(7)	Si(1)-C(2)	1.892(6)
Si(2)-C(20)	1.872(9)	Si(2)-C(20)#2	1.872(9)
Si(2)-C(16)	1.881(6)	Si(2)-C(16)#2	1.881(6)
N(3)-Ag(1)-N(1)	173.6(2)	N(2)#1-Ag(2)-N(2)	176.8(3)
C(14)-Si(1)-C(7)	111.5(3)	C(14)-Si(1)-C(11)	95.4(4)
C(7)-Si(1)-C(11)	113.6(3)	C(14)-Si(1)-C(2)	113.7(3)
C(7)-Si(1)-C(2)	108.1(2)	C(11)-Si(1)-C(2)	114.1(3)
C(20)-Si(2)-C(20)#2	97.4(8)	C(20)-Si(2)-C(16)	111.7(4)
C(20)#2-Si(2)-C(16)	113.1(4)	C(20)-Si(2)-C(16)#2	113.1(4)
C(20)#2-Si(2)-C(16)#2	111.7(4)	C(16)-Si(2)-C(16)#2	109.5(3)
C(1)-N(1)-Ag(1)	120.8(4)	C(5)-N(1)-Ag(1)	119.0(4)
C(10)-N(2)-C(6)	117.3(6)	C(10)-N(2)-Ag(2)	122.4(5)
C(6)-N(2)-Ag(2)	119.4(4)	C(19)-N(3)-C(15)	116.6(5)
C(19)-N(3)-Ag(1)	123.8(5)	C(15)-N(3)-Ag(1)	119.6(4)

Symmetry transformations used to generate equivalent atoms: #1 $x, -y, -z+1$ #2 $-x, y, -z+3/2$

or ethanol instead of methanol, the same crystals were obtained.

Crystallographic Structure Determination. A colorless crystal was wedged in a Lindemann capillary with mother solvent. X-ray data were collected on a Bruker SMART automatic diffractometer with a graphite-monochromated Mo K α 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 structure was solved by the SHELXS 97 and refined by SHELXL 97.²⁷ The non-hydrogen atoms were refined anisotropically, and 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 were given in Table 1. The chiral space group was determined by the intensities of Friedel pairs.

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-232275). 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).

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