Polymorphism of Molecular Rectangle *via* Flexible Argentophilic Interaction

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Crystallization is a process taken for granted for most chemists since it is a standard method for purifying solid samples. During the process, a compound is sometimes crystallized in more than one distinct crystal morphology. This situation leads to the formation of polymorphs, that is, supramolecular isomers differing in solid state packing. In the last two decades, the polymorphic interest has been a sharp rise for the development of a variety of desirable materials such as molecular switch, sensor etc.[1,2] Polymorphism can profoundly influence the physicochemical properties of solid materials[3] since polymorphs display different density, hardness, solubility, opto-electrical properties, and thermodynamic stability. The preferential growth of a particular form can often be rationalized by the consideration of conformational equilibria or changes in patterns of weak interactions.[1] Recently, the anion-dependent structures and related properties of silver(I) pseudohalides with 1,3-bis(4-pyridyl)tetramethyldisiloxane were published as a communication.[4]

In this context, we report *an interesting polymorphism induced by labile transannular argentophilic interaction* in silver(I) perchlorate with 1,3-bis(4-pyridyl)tetramethyldisiloxane (L). In particular, the induction and modulation of such a d[10] argentophlic interaction is a thematic issue in silver chemistry.[5-12]

(L)
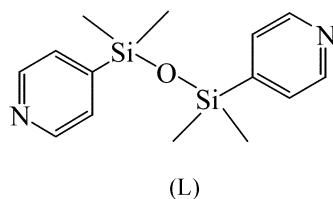
Experimental Section

Materials and Measurements. Silver(I) perchlorate was purchased from Aldrich and, and used without further purification. 1,3-Bis(4-pyridyl)tetramethyldisiloxane (L) was prepared according to our previous procedure.[4] Elemental microanalyses (C, H, N) were performed at the Advanced Analysis Center at KIST using a Perkin-Elmer 2400 CHNS Analyzer. X-ray powder diffraction data were recorded on a Rigaku RINT/DMAX-2500 diffractometer at 40 kV, 126 mA for Cu Kα. Thermal analyses (TGA and

DSC) 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.

Preparation of [AgL]$_2$(ClO$_4$)$_2$. An ethanol solution (5 mL) of L (58 mg, 0.2 mmol) was slowly diffused into an aqueous solution (5 mL) of AgClO$_4$ (41 mg, 0.2 mmol). Colorless crystals of [AgL]$_2$(ClO$_4$)$_2$ formed at the interface, and were obtained in 3 days in 71% yield. Anal. Calcd for C$_{14}$H$_{20}$N$_2$ClO$_5$Si$_2$Ag: C, 33.91; H, 4.07; N, 5.65. Found: C, 33.70; H, 4.08; N, 5.63. IR (KBr, cm^{-1}): ν(ClO$_4$), 1088 (s). Two shapes of crystals of needles and plates in a 2 : 1 ratio were obtained.

Crystallographic Structure Determination. A colorless crystal of plate form wedged in a Lindemann capillary with mother solvent. X-ray data were collected on a Bruker SMART automatic diffractometer with a graphite-mono-chromated Mo Kα radiation (λ = 0.71073 Å) and a CCD detector at ambient temperature. The 45 frames of two

Table 1. Crystallographic Data for Plate Crystal of [AgL]$_2$(ClO$_4$)$_2$

formula	C$_{28}$H$_{40}$N$_4$O$_{10}$Cl$_2$Si$_4$Ag$_2$
f.w.	991.64
space group	$P\bar{1}(bar)$
a, Å	10.562(1)
b, Å	14.239(2)
c, Å	14.554(2)
α, deg	71.593(2)
β, deg	84.042(3)
γ, deg	81.304(2)
V, Å^3	2049.2(4)
Z	2
d_{cal}, g cm^{-3}	1.607
m, mm^{-1}	1.256
Crystal size (mm^3)	0.1 × 0.3 × 0.3
Completeness to theta = 27.46	92.6%
Data/restraints/parameters	9415 / 0 / 451
R {I > 2σ(I)}	R$_1$ = 0.0505
	wR$_2$ = 0.1110

R$_1$ = Σ | Fo|–|Fc|| / Σ Fo|. wR$_2$ = Σw(Fo^2–Fc^2)^2/ΣwFo^2)$^{1/2}$

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.[15] 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.

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-252062). 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).

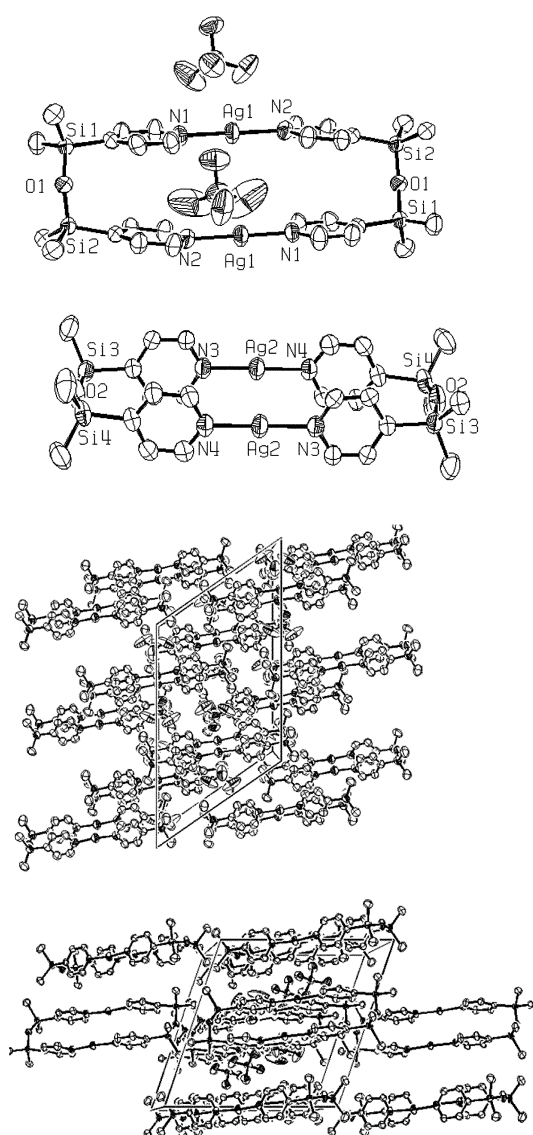**Figure 1.** ORTEP view of plate [AgL]₂(ClO₄)₂, indicating two inequivalent molecules in the unit cell (top). Packing diagram of needle (middle) and plate crystals (bottom). For each structure, hydrogen atoms are omitted for clarity.

Results and Discussion

Slow diffusion of $AgClO_4$ with L afforded discrete cyclic molecules in contrast to general bipyridyl analogues.[9,11,12,14,15] The diffusion reaction was not significantly affected by the reaction condition such as reactant mole ratios, solvents, and concentrations, indicating that the discrete cyclic compound is a favorable species. The product is a colorless crystalline solid that is hardly soluble in water and common organic solvents. The most salient feature is that two shapes of needle and plate crystals are obtained in a 2 : 1 ratio. The structure of the needle crystal (monoclinic *C2/c*) was immediately published as a communication.[1] To elucidate the detailed structure of the plate crystal, single crystal X-ray diffraction was performed. The X-ray characterization (*P1* bar) has provided the composition of [AgL]₂(ClO₄)₂ (Figure 1). Relevant bond distances and angles are listed in Table 2. For both shape crystals, the basic molecular structure is a cyclic dimer. That is, an unusual horse-shoe tectonic L connects two Ag(1) ions (Ag–N = 2.142(5)–2.176(4) Å) to form a 24-membered macrocycle. However, the plate crystals have two inequivalent molecules in the unit cell in contrast to the needle crystals. Of course, the packing of the plate crystal is substantially different from that of needle crystals, presumably due to the flexible 24-membered macrocycle. The Ag···Ag distances of the two inequivalent molecules (3.53(1) Å; 4.28(1) Å) are considerably different. Thus, one molecule is close to a rectangle, and the other is a parallelogram rather than a rectangle. The parallelogram cyclodimer seems to be induced by elongation of the Ag···Ag distance along with the retention of the π–π stackings (~3.6 Å). Such a fact indicates that the weak transannular Ag–Ag interaction is susceptible to the surroundings. The distance of 3.53(1) Å is in the range of van der Waals interaction, whereas that of 4.28(1) Å is out of the interaction range.[1]

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

Ag(1)-N(1)	2.163(4)
Ag(1)-N(2)#1	2.176(4)
Ag(2)-N(4)#2	2.142(5)
Ag(2)-N(3)	2.156(5)
N(2)-Ag(1)#1	2.176(4)
N(4)-Ag(2)#2	2.142(5)
N(1)-Ag(1)-N(2)#1	173.30(19)
N(4)#2-Ag(2)-N(3)	171.07(19)
C(1)-N(1)-Ag(1)	120.6(4)
C(6)-N(2)-Ag(1)#1	121.3(4)
C(10)-N(2)-Ag(1)#1	121.7(4)
C(15)-N(3)-Ag(2)	121.5(4)
C(19)-N(3)-Ag(2)	120.5(4)
C(20)-N(4)-Ag(2)#2	123.0(5)
C(24)-N(4)-Ag(2)#2	120.1(4)

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

Scheme 1

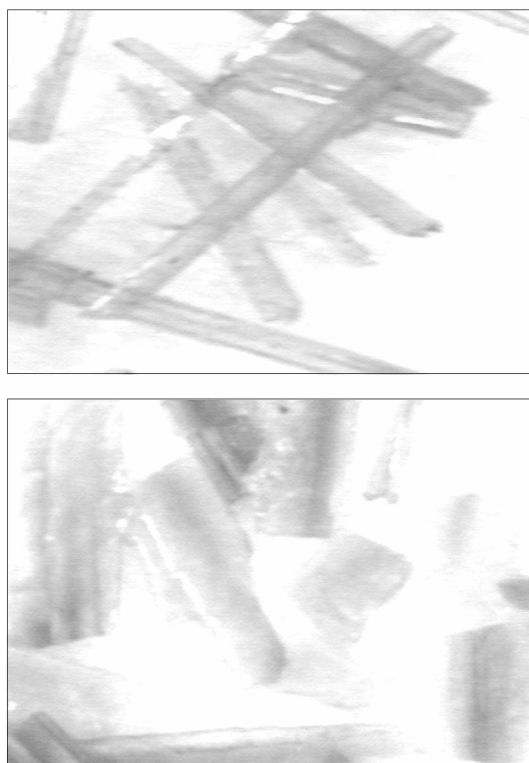**Table 3.** Comparison of Two Shapes of Crystals

shape	Needle*	Plate
space group	C2/c	P1(bar)
Ag···Ag distance (Å)	3.41(1)	3.53(1). 4.29(1)
Molecular shape	rectangle	rectangle. parallelepiped
Density	1.597	1.607

*ref. 4

shoe tectonic L and the linear or T-shaped geometric unit Ag(1) ion seems to produce the discrete cyclodimers instead of coordination polymers. The horse-shoe tectonic may be induced by the intracyclic $\pi-\pi$ along with the argentophlic interactions. The felicitous tuning of the Ag···Ag distance can be attributed to the nonrigidity of 24-membered macrocycle

In conclusion, the present cyclodimeric molecule is a good example of polymorphism that occurs via labile structural feature of molecular rectangle. Since such weak metal-metal interactions play an important role in the kinetic and thermodynamic stabilization, this polymorphism will be intended to contribute to the development of desirable materials via structure vs polymorphs.

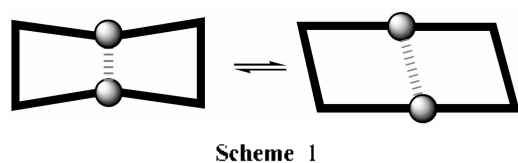**Figure 2.** Morphology of cyclodimeric [AgL]₂(ClO₄)₂, needle form and plate form.

The weak Ag–Ag interaction (Scheme 1) may trigger a keen competition among the transannular Ag–Ag interactions, intraligand $\pi-\pi$ interactions, and electrostatic interactions between cationic skeleton and its counteranions, and ultimately induce the polymorphism. This is a good example of the polymorph via flexible Ag–Ag interaction. The argentophilic interaction of this compound can be changed without any particular strain. The two shapes of crystals was compared and listed in Table 3. In particular, the understanding of closed-shell d¹⁰ Ag–Ag interactions is a very important issue since the interactions give rise to intriguing supramolecular motifs, crystal packing, and specific photophysical properties.[5-12] The control of polymorphism may be a significant work. A preliminary experiment indicates that the ratio of two crystals is dependent upon crystallization-solvents.

On the other hand, a suitable combination of the horse-

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