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Anion Effects on the Formation of Cross-Linked Argentophilic Interaction. Synthesis and Structural Properties of AgX Bearing Bis(3-pyridyl)dimethylsilane ($X^- = CF_3SO_3^-$, PF_6^-, and NO_3^-)

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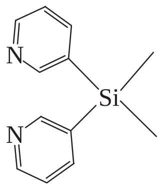
Anion effects on the formation of a cross-linked Ag–Ag interaction in the molecular construction of a series of AgX complexes with bis(3-pyridyl)dimethylsilane (L) ($X^- = CF_3SO_3^-$, PF_6^-, and NO_3^-) have been carried out. The slow diffusion of an organic solution of L into an aqueous solution of AgX afforded [Ag(L)]X or [Ag(X)(L)]. Each L connected two Ag(I) ions (Ag–N = 2.110(5)–2.161(4) Å) to form a wave strand. For $CF_3SO_3^-$ and PF_6^- anions, each single strand cross-linked the adjacent single strands via an argentophilic interaction (Ag–Ag = 3.0551(7) Å for $CF_3SO_3^-$, 3.279(1) Å for PF_6^-) to produce unique 2D sheets. In contrast, for the NO_3^- anion, the anion acts as a ligand ($Ag–O_3N = 2.61–2.79$ Å) instead of the argentophilic interaction (Ag···Ag = 3.351(1) Å). That is, a small coordinating anion is an obstacle to form the argentophilic interaction, whereas a big noncoordinating anion favors the argentophilic interaction in the present molecular construction. For all complexes, the geometry around the Ag(I) ion is a typical T-shaped arrangement. The thermal stability can be explained in terms of the structural properties, including the argentophilic interaction.

A thematic issue in the molecular construction of silver(I) compounds is understanding closed-shell d^{10} Ag–Ag interactions and π–π interactions that give rise to intriguing supramolecular motifs, crystal packing, and specific photophysical properties.[1–6] Such noncovalent weak interactions have often been studied to deduce general structure–stability relationships. The results can be extended beyond the initial goal to diverse areas, such as quantum-mechanical calculations, spectroscopic studies, molecular biology, and recognition materials.[2,7,8] Furthermore, some counteranions have significantly affected the modulation and induction of skeletal structures, since the anions have many features, such as negative charges, big sizes, a wide range of geometries, delicate solvent effects, and strong pH dependence.[9–11] Recent developments in anion chemistry include exciting advances in anion template assembly, ion-pair recognition, and the function of supramolecular materials.[12–15] In particular, the exploitation of silicon-containing pyridine-based ligands has given interesting coordinating natures.[16–20] The silicon-containing tectonic ligands possess manageable properties in the facets of a potential bridging ability, flexible tetrahedral angles around the silicon, an easy control of length, conformational non-rigidity, and electronic effects of the silicone group.

In an effort to observe the anion effects on cross-linked Ag–Ag interactions, the reaction of AgX ($CF_3SO_3^-$, PF_6^-, and NO_3^-) with bis(3-pyridyl)dimethylsilane (L) was carried out. We report on the syntheses and structural properties of [Ag(L)]X or [Ag(X)(L)]. The Ag(I) ion has been employed as various directional units, such as linear, T-shaped, and tetrahedral geometry.[21,22] Bis(4-pyridyl)dimethylsilane has been known,[20] but bis(3-pyridyl)dimethylsilane (L) is a new ligand (Chart 1).



L

Chart 1.

Experimental

Materials and Measurements. AgX ($X^- = CF_3SO_3^-$, PF_6^-, and NO_3^-) were purchased from Strem Chemicals, and were 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.

Preparation of Bis(3-pyridyl)dimethylsilane (L). The new ligand was prepared according to a literature procedure:[20] to a solution of 3-bromopyridine (7 mmol) in dry ethyl ether (20 mL) un-

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Table 1. Crystallographic Data

	$[CF_3SO_3]$[a)]	$[PF_6]$[b)]	$[NO_3]$[c)]
Formula	$C_{13}H_{14}N_2O_3F_3SSiAg$	$C_{12}H_{14}N_2PF_6SiAg$	$C_{24}H_{28}N_6O_6Si_2Ag_2 \cdot H_2O$
fw	465.23	467.18	786.46
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a/Å	11.1123(3)	10.930(3)	20.495(2)
b/Å	14.0514(5)	14.192(3)	7.3163(6)
c/Å	11.6570(3)	11.097(3)	20.752(2)
β/deg	103.953(2)	106.79(2)	107.108(1)
V/Å^3	1766.46(9)	1647.9(6)	2974.0(4)
Z	4	4	4
D_{calcd}/g cm^{-3}	1.749	1.883	1.756
μ/mm^{-1}	1.369	1.450	1.450
$R\{I > 2\sigma(I)\}$	$R1$[d)] = 0.0514	0.0408	0.0480
	$wR2$[e)] = 0.1473	0.1056	0.1258
R(all data)	$R1$[d)] = 0.0644	0.0420	0.0791
	$wR2$[e)] = 0.1655	0.1068	0.1482

a) $[Ag(L)](CF_3SO_3)$. b) $[Ag(L)](PF_6)$. c) $[Ag(NO_3)(L)]$. d) $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. e) $wR2 = \Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma wF_o{}^2)^{1/2}$.

der 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 this temperature for 1 h. 1,3-Dichlorodimethylsilane (3.2 mmol) was slowly added to the yellow suspension for 2 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 was then dried over $MgSO_4$. The crude product was purified by column chromatography on silica gel with ethyl acetate. The solvent was evaporated to obtain a viscous liquid in 62% yield. Anal. Calcd for $C_{12}H_{14}N_2Si_2$: C, 67.24; H, 6.58; N, 13.07%. Found: C, 67.10; H, 6.48; N, 12.90%. ^1H NMR (300.00 MHz, $CDCl_3$, $SiMe_4$): δ 0.63 (s, 6H), 7.14 (q, 2H), 7.65 (dt, $J = 2.0$ Hz, $J = 6.0$ Hz, 2H), 8.48 (dd, $J = 2.0$ Hz, $J = 4.0$ Hz, 2H), 8.59 (s, 2H). ^{13}C NMR (125.76 MHz, $CDCl_3$, Me_4Si): δ 2.73, 123.51, 132.10, 141.85, 150.70, 154.55. EI-MS (70 eV): 214 [M^+].

$[Ag(L)](CF_3SO_3)$. A methanol solution of L (43 mg, 0.20 mmol) was slowly diffused into an aqueous solution of $AgCF_3SO_3$ (51 mg, 0.20 mmol). Colorless crystals of $[Ag(L)](CF_3SO_3)$ formed at the interface, and were obtained in 72% yield based on Ag(I) salt. mp 287 °C (dec). Anal. Calcd for $C_{13}H_{14}N_2O_3F_3SSiAg$: C, 33.13; H, 2.99; N, 5.94%. Found: C, 33.0; H, 2.89; N, 5.89%. IR (KBr, cm^{-1}): $\nu(CF_3SO_3)$, 826(s).

$[Ag(L)](PF_6)$. This reaction was carried out in a similar method of $[Ag(L)](CF_3SO_3)$. Yield: 70%. mp 249 °C (dec). Anal. Calcd for $C_{12}H_{14}N_2PF_6SiAg$: C, 30.85; H, 3.02; N, 6.00%. Found: C, 30.30; H, 3.08; N, 6.11%. IR (KBr, cm^{-1}): $\nu(PF_6)$, 846(s).

$[Ag(NO_3)(L)]$. A methanol solution (6 mL) of L (43 mg, 0.20 mmol) was slowly diffused into an aqueous solution (6 mL) of $AgNO_3$ (32 mg, 0.20 mmol). Colorless crystals of $[Ag(NO_3)(L)]$ formed at the interface, and were obtained in 6 d in 60% yield. mp 230 °C (dec). Anal. Calcd for $C_{12}H_{14}N_3O_3SiAg \cdot 0.5H_2O$: C, 36.65; H, 3.84; N, 10.69%. Found: C, 36.20; H, 3.79; N, 10.34%. IR (KBr, cm^{-1}): $\nu(NO_3)$, 1384(s).

Crystallographic Structure Determination. X-ray data were collected on a Bruker SMART automatic diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and a CCD detector at ambient temperature. Then, 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 absorption effects were corrected by the empirical ψ-scan method. The structures were solved by the direct method (SHELXS 97) and refined by full-matrix least-squares techniques (SHELXL 97).[23] The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed at the calculated positions and refined only for the isotropic thermal factors. The crystal parameters and procedural information corresponding to data collection and structure refinement are given in Table 1. For $[Ag(NO_3)(L)]$, two oxygen atoms (O(4) and O(6)) of one nitrate were disordered.

Further details concerning the crystal-structure investigation for $[Ag(L)](CF_3SO_3)$ (CCDC No. 273541), $[Ag(L)](PF_6)$ (CCDC No. 273540), and $[Ag(NO_3)(L)]$ (CCDC No. 273539) are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

Results and Discussion

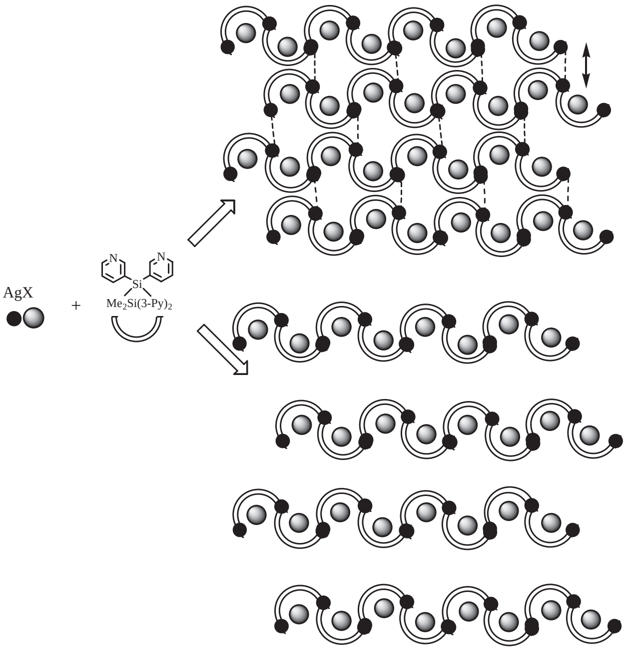
Synthesis. A new ligand of bis(3-pyridyl)dimethylsilane (L) was smoothly obtained in 62% yield. The slow diffusion of an organic solution of L into an aqueous solution of AgX ($X^- = CF_3SO_3{}^-$, $PF_6{}^-$, and $NO_3{}^-$) afforded [Ag(L)]X or [Ag(X)(L)] (Scheme 1). The reaction was originally accomplished in a 1:1 mole ratio of Ag(I) and L, but the products were not significantly affected by a change of the mole ratio. Moreover, when acetone or ethanol was used as a solvent instead of methanol, the same products were obtained. Each structure has basically the same skeleton, but the Ag–Ag interaction is strongly dependent upon the nature of the anions, as will be explained later. For relatively big noncoordinating anions, $CF_3SO_3{}^-$ and $PF_6{}^-$, a cross-linked Ag–Ag interaction exists to form unique 2D sheets. However, a small coordinating anion, $NO_3{}^-$, interacts with the Ag(I) ion instead of the cross-linked Ag–Ag interaction. The crystalline products are stable and are insoluble in water and common organic solvents.

Structures. The X-ray structure on a single crystal of $[Ag(L)](CF_3SO_3)$ has provided unique coordination polymers, as depicted in Fig. 1. Relevant structural data are listed in

Table 2. Each L connects two Ag(I) cations (Ag–N(1) = 2.147(3) Å, Ag–N(2) = 2.157(3) Å) to form a wave strand. Each single strand cross-links the adjacent strands via an argentophilic interaction (Ag–Ag = 3.0551(7) Å) to form a 2D sheet. Thus, the geometry around the Ag(I) ion approximates a T-shaped arrangement (N(1)–Ag–N(2) = 169.0(1)°; N(1)–Ag(1)–Ag(1)′ = 98.3(1)°; N(2)–Ag(1)–Ag(1)′ = 92.05(9)°). The slightly bent angle of N(1)–Ag–N(2) (169.0(1)°) is evidence of the presence of the Ag–Ag interaction. The triflate anion does not significantly interact with the Ag(I) ion, and thus acts as a simple counteranion (the shortest distance of Ag···O = 2.798 Å). Thus, the 2D sheet consists peanut-shape motifs, and the anions are nestled in a peanut shape. The sheets are stacked in the abab… layers mode. The layer thickness is similar to the distance of the π–π interaction.

The crystal structure of [Ag(L)](PF$_6$) is very similar to the structure of [Ag(L)](CF$_3$SO$_3$) (Fig. 2). However, the Ag–Ag distance increases by 0.224 Å (3.279(1) Å) relative to that (3.0551(7) Å) of [Ag(L)](CF$_3$SO$_3$). Thus, the N(1)–Ag–N(2) angle is also enlarged to 175.2(2)°. Relevant structural data are listed in Table 2. The PF$_6{}^-$ anion acts as a simple counteranion (the shortest distance of Ag···F = 2.96 Å).

The structure of [Ag(NO$_3$)(L)] is shown in Fig. 3, and relevant structural data are listed in Table 2. There are two independent units in the asymmetric region of the monoclinic unit cell. Each L connects two Ag(I) ions (Ag–N = 2.154(4)–2.161(4) Å) to form a wave strand. The distance of Ag–O$_3$N (2.61 and 2.79 Å) indicates that the NO$_3{}^-$ anion acts as a ligand rather than a counteranion. The slightly bent N–



Scheme 1.

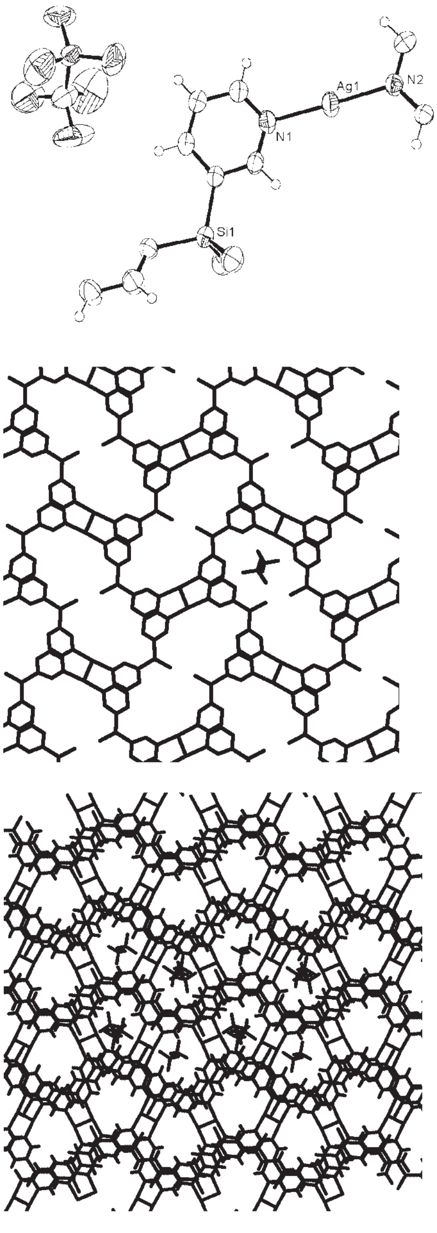


Fig. 1. Asymmetric unit (top), infinite structure (middle), and two infinite layers (bottom) of [Ag(L)](CF$_3$SO$_3$).

Table 2. Selected Bond Parameters and Structural Features

	[CF$_3$SO$_3$]$^{a)}$	[PF$_6$]$^{b)}$	[NO$_3$]$^{c)}$
Ag–N/Å	2.147(3), 2.157(3)	2.110(5), 2.114(4)	2.154(4)–2.161(4)
N–Ag–N/°	169.0(1)	175.2(2)	161.6(1), 171.7(1)
C–Si–C/°	107.1(2)–113.0(3)	107.7(3)–111.8(2)	107.0(2)–111.7(2)
Ag···X/Å	2.83	2.96	2.61, 2.79
Ag···Ag/Å	3.0551(7)	3.279(1)	3.351(1)
Geometry	T-shape	T-shape	T-shape

a) [Ag(L)](CF$_3$SO$_3$). b) [Ag(L)](PF$_6$). c) [Ag(NO$_3$)(L)].

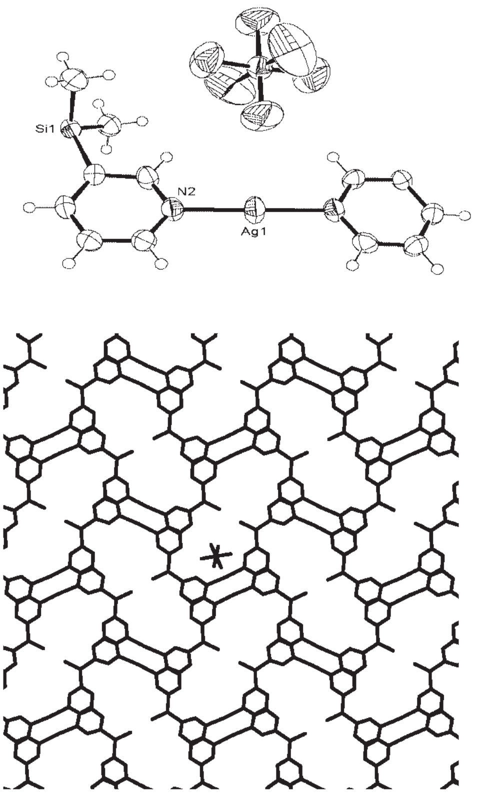


Fig. 2. Asymmetric unit (top) and infinite structure (bottom) of [Ag(L)](PF_6).

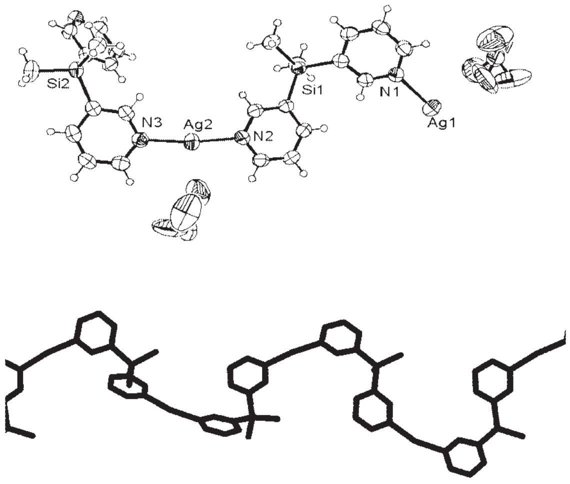


Fig. 3. Asymmetric unit (top) and infinite structure (bottom) of [Ag(NO_3)(L)].

Ag–N angles (161.6(1)° and 171.7(1)°) are due to the Ag–O_3N electrostatic interaction. Thus, the interstrand Ag–Ag distance is much longer (3.351(1) and 3.913(1) Å) than those of [Ag(L)](PF_6) and [Ag(L)](CF_3SO_3). The overall skeleton of [Ag(NO_3)(L)] approximates a single wave strand instead of a 2D sheet.

Construction Principle. The skeleton of all the compounds is a single wave strand, but the cross-linked argentophilic interaction is strongly dependent on the nature of the anions. The formation of the strand may be attributed to a suitable combination of the skewed conformer of L and the potential linear geometry around the N–Ag–N bonds. In particular, all of the compounds are exclusively constructed irrespective of the mole ratio of the reactants, the solvent types, and the concentrations. Each single wave strand cross-links the adjacent strands via argentophilic interactions to form a unique molecular sheet. For the $CF_3SO_3^-$ and PF_6^- compounds, the argentophilic distances (3.0551(7) and 3.279(1) Å) are similar to the known closed-shell d^{10} Ag–Ag interactions.[4] The argentophilic interactions are longer than the Ag–Ag distance in silver metal (2.89 Å),[24] but are shorter than the van der Waals radii (3.44 Å).[25] In contrast, for the NO_3^- compound, the Ag···Ag distance (3.351(1) Å) is much longer than those of the $CF_3SO_3^-$ and PF_6^- analogues. Such results may be explained by the following nature of anions. The big $CF_3SO_3^-$ and PF_6^- anions that have been considered as common "non-coordinating" anions[26] have little tendency to serve as ligands in the present structures. Thus, such non-coordinating anions afford the relatively short Ag–Ag distances. The small coordinating NO_3^- anion (Ag–O_3N = 2.61–2.79 Å) gives the long Ag···Ag distance. The metal–metal interaction of the present products appears to be delicately associated with the coordinating nature and size of anions. For the present system, π–π interactions also exist, and the interactions may play an important role in the formation of each structure. The formation of stable Ag–N bonds, Ag–Ag interactions, and π–π interactions may be partly indebted to the electronic effects of the silicon-containing ligand. For instance, Ag(I) complexes with silicon-containing ligands, such weak Ag–Ag interactions and π–π interactions, have been frequently observed, presumably owing to the donating ability of the silicon atom.[19]

Stability and Thermal Properties. All compounds are insoluble in water and common organic solvents, but are easily dissolved in polar organic solvents, such as dimethyl sulfoxide, *N*,*N*-dimethylformamide, and acetonitrile. The products seem to be dissociated in the solution. The products are air-stable, but slowly turn to gray powder under light. The thermal analyses were used to establish the relationship between the structure and the thermal properties.[27,28] The thermal stabilities of the present compounds are dependent upon each skeletal structure (Fig. 4). The decomposition temperature of the 1D wave strand, [Ag(NO_3)(L)] (230 °C) is lower than those of the 2D structures, [Ag(L)](PF_6) (249 °C) and [Ag(L)](CF_3SO_3) (287 °C). The collapse temperature of [Ag(NO_3)(L)] is relative

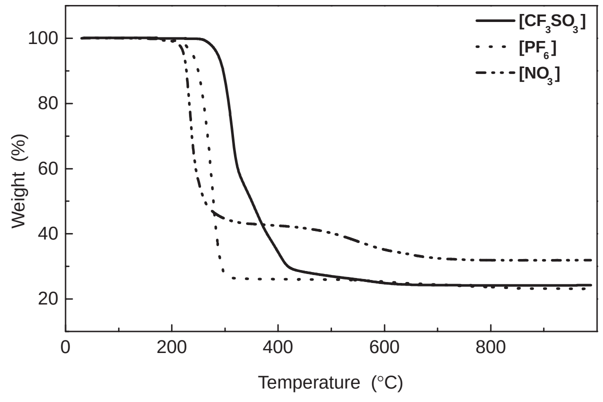


Fig. 4. Thermogravimetric analyses of [Ag(L)](CF_3SO_3) (—), [Ag(L)](PF_6) (···), and [Ag(NO_3)(L)] (–··).

to the $[Ag_3(L)_4](NO_3)_3$ (231 °C).[18] Furthermore, $[Ag(L)](CF_3SO_3)$ (287 °C) is more stable than $[Ag(L)](PF_6)$ (249 °C). The volume expansion due to thermal energy collapses the compounds, resulting in a change from a highly ordered arrangement to a more random state. Thus, the present results indicate that the Ag–Ag argentophilic strength is directly dependent on the thermal stability of the present compounds.

In conclusion, the new silicon-based bipyridine spacer is a fascinating tectonic without any particular strain in the construction of a stable wave skeleton. The silicon-containing ligand induces a ligand-unsupported cross-linked Ag–Ag interaction. Furthermore, the nature of the anion tunes the argentophilic interaction. The present results may contribute to the development of rational molecular-based materials of multidimensional coordination polymers.

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