

Ring-Conformations *via* the Competition of Electrostatic Interaction and Argentophilic Interaction. Cyclodimeric Structures of Silver Trifluoromethanesulfonate Containing Isonicotinate Ester Ligands

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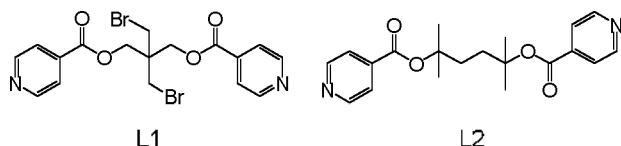
Metallacyclodimers, $[\text{Ag}(\text{OTf})(\text{L1})_2]$ and $[\text{Ag}(\text{L2})_2(\text{OTf})_2]$ ($\text{L1} = 1,3\text{-dibromo-2,2-bis}[(\text{isonicotinoyloxy})\text{methyl}]\text{propane}$; $\text{L2} = 2,5\text{-dimethyl-2,5-bis}[(\text{isonicotinoyloxy})\text{hexane}]$) were constructed and characterized. The crystal structure of $[\text{Ag}(\text{OTf})(\text{L1})_2]$ reveals a 32-membered cyclodimer, whereas that of $[\text{Ag}(\text{L2})_2(\text{OTf})_2]$ shows a linked 34-membered cyclodimer chain *via* intercylic argentophilic ($\text{Ag}\cdots\text{Ag}$) interactions. $[\text{Ag}(\text{OTf})(\text{L1})_2]$ affords "intramolecular $\pi\text{-}\pi$ interaction cyclodimer" whereas $[\text{Ag}(\text{L2})_2(\text{OTf})_2]$ produces a racemic mixture of "twisted cyclodimer". Ring-conformation of the cyclodimers was affected *via* the competition of electrostatic interaction and argentophilic interaction.

Key Words: Isonicotinoyl ligands. Metallacyclodimers. Ring-conformation. Silver(I) complexes

Introduction

The rational design and construction of metallacycles is a challenging and fruitful field since the macrocyclic molecules have various potential applications such as separation science, harmful materials adsorption, molecular containers, ion exchangers, and luminescent sensing.¹⁻⁵ Thus, various kinds of metallacyclic molecules have been synthesized by the coordinations of metal ions with organic tectonics.⁶⁻¹⁰ Appropriate angles, lengths, and flexible components of multidentate N-donor linkers play key important roles in the construction of the tailor-made metallacyclic molecules.^{4,11} However, the constructions of specific metallacycles are often serendipitous owing to the coexistence of specific noncovalent interactions such as $\pi\text{-}\pi$ stackings, metal-metal interactions, and hydrogen-bonds.⁵ Recently, we have demonstrated that various (iso)nicotinoyl linkers are useful tectonics for desirable cyclic skeletons.¹²⁻¹⁵ Silver(I) ion has been employed as angular directional units of linear or T-shaped geometry.^{16,17} In our recent report, we have demonstrated the delicate structural difference between the two metallacyclic silver(I) complexes *via* anion effects for AgX ($\text{X}^- = \text{ClO}_4^-$ and BF_4^-) complexes containing isonicotinoyl-containing ligands.¹⁵ These ligands are adjustable in their potential bridging ability and length, possess flexible angles, and are conformationally nonrigid.¹²⁻¹⁵

As a part of our continuing interest, we report here delicate difference on ring-conformations *via* the competition of electrostatic interaction and argentophilic interaction for metallacyclic Ag(I) complexes containing 1,3-dibromo-2,2-bis[(isonicotinoyloxy)methyl]propane (L1) and 2,5-dimethyl-2,5-bis[(isonicotinoyloxy)hexane] (L2).



Experimental Section

Materials and Measurements. All chemicals including AgOTf ($\text{OTf}^- = \text{CF}_3\text{SO}_3^-$, trifluoromethanesulfonate) were purchased from Aldrich Chemicals, and used without further purification. 1,3-Dibromo-2,2-bis[(isonicotinoyloxy)methyl]propane (L1) and 2,5-dimethyl-2,5-bis[(isonicotinoyloxy)hexane] (L2) were prepared by the literature method.¹² Anion exchange was accomplished according to a reference procedure.¹⁷ Elemental microanalyses (C, H, N) were performed on crystalline samples by the Pusan Center at KBSI using a Vario-EL III. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury Plus 300 operating at 300.00 and 75 MHz, respectively, and the chemical shifts were relative to the internal Me_4Si . Infrared spectra were obtained on a Nicolet 380 FT-IR spectrophotometer with samples prepared as KBr pellets. Thermal analyses were carried out under a dinitrogen atmosphere at a scan rate of $10^\circ\text{C}/\text{min}$ using a Labsys TGA-DSC 1600.

$[\text{Ag}(\text{OTf})(\text{L1})_2]$. A methanol solution of AgOTf was slowly diffused into a dichloromethane solution of 1,3-dibromo-2,2-bis[(isonicotinoyloxy)methyl]propane (L1) in the mole ratio of 1 : 1. Yield: 70% based on Ag(I) salt. Calcd for $\text{C}_{36}\text{H}_{32}\text{N}_4\text{O}_{14}\text{F}_6\text{S}_2\text{Br}_4\text{Ag}_2$: C, 29.65; H, 2.21; N, 3.84. Found: C, 30.10; H, 2.18; N, 3.79. IR (KBr, cm^{-1}): 3546, 1736, 1410, 1269 (OTf^-), 1169, 1115, 1039, 854, 758, 703, 636.

$[\text{Ag}(\text{L2})_2(\text{OTf})_2]\cdot\text{CH}_3\text{OH}$. A methanol solution of AgOTf was slowly diffused into a dichloromethane solution of 2,5-dimethyl-2,5-bis[(isonicotinoyloxy)hexane] (L2) in the mole ratio of 1 : 1. Yield: 83% based on Ag(I) salt. Calcd for $\text{C}_{44}\text{H}_{52}\text{N}_4\text{O}_{15}\text{F}_6\text{S}_2\text{Ag}_2$: C, 41.03; H, 4.16; N, 4.45. Found: C, 40.80; H, 4.15; N, 4.50. IR (KBr, cm^{-1}): 1718, 1562, 1406, 1300, 1273, 1255 (OTf^-), 1165, 1128, 1045, 760, 652 (OTf^-).

X-ray Crystallography. All X-ray data were collected on a Bruker SMART automatic diffractometer with a graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and a CCD detector at ambient temperature. The 45 frames of two dimensional diffraction images were collected and processed to

Table 1. Crystal Data and Structure Refinements for $[\text{Ag}(\text{OTf})(\text{L1})_2]$ and $[\text{Ag}(\text{L2})_2](\text{OTf})_2 \cdot \text{CH}_3\text{OH}$.

	$[\text{Ag}(\text{OTf})(\text{L1})_2]$	$[\text{Ag}(\text{L2})_2](\text{OTf})_2 \cdot \text{CH}_3\text{OH}$
formula	$\text{C}_{36}\text{H}_{32}\text{N}_4\text{O}_{14}\text{F}_6\text{S}_2\text{Br}_4\text{Ag}_2$	$\text{C}_{43}\text{H}_{32}\text{N}_4\text{O}_{15}\text{F}_6\text{S}_2\text{Ag}_2$
M_w	1458.16	1258.75
cryst syst	Orthorhombic	Orthorhombic
space group	<i>Pbcn</i>	<i>Pbcn</i>
$a/\text{\AA}$	21.5082(7)	12.5883(5)
$b/\text{\AA}$	9.9497(3)	25.6794(1)
$c/\text{\AA}$	21.4562(7)	16.2029(6)
$V/\text{\AA}^3$	4591.6(3)	5237.7(4)
Z	4	4
density/ Mg/m^3	2.109	1.596
μ/mm^{-1}	4.518	0.915
$F(000)$	2832	2552
GOF on F^2	1.087	1.030
$R_1 [I > 2\sigma(I)]^a$	0.0247	0.0463
wR_2 (all data) ^b	0.0558	0.1308

$$^a R_1 = \frac{\sum |F_o| - F_d}{\sum |F_o|}, \quad ^b wR_2 = \left(\frac{\sum (F_o^2 - F_c^2)^2}{\sum w F_o^2} \right)^{1/2}$$

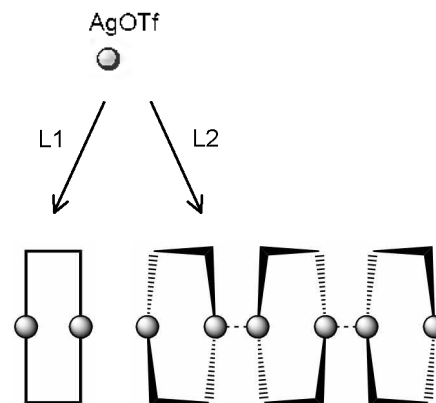
Table 2. Selected Bond Lengths (\AA) and Angles ($^\circ$) of $[\text{Ag}(\text{OTf})(\text{L1})_2]$ and $[\text{Ag}(\text{L2})_2](\text{OTf})_2$.

	$[\text{Ag}(\text{OTf})(\text{L1})_2]$	$[\text{Ag}(\text{L2})_2](\text{OTf})_2$
Ag(1)-N(1)	2.200(3)	2.133(4)
Ag(1)-N(2)	2.190(3)	2.141(4)
Ag(1)···O(5)	2.664	
N(1)-Ag(1)-N(2)	176.19(1)	174.22(2)

obtain the cell parameters and orientation matrix. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the empirical method. The structures were solved by the direct method (SHELXS 97) and refined by full-matrix least squares techniques (SHELXL 97).¹⁸ The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions and refined using a riding model. The crystal parameters and procedural information corresponding to the data collection and structure refinement were listed in Table 1 and the relevant structural data were listed in Table 2. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-720474 and CCDC-741990). 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).

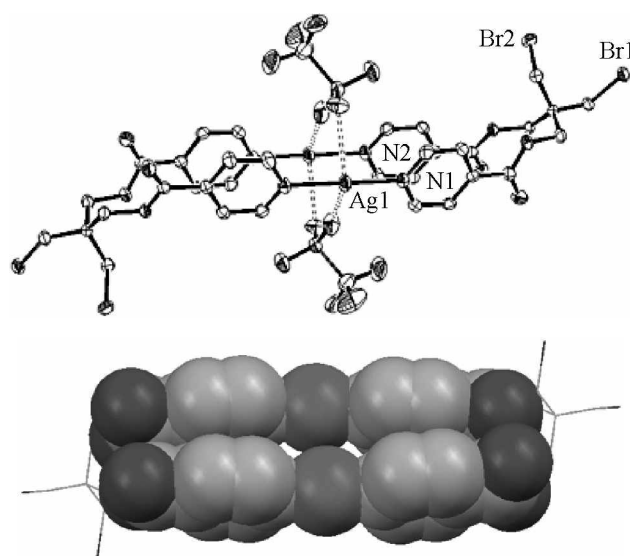
Results and Discussion

Synthesis and Properties of Silver(I) Metallacyclic Complexes. The slow diffusion of AgOTf in methanol with L in dichloromethane produced colorless crystals consisting of metallacyclodimers (Scheme 1). The reactions were originally carried out at the mole ratio of 1 : 1, but the formation of the

**Scheme 1**

products was not significantly affected by the change of reactant mole ratio and concentration, indicating that the products are thermodynamically favorable species. The products are metallacyclodimers instead of polymeric species. Both products are insoluble in water and common organic solvents, but are easily dissociated in polar organic solvents, such as dimethyl sulfoxide, *N,N*-dimethylformamide, and acetonitrile. The crystalline products are air-stable, but slowly turn to gray powder under light. The elemental analyses and IR spectra are consistent with the cyclodimeric structures. Strong stretching frequency of OTf⁻ anions appears at around 1250 - 1270 cm^{-1} .

Crystal Structures. X-ray characterizations on both single crystals have provided metallacyclodimers, and their relevant bond lengths and angles are listed in Table 2. The X-ray crystal structure of $[\text{Ag}(\text{OTf})(\text{L1})_2]$ shows a discrete metallacyclodimer as depicted in Figure 1. Each L1 connects two Ag(I) cations ($\text{Ag-N} = 2.190(3) - 2.200(3) \text{\AA}$) to form a 32-membered cyclodimer. The triflate anion slightly interacts with the Ag(I) ion ($\text{Ag(1)} \cdots \text{O(5)} = 2.66$; $\text{Ag(1)} \cdots \text{O(6)} = 2.81 \text{\AA}$), and thus acts as a ligand rather than a counteranion, and hence the geo-

**Figure 1.** ORTEP drawing (top) and space-filling diagram showing the π - π interaction (bottom) of $[\text{Ag}(\text{OTf})(\text{L1})_2]$. Hydrogen atoms (top and bottom) and counteranions (bottom) are omitted for clarity.

metry around the Ag(I) ion approximates a T-shaped arrangement ($N(1)-Ag-N(2) = 176.2(1)^\circ$, $N(1)-Ag(1)\cdots O(5) = 89.28(1)^\circ$, $N(2)-Ag(1)\cdots O(5) = 87.70(1)^\circ$). The L1 ligand acts as a horse-shoe tectonic, which is useful for the construction of molecular rectangles.¹⁵ The metallacyclodimer may be stabilized *via* an intramolecular face-to-face $\pi-\pi$ stacking ($N(1)\cdots N(2) = 4.023(4)$ Å, dihedral angle = $10.0(2)^\circ$, center to center = 3.81 Å). The most salient feature is that the intramolecular $Ag\cdots Ag$ argentophilic interaction (4.167(1) Å) is longer than the face-to-face stacking. The bite size of triflate (the angle of $O-S-O = 113.60(2)^\circ$) that electrostatically interacts with Ag(I) ion makes the longer argentophilic interaction.⁶

The crystal structure of $[Ag(L2)]_2(OTf)_2$ reveals that the crystal consists of the similar metallacyclodimer ($Ag(1)-N(1) = 2.133(4) - 2.141(4)$ Å) (Figure 2). However, the triflate anion was considered as a counteranion rather than a coordinating ligand (the shortest distance of $Ag\cdots O = 3.000(5)$ Å). Instead, intermolecular argentophilic interaction between the adjacent metallacyclodimers (3.369(1) Å) exists to lead a linked-ring chain. The L2 ligand acts as a horse-shoe tectonic to form a 34-membered ring. An important feature is that the metallacyclodimer is a twisted conformer. R- and S-form are alternatively arranged to finally a racemic mixture. The distorted bond angle of $N(1)-Ag(1)-N(2)$ ($174.22(2)^\circ$) form ideal linear

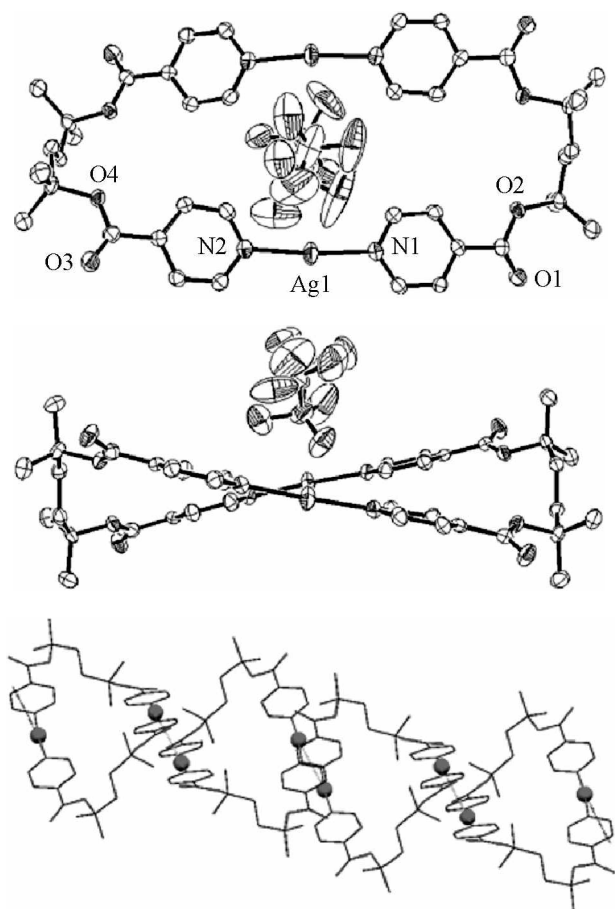


Figure 2. ORTEP drawing (top, top view; middle, side view) and packing diagram showing the racemic mixture (bottom) of $[Ag(L2)]_2(OTf)_2$.

geometry supported the presence of the argentophilic interaction. Thus, an intermolecular face-to-face interaction (3.52(2) Å, dihedral angle = $4.4(2)^\circ$) was observed to further stabilize this polymeric skeleton.

Thermal Properties and Anion Exchange. The thermogravimetric analysis (TGA) curves of $[Ag(OTf)(L1)]_2$ and $[Ag(L2)]_2(OTf)_2$ indicated a similar decomposition pattern as depicted in Figure 3. $[Ag(OTf)(L1)]_2$ is stable up to 276 °C whereas $[Ag(L2)]_2(OTf)_2$ is collapsed at 178 °C. The difference may be affected by the skeletal structure including $\pi-\pi$ interaction, argentophilic interaction, and intermolecular interaction. We attribute the formation of each structure to the felicitous "metallacyclic conformation" rather than the "argentophilic interaction" character. The decomposition temperature of $[Ag(OTf)(L1)]_2$ is much higher than that of $[Ag(L2)]_2(OTf)_2$. The thermal stability can be explained in terms of the structural properties including the ring size and anion stability.

In order to measure the different exchangeability of anions, the anion exchanges of both compounds with $NaPF_6$ were carried out in aqueous solution.¹⁷ The anion exchange of $[Ag(OTf)(L1)]_2$ with $NaPF_6$ is slower than that of $[Ag(L2)]_2(OTf)_2$ with $NaPF_6$. To investigate the exchange procedure, the anion exchanges of both products with PF_6^- was monitored by the characteristic IR bands of anions (Figure 4). The anion exchange in water at room temperature was checked after 3 h, 6 h, 9 h, 1 day, and 2 days. The infrared spectra show the gradual disappearance of intense OTf^- bands ($1200 - 1300\text{ cm}^{-1}$) and the appearance and growth of new PF_6^- peaks ($800 - 900\text{ cm}^{-1}$). The anion exchange of $[Ag(L2)]_2(OTf)_2$ with $NaPF_6$ was completely accomplished within 3 h, but the anion exchange of $[Ag(OTf)(L1)]_2$ with $NaPF_6$ was partly carried out even for 2 days. Such a fact is consistent with that, for $[Ag(OTf)(L1)]_2$, OTf^- acts as a ligand rather than a counteranion whereas, for $[Ag(L2)]_2(OTf)_2$, OTf^- acts as a counteranion rather than a coordinating ligand. Thus, the anion exchange seems to be significantly affected to the nature of anions, presumably due to the $CF_3SO_3^- \cdots Ag(I)$ interactions. During the anion exchange, the other peaks of the IR spectrum remain virtually unchanged, suggesting that the metallacyclic skeleton is retained after the anion exchange. Thus, the anion exchange may be applied as a tailored strategy for the determination of the

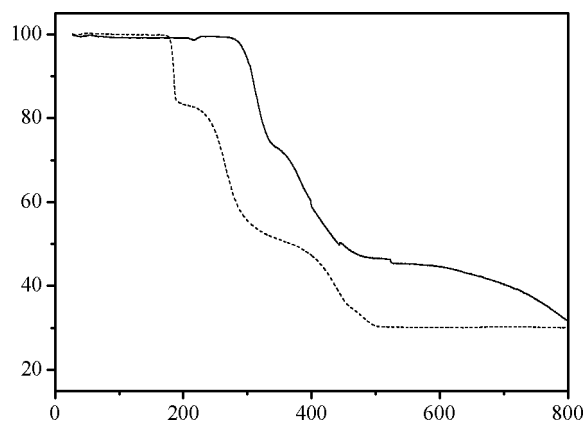


Figure 3. TGA curves of $[Ag(OTf)(L1)]_2$ (solid line) and $[Ag(L2)]_2(OTf)_2$ (dashed line).

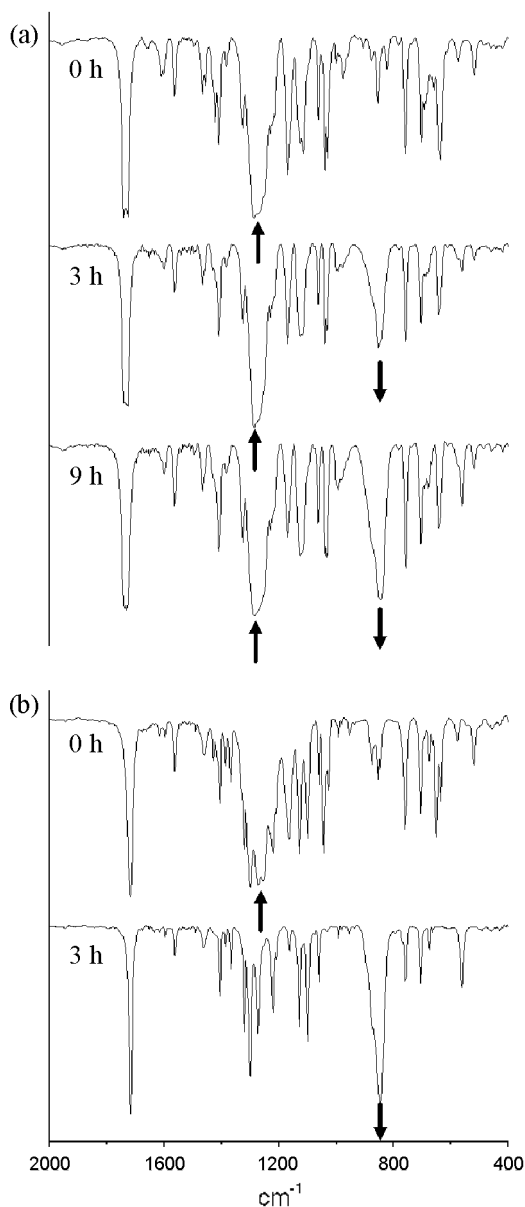


Figure 4. IR spectra during the anion exchange of $[\text{Ag}(\text{OTf})(\text{L}1)]_2$ with NaPF_6 after 0 h, 3 h, and 9 h (a), and the anion exchange of $[\text{Ag}(\text{L}2)]_2(\text{OTf})_2$ with NaPF_6 after 0 h and 3 h (b).

metallophilicity of anions.

Construction Principle. The metallacyclodimeric skeleton was favorably formed irrespective of solvents, concentrations, and mole ratios. Why is the metallacyclodimeric species so effectively constructed? Both compounds do not reveal significant angle strains. Of course, a suitable combination of the appropriate length and non-rigid conformation of spacer ligands and the potential linear geometry of Ag(I) ion may contribute to a driving force for the formation of the metallacycles. That is, the Ag–N bonds are indispensable to the macrocyclic ring, and the formation of the cyclodimer may be attributed to both the π - π and the weak argentophilic interactions. The horse-shoe tectonic seems to play an important role in the formation of discrete cyclic molecules instead of infinite linear polymers.

The same reaction with L2 gave a twisted metallacyclo-

dimer whereas the reaction of L1 produces “ π - π interaction metallacyclodimer”. What is the critical driving force for the delicate conformational differences between both complexes? Delicate structural difference of the linkers results in the formation of significantly different conformation. To date, the structures of the known silver(I) compounds with pyridyl linkers have been greatly affected by π - π and Ag \cdots Ag interactions.¹⁹ Besides the factors, competition between electrostatic interaction between Ag(I) and anions and intermolecular argentophilic interaction (Ag(I) \cdots Ag(I)) is another very important factor for the formation of the conformation.

Conclusions

The self-assemblies of AgOTf with isonicotinoyl linkers afforded an interesting pair of metallacyclic complexes. Formation of two different conformations between $[\text{Ag}(\text{OTf})(\text{L}1)]_2$ and $[\text{Ag}(\text{L}2)]_2(\text{OTf})_2$ is a good example to show that the conformation be controlled *via* the competition of an ionic electrostatic interaction and an argentophilic interaction. The molecular metallacycles may contribute to the development of bond tunable-based materials such as sensor, recognition materials, or molecular switch.

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