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Regioisomer-Dependent Endo- and Exocyclic Coordination of Bis-Dithiamacrocycles

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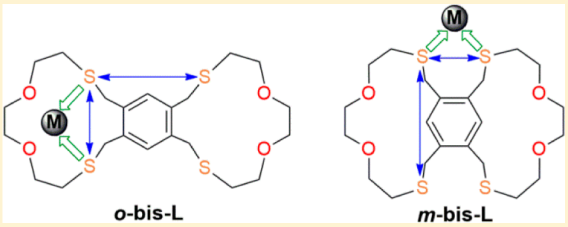
Supporting Information

ABSTRACT: Syntheses of the regioisomers of bis-dithiamacrocycle and the regioisomer-controlled endo- and exocyclic coordination behaviors are reported. Direct bis-cyclization reaction of 1,2,4,5-tetra(bromomethyl)benzene with 3,6-dioxa-1,8-octanedithiol led to a mixture of two bis-dithiamacrocycle regioisomers (*ortho*-type; ***o*-bis-L** and *meta*-type; ***m*-bis-L**) which were separated by recrystallization and column chromatography. When the two isomers were reacted with $AgPF_6$, ***o*-bis-L** gave an endocyclic one-dimensional (1-D) coordination polymer $\{[Ag_3(\textit{o}\text{-bis-L})_2(CH_3CN)](PF_6)_3{\cdot}2CH_3CN\}_n$ (**1**) with a 3:2 (metal-to-ligand) stoichiometry, while ***m*-bis-L** afforded an exocoordination-based 1-D polymeric complex $\{[Ag(\textit{m}\text{-bis-L})](PF_6)\}_n$ (**2**) with a 2:2 stoichiometry. The observed endo- and exocoordination modes depending on the isomers were discussed in terms of the S···S distances in the bis-dithiamacrocycle isomers. Due to the closer S···S distance in each macrocyclic ring, ***o*-bis-L** is suitable for the endocoordination. However, ***m*-bis-L** forms an exocyclic complex because the S···S distance between two macrocyclic rings is shorter than that in one macrocyclic ring. NMR experiments also revealed that ***o*-bis-L** and ***m*-bis-L** form the endo- and the exocyclic complexes, respectively, in solution.



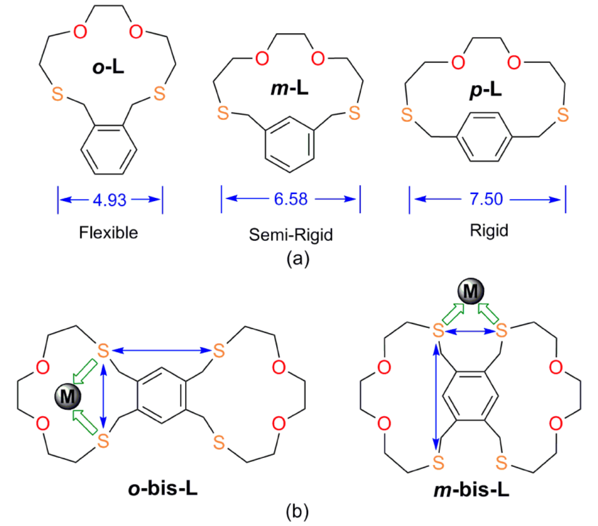
■ INTRODUCTION

The structural modification of macrocyclic ligands has been an important strategy for the construction of novel metallosupramolecular species because this approach can lead to a considerable variety of coordination modes and geometries.[1] So often, such macrocyclic ligands employ an aromatic subunit as a ring member to control conformational rigidity, cavity size, reactivity, solubility, and so on. Thus, the strategy for the preparation of novel coordination species for the macrocyclic ligands involves the structural modification of the aromatic subunit.[2−4] In this regard, the benzo-macrocycle isomers obtained by changing the substitution position in the aromatic subunit have been considered in this approach.[2,4]

Recently, we have reported the NS_2-macrocyclic isomers with a xylyl subunit in *ortho*-, *meta*-, and *para*-positions and their soft metal complexes exhibiting unique network patterns.[4a] In this case, the sulfur donor in the macrocyclic ring tends to lead the coordination of a metal ion to the exocyclic mode (metal outside the cavity) due to its sufficient lone pair electron density.[5,6] Thus, how to control the endo- and the exocyclic coordination and to apply this behavior to the design of new supramolecular system also became our challenging task.[6]

We have established several strategies to control the endo- and the exocoordination modes of the macrocyclic complex system by anion[7] and ligand design.[8] We have also introduced the O_2S_2-macrocyclic isomers (***o*-L**, ***m*-L**, and ***p*-L** in Scheme 1a)[9] and their thiaphilic metal complexes with the endo- and/or the exocyclic coordination modes, depending on the conformational ring rigidity and the S···S distances in the ring cavity arising from the substitution position in the aromatic subunit of the isomers.

Scheme 1. (a) Three Regioisomers of the O_2S_2-Macrocycle with Different S···S Distances (Å) and (b) Two Regioisomers of the Bis-O_2S_2-Macrocycle and their Expected Coordination Modes Due to the Different S···S Distances



On the other hand, binuclear macrocyclic complexes are one of the coordination systems of interest in diverse areas, such as

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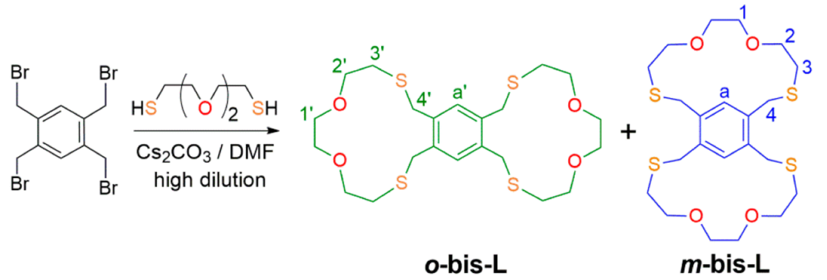
Scheme 2. Synthesis of a Mixture of **o-bis-L** and **m-bis-L** via Bis-Cyclizations



electron transport, charge transfer, and allosteric behavior in biochemical systems.[10] Loeb and Shimizu reported the *meta*-type bis-S_3- and bis-OS_2-macrocycles and their binuclear complexes in which two thiaphilic metal ions are coordinated in the endocyclic mode.[2]

Hence, we reasoned that the cooperation of two dithiamacrocycle rings to the aromatic center in different substitution position might induce the controlled endo- and exocyclic products as depicted in Scheme 1b. In this work, we therefore propose two macrocycle regioisomers **o-bis-L** and **m-bis-L** in which two O_2S_2 donor rings are disubstituted in different aromatic positions (**o-bis-L**, 1,2-disubstitution; **m-bis-L**, 1,3-disubstitution). Accordingly, the S···S distance inside the ring cavity in **o-bis-L** is expected to be much shorter than that in **m-bis-L**, and their ring rigidities can be assumed to be **m-bis-L** > **o-bis-L**. Furthermore, the proposed two regioisomers can be obtained through a one-pot reaction from the commercial reagents followed by an appropriate separation process. We report the syntheses and the separation of the bis-macrocycle regioisomers and their endo- and exocyclic silver(I) complexes, with emphasis on the different coordination modes associated with the structural conformations of the isomers.

■ RESULTS AND DISCUSSION

Synthesis and Separation of Macrocycle Isomers (o-bis-L and m-bis-L). Unlike the individual synthetic procedures for the monocyclic isomers **o-**, **m-**, and **p-L** shown in Scheme 1,[4a] in principle, the bis-cyclization reaction of 1,2,4,5-tetra(bromomethyl)benzene with 3,6-dioxa-1,8-octane-dithiol can lead to both *ortho-* (**o-bis-L**) and *meta*-type (**m-bis-L**) bis-macrocycle isomers via 1,2- and 1,3-bis-cyclizations, respectively (Scheme 2).

For the synthesis of the bis-thiamacrocyclic ligands, as mentioned, the reaction of 1,2,4,5-tetra(bromomethyl)benzene with 2 equiv of 3,6-dioxa-1,8-octanedithiol was carried out in the presence of Cs_2CO_3 in DMF under the high dilution condition. The ^{1}H NMR spectrum of this crude product mixture revealed the presence of two isomers in a 1:4 ratio (Figure 1b). The small signals at 2.9–3.4 ppm in Figure 1b seem to be derived from the unidentified byproducts including the decomposed chemicals.

The minor product **o-bis-L** exhibits a general downfield shift compared to those of **m-bis-L**. These two isomers in the mixture were separated using their differential solubility and recrystallization, coupled with the column chromatography on silica gel. The ^{1}H and ^{13}C NMR spectra of **o-bis-L** and **m-bis-L** clearly show the success of the separation of each component from the mixture (Figure 1, and Figures S1 and S2 in the Supporting Information). No 1,4-bis-cyclization product (**p-bis-L**) was isolated from this reaction nor observed in the ^{1}H NMR spectrum of the reaction mixture.

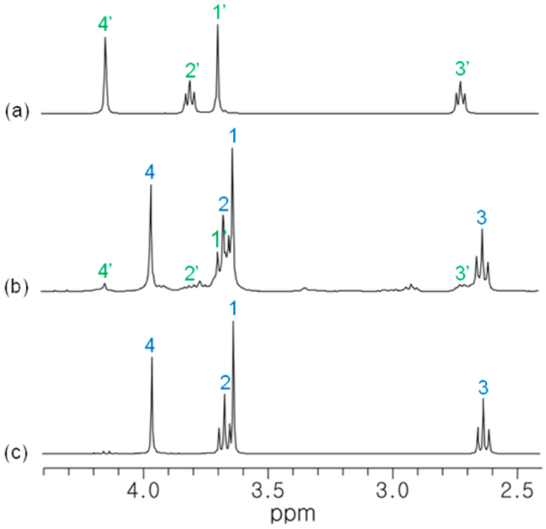


Figure 1. ^{1}H NMR spectra of the aliphatic region for (a) **o-bis-L**, (b) a crude mixture of **o-bis-L** and **m-bis-L**, and (c) **m-bis-L** in $CDCl_3$.

Synthesis and Structural Characteristics of Silver(I) Complexes (1 and 2). Complexation of both isomers **o-bis-L** and **m-bis-L** with $AgPF_6$ yielded colorless precipitates. Vapor diffusion of diethyl ether to the acetonitrile solution of each complex of **o-bis-L** and **m-bis-L** gave crystalline products **1** and **2**, respectively. The purity of each product was confirmed by comparing the simulated powder X-ray diffraction (PXRD) pattern from the single crystal X-ray data with the synthesized bulk sample (Supporting Information Figure S3).

Single crystal X-ray analysis revealed that **1** crystallizes in the monoclinic space group *P*2/*c* and adopts a 1-D polymeric structure with a formula $\{[Ag_3(\textbf{o-bis-L})_2(CH_3CN)](PF_6)_3\cdot 2CH_3CN\}_n$ (Figure 2 and Figure S4 in the Supporting Information). Selected geometric parameters of **1** are presented in Table S2. The asymmetric unit of **1** in the complex part contains two ligand molecules (a half molecule of ligand I, a half molecule of ligand II, and one molecule of ligand III), three Ag atoms (Ag1, Ag2, and Ag3), and one coordinated acetonitrile molecule. The three crystallographically independent Ag atoms are differentiated by their bridging (Ag1 and Ag2) and terminal (Ag3) coordination modes (Figure 2a).

The local coordination environment of the two bridging Ag atoms (Ag1 and Ag2) is similar (Figure 2c). For example, each endocyclic Ag atom is coordinated by the O_2S_2-donor set from ligand I or ligand II in a stair-like arrangement, and the fifth coordination site is completed by one S donor from one cyclic ring in ligand III via Ag–S bond, resulting in the formation of the 1-D polymeric chain. The Ag1 and Ag2 atoms are positioned 1.069(2) and 1.120(1) Å from each O_2S_2 plane

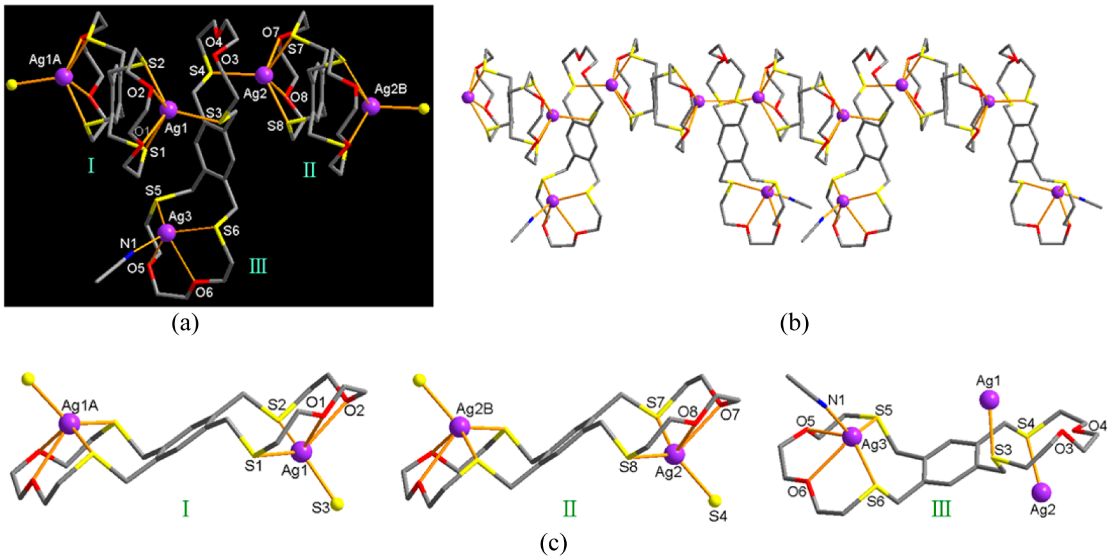


Figure 2. Endocyclic 1-D coordination polymer **1**, $\{[Ag_3(\textbf{\textit{o}-bis-L})_2(CH_3CN)](PF_6)_3 \cdot 2CH_3CN\}_n$: (a) core coordination environment, (b) general view of 1-D network structure, (c) local coordination environment of each silver(I). Noncoordinating anions and solvent molecules are omitted.

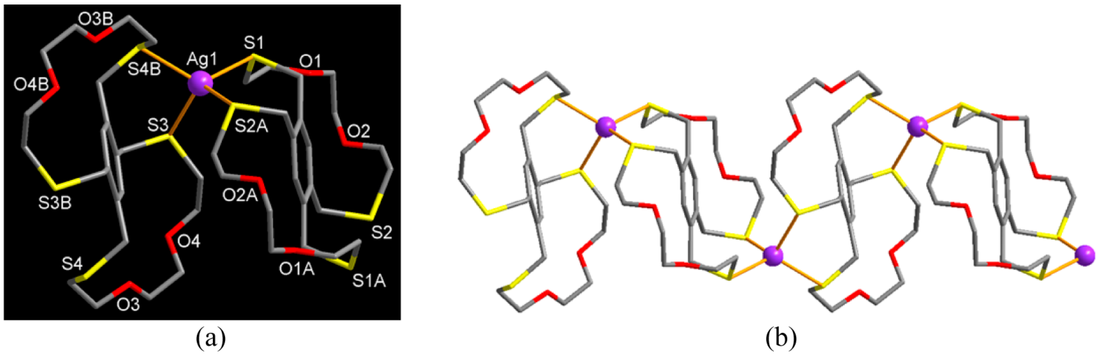


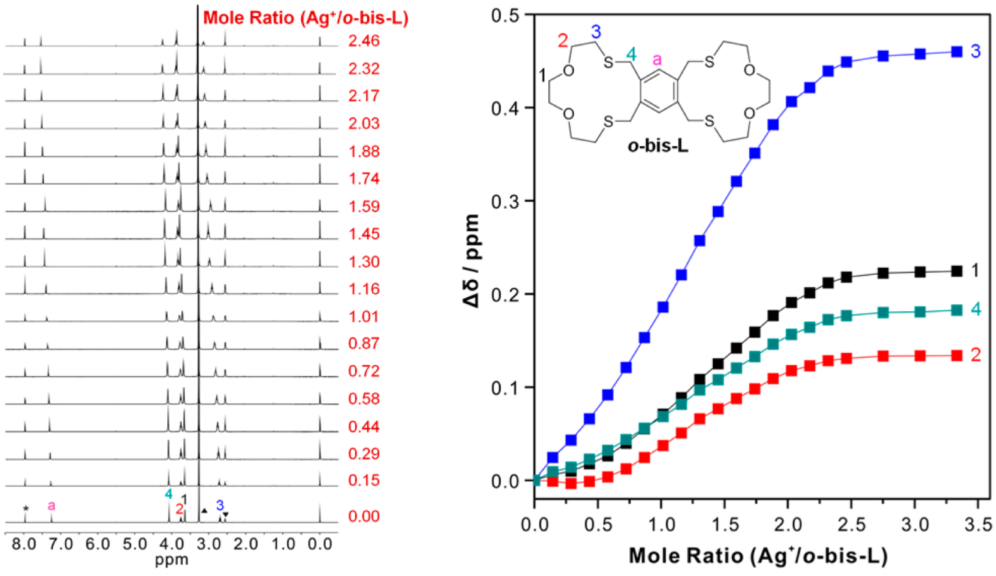
Figure 3. Exocyclic 1-D coordination polymer **2**, $\{[Ag(\textbf{\textit{m}-bis-L})]PF_6\}_n$: (a) core coordination unit and (b) general view of 1-D zigzag network structure. Noncoordinating anions are omitted.

toward ligand III, adopting a perching conformation. The Ag3 atom is also five-coordinate, being coordinated by the O_2S_2-donor from another ring in the ligand III. Unlike Ag1 and Ag2 atoms, the coordination sphere of Ag3 atom is completed by one acetonitrile solvent molecule with the silver(I) positioned 1.025(2) Å from the O_2S_2 plane toward the solvato-ligand, adopting a perching conformation.

Sometimes, it is hard to distinguish a square pyramid (SP) and a trigonal bipyramid (TBP) for a distorted five coordinate complex. Addison's group[11] proposed the simple distortion parameter τ, which serves a measure of the degree of SP versus TBP geometry adopted by the five-coordinate copper(II) complex. According to the definition $[\tau = (\theta_1 - \theta_2)/60]$, where θ_1 is the largest and θ_2 is the second largest basal angle, a perfect SP is characterized by $\tau = 0$, while $\tau = 1$ means a perfect TBP. In **1**, the τ values for Ag1, Ag2, and Ag3 atoms are 0.18, 0.14, and 0.21, respectively. Therefore, all silver(I) centers in **1** can be described as being in a distorted square pyramidal environment.

The Ag−S bond distances [2.509(3)−2.570(2) Å] in **1** are typical, and the Ag−N bond distance [2.240(8) Å] is also within the normal literature range for this bond type.[12] The Ag−O bond distances [2.671(6)−2.804(5) Å] in this structure lie in the longer end of the database range (2.40−3.06 Å).[13] In the overall structure, Ag1 and Ag2 atoms are fully shielded from further interaction with solvent or anions by the endocyclic coordination of each ligand as well as the adjacent ligand resulting in the alternate perpendicular arrangement of the ligands. Consequently, the preferred endocoordination mode of ***o*-bis-L** in **1** presumably reflects that when the separation between two sulfur donors is small in the macrocyclic cavity, the two sulfurs will cooperate to chelate to one metal ion as depicted in Scheme 1b (left).

Single crystal X-ray analysis revealed that **2** crystallizes in the triclinic space group $P\bar{1}$. In marked contrast to the endocyclic coordination mode in **1**, compound **2** adopts an exocyclic 1-D coordination polymer of a formula $\{[Ag(\textbf{\textit{m}-bis-L})]PF_6\}_n$, in which no anion and solvent molecules are presented in the coordination sphere (Figure 3 and Figure S5 in the Supporting Information). In the complex part, the asymmetric unit of **2** contains a half molecule of ligand I, a half molecule of ligand II, and one Ag atom. So, the structural unit in Figure 3 is generated through an inversion symmetry. In **2**, each Ag atom which lies outside the cavity is bonded to two sulfur donors from one ligand molecule (molecule I) and two sulfur donors from another ligand molecule (molecule II) to form a distorted tetrahedral environment, with "tetrahedral angles" falling in the range 101.6(5)° for (S4A−Ag1−S3) to 127.3(4)° for (S1−Ag1−S4A). These deviations are due to the formation of the seven membered ring [Ag1−S3−C−C−C−C−S4A] via Ag−S



(a) (b)

Figure 4. (a) ^{1}H NMR spectra of ***o*-bis-L** following the stepwise addition of $AgPF_6$ in DMSO-d_6/$CDCl_3$ (6:4) and (b) their titration curves for each protons in ***o*-bis-L**. Residual solvent peaks: * $CHCl_3$, ▲ DMSO, and ▼ HDO. [***o*-bis-L**] = 6.0 × 10^{-3} M, [$AgPF_6$] = 0−1.82 × 10^{-2} M.

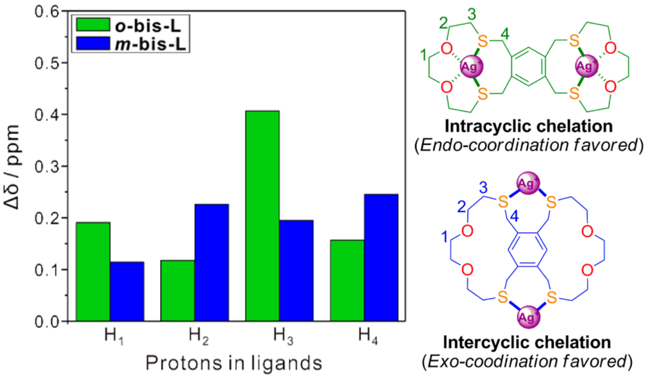
bonds. The Ag−S bond distances [2.528(1)−2.590(1) Å] in **2** are also typical; thus, their average [2.566(1) Å] is similar to that of **1** [2.535(2) Å].

In the present work, we proposed a couple of regioisomers which are expected to form the controlled endo- or exocoordinated product. This approach was realized, and two types of 1-D polymeric products whose linking patterns are based on the endo- or the exocoordination were isolated and structurally characterized. The structural comparison of **1** and **2** reveals that even a small isomeric structural change resulted in a large effect on the topology of the products. First of all, the S···S distance in each cavity is 4.128(3)−5.636(3) Å [av 4.882(3) Å] for **1** and 6.984(2)−7.179(2) Å [av 7.082(2) Å] for **2**. In addition, with the expected larger ring strain due to the *meta*-substitution, the conformational ring flexibility can be assumed to be ***o*-bis-L** > ***m*-bis-L**. Thus, the formation of the resulting endo- and exocyclic products of the thiaphilic metal ion complexes is influenced by the regioisomerism of the bis-dithiamacrocycle system. As far as we are aware, this is the first example of the macrocyclic complexes in which the regioisomers of the ligand control the endo- and the exocoordination modes.

NMR Study of the Silver(I) Complexations in Solution. In an extension of the solid state study on the endo- and the exocyclic silver(I) complexes depending on the isomers ***o*-bis-L** and ***m*-bis-L**, the related ^{1}H NMR experiments were performed in solution to obtain the information on the complexation behavior including the binding mode.[14] The ^{1}H NMR titration of ***o*-bis-L** with $AgPF_6$ was performed in DMSO-d_6/$CDCl_3$ (6:4) (Figure 4). In the case of ***m*-bis-L**, however, due to the low solubility of this ligand and the precipitation during the titration, the complete titration was not possible. In the NMR titration, the signals of the methylene protons (H_{1-4}) and the aromatic protons (H_a) for ***o*-bis-L** are well resolved and readily identified (Figure 4a). The chemical shift change (Δδ, ppm) of each peak was measured as a function of the mole ratio of Ag(I) to ligand (Ag$^+$/***o*-bis-L**) (Figure 4b). Upon stepwise addition of $AgPF_6$ (0−3.4 equiv) to the ligand solution, the signals for all protons shifted downfield, in keeping with the occurrence of the silver(I) complex formation, with the ligand exchange rate being fast on the NMR time scale. The titration curves (Figure 4b) show that the plots for all proton signals exhibit no more silver(I)-induced shifts above a mole ratio (Ag$^+$/***o*-bis-L**) of 2.0, indicating a 2:1 (metal-to-ligand) stoichiometry for the complex. The complexation induced shifts follow the order $H_3 \gg H_1 > H_4 > H_2$. Notably, the observed largest downfield shift for H_3 adjacent to the S donor is in accord with the silver(I) being strongly bound to the sulfur donor. Also, the second largest downfield shift for H_1 between two oxygen donors also shows the contribution of the O donors to the coordination, reflecting the metal ion's position inside the cavity (the endocyclic coordination).

From the titration data in Figure 4b, the stability constants (at 23 °C) of the complexation between silver(I) and ***o*-bis-L** were obtained by using HyperNMR2008 software.[15] This complexation could not be described using a 1:1 or a 2:1 (metal-to-ligand) binding model. Instead, a good fit of the data was obtained with the 1:1 and the 2:1 binding model (Figures S6−S8 in the Supporting Information), and this yields the stepwise log K values of 6.8 ± 0.1 (log K_{11}) and 6.6 ± 0.2 (log K_{21}), and the overall stability constant (log K_{overall}) of 13.4 ± 0.2, suggesting the formation of a stable endocyclic disilver(I) complex due to the synergic effect of Ag−S and Ag−O bonds in solution.

Due to the solubility problems, as mentioned above, the complete NMR titration for ***m*-bis-L** was not possible. As an alternate way, the comparative NMR experiment for ***m*-bis-L** before and after addition of 2.0 equiv of $AgPF_6$ was performed for the comparison with the corresponding data of ***o*-bis-L** (Figure 5a). In this condition, all protons in ***m*-bis-L** also show a downfield shift, suggesting the quite stable complex formation in this case. The order of magnitude of the induced chemical shifts is $H_4 > H_2 > H_3 \gg H_1$, in accord with silver(I) being strongly bound by the sulfur donors and with the oxygen atoms interacting weakly with silver(I). In the disilver(I) complexation with ***m*-bis-L**, unlike ***o*-bis-L**, the benzylic proton H_4 shows the largest shift and the methylene proton H_1 adjacent to the O donor shows the smallest shift, reflecting the silver(I)



(a) (b)

Figure 5. (a) Silver(I)-induced chemical shifts of the protons in ***o*-bis-L** (green bars) and ***m*-bis-L** (blue bars) upon addition of 2 equiv of $AgPF_6$ and (b) the proposed structures of disilver(I) complexes showing different coordination modes.

coordinate from outside the cavity rather than inside as proposed in Figure 5b. Although the above NMR data, especially the later one, do not give much information for the complexation behaviors in solution, it is possible to conclude that the proposed regioisomers' approach can control the endo and the exocoordination modes for the thiaphilic host−guest system both in solid and solution states.

■ CONCLUSION

We present the synthesis of a mixture of two regioisomers (***o*-bis-L** and ***m*-bis-L**) of monobenzo-bis-thiamacrocycle and their separation. While ***o*-bis-L** forms a typical endocyclic silver(I) complex, ***o*-bis-L** allowed us to prepare an exocyclic silver(I) complex in the solid state. From these results, it is concluded that the endo- and the exocyclic coordination modes can be controlled by the regioisomers of the bis-dithiamacrocycle, in association with the dependence of the S···S distances in the bis-macrocycles. According to the NMR studies, similar coordination behaviors were also observed in solution. Further investigations of the novel supramolecular complexes involving the coordination modes based on the regioisomers of the bis-macrocycle systems and their potential application are in progress.

■ EXPERIMENTAL SECTION

General. All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. The ^1H NMR spectra were recorded by using a Bruker Advance-300 (300 MHz) NMR spectrometer with tetramethylsilane (TMS) as internal standard. The ESI mass spectra were obtained by using a Thermo Scientific LCQ Fleet spectrometer. The high resolution mass spectrum (HRMS) was obtained on a JEOL JMS-700 spectrometer. The FT-IR spectrum was measured by using a Thermo Fisher Scientific Nicolet *i*S 10 FT-IR spectrometer. The elemental analysis was carried out by using a LECO CHNS-932 elemental analyzer.

Synthesis and Characterization of *m*-bis-L. 1,2,4,5-Tetra-(bromomethyl)benzene (2.00 g, 4.45 mmol) and 3,6-dioxa-1,8-octanedithiol (2.03 g, 11.13 mmol) were dissolved in DMF (50 mL) and added over three days, to a suspension of Cs_2CO_3 (8.80 g, 27.01 mmol) in DMF (1500 mL) stirring at 55 °C. Upon completion of addition, the DMF was removed in vacuum, and the resulting yellowish residue was dissolved in $CHCl_3$ (100 mL) and filtered. The $CHCl_3$ solution was washed with 0.1 M NaOH and distilled water (300 mL) and then dried over anhydrous $MgSO_4$. The solvent was removed in vacuum to obtain the crude product as a viscous oil and a solid mixture. The ^1H NMR spectrum of the crude product was revealed as a mixture of two isomers (***o*-bis-L** and ***m*-bis-L**) in a 1:4 ratio. The recrystallization of the crude mixed product from dichloromethane/ethanol (1:9) yielded ***m*-bis-L** as a white microcrystalline solid which still contains a small amount of ***o*-bis-L**. The flash column chromatography (SiO_2; DCM/ethyl acetate 9:1) of the recrystallized solid product afforded ***m*-bis-L** in pure form as a white solid. Yield 574 mg (26%). Mp: 205−207 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.39 (s, 2 H, Ar), 3.96 (s, 8 H, $ArCH_2S$), 3.67 (t, 8 H, SCH_2CH_2O), 3.63 (s, 8 H, OCH_2CH_2), 2.63 (t, 8 H, SCH_2CH_2O). ^{13}C NMR (300 MHz, $CDCl_3$): 135.0, 134.7, 71.8, 70.7, 32.8, 30.2. IR (KBr pellet): 3042, 2914, 2887, 1508, 1469, 1451, 1424, 1405, 1368, 1351, 1291, 1131, 1104, 1070, 1031, 908, and 709 cm^{-1}. HRMS (EI) Calcd for $C_{22}H_{34}O_4S_4$ (M^+): 490.1340. Found: 490.1340.

Synthesis and Characterization of *o*-bis-L. After isolating the ***m*-bis-L**-rich content from the mixed crude product by the recrystallization in the above procedure, the filtrate was found to contain a higher content of ***o*-bis-L**. So, the solvent was removed from the filtrate to give a yellow viscous oil, and then the residue was recrystallized from ethanol giving a colorless solid. The flash column chromatography (SiO_2; n-hexane/ethyl acetate 7:3) afforded ***o*-bis-L** in pure form as a white solid. Yield 42.7 mg (2%). Mp: 181−183 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.35 (s, 2 H, Ar), 4.14 (s, 8 H, $ArCH_2S$), 3.80 (t, 8 H, SCH_2CH_2O), 3.69 (s, 8 H, OCH_2CH_2), 2.72 (t, 8 H, SCH_2CH_2O). ^{13}C NMR (300 MHz, $CDCl_3$): 136.0, 132.7, 73.3, 70.2, 34.9, 32.5. IR (KBr pellet): 3009, 2862, 1500, 1471, 1429, 1369, 1351, 1293, 1228, 1193, 1112, 1033, 977, 917, and 907 cm^{-1}. Anal. Calcd for $[C_{22}H_{34}O_4S_4]$: C, 53.86; H, 6.94; S, 26.12. Found: C, 54.11; H, 7.07; S, 26.17%. ESI mass spectrum *m*/*z*: 513.25 $[M + Na]^+$.

Preparation of 1, $\{[Ag_3(\textit{o}\text{-bis-L})_2(CH_3CN)](PF_6)_3\cdot 2CH_3CN\}_n$. $AgPF_6$ (26.1 mg, 0.103 mmol) in methanol (1 mL) was added to ***o*-bis-L** (10.1 mg, 0.021 mmol) in chloroform (1 mL). The colorless precipitate obtained was separated and dissolved in acetonitrile. The vapor diffusion of diethyl ether into the acetonitrile solution afforded a crystalline product **1** suitable for the X-ray analysis. Yield (17%). Mp: 220−222 °C (decomp). IR (KBr pellet): 2909, 2866, 2363, 2345, 1290, 1115, 1065, 1028, and 840 (PF_6^-) cm^{-1}. Anal. Calcd for $\{[Ag_3(\textit{o}\text{-bis-L})_2](PF_6)_3\}_n$, $[C_{44}H_{68}Ag_3F_{18}O_8P_3S_8]$: C, 30.37; H, 3.94; S, 14.74. Found: C, 30.00; H, 4.02; S, 14.29%. For the elemental analysis, drying the product under vacuum at 70 °C for 24 h led to loss of acetonitrile molecules to yield $[Ag_3(\textit{o}\text{-bis-L})_2(PF_6)_3]_n$.

Preparation of 2, $\{[Ag(\textit{m}\text{-bis-L})]PF_6\}_n$. $AgPF_6$ (26.1 mg, 0.103 mmol) in methanol (0.7 mL) was added to ***m*-bis-L** (10.1 mg, 0.021 mmol) in chloroform (0.7 mL). The colorless precipitate obtained was separated and dissolved in acetonitrile. The vapor diffusion of diethyl ether into the acetonitrile solution afforded a crystalline product **2** suitable for the X-ray analysis. Yield (12%). Mp: 217−219 °C (decomp). IR (KBr pellet): 2920, 2862, 2361, 2345, 1637, 1438, 1298, 1131, 1108, 1030, 869, and 842 (PF_6^-) cm^{-1}. Anal. Calcd for $[C_{22}H_{36}AgF_6O_5PS_4]$ ($\{[Ag(\textit{m}\text{-bis-L})]PF_6\}_n\cdot H_2O$): C, 34.70; H, 4.76; S, 16.84; Found: C, 34.48; H, 4.58; S, 16.95%. Because of the hygroscopic property, one water molecule for each formula unit was found in the elemental analysis.

X-ray Crystallographic Analysis. The crystal data for **1** and **2** were collected on a Bruker SMART APEX II ULTRA diffractometer equipped with the graphite monochromated Mo Kα radiation (λ = 0.710 73 Å) generated by a rotating anode. The cell parameters for the compounds were obtained from a least-squares refinement of the spot (from 36 collected frames). Data collection, data reduction, and semiempirical absorption correction were carried out using the software package of APEX2.[16] All of the calculations for the structure determination were carried out using the SHELXTL package.[17] In all cases, all nonhydrogen atoms were refined anisotropically, and all hydrogen atoms were placed in idealized positions and refined isotropically in a riding manner along with their respective parent atoms. Since the lattice solvent (two acetonitrile) molecules in **1** are highly disordered, the contribution of solvent electron density was removed by the SQUEEZE routine in PLATON.[18] In addition, the crystal quality of **1** is not so good, and this is probably because the crystal has a needle shape. Because of these reasons, we were not able to collect the necessary number of high-angle (2θ) diffraction data. We repeated the preparation of the single crystals and the data collection, but no significant improvement was observed. So, it has a somewhat larger wR_2 value (~20%). In **2**, one PF_6^- ion (F3 and F4 atoms) is highly disordered, and the O3 and C8 atoms in the macrocyclic ring are also disordered in two positions (55:45) (Supporting Information). Relevant crystal data collection and refinement data for the crystal structures of **1** and **2** are summarized in Supporting Information Table S1.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of ligands, crystal structures for **1** and **2**, HyperNMR output for the NMR titration data. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 921862 (**1**) and 921863 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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