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Article

Discrete Mercury(II) Complexes, One-Dimensional and Palladium(II)-Mediated Two-Dimensional Silver(I) Coordination Polymers of NS_2-Macrocycle: Synthesis and Structural Characterization

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A range of thiaphilic mononuclear (Hg^{2+} and Ag^{+}) and heterobinuclear (Ag^{+}/Pd^{2+}) complexes (**1**−**6**) of an NS_2-donor macrocycle **L** with discrete and networked forms were prepared and structurally characterized. Reaction of **L** with $HgCl_2$ afforded a unique 1:1 (cationic/anionic) complex $[Hg_2(\mathbf{L})Cl_5][Hg(\mathbf{L})Cl]$ (**1**). Reaction of **L** with $Hg(ClO_4)_2$ yielded the sandwich-type 1:2 (metal-to-ligand) complex $[Hg(\mathbf{L})_2](ClO_4)_2$ (**2**). Contrasting with the mercury(II) salts, the reactions of **L** with AgX ($X{=}NO_3^{-}$ and $CF_3SO_3^{-}$) yielded an isostructural one-dimensional (1D) zigzag networks $[Ag(\mathbf{L})X]_n$ (**3**; $X{=}NO_3^{-}$ and **4**; $X{=}CF_3SO_3^{-}$) in which each ring of **L** is exo-coordinated via two S atoms and one N atom to a silver ion which is also bound to one S atom in the neighboring **L** such that the overall coordination geometry about each silver is four-coordinate. Whereas, reaction of **L** with K_2PdCl_4 gave a discrete exocyclic complex **5**, [*cis*-$Cl_2Pd(\mathbf{L})$]. Through a successive reaction of the complex **5** with $AgNO_3$, a heterobinuclear two-dimensional (2D) coordination polymer **6**, $[Pd(\mathbf{L})Ag_{2.5}(NO_3)_{4.5}(H_2O)_{0.5}]_n$, utilizing exocyclic Pd(II) and Ag(I) was isolated and characterized.

Introduction

The field of supramolecular chemistry based on the macrocyclic ligand system has advanced to a stage at which it is quite possible to control the self-assembled structures with specific topologies.[1] On the basis of a prior study,[2] the use of macrocyclic thioethers as building blocks gives the possibility of promoting formation of a framework owing to the unique exo-coordinating nature. Thus, the careful selection of the building blocks including the thiamacrocycles make it possible to produce a large number of coordination topologies.

Our particular interest has been the coordination of the heterodonor macrocycles such as thiaoxa- or thiaaza-macrocycles with thiaphilic metals to construct the new types of homo- and heterobinuclear network compounds.[3] The versatility of sulfur-containing macrocycles makes them useful for a range of products because the sulfur donor is expected to favor binding toward softer metals such as Pd(II), Pt(II), and Ag(I) in either an exo- or an endocyclic mode. Indeed, a range of mono and multinuclear complexes of thiamacrocycles with exo-coordination have been reported by us[4] and others.[5] On the other hand, the Loeb[6a] and

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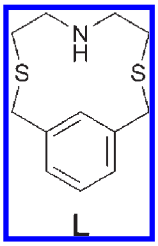
Habata[6b] groups reported endocyclic disilver(I) complexes of large dibenzo-S_6 and N_2S_6 macrocycles, respectively.

A strategy for the preparation of a heterobinuclear complex is the use of metal complexes as ligands (so-called metalloligands), that is to say, metal complexes containing potential donor atoms or those with available coordination sites. We are interested in extending the metalloligand approach in connection with the preparation of novel heterobinuclear macrocyclic network compounds. Furthermore, we have suggested that such endo- and exo-coordination can be controllable by the discriminative coordination ability of anions employed.[7] As an extension, we have recently proposed one *N*-azo-coupled NS_2O_2-macrocycle system, which serves to illustrate how the coordinating ability of the anion controls the color change through formation of endo- or exometal complexes.[8] We have also tried to merge the endo- and exo-coordination to generate the heterobinuclear species which have two different metal species in endo- and exo- manner, respectively. The preliminary result of our efforts in the formation of such a heterobinuclear network with endo- and exocyclic coordination of Pd(II)/Ag(I) in a dibenzo-O_2S_3 macrocycle has recently been communicated.[9] On the other hand, we recently introduced the three positional (*ortho*, *meta*, and *para*) isomers of the NS_2-macrocycle including **L** (*meta*-form) and their metallosupramolecules.[10]

Inspired by this consideration, we planned to extend our preparative work from discrete homo- to continuous heteronuclear species by employing a semirigid NS_2-donor macrocycle **L** because of its xylyl subunit in the *meta*-position. Herein, we present the synthesis and structural characterization of the supramolecular complexes for **L** with emphasis on the networking of the macrocycles by means of exocyclic coordination.



L

Experimental Section

General Information. All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. Mass spectra were obtained on a Applied Biosystems QTRAP 3200 spectrometer at the Central Laboratory of Gyeongsang National University. The FT-IR spectra were measured with a Shimadzu FT-IR 8100 spectrometer. The elemental analysis was carried out on a LECO CHNS-932 elemental analyzer.

Synthesis of Mercury(II) Complexes (1 and 2). The NS_2-donor macrocycle **L** was prepared as described previously by us.[9] To the stirring solution of **L** (20.3 mg, 0.08 mmol) in dichloromethane (1 mL) was added to mercury(II) salts [0.09 mmol, **1**: $HgCl_2$ (24.4 mg) and **2**: $Hg(ClO_4)_2$ (36.0 mg)] in methanol (2 mL) afforded colorless precipitate. After the filtration, the vapor diffusion of diethyl ether to *N*,*N*-dimethylformamide (DMF) solution gave rise to colorless crystalline complexes **1** and **2**.

$[Hg_2(L)Cl_5][Hg(L)Cl]$ (1). Mp: 192−193 °C (decomp.), ESI-MS: *m*/*z* 987 $[Hg_2(\mathbf{L})_2Cl_3]^+$, 476 $[Hg(\mathbf{L})Cl]^+$. IR (KBr, cm^{-1}): 3110, 2912, 2352, 1670, 1517, 1423, 2118, 1143, 1060, 954, 779, 702. Anal. Calcd for $C_{24}H_{34}N_2S_4Hg_3Cl_6$: C, 22.29; H, 2.65; N, 2.17; S, 9.92. Found: C, 21.85; H, 2.37; N, 1.98; S, 9.82%.

$[Hg(L)_2](ClO_4)_2$ (2). ESI-MS: *m*/*z* 779 $[Hg(\mathbf{L})_2ClO_4]^+$, 340 $[Hg(\mathbf{L})_2]^{2+}$. IR (KBr, cm^{-1}): 3186, 2914, 2345, 1431, 1097 (ClO_4^-), 617. Anal. Calcd for $C_{24}H_{34}N_2S_4HgCl_2O_8$: C, 32.82; H, 3.90; N, 3.19; S, 14.60. Found: C, 32.43; H, 3.79; N, 2.96; S, 14.82%.

Caution! *Perchlorate salts of metal complexes are potentially explosive and should be handled with great care.*

Synthesis of Silver(I) Complexes (3 and 4). To the stirring solution of **L** (20.2 mg, 0.08 mmol) in dichloromethane (1 mL) was added to silver(I) salts [0.08 mmol, **3**: $AgNO_3$ (13.6 mg) and **4**: $AgCF_3SO_3$ (20.6 mg)] in methanol (2 mL) afforded a colorless precipitate. After the filtration, the vapor diffusion of diethyl ether to DMSO solution gave rise to colorless crystalline products **3** and **4**.

$\{[Ag_2(L)_2](NO_3)_2\}_n$ (3). Mp: 194−195 °C (decomp.). IR (KBr, cm^{-1}): 3431, 2833, 1625, 1361 (NO_3^-), 1089, 908, 808, 715. Anal. Calcd for $C_{24}H_{34}Ag_2N_4O_6S_4$: C, 35.22; H, 4.19; N, 6.84; S, 15.67. Found: C, 35.37; H, 4.20; N, 6.75; S, 15.86%.

$\{[Ag(L)]CF_3SO_3\}_n$ (4). Mp: 225−226 °C (decomp.). IR (KBr, cm^{-1}): 3294, 3026, 2927, 2842, 1263, 1164, 1024, 918, 808 ($CF_3SO_3^-$), 632. Anal. Calcd for $C_{12}H_{17}NS_2AgCF_3SO_3$: C, 31.46; H, 3.45; N, 2.82; S, 19.38. Found: C, 31.07; H, 3.59; N, 2.98; S, 19.35%.

Synthesis of Pd(II) Complex [*cis*-$Cl_2Pd(L)$] (5). Addition of K_2PdCl_4 (68.9 mg, 0.21 mmol) in aqueous solution to the stirring solution of **L** (50.4 mg, 0.21 mmol) in dichloromethane afforded a yellow precipitate. After the filtration, vapor diffusion of diethyl ether into DMSO solution afforded the crystalline product **5**. Mp: 229−230 °C (decomp.). IR (KBr, cm^{-1}): 3302, 2903, 2345, 1701, 1606, 1510, 1431, 702. ESI-MS: *m*/*z* 380 $[Pd(\mathbf{L})Cl]^+$. Anal. Calcd for $C_{12}H_{17}NS_2PdCl_2$: C, 34.59; H, 4.11; N, 3.36; S, 15.39. Found: C, 34.52; H, 4.40; N, 3.45; S, 15.06%.

Synthesis of Pd(II)/Ag(I) Complex $[Pd(L)Ag_{2.5}(NO_3)_{4.5}(H_2O)_{0.5}]_n$ (6). To the stirring solution of **5** (8.5 mg, 0.02 mmol) in dichloromethane (2 mL) was added to excess of $AgNO_3$ (13.93 mg, 0.08 mmol) in dichloromethane/methanol (1:1, 2 mL). After the filtration, the slow evaporation of the filtrate afforded pale-yellow crystalline **6** suitable for X-ray analysis. IR (KBr, cm^{-1}): 2397, 2358, 1760, 1378, 1353, 1306, 828, 805.

Crystallographic Structure Determinations. All data were collected on a Bruker Smart diffractometer equipped with a graphite monochromated Mo Kα (λ = 0.71073 Å) radiation source and a CCD detector. The 45 frames of two-dimensional (2D) diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The first 50 frames were retaken after complete data collection. The crystal showed no significant decay. The frame data were processed to give structure factors using the SAINT software.[11] The structure was solved by direct methods and refined by full matrix least-squares methods on F^2 for all data using the SHELXTL software.[12] The nonhydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and refined with a riding model with U_{iso} constrained to be 1.2 times U_{eq} of the parent atom (Table 1).

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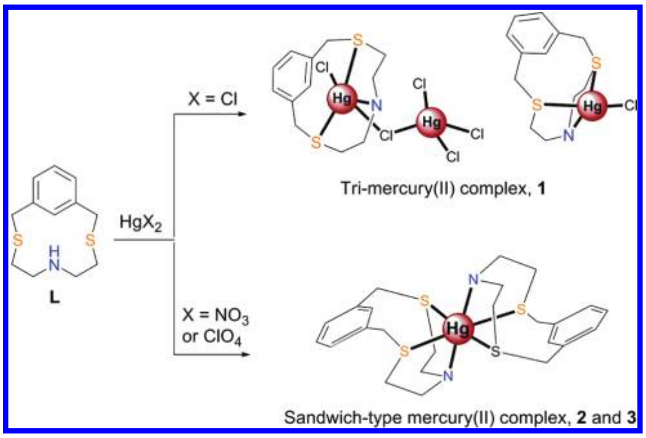
[12] *SHELXTL*: Structure Determination Programs, Ver. 5.16; Bruker Analytical X-ray Instruments: Madison, WI, 1998.

Table 1. Crystal and Experimental Data for **1**−**6**

	1	**2**	**3**	**4**	**5**	**6**
formula	$C_{24}H_{34}C_{l6}Hg_3N_2S_4$	$C_{12}H_{17}ClHg_{0.5}NO_4S_2$	$C_{24}H_{34}Ag_2N_4O_6S_4$	$C_{13}H_{17}AgF_3NO_3S_3$	$C_{12}H_{17}Cl_2NPdS_2$	$C_{12}H_{18}Ag_{2.5}$-$N_{5.5}O_{14}PdS_2$
formula weight	1293.24	439.13	818.53	496.33	416.69	903.51
temperature (K)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	Cc	$P2_1/c$	$P2_1/c$	$P2_1/c$
Z	4	4	4	4	4	4
a (Å)	17.0810(11)	10.0970(10)	10.7933(12)	12.3784(8)	8.9062(6)	14.5640(5)
b (Å)	8.2239(6)	11.3304(11)	10.8604(12)	7.8493(5)	12.0658(8)	11.7938(4)
c (Å)	24.7326(17)	13.6241(13)	24.337(3)	18.5551(12)	14.4428(9)	13.6829(5)
β (deg)	96.7250(10)	94.290(2)	95.103(2)	99.6660(10)	104.5340(10)	98.3430(10)
V (Å^3)	3450.3(4)	1554.3(3)	2841.5(5)	1777.3(2)	1502.36(17)	2325.37(14)
D_x (g/cm^3)	2.490	1.877	1.913	1.855	1.842	2.581
R	0.0423	0.0288	0.0531	0.0801	0.0434	0.0302
wR	0.0947	0.0578	0.1277	0.1395	0.0758	0.0654

Scheme 1. Discrete-Type Mercury(II) Complexes **1** and **2** Prepared



Results and Discussion

Preparation and Structural Description of Mercury(II) Complexes (1 and 2). Self-assembly reactions of **L** with mercury(II) salts with two different anions were attempted (Scheme 1). First, a colorless precipitate was obtained by mixing equimolar amounts of **L** and $HgCl_2$ in dichloromethane/methanol. Vapor diffusion of diethyl ether into a DMF solution gave rise to a crystalline product **1**. X-ray analysis reveals that **1** consists of one anionic part $[Hg_2(\mathbf{L})Cl_5]^-$ and one cationic part $[Hg(\mathbf{L})Cl]^+$ (Figure 1a).[13] In the anionic part, two local Hg centers (Hg1 and Hg2) are linked by a chlorine atom (Cl2). The Hg1 is effectively five-coordinated, with the coordination geometry best described as distorted trigonal bipyramidal. The S1, S2, and Cl2 atoms define the equatorial plane, with the axial positions occupied by N1 and Cl1 [N1−Hg1−Cl1, 174.4(2)°]. The Hg2, which lies outside the cavity, is bonded to three terminal Cl atoms and one bridging μ_2-Cl atom to form a distorted tetrahedral environment, with tetrahedral angles falling in the range of 97.0(1)−124.7°(1) (Table 2).

In the cationic part, the Hg3 atom is bound to one Cl atom and NS_2 donors of **L** that exhibit a bent arrangement. The bond angles around the Hg3 atom vary as 80.0(2)−168.9(2)° because of the pairwise interactions via Hg3···Cl6A (see Figure 1b). Therefore, the local coordination geometry of the Hg3 atom cannot de described simply in terms of a regular polyhedron.

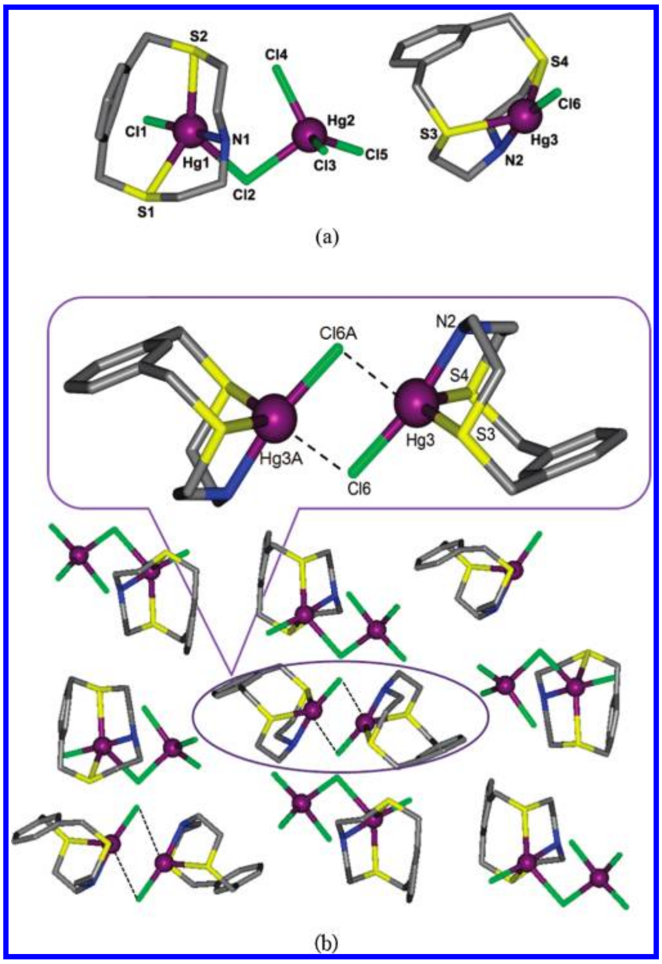


Figure 1. Crystal structure of the 1:1 (cationic/anionic) complex **1**, $[Hg_2(\mathbf{L})Cl_5][Hg(\mathbf{L})Cl]$: (a) asymmetric unit and (b) packing diagram showing intermolecular Hg···Cl interactions (dashed lines, 3.194 Å). Hydrogen atoms are omitted.

To examine the role of anions in the formation of mercury(II) complexes for **L**, the reaction was also carried out with $Hg(ClO_4)_2$. The reaction of **L** with equimolar amount of $Hg(ClO_4)_2$ in dichloromethane/methanol afforded a colorless precipitate. Vapor diffusion of diethyl ether into DMF solution of the precipitate gave rise to a crystalline product **2**. X-ray analysis reveals that **2** is a 1:2 (mercury-to-ligand) sandwich-type complex of formula

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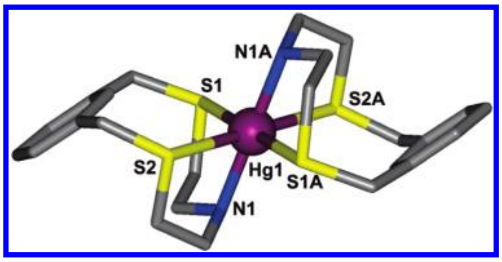


Figure 2. Crystal structure of the 1:2 [Hg(II):ligand] sandwich-type complex **2**, $[Hg(\mathbf{L})_2](ClO_4)_2$. Hydrogen atom and non-coordinating anions are omitted.

Table 2. Selected Bond Lengths (Å), Bond Angles (deg) and Torsion Angles (deg) for **1**, $[Hg_2(\mathbf{L})Cl_5][Hg(\mathbf{L})Cl]$

Hg1−N1	2.222(8)	Hg1−S1	2.899(3)
Hg1−S2	2.868(3)	Hg1−Cl1	2.354(3)
Hg1−Cl2	2.816(3)	Hg2−Cl2	2.609(2)
Hg2−Cl3	2.504(3)	Hg2−Cl4	2.472(3)
Hg2−Cl5	2.385(3)	Hg3−Cl6	2.342(3)
Hg3−N2	2.201(8)	Hg3−S3	2.809(3)
Hg3−S4	2.884(2)		
N1−Hg1−Cl1	174.4(2)	N1−Hg1−S2	79.2(2)
Cl1−Hg1−S2	99.7(1)	N1−Hg1−S1	78.9(2)
Cl1−Hg1−S1	97.6(1)	S2−Hg1−S1	126.3(1)
Cl5−Hg2−Cl4	124.7 (1)	Cl5−Hg2−Cl3	118.3(1)
Cl4−Hg2−Cl3	101.0(1)	Cl5−Hg2−Cl2	111.2(1)
Cl4−Hg2−Cl2	99.9(1)	Cl3−Hg2−Cl2	97.0(1)
N2−Hg3−Cl6	168.9(2)	N2−Hg3−S3	80.0(2)
Cl6−Hg3−S3	102.3(4)	N2−Hg3−S4	80.1(2)
Cl6−Hg3−S4	106.5(2)	S3−Hg3−S4	125.5(4)
Hg2−Cl2−Hg1	98.4(0)		
S1−C4−C5-N1	65(1)	N1−C6−C7-S2	59(1)
S3−C16−C17-N2	−61(1)	N2−C18−C19	−62(1)

$[Hg(\mathbf{L})_2](ClO_4)_2$ (Figure 2). The ESI-mass spectrum of **L** with 1 equiv of $Hg(ClO_4)_2$ was dominated by peaks for sandwich-type (1:2) species such as $[Hg(\mathbf{L})_2]^{2+}$ (*m*/*z* 340.0), $[Hg(\mathbf{L}+H)_2(ClO_4)_2]^{2+}$ (*m*/*z* 440.0) and $[Hg(\mathbf{L})_2\text{-}H(ClO_4)_2]^{+}$ (*m*/*z* 879.0) (see Supporting Information). The coordination of each **L** to the mercury(II) center is via facial arrangement of two sulfur and one nitrogen donors. So the coordination geometry can best be described as a distorted octahedron with four sulfur donors from two ligands defining the square-equatorial plane and the axial positions occupied by the remaining two nitrogen atoms (∠N1−Hg1−N1A 180.0(2)°). The bite angles around the Hg atom vary considerably, ranging from 66.9(1)° (S1−Hg1−S2A) to 113.1(1)° (S1−Hg1−S2). The Hg−S bond lengths (Hg1−S1 3.071(1) Å and Hg1−S2 2.936(1) Å) are longer than reported previously for such bonds (2.6−2.8 Å)[14] because of the steric hindrance between two macrocycles which sandwich the Hg atom. The Hg−N bond length (2.164(3) Å), however, is slighly shorter than those in the nomal range for this bond type (Table 3).

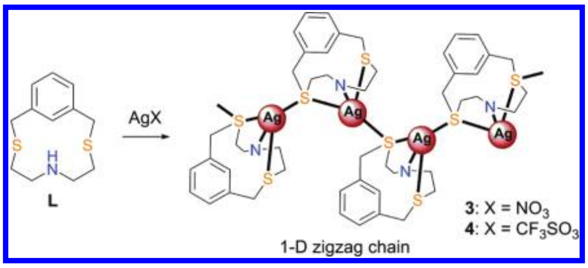
Unlike **1**, the mercury(II) center in **2** is fully shielded by the two facially bound macrocycles. Therefore, a comparison of the coordination modes between the anion-coordinated 1:1 (cationic/anionic) form in **1** and the anion-free sandwich form in **2** supports the idea that the anion-coordination ability is an important controlling factor.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for **2**, $[Hg(\mathbf{L})_2](ClO_4)_2$[a]

Hg1−N1	2.164(3)	Hg1−S1	3.071(1)
Hg1−S2	2.936(1)		
N1−Hg1−N1A	180.0(2)	N1−Hg1−S2	77.9(1)
N1A−Hg1-S2	102.1(1)	S2−Hg1−S2A	180.0(1)
N1−Hg1−S1	78.9(1)	N1A−Hg1-S1	101.1(1)
S2−Hg1−S1	113.1(1)	S2A−Hg1-S1	66.9(1)

[a] Symmetry operation: (A) $-x+1,-y+1,-z$.

Scheme 2. Silver(I) Coordination Polymers (**3** and **4**) Prepared



Preparation and Structural Description of Silver(I) Complexes (3 and 4). Having obtained two anion-dependent mercury(II) complexes, we proceeded to the preparation of corresponding complexes by employing silver(I) salts (nitrate and triflate; Scheme 2). Contrary to our expectations, however, the X-ray analysis for **3** (nitrate, Figure 3a) and **4** (triflate, Figure 3b) revealed that there is no major difference in the crystal structures except the existence of an inversion center in **4** (see Table 4). The potential inversion symmetry of the complex cation part in **3** is broken by the Ag···ONO_2 interaction[15] (Ag2···O4 3.037 Å, see dashed line in Figure 3a). The distance between Ag1 and the neighboring NO_3^- ion (not shown, 3.496 Å) is longer than the former one. In both cases, each metal center is in a highly distorted tetrahedral environment defined by two S atoms and one N atom from one facially coordinated **L** and one S atom from an adjacent **L** which has an exodentate conformation, resulting in the zigzag-type chain structure. For example, the bond angles around the Ag atoms in **3** vary from 76.0(2)° (N1−Ag1−S2) to 149.9(2)° (N1−Ag1−S4) for Ag1 atom, and from 75.7(2)° (N2−Ag2−S4) to 124.48(6)° (S3−Ag2−S4) for Ag2 atom, respectively. These large deviations of the angles from the regular tetrahedron are due to the formation of the pentagonal rings via Ag−S and Ag−N bonds together with the steric hindrance between two adjacent ligands linked with Ag atom.

Preparation and Structural Description of Palladium(II) and Heterobinuclear Palladium(II)/Silver(I) Complexes (5 and 6). As part of our ongoing strategy for the preparation of heterobinuclear complexes, we were interested in the palladium complexes as the metalloligand system which has potential donor atoms or those with available

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[15] (a) Zou, R.-Q.; Li, J.-R.; Xie, T.-B.; Zhang, R.-H.; Bu, X.-H. *Cryst. Growth Des.* **2004**, *4*, 79. (b) Su, C.-Y.; Liao, S.; Zhu, H.-L.; Kang, B.-S.; Chen, X.-M.; Liu, H.-Q. *J. Chem. Soc., Dalton Trans.* **2000**, 1985.

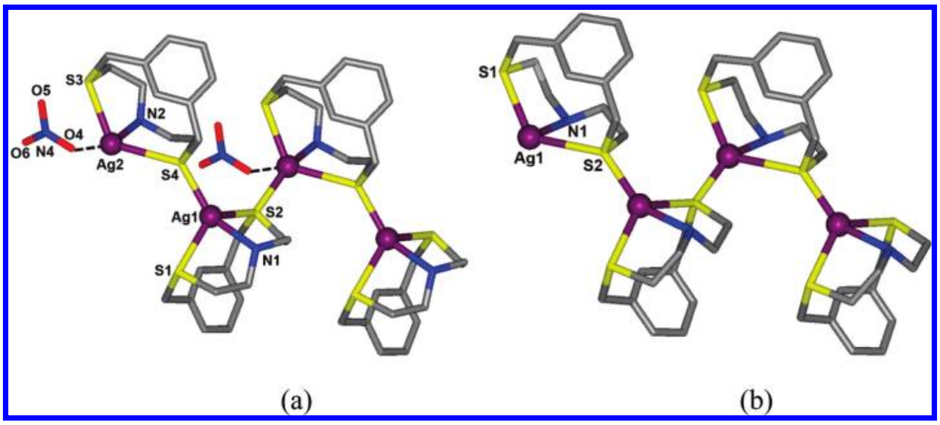


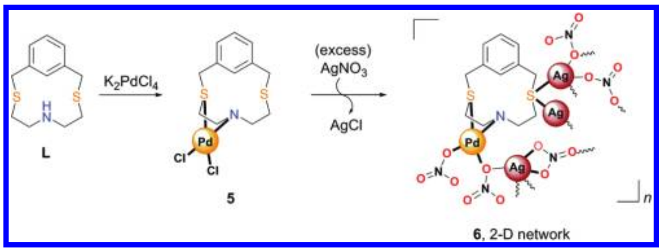
Figure 3. 1D zigzag structures of (a) **3**, $\{[Ag_2(\mathbf{L})_2](NO_3)_2\}_n$, and (b) **4**, $\{[Ag(\mathbf{L})]CF_3SO_3\}_n$. Hydrogen atoms and non-coordinating anions (except the NO_3^- ion in **3**) are omitted.

Table 4. Comparison of the Selected Bond Lengths (Å) and Bond Angles (deg) for **3**, $\{[Ag_2(\mathbf{L})_2](NO_3)_2\}_n$ and **4**, $\{[Ag(\mathbf{L})]CF_3SO_3\}_n$[a]

	3 (X = NO_3)	**4** (X = OTf)
Ag1−N1	2.312(8)	2.325(6)
Ag1−S2A		2.485(2)
Ag1−S1	2.696(3)	2.694(2)
Ag1−S2	2.896(3)	2.911(2)
Ag1−S4	2.459(3)	
Ag2−N2	2.319(8)	
Ag2−S2A	2.458(3)	
Ag2−S3	2.690(3)	
Ag2−S4	2.912(3)	
N1−Ag1−S2A		152.6(2)
N1−Ag1−S1	80.7(2)	80.6(2)
S2A−Ag1-S1		116.6(1)
N1−Ag1−S2	75.9(2)	74.3(2)
S2A−Ag1-S2		106.0(1)
S1−Ag1−S2	124.6(1)	127.9(1)
N1−Ag1−S4	150.1(2)	
S4−Ag1−S1	119.2(1)	
S4−Ag1−S2	105.0(1)	
N2−Ag2−S2A	150.3(3)	
N2−Ag2−S3	80.7(2)	
S2A−Ag2-S3	119.9(1)	
N2−Ag2−S4	75.5(2)	
S2A−Ag2-S4	104.4(1)	
S1−Ag1−S2	127.9(1)	

[a] Symmetry operation: (A) $x-1/2$, $y+1/2$, z (**3**) and $-x$, $y-1/2$, $-z+1/2$ (**4**).

Scheme 3. Palladium(II) Complex (**5**) and Pd(II)/Ag(I) Coordination Polymer (**6**) Prepared



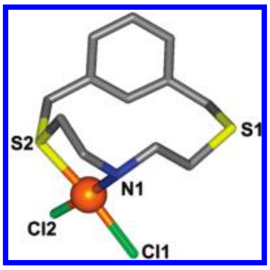


Figure 4. Molecular structure of exo-coordinated **5**, $[cis\text{-}Cl_2Pd(\mathbf{L})]$.

coordination sites (Scheme 3). On the basis of this consideration, we carried out the reaction of **L** in dichloromethane with equimolar amount of K_2PdCl_4 in water, resulting in an orange-colored precipitate. Vapor diffusion of diethyl ether into DMSO solution of the precipitate gave the crystalline product **5**. The ESI-mass spectrum of **5** showed an intense peak at m/z 380 corresponding to $[cis\text{-}ClPd(\mathbf{L})]^+$. The crystallographic analysis reveals that **5** is an exodentate complex of formula $[Pd(\mathbf{L})Cl_2]$ (Figure 4). The Pd atom is outside the cavity in a *cis*-type square-planar arrangement coordinated by one sulfur and one nitrogen donors from **L**. Two chlorine atoms are occupying the rest of two binding sites. Notably, one sulfur atom (S1) remains uncoordinated. Because of this, one can consider **5** as a metalloligand to prepare the novel heterobinuclear complexes by successive reactions with soft metal salts.

Indeed, the reaction of **5** with excess amount of $AgNO_3$ afforded meaningful product. In this case, the AgCl precipitate formed quantitatively was removed by filtration. Slow evaporation of the filtrate afforded the orange-colored crystalline product **6**, in which it crystallizes as a 2D network of formula $[Pd(\mathbf{L})Ag_{2.5}(NO_3)_{4.5}(H_2O)_{0.5}]_n$ involving the heterobinuclear Pd(II)/Ag(I) complex unit (Figure 5). The structural unit shown in Figure 5a is generated through a center of symmetry. In this case, the nitrate ions in **6** function not only as chelate ligands but also as bridging ligands, thus networking the macrocycles to form a 2D coordination polymer. The structure shows unusual arrangement, with the Pd atom coordinated in an exo-fashion to the ring via SN donors and all of the Ag atoms in an exo-fashion to the ring. The Pd atom in **6** remains also in a *cis*-type square-planar arrangement, but two *cis*-coordinated Cl atoms in **5** were replaced by two nitrate ions. Importantly, all of the Ag atoms show very different coordination environments. In fact, Ag1 atom is five-coordinated by one bidentate and four monodentate nitrate ions with an irregular geometry. Ag2 atom is four-coordinated by one S donor from **L** and three monodentate nitrate ions, forming a distorted tetrahedral geometry with the "tetrahedral" angles falling in the range 101.4(1)−133.2(3)°. Meanwhile, the Ag3

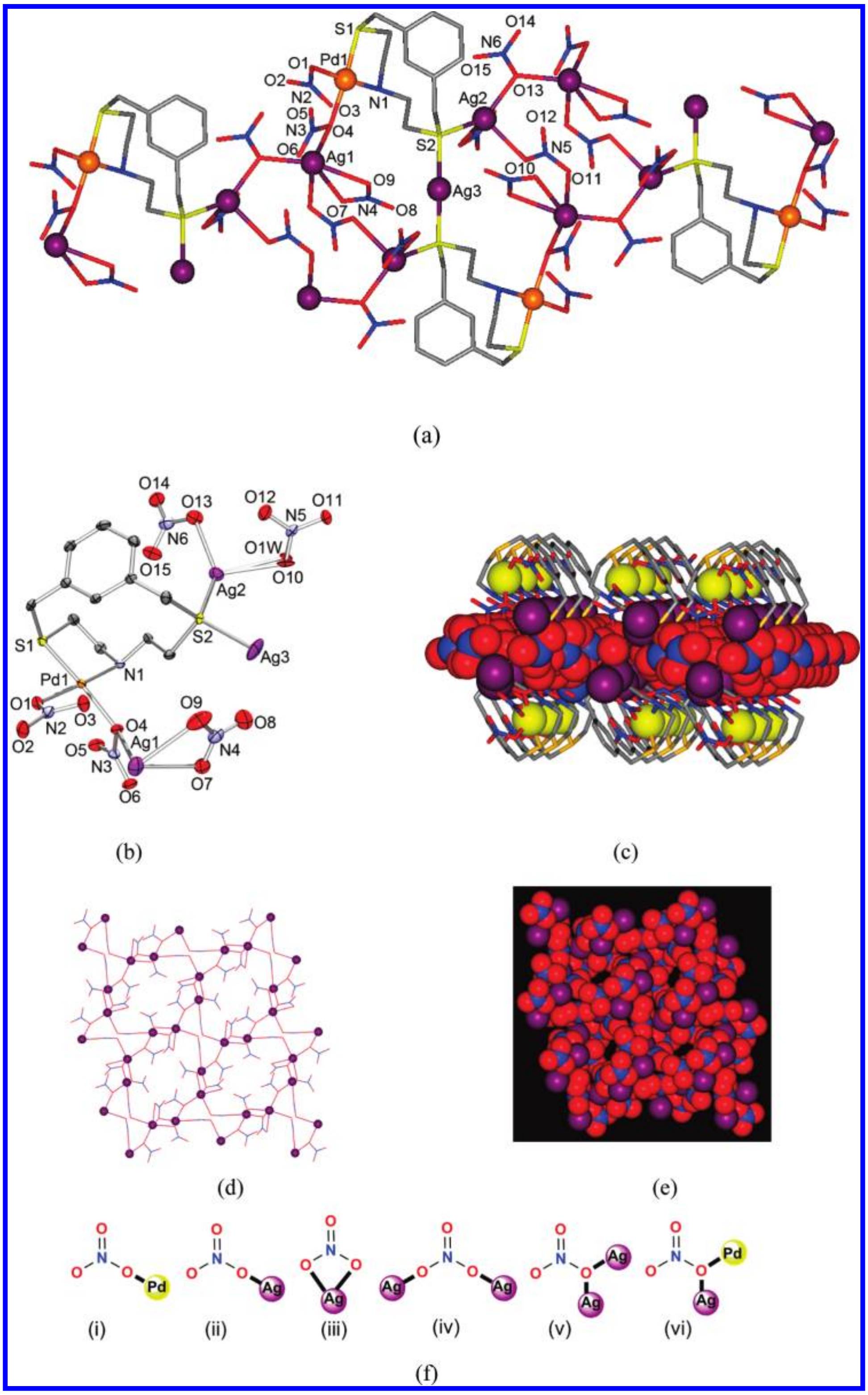


Figure 5. Structures of (a) a 2D heterobinuclear network of **6**, $[Pd(\mathbf{L})Ag_{2.5}(NO_3)_{4.5}(H_2O)_{0.5}]_n$, and (b) its asymmetric unit. (c) Side view of the 2D network of **6** showing the array of exocyclic Pd(II) complex units linked up and down of the $[Ag_{2.5}(NO_3)_{4.5}]_n$ square-grid sheet. Top view of the square-grid sheet with (d) ball-and-stick and (e) space-filling representations (Key: Pd, yellow; Ag, violet; N, light blue; O, red). (f) Coordination modes of the nitrate ions in **6**.

atom links two ligand molecules via S2−Ag3−S2′ motif (bond angle: 180.00°(2)). Because of the nitrate ions with six coordination modes which link each metal center (Figure 5f), the 2D sheet layer structure of **6** with exocyclic Pd(II) complex array onto the layer from both sides was obtained (Tables 5 and 6).

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for **5**, [*cis*-$Cl_2Pd(\mathbf{L})$]

Pd1−N1	2.051(4)	Pd1−Cl1	2.316(1)
Pd1−S2	2.264(1)	Pd1−Cl2	2.299(1)
N1−Pd1−S2	87.5(1)	N1−Pd1−Cl1	91.1(1)
N1−Pd1−Cl2	176.6(1)	S2−Pd1−Cl1	172.6(1)
S2−Pd1−Cl2	89.2(1)	Cl2−Pd1−Cl1	92.3(1)

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) for **6**, $[\mathrm{Pd}(\mathbf{L})\mathrm{Ag}_{2.5}(\mathrm{NO}_3)_{4.5}(\mathrm{H}_2\mathrm{O})_{0.5}]_n$

Pd1−N1	2.029(3)	Ag2−O10	2.47(3)
Pd1−O1	2.051(3)	Ag2−S2	2.472(1)
Pd1−O4	2.080(3)	Ag1−O4	2.441(3)
Pd1−S1	2.245(1)	Ag1−O7	2.538(4)
Pd2−S2	2.455(1)	Ag2−O13	2.307(3)
Ag2−O1W	2.55(3)	Ag(3)−S(2)	2.456(1)
O4−Pd1−S1	170.4(1)	O4−Ag1−O7	82.7(1)
O13−Ag2−S2	133.2(1)	Pd2−S2−Ag2	117.3(1)
N1−Pd1−O1	176.9 (1)	Pd1−O4−Ag1	132.8(2)
O1−Pd1−S1	89.4(1)	N1−Pd1−O4	89.6(1)
O3−Ag2−O10	98.7(7)	O1−Pd1−O4	93.4(2)
S2−Ag2−O10	112.5(1)	N1−Pd1−S1	87.5(1)
O13−Ag2−O10	101.4(5)	O10−Ag2−S2	109.2(7)
O13−Ag2−O1W	95.1(5)	O10−Ag2−O1W	7.0(12)
S2−Ag2−O1W	116.1(7)	Ag3−S2−Ag2	117.3(1)

In summary, we employed the semirigid NS_2-donor macrocyclic ligand **L**, and its thiaphilic metal complexes with different types of coordination modes (endo- and exo-) and topologies (discrete, 1D and 2D networks) were presented. Mercury(II) showed anion-dependent products in the reactions of **L** because of the discriminated coordination ability of anions used. In the case of silver(I), however, anion-independent 1D zigzag polymeric chain compounds were isolated. We were able to prepare the silver(I)/palladium(II) heterobinuclear complex with a 2D network by using [*cis*-$\mathrm{Cl}_2\mathrm{Pd}(\mathbf{L})$] as a metalloligand. Compared with the direct assembly of the ligand and salt system, the proposed metalloligand approach based on the exo-coordination provides an opportunity for compound construction of a higher level of sophistication.

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Supporting Information Available: X-ray data in CIF format and additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.