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Copper(I), Silver(I), and Palladium(II) Complexes of a Thiaoxamacrocycle Displaying Unusual Topologies

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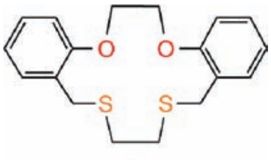
Coordination behavior of the 14-membered dibenzo-O_2S_2 macrocycle, **L**, with the soft metal ions such as Pd(II), Cu(I), and Ag(I) is reported. The X-ray structures of the complexes have been determined, and a range of less common structural types, including mono-, di-, and multinuclear species with discrete and continuous forms were obtained. A two-step approach via reaction of dichloro-palladium(II) complex of **L** as a metalloligand, with **L** through a treatment of silver(I) perchlorate, led to the formation of bis(ligand) monopalladium(II) complex, $[Pd(\mathbf{L})_2]\cdot 2ClO_4\cdot 2CH_3NO_2$ (**1**). In this case, the square-planar stereochemical demand of Pd(II) coupled with the coordination of the S_2-donors of **L** to a metal center results in the formation of the bis(ligand)-type mononuclear complex. In **1**, the ether oxygens of the ring are unbound. **L** reacts with CuBr to yield related 2:2:2 (metal/ligand/anion) complex of type $[Cu_2Br_2(\mathbf{L})_2]$ (**2**), in which two ligand molecules are linked by a rhomboid-type Cu$-$Br$_2$$-$Cu cluster unit. However, the parallel reaction with CuI afforded the mixture of the isostructural 2:2:2 type complex $[Cu_2I_2(\mathbf{L})_2]$ (**3a**) and double-stranded 1D coordination polymer $\{[Cu_2I_2(\mathbf{L})_2]\cdot 2CH_3CN\}_n$ (**3b**). The framework of **3b** contains four bridging **L** coordinated to a rhomboidal Cu$-$I$_2$$-$Cu motif through the exomonodentate Cu$-$S bonds. Again, the ether oxygens do not coordinate in copper(I) halide complexes. The observed different reactivity between copper(I) bromide and copper(I) iodide was also confirm by an XRPD measurement. Unlike the Pd(II) and Cu(I) cases, **L** afforded an unusual tris(**L**)-disilver(I) (club-sandwich-type) complex $[Ag_2(\mathbf{L})_3](PF_6)_2$ (**4**) on its reaction with $AgPF_6$. Each silver adopts a trigonal planar coordination environment with coordination sites occupied by two S atoms from one terminal ligand, and by one S atom from the bridging ligand; once again the ether oxygens are not coordinated. An NMR titration of the formation of complex **4** confirmed that the Ag/**L** stoichiometry of 2:3 found in the solid state is also maintained in solution.

Introduction

Unlike all oxygen-donor crown ethers, thiacrown analogues show a tendency to bind to thiaphilic metal ions to form exocyclic complexes,[1] since S$\cdots$S repulsion in the thiacrowns stabilizes the formation of *trans* torsion angles about each S-$(CH_2)_2$-S segment. As a consequence, such *exodentate* coordination tends to lead to the formation of diverse types of coordination polymers,[2] as well as to discrete metallosuprastructures bearing less-common stoichiometries.[3] From our studies so far on sulfur-containing mixed donor macrocycles[4] it is clear that the formation of corresponding discrete complexes is influenced not only by the stereochemical demand of the thiaphilic soft metal ion but also by the steric requirement of the ligand. As a result, we were motivated to prepare new discrete thiaphilic metal complexes of the O_2S_2-macrocycle **L** with unusual topologies and stoichiometries such as bis- and tris(macrocycle) species shown in Schemes 1$-$3 that include the rare "club-sandwich" Ag(I) complex.



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[1] (a) Wolf, R. E., Jr.; Hartman, J. R.; Storey, J. M. E.; Foxman, B. M.; Cooper, S. R. *J. Am. Chem. Soc.* **1987**, *109*, 4328. (b) Hill, S. E.; Feller, D. *J. Phys. Chem. A* **2000**, *104*, 652.

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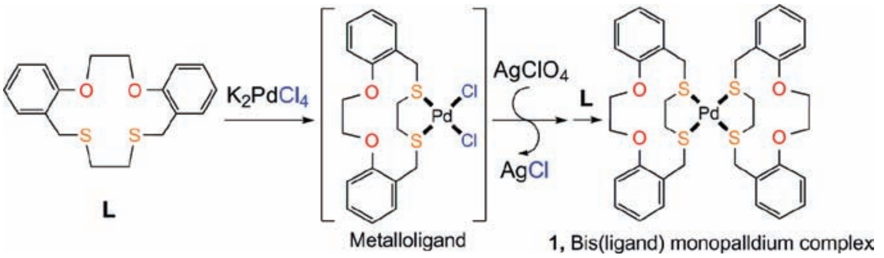
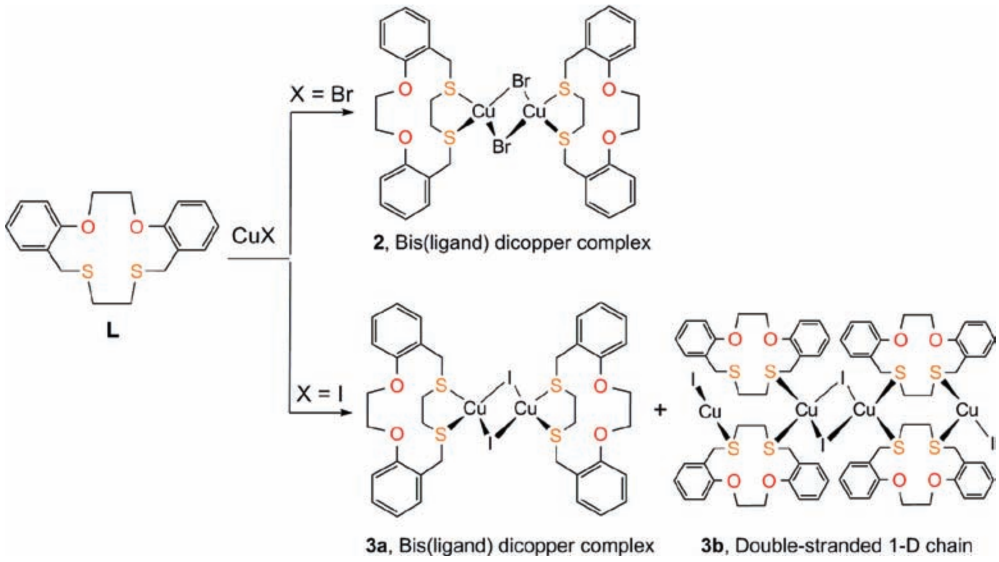
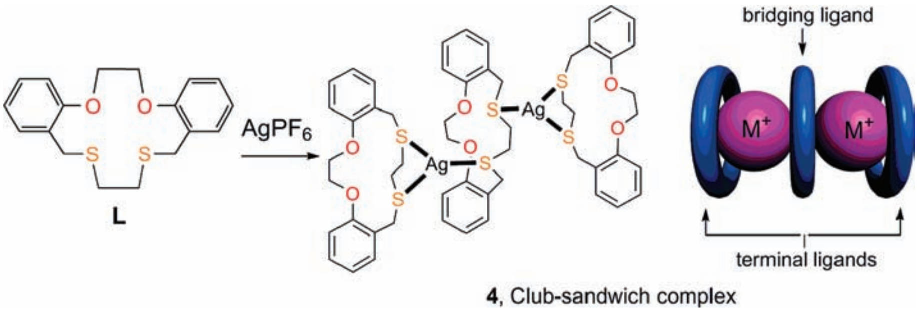
Scheme 1. Palladium(II) Complex Prepared



Scheme 2. Copper(I) Halide Complexes Prepared



Scheme 3. Silver(I) Complex Prepared



Experimental Section

General Procedures. All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. NMR spectra were recorded on a Bruker 300 spectrometer (300 MHz), and mass spectra were obtained on a JEOL JMS-700 spectrometer. 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. The X-ray powder diffraction (XRPD) experiments were performed in a transmission mode with a Bruker GADDS diffractometer equipped with graphite monochromated Cu Kα radiation ($\lambda = 1.54073$ Å).

Preparation of $[Pd(L)_2]\cdot 2ClO_4\cdot 2CH_3NO_2$ (1). Reaction of K_2PdCl_4 (19.6 mg, 0.060 mmol) and **L** (20.0 mg, 0.060 mmol) yielded an orange precipitate. The solid product was dissolved in methanol and then treated with $AgClO_4$. The AgCl precipitate that formed was removed by filtration. The addition of 1 equiv of **L** to the filtrate resulted in an orange solid which was dissolved in nitromethane. Vapor diffusion of diethyl ether into this solution afforded **1** as a crystalline product which was suitable for X-ray analysis (75%). Mp: 236−237 °C (decomp.). IR (KBr pellet): 3011, 2939, 1599, 1491, 1454, 1248, 1092 (ClO_4^-), 928, 754, 623 cm^{-1}. Anal. Calcd for $[C_{36}H_{40}Cl_2O_{12}PdS_4]$: C, 44.56; H, 4.16; S, 13.22. Found: C, 44.52; H, 4.27; S, 13.45%. ^1H NMR (300 MHz, CD_3CN, 25 °C): $\delta = 7.32$ (m, 8H), 7.09 (d, 4H), 7.00 (t, 4H), 4.43 (s, 8H), 3.95 (s, 8H), 2.88 (s, 8H). Mass spectrum *m*/*z* (FAB): 869.11 $[Pd(L)_2(ClO_4)]^+$, 385.065 $[Pd(L)_2]^{2+}$.

Preparation of $[Cu_2Br_2(L)_2]$ (2). A dichloromethane (2 mL) solution of **L** (15.0 mg, 0.045 mmol) was allowed to diffuse slowly to an acetonitrile (2 mL) solution of CuBr (6.47 mg, 0.045 mmol) in a capillary tube (i.d. 5 mm). Slow evaporation of the solution afforded the colorless crystalline product **2** suitable for X-ray analysis (90%). Mp: 213−214 °C (decomp.). IR (KBr pellet): 3003, 2941, 1582, 1489, 1448, 1400, 1242, 1225, 1190, 1107, 1068, 1057, 918, 829, 777, 748 cm^{-1}. Anal. Calcd for

Table 1. Crystal and Experimental Data for **1**−**4**

	1	**2**	**3a**	**3b**	**4**
formula	$C_{38}H_{46}Cl_2N_2O_{16}PdS_4$	$C_{18}H_{20}BrCuO_2S_2$	$C_{36}H_{40}Cu_2I_2O_4S_4$	$C_{20}H_{23}CuIN\ O_2S_2$	$C_{54}H_{60}Ag_2F_{12}O_6P_2S_6$
formula weight	1092.31	475.91	1045.80	563.95	1503.06
temperature	173(2)	173(2)	173(2)	298(2)	298(2)
crystal system	rhombohedral	monoclinic	monoclinic	monoclinic	monoclinic
space group	$R\bar{3}$	$P2_1/n$	$P2_1/n$	$C2/c$	$P2_1$
Z	9	4	6	8	2
a (Å)	30.9427(8)	11.5981(8)	20.1114(19)	27.736(2)	11.8135(10)
b (Å)	30.9427(8)	8.3384(6)	8.6467(8)	8.4417(7)	23.679(2)
c (Å)	12.6888(6)	19.4876(14)	34.485(3)	21.9823(18)	12.2325(11)
α (deg)	90	90	90.00	90	90
β (deg)	90	97.7430(10)	99.883(2)	121.2280(10)	106.928(2)
γ (deg)	120	90	90.00	90	90
V (Å^3)	10521.3(6)	1867.5(2)	5907.9(10)	4401.2(6)	3273.6(5)
D_{calc} (g/cm^3)	1.552	1.693	1.764	1.702	1.525
$2\theta_{max}$ (deg)	55.00	55.00	54.00	56.52	55.00
R	0.0604	0.0321	0.0508	0.0565	0.0682
wR	0.1477	0.0604	0.1124	0.1290	0.1603
no. of reflections used [$>2\sigma(I)$]	5361 [R(int) = 0.1327]	4223 [R(int) = 0.0381]	12203 [R(int) = 0.0602]	5347 [R(int) = 0.0789]	12550 [R(int) = 0.0724]
diffractometer	Bruker SMART CCD	Bruker SMART CCD	Bruker SMART CCD	Bruker SMART CCD	Bruker SMART CCD
structure determination	SHELXTL	SHELXTL	SHELXTL	SHELXTL	SHELXTL
refinement	full-matrix	full-matrix	full-matrix	full-matrix	full-matrix

[$C_{36}H_{40}Br_2Cu_2O_4S_4$]: C, 45.43; H, 4.24; S, 13.47. Found: C, 45.60; H, 4.37; S, 13.79%. Mass spectrum m/z (FAB) 395.07 [$Cu_2(\mathbf{L})_2$]$^{2+}$.

Preparation of Mixture of [$Cu_2I_2(L)_2$] (3a) and {[$Cu_2I_2(L)_2$]·2CH_3CN}$_n$ (3b). A dichloromethane (2 mL) solution of **L** (15.0 mg, 0.045 mmol) was allowed to diffuse slowly to an acetonitrile (2 mL) solution of CuI (8.59 mg, 0.045 mmol) in a capillary tube (i.d. 5 mm). Slow evaporation of the solution afforded the colorless crystalline product suitable for X-ray analysis (75%). Single-crystal X-ray analysis and XRPD results confirmed that the product is a two component mixture: a discrete dimeric complex (**3a**) and a double stranded one-dimensional (1D) polymer (**3b**). Separation of the mixed product into two pure components was not available.

Preparation of [$Ag_2(L)_3$](PF_6)$_2$ (4). $AgPF_6$ (15.2 mg, 0.060 mmol) in methanol (2 mL) was added to a solution of **L** (20.0 mg, 0.060 mmol) in acetonitrile. Slow evaporation of the solution afforded the colorless crystalline product **4** suitable for X-ray analysis (50%). Mp: 150−151 °C (decomp.). IR (KBr pellet) 2932, 1599, 1587, 1493, 1452, 1292, 1248, 1231, 1188, 1103, 1051, 939, 841 (PF_6^-), 754, 557 cm^{-1}. Anal. Calcd for [$C_{55}H_{68}Ag_2F_{12}O_9P_2S_6$]: C, 42.04; H, 4.36; S, 12.24. Found: C, 41.99; H, 3.99; S, 12.37%. ^{1}H NMR (300 MHz, CD_3CN, 25 °C): δ = 7.30 (m, 12H), 7.08 (d, 6H), 7.99 (t, 6H), 4.42 (s, 12H), 3.91 (s, 12H), 2.83 (s, 12H).

X-ray Crystallographic Analysis. All data were collected on a Bruker SMART CCD diffractometer equipped with graphite monochromated Mo K$_\alpha$ radiation (λ = 0.71073 Å). The cell parameters for the compounds were obtained from a least-squares refinement of the spot (from 45 collected frames) using the SMART program. The intensity data were processed using the Saint Plus program. All of the calculations for the structure determination were carried out using the SHELXTL package (version 6.22).[5] Absorption corrections were applied by using XPREP and SADABS.[6] In most cases, hydrogen positions were input and refined in a riding manner along with the attached carbons. Relevant crystal data collection and refinement data for the crystal structures of **1**, **2**, **3a**, **3b**, and **4** are summarized in Table 1.

Results and Discussion

Preparation and Structural Description of Palladium(II) Complex. The macrocycle **L** was synthesized as described previously by us.[7] The O_2S_2 macrocycle derivatives including **L** are expected to react with metals favoring square-planar geometry, such as palladium(II), to induce formation of bis(macrocycle) complexes.[8] As depicted in Scheme 1, a metalloligand-mediated two-step approach was employed to prepare the bis(macrocycle) monopalladium(II) complex **1**.

Reaction of K_2PdCl_4 and **L** yielded an orange precipitate which was dissolved in methanol, and the solution treated with $AgClO_4$. The AgCl precipitate that formed was removed by filtration. The addition of 1 equiv of **L** to the filtrate resulted in an orange solid which was dissolved in nitromethane; vapor diffusion of diethyl ether into this solution gave crystalline product **1**. X-ray analysis of **1** revealed it to have the formula [$Pd(\mathbf{L})_2$]·2ClO_4·2CH_3NO_2 in which Pd(II) is coordinated by two pairs of sulfur atoms from two **L** (Figure 1, Table 2). The two oxygen donors from each ligand remain uncoordinated. The Pd atom lies outside the macrocyclic cavities of both **L**, with each macrocycle adopting a bent configuration. Around the Pd atom, the bond distances [Pd1−S1 2.307(2) and Pd1−S2 2.324(2) Å] and bond angles [S1−Pd1−S2 89.1(1) and S1−Pd1−S2A 90.9(1)°] are similar, confirming that the structure is close to regular square-planar. Consequently, the square-planar stereochemical demand of Pd(II) coupled with the sole coordination of the S_2-donors of **L** to a single metal center results in the formation of the bis(macrocycle) monopalladium(II) complex.

Preparation and Structural Description of Copper(I) Halide Complexes. In complexation of **L** with copper(I) halide system, we were able to prepare one copper(I)

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[5] Sheldrick, G. M. *SHELXTL-PC* , version 6.22; Bruker-Analytical X-ray Services: Madison, WI, 2001.

[6] Sheldrick, G. M. *SADABS*; University of Göttingen: Göttingen, Germany, 2000.

[7] Lee, S. Y.; Seo, J.; Yoon, I.; Kim, C.-S.; Choi, K. S.; Kim, J. S.; Lee, S. S. *Eur. J. Inorg. Chem.* **2006**, 3525.

[8] (a) Lee, S. Y.; Park, K.-M.; Lee, S. S. *Inorg. Chem. Commun.* **2008**, *11*, 307. (b) Lee, S. Y.; Park, S.; Lee, S. S. *Inorg. Chim. Acta* **2009**, *362*, 1047.

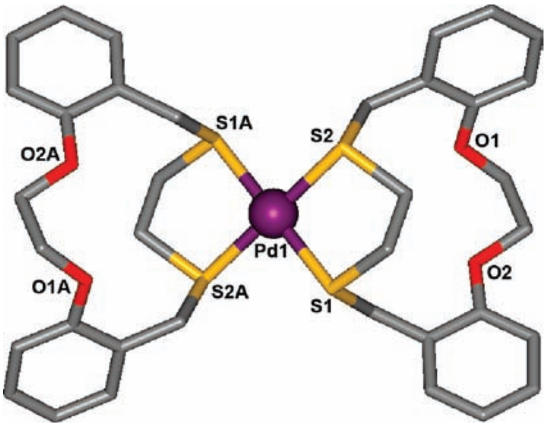

Figure 1. Crystal structure of the 1:2 [Pd(II)/ligand] bis(macrocycle) mononuclear complex **1**, [Pd(**L**)$_2$]·2ClO$_4$·2CH$_3$NO$_2$. Non-coordinating anions and solvent molecules are omitted.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for **1**[a]

Pd1−S1	2.307(2)	Pd1−S2	2.324(2)
S1−Pd1−S2	89.1(1)	S1−Pd1−S2A	90.9(1)
S1−Pd1−S1A	180.0(1)		

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

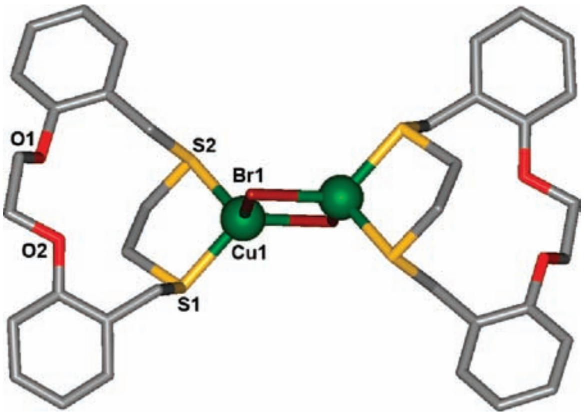

Figure 2. Crystal structure of the 2:2:2 [Cu(I)/anion/ligand] bis-(macrocycle) dinuclear complex **2**, [Cu$_2$Br$_2$(**L**)$_2$]. Hydrogen atoms are omitted.

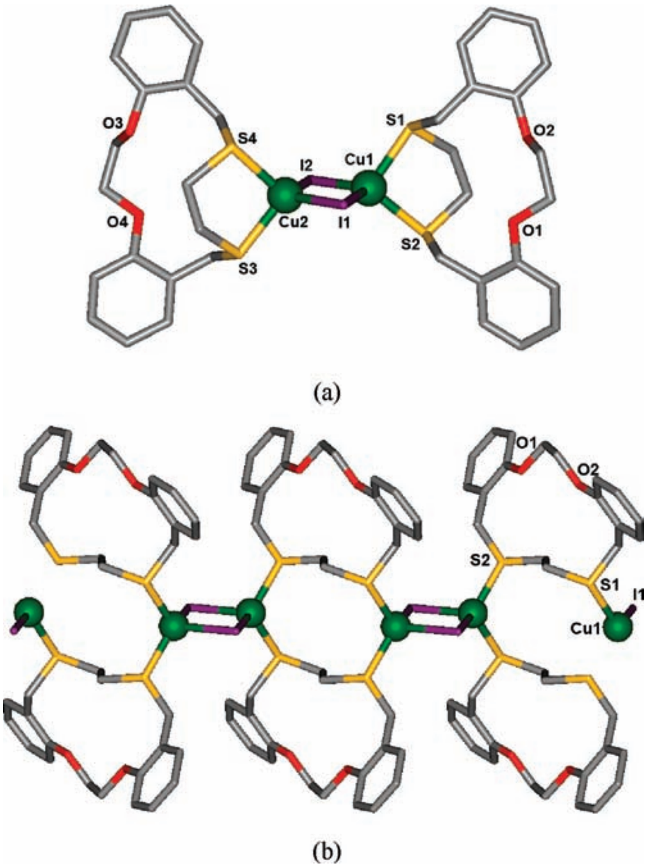

Figure 3. Crystal structures of (a) **3a**, [Cu$_2$I$_2$(**L**)$_2$], and **3b**, {[Cu$_2$I$_2$(**L**)$_2$]·2CH$_3$CN}$_n$. Hydrogen atoms and solvent molecules are omitted.

bromide complex **2** and two copper(I) iodide complexes **3a** and **3b** (Scheme 2). Each structure was characterized by single-crystal X-ray analysis (Figures 2 and 3) and the purity of each reaction product was checked by XRPD patterns (Figure 4).

A dichloromethane solution of **L** was allowed to diffuse slowly to an acetonitrile solution of 1 equivalent of CuBr in a capillary tube. Slow evaporation of the solution afforded the colorless crystalline product **2** suitable for X-ray analysis. The complex **2** crystallizes in a cofacial dimeric form, with two **L** sandwich an Cu−Br$_2$−Cu core forming a discrete complex with formula [Cu$_2$Br$_2$(**L**)$_2$] (Figure 2, Table 3). The comparison of XRPD results for the synthesized product with the simulated data for **2** confirmed that the product prepared is pure (Figure 4a). The structure contains a rhomboidal Cu−Br$_2$−Cu core connecting two bound macrocycles through Cu−S bonds. Each Cu(I) is four coordinate being bound to two exo-oriented sulfur atoms from two different macrocycles and the two bridging Br atoms; both macrocyclic rings adopt a bent configuration. Thus, the coordination sphere of the Cu center is distorted tetrahedral, with the "tetrahedral" angles falling in the range 93.6(1)−113.2(1)°.

Next, the reaction of **L** with CuI yielded a colorless crystalline product whose X-ray analysis confirmed a mixture of two different species: a discrete dimeric complex (**3a**) and a double stranded 1D polymer (**3b**) (Figure 3). The comparison of the XRPD result for the synthesized product with the simulated data for **3a** and **3b** also confirmed that the product prepared is the binary mixture (Figure 4b). Separation of the mixed products into two pure components was not available. Similar to **2**, the complex **3a** crystallizes in a cofacial dimeric form, with two **L** sandwich an Cu−I$_2$−Cu core forming a discrete complex with formula [Cu$_2$I$_2$(**L**)$_2$] (Figure 3a, Table 4).

X-ray analysis revealed that **3b** has a double-stranded polymeric chain structure (Figure 3b, Table 5). The framework contains four bridging **L** coordinated to a rhomboidal Cu−I$_2$−Cu motif through the exomonodentate Cu−S bonds. The Cu(I) coordination sphere is a distorted tetrahedral shape, with the "tetrahedral" angles falling in the range 92.5(1)−117.5(1)°. It is noted that we also recently reported the synthesis and structure of the closely related chloro-containing Hg(II) complex, [Hg$_2$Cl$_4$(**L**)$_2$], incorporating five-coordinate Hg(II);[9] it is interesting that such similar structures should be obtained

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[9] Lee, S. Y.; Park, S.; Kim, H. J.; Jung, J. H.; Lee, S. S. *Inorg. Chem.* **2008**, *47*, 1913.

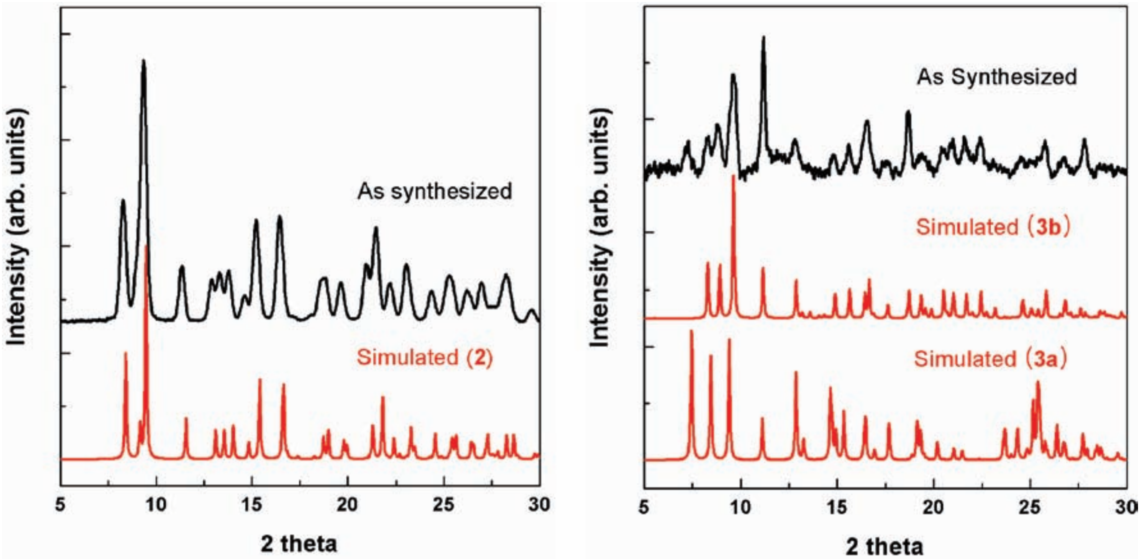

Figure 4. Comparison of XRPD patterns for (a) CuBr complex (**2**) and (b) CuI complexes: (top) as synthesized and (bottom) simulated from the single-crystal X-ray data.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for **2**[a]

Cu1−S1	2.311(1)	Cu1−S2	2.336(1)
Cu1−Br1	2.488(1)	Cu1−Br1A	2.434(1)
S1−Cu1−S2	93.6(1)	S1−Cu1−Br1	113.2(1)
S2−Cu1−Br1	108.3(1)	Br1−Cu1−Br1A	107.3(1)
S1−Cu1−Br1A	110.2(1)		

[a] Symmetry operation (A) $-x + 2, -y, -z$.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for **3a**

Cu1−S1	2.335(2)	Cu1−S2	2.359(2)
Cu1−I1	2.588(1)	Cu1−I2	2.628(1)
Cu2−S3	2.343(3)	Cu2−S4	2.347(2)
Cu2−I2	2.594(1)	Cu2−I1	2.604(1)
S1−Cu1−S2	92.5(1)	S1−Cu1−I1	115.8(1)
S2−Cu1−I1	109.9(1)	S1−Cu1−I2	104.2(1)
S2−Cu1−I2	114.3(1)	I1−Cu1−I2	117.5(1)
S3−Cu2−S4	93.1(1)	S3−Cu2−I2	112.8(1)
S4−Cu2−I2	111.3(1)	S3−Cu2−I1	107.2(1)
S4−Cu2−I1	111.4(1)	I2−Cu2−I1	118.2(1)

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for **3b**[a]

Cu1−S1	2.336(2)	Cu1−S2A	2.307(2)
Cu1−I1	2.681(1)		
S2A−Cu1−S1	105.9(1)	S2A−Cu1-I1B	121.6(1)
S2A−Cu1-I1	105.5(1)	S1−Cu1−I1	102.3(1)
S1−Cu1−I1B	113.9(1)		

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

from such diverse metal ions from otherwise the one assembly reaction. The bond distances to sulfur (Cu1−S1 2.335(2) Å, Cu1−S2 2.359(2) Å) are reasonably similar and compare well to those found in other copper(I)-thiamacrocyclic complexes.[4f] Each Cu(I) which lies outside the cavity is coordinated to the two S atoms of from two facing **L**. In **3b**, every to two adjacent ligands coordinated to one Cu(I) arranged in the opposite direction. Accordingly, an alternating arrangement of a pair of S-$(CH_2)_2$-S segment including Cu atom forms an extra metallacyclic cavity, corresponding to a 10-membered ring.

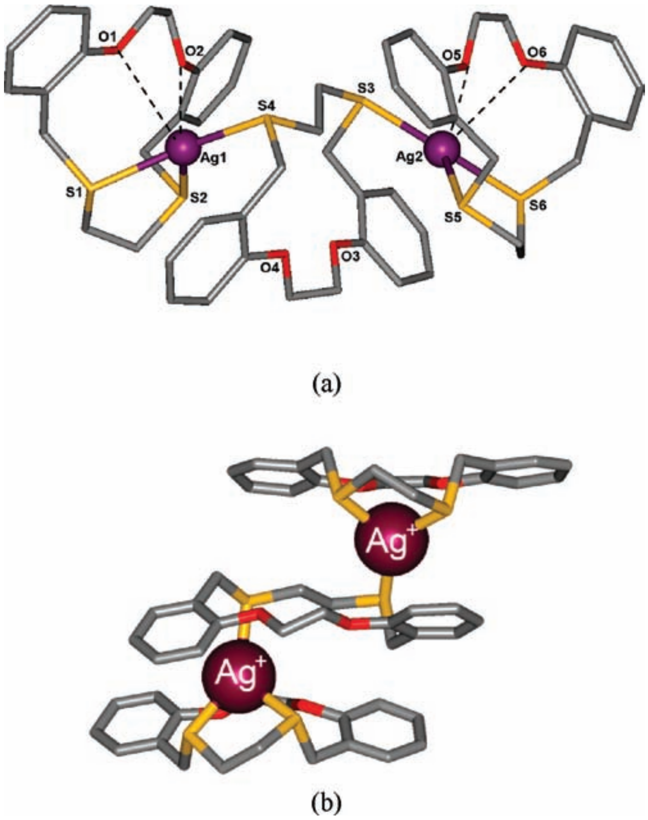

Figure 5. Crystal structure of the 2:3 [Ag(I):ligand] club-sandwich-type complex **4**, $[Ag_2(\mathbf{L})_3](PF_6)_2$: (a) top view (ORTEP drawing) and (b) side view (stick drawing except metal ions). Hydrogen atoms, non-coordinating anions, and solvent molecules are omitted.

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) for **4**

Ag1−S1	2.540(4)	Ag1−S2	2.590(4)
Ag1−S4	2.457(4)	Ag2−S3	2.461(3)
Ag2−S5	2.588(4)	Ag2−S6	2.532(4)
Ag1···O1	2.924(13)	Ag1···O2	3.002(9)
Ag2···O5	2.803(11)	Ag2···O6	2.982(14)
S4−Ag1−S1	145.7(1)	S4−Ag1−S2	121.4(1)
S1−Ag1−S2	86.6(1)	S3−Ag2−S6	136.9(1)
S3−Ag2−S5	133.4(1)	S6−Ag2−S5	85.8(1).

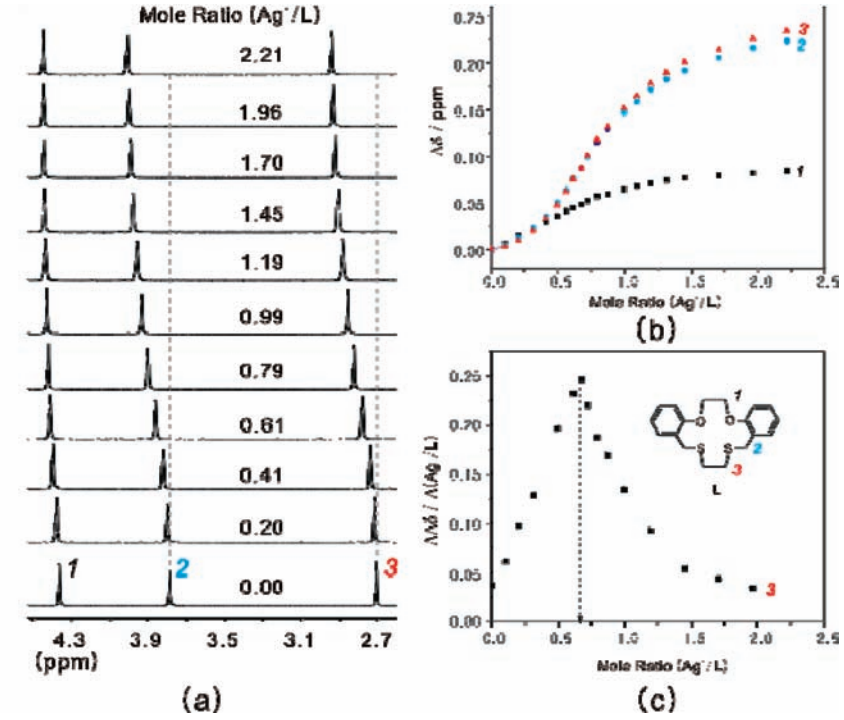

Figure 6. (a) ^{1}H NMR spectra of **L** following stepwise addition of $AgPF_6$, (b) the titration curves for addition of $AgPF_6$ to **L** in CD_3CN, and (c) first derivative titration curve for H_3.

Preparation and Structural Description of Silver(I) Complex. Unlike the above Pd(II) and Cu(I) cases, **L** afforded an unusual tris(macrocycle) dinuclear complex **4** on its reaction with $AgPF_6$ in a mixture of methanol and acetonitrile (Scheme 3).

Crystal structural analysis revealed that **4** is a triple decker club-sandwich complex[10] consisting of two silver(I) ions and three **L** with formula $[Ag_2(\mathbf{L})_3](PF_6)_2$ (Figure 5, Table 6). Two Ag atoms are crystallographically independent, but their coordination environments are not so significantly different. In **4**, each Ag atom is in a trigonal planar coordination environment with coordination sites occupied by two S atoms from one terminal ligand, and by one S atom from the bridging ligand. The coordination sphere of each three-coordinated Ag atom is considerably distorted [bond angles: S1−Ag1−S2 86.6(1)°, S2−Ag1−S4 121.4(1)°, and S1−Ag1−S4 145.7(1)°]. This distortion is attributed to the interactions of Ag1···O1 (2.924 Å) and Ag1···O2 (3.002 Å) forcing the Ag1 atom out of the trigonal S_3-coordination plane by 0.33 Å toward the terminal ligand (see dashed lines in Figure 5a). In the case of the Ag2 atom, the metal-donor bond angles show a typical Y-shaped geometry [S3−Ag2−S5 133.4(1)°, S3−Ag2−S6 136.9(1)°, and S5−Ag2−S6 85.8(1)°] due to Ag···O interactions (Ag2···O5 2.803 and Ag2···O6 2.982 Å). The Ag−S distances in the terminal ligands (2.53−2.59 Å) are longer than those in the bridging ligand (2.46 Å).

In marked contrast to Pd(II) (d^8), Ag(I) (d^{10}) has weaker stereochemical demands, often producing complex geometries largely dictated by the conformational preferences of the ligand rather than the geometric demands of the metal center. Notably, the conformations of two terminal ligands and one bridging ligand in **4** are significantly different. For example, torsion angles between two S donors in terminal ligands show *gauche* conformation [S1−C−C−S2 −56.79°, S5−C−C−S6 57.95°] but the bridging ligand adopts *anti* arrangement [S3−C−C−S4 −173.78°]. In fact, some sandwich-like complexes (metal-to-ligand 1:2) formed by benzo-15-crown-5,[11a−c] dibenzo-18-crown-6,[11d] and dicyclohexyl-18-crown-6[11e] with larger alkali metal ions have been reported. The club-sandwiches,[12] however, have appeared on the stage after many twists and turns because the macrocyclic ligand in the middle of system (bridging ligand) cannot be expected to make effective metal-to-donor contacts on two axial sides at a time. Because of this reason, only a limited number of examples of the club-sandwich complexes based on $[Cs_2(18\text{-crown-}6)_3]^{2+}$ are known.[11a−d] In case of soft acid−base complex systems, to the best of our knowledge, only two club-sandwich complexes have been reported by the Schröder,[13a] and Holdt[13b] groups.

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NMR Titration Study for Silver(I) Complexation. To explore the complexation behavior of **L** with silver(I) in solution and also for comparison with that in the solid state, an ^{1}H NMR titration was performed in CD_3CN (Figure 6a). Upon stepwise additions of $AgPF_6$ (0−2.3 equiv) to the ligand solution, the signals of all methylene protons of **L** shifted downfield. The signals of the three methylene protons (H_{1-3}) in **L** were well resolved and readily identified (Figure 6a). For these, the order of magnitude of the chemical shift variation is H_3, $H_2 \gg H_1$, in keeping with silver(I) being more strongly coordinated by S than O, in accord with the solid state structure of **4**. The titration curves show no clear break point in the range investigated, suggesting that the coexistence of more than one overlapping species corresponding to different M/**L** ratios (Figure 6b). However, the first derivative titration curve for H_3 shown in Figure 6c unambiguously shows a maximum at a mole ratio (metal-to-ligand) of 0.67, suggesting the formation of a complex with a 2:3 stoichiometry, similar to that found in the solid state.

Conclusions

The assembly reactions of the dibenzo-O_2S_2 macrocycle **L** with the chosen thiaphilic metals provide a facile means of generating less common bis- and tris(macrocycle) complexes with unusual topologies. From these results, it is concluded that a combination of the stereochemical demand of the thiaphilic metal ion coupled with the tendency for exo-coordination of the S donors of the proposed thiamacrocycle combine to direct both the observed variation in the complex stoichiometries as well as the final structures of the respective complexes.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.