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Articles

Preparation and Crystal Structures of Silver(I), Mercury(II), and Lead(II) Complexes of Oxathia-Tribenzo-Macrocycles

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An investigation of the coordination behavior of sulfur-containing mixed-donor tribenzo-macrocycles $\mathbf{L^1}$-$\mathbf{L^3}$ ($\mathbf{L^1}$: 20-membered O_3S_2, $\mathbf{L^2}$: 20-membered O_2S_3, and $\mathbf{L^3}$: 23-membered O_4S_2) with d^{10}-metal (Ag^+, Hg^{2+}, and Pb^{2+}) salts is reported. The X-ray structures of five complexes (**1**-**5**) with different structural types and stoichiometries, including mono- to dinuclear species have been determined. Reactions of $\mathbf{L^2}$ and $\mathbf{L^3}$ with the silver(I) salts (PF_6^- and SCN^-) afforded two dinuclear 2:2 (metal-to-ligand) complexes with different arrangements: a sandwich-type cyclic dinuclear complex $[Ag_2(\mathbf{L^2})_2](PF_6)_2\cdot 3CH_2Cl_2$ (**1**) and a linear dinuclear complex $[Ag_2(\mathbf{L^3})_2(SCN)_2]$ (**2**), in which two monosilver(I) complex units are linked by an Ag-Ag contact. Reactions of $\mathbf{L^1}$ and $\mathbf{L^2}$ with mercury(II) salts (SCN^- and Cl^-) gave a mononuclear 1:1 complexes $[Hg(\mathbf{L^1})(SCN)_2]$ (**3**) and $[Hg(\mathbf{L^2})Cl_2]$ (**4**) with anion coordination in both cases. $\mathbf{L^2}$ reacts with lead(II) perchlorate to yield a mononuclear sandwich-type complex $[Pb(\mathbf{L^2})_2(ClO_4)_2]$ (**5**), giving an overall metal coordination geometry of eight with a square antiprism arrangement. From these results, the effects of the donor variation and the anion-coordination ability on the resulting topologies of the soft metal complexes are discussed.

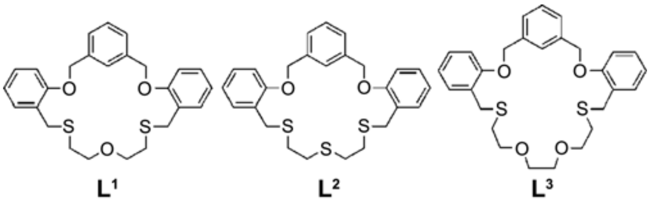
Key Words : Macrocyclic complex, Silver, Mercury, Lead, X-ray crystal structure

Introduction

Unlike the oxygen-type macrocycles (crown ethers), sulfur-donor macrocycles (thiamacrocycles) favor the adoption of exo-coordination in which the sulfur donors are oriented out of the macrocyclic cavity.[1] Because of this reason, coordinating behavior of the thiamacrocycles toward soft *d*-block metal ions give rise to supramolecular complexes with diverse topologies.[2] For example, such exocyclic coordination tends to lead to the formation of coordination polymers with unusual structures, as well as to discrete metallosupramolecules bearing less-common stoichiometries.[2,3]

We have reported that variation of the X donor in O_2S_2X macrocycles (X = S, NH, or O) triggers marked changes in the coordination geometries of the corresponding Ag(I) complexes.[3c] Recently, we have reported the synthesis and crystal structures of four sulfur-containing tribenzo-macrocycles including $\mathbf{L^1}$-$\mathbf{L^3}$ (Scheme 1) and their polymeric and discrete complexes of silver(I) salts and copper(I) iodide with less common topologies such as cyclic dimer, endo/exocyclic 1D polymer, and dinuclear sandwich.[4] In this case, tuning of sulfur-to-sulfur distance in the dithiamacrocycles is effective to discriminate the product because of the different exo-coordination modes. Very recently, we also reviewed on the exocyclic coordination based networking of thiamacrocycles.[5]

The continuing interest in metallosupramolecular assemblies incorporating sulfur-containing tribenzo-macrocycles $\mathbf{L^1}$-$\mathbf{L^3}$ has prompted us to investigate some more d^{10} soft metal complexes for these ligands. Here we report the preparation and crystal structures of the discrete type silver(I), mercury(II), and lead(II) complexes with less common structures including cyclic dimer and sandwich-type species. In particular, the lead(II) perchlorate complex isolated is the first case of the sandwich-type macrocyclic lead(II) complex with a square antiprism geometry.



Scheme 1. Oxathia-tribenzo-macrocycles $\mathbf{L^1}$-$\mathbf{L^3}$ used in this work.

Experimental

General. All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. The FT-IR spectra were measured with a Thermo Scientific Nicolet iS10 spectrophotometer. The electrospray ionization (ESI) mass spectra were obtained on a Thermo Scientific LCQ Fleet spectrometer. The tribenzo-macrocycles $\mathbf{L^1}$-$\mathbf{L^3}$ were prepared as described by us previously.[4]

Caution: The perchlorate-containing complex is potentially explosive and appropriate precautions should be taken during its preparation, handling, and storage.

Preparation of 1, $[Ag_2(L^2)_2](PF_6)_2 \cdot 3CH_2Cl_2$. Silver(I) hexafluorophosphate (18 mg, 0.071 mmol) in methanol (1 mL) was added to a solution of $\mathbf{L^2}$ (30 mg, 0.064 mmol) in dichloromethane (1 mL). Slow evaporation of the solution afforded colorless crystalline product **1** suitable for X-ray analysis. mp 185-187 °C (decomp). IR (KBr pellet): 2924, 1600, 1493, 1454, 1291, 1244, 1104, 1047, 1009, 843 (PF_6^-), 755, 701 cm^{-1}. Anal. Calcd for $[C_{53}H_{58}O_4S_6Cl_2P_2F_{12}Ag_2]$ ($[Ag_2(L^2)_2](PF_6)_2 \cdot CH_2Cl_2$): C, 40.74; H, 3.68; S, 12.31. Found: C, 41.10; H, 3.85; S, 12.32%. MS (ESI) *m/z*: 575.00 $[Ag(\mathbf{L^2})]^+$.

Preparation of 2, $[Ag_2(L^3)_2(SCN)_2]$. Silver(I) thiocyanate (11 mg, 0.066 mmol) in methanol (1 mL) was added to $\mathbf{L^3}$ (30 mg, 0.060 mmol) in dichloromethane (1 mL). Slow evaporation of the solution afforded colorless crystalline product **2** suitable for X-ray analysis. mp 126-128 °C (decomp). IR (KBr pellet): 3076, 3034, 2921, 2847, 2088 (SCN^-), 1598, 1493, 1373, 1288, 1246, 1136, 1100, 1006, 897, 750, 695 cm^{-1}. Anal. Calcd for $[C_{30}H_{32}O_4S_3NAg]$: C, 52.57; H, 4.87; N, 2.11. Found: C, 52.57; H, 4.81; N, 2.13%. MS (ESI) *m/z*: 603.17 $[Ag(\mathbf{L^3})]^+$.

Preparation of 3, $[Hg(L^1)(SCN)_2]$. Mercury(II) thiocyanate (23 mg, 0.073 mmol) in methanol (1 mL) was added to $\mathbf{L^1}$ (30 mg, 0.066 mmol) in dichloromethane (1 mL). Slow evaporation of the solution afforded colorless crystalline product **3** suitable for X-ray analysis. mp 163-165 °C (decomp). IR (KBr pellet): 3034, 2915, 2870, 2113 (SCN^-), 1598, 1494, 1453, 1292, 1240, 1114, 1009, 761, 703 cm^{-1}. Anal. Calcd for $[C_{28}H_{28}O_3S_4N_2Hg]$: C, 43.71; H, 3.67; N, 3.64; S, 16.67. Found: C, 43.75; H, 3.67; N, 3.64; S, 16.90%. MS (ESI) *m/z*: 711.67 $[Hg(\mathbf{L^1})(SCN)]^+$.

Preparation of 4, $[Hg(L^2)Cl_2]$. Mercury(II) chloride (19 mg, 0.070 mmol) in methanol (1 mL) was added to $\mathbf{L^2}$ (30 mg, 0.064 mmol) in dichloromethane (1 mL). Slow evaporation of the solution afforded colorless crystalline product **4** suitable for X-ray analysis. mp 157-159 °C. IR (KBr pellet): 3056, 2930, 2876, 2361, 2344, 1701, 1492, 1453, 1375, 1243, 1098, 1010, 754, 705 cm^{-1}. Anal. Calcd for $[C_{26}H_{28}O_2S_3Cl_2Hg]$: C, 42.19; H, 3.81; S, 12.99. Found: C, 41.74; H, 3.73; S, 13.28%. MS (ESI) *m/z*: 704.92 $[Hg(\mathbf{L^2})Cl]^+$.

Preparation of 5, $[Pb(L^2)_2(ClO_4)_2]$. Lead(II) perchlorate trihydrate (28 mg, 0.070 mmol) in acetonitrile (1 mL) was added to $\mathbf{L^2}$ (30 mg, 0.064 mmol) in dichloromethane (1 mL). Slow evaporation of the solution afforded colorless crystalline product **5** suitable for X-ray analysis. mp 179-181 °C (decomp). IR (KBr pellet): 3034, 2922, 2346, 1599, 1493, 1454, 1376, 1288, 1239, 1100 (ClO_4^-), 1047, 843, 753, 627 cm^{-1}. Anal. Calcd for $[C_{52}H_{56}O_{12}S_6Cl_2Pb]$: C, 46.49; H, 4.20; S, 14.32. Found: C, 46.57; H, 4.10; S, 14.82%. MS (ESI) *m/z*: 775.00 $[Pb(\mathbf{L^2})(ClO_4)]^+$.

X-ray Crystallographic Analysis. All data were collected on a Bruker SMART APEX2 ULTRA diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) generated by a rotating anode. Data collection, data reduction, and semiempirical absorption correction were carried out using the software package APEX2.[6] All of the calculations for the structure determination were carried out using the SHELXTL package.[7] In all cases, all non-hydrogen 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. Relevant crystal data collection and refinement data for the crystal structures are summarized in Table 1.

Table 1. Crystal and Experimental Data for **1-5**

	1	**2**	**3**	**4**	**5**
Formula	$C_{55}H_{62}Ag_2Cl_6F_{12}O_4P_2S_6$	$C_{29}H_{32}AgNO_4S_3$	$C_{28}H_{28}HgN_2O_3S_4$	$C_{26}H_{27}Cl_2HgO_2S_3$	$C_{52}H_{56}Cl_2O_{12}PbS_6$
Formula weight	1697.79	662.61	769.35	739.15	1343.42
Temperature	173(2)	173(2)	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	P-1	P-1	$C2/c$	P-1
Z	2	2	2	8	2
a (Å)	10.7465(2)	9.6453(2)	9.7560(2)	20.4587(8)	9.9175(8)
b (Å)	20.8933(4)	12.1962(3)	12.3833(3)	10.5713(4)	16.7177(12)
c (Å)	15.4189(2)	12.8508(3)	12.9441(3)	25.9179(10)	17.0542(13)
α (°)	90	83.9780(10)	90.0580(10)	90	82.627(2)
β (°)	100.4930(10)	88.1440(10)	100.6880(10)	100.438(2)	74.862(2)
γ (°)	90	69.6660(10)	109.6140(10)	90	87.164(2)
V (Å^3)	3404.11(10)	1409.68(6)	1444.12(6)	5512.6(4)	2706.5(4)
D_{calc} (g/cm^3)	1.656	1.561	1.769	1.781	1.648
$2\theta_{max}$ (°)	52.00	52.00	52.00	52.00	52.00
GOF	1.048	1.137	1.094	1.034	1.040
R_1, wR_2 [$I > 2\sigma(I)$]	0.0462, 0.1260	0.0223, 0.0590	0.0206, 0.0521	0.0241, 0.0565	0.0199, 0.0475
R_1, wR_2 [all data]	0.0539, 0.1331	0.0235, 0.0599	0.0216, 0.0526	0.0289, 0.0592	0.0228, 0.0489
No. reflns used [$> 2\sigma(I)$]	6672 [R_{int} = 0.0236]	5530 [R_{int} = 0.0238]	5645 [R_{int} = 0.0389]	5404 [R_{int} = 0.0320]	10631 [R_{int} = 0.0230]

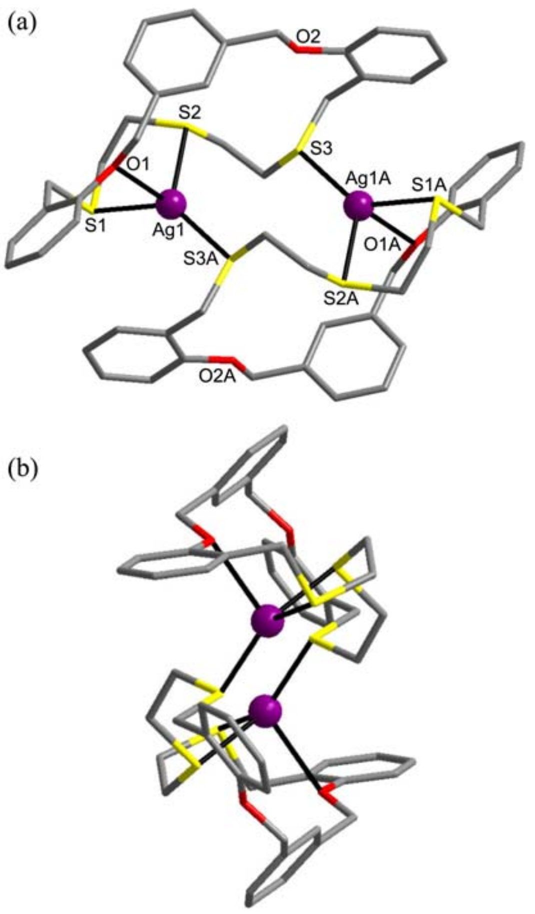


Figure 1. Crystal structure of **1**, $[\mathrm{Ag_2}(\mathbf{L}^2)_2](\mathrm{PF_6})_2\cdot 3\mathrm{CH_2Cl_2}$: (a) front view and (b) side view. Non-coordinating anions and solvent molecules are omitted.

Results and Discussion

Preparation and Structures of the Silver(I) Complexes (1 and 2). On complexation with silver(I) salts (hexafluorophosphate and thiocyanate), two supramolecular complexes (**1** and **2**) were obtained for $\mathbf{L}^2$ and $\mathbf{L}^3$. The preparation of the corresponding silver(I) complexes with $\mathbf{L}^1$ was not possible.

Colorless crystalline complex **1** suitable for X-ray analysis was obtained by slow evaporation of the reaction mixture of silver(I) hexafluorophosphate and $\mathbf{L}^2$ in methanol/dichloromethane at room temperature. Interestingly, the X-ray analysis revealed that **1** is a cyclic dimer complex with the formula being $[\mathrm{Ag_2}(\mathbf{L}^2)_2](\mathrm{PF_6})_2\cdot 3\mathrm{CH_2Cl_2}$ (Figure 1). The selected geometric parameters are presented in Table 2. The asymmetric unit in the complex part contains one $\mathbf{L}^2$ and one Ag atom. The structural unit in Figure 1 is generated through inversion symmetry. The structure consists of a dimeric arrangement in which two macrocycles are sandwiching two Ag atoms. Each four-coordinated Ag atom lies outside the macrocyclic cavity and is bonded to $\mathrm{S_2O}$ atoms from one $\mathbf{L}^2$ and one S atom from a different $\mathbf{L}^2$, resulting in the formation of a 10-membered metallacycle. The 'tetrahedral' bond angles around the Ag atom vary from 82.2(1)° (O1-Ag1-S1) to 135.4(1)° (S1-Ag1-S3A). These large deviations of the angles from the regular tetrahedron are due to the formation of the penta- and hexagonal rings *via* Ag1-S1, Ag1-S2, and Ag-O1 bonds together with the steric hindrance between two adjacent ligands linked with Ag atom. The Ag-S bond distances [2.415(1)-2.534(1) Å] are typical for such bonds. The separation of the two Ag atoms (Ag1···Ag1A, 5.220 Å) is far outside the range expected for an agentophilic interaction.[8] The preference for the cyclic dimer-type dinuclear complex formation may be associated with the donor atoms of $\mathbf{L}^2$ which allows ready metal coordination to all three consecutive sulfur donors. In addition, the lower coordination ability of the anion induces the formation of the anion-free complex cation.

Table 2. Selected bond lengths (Å) and bond angles (°) for **1**, $[\mathrm{Ag_2}(\mathbf{L}^2)_2](\mathrm{PF_6})_2\cdot 3\mathrm{CH_2Cl_2}$

Ag1-S1	2.522(1)	Ag1-S2	2.534(1)
Ag1-S3A	2.415(1)	Ag1-O1	2.647(3)
S1-Ag1-S2	88.5(1)	S1-Ag1-O1	82.2(1)
S1-Ag1-S3A	135.4(1)	S2-Ag1-O1	95.1(1)
S2-Ag1-S3A	126.2(1)	O1-Ag1-S3A	116.3(1)

symmetry operations: (A) $-x+1$, $-y$, $-z$

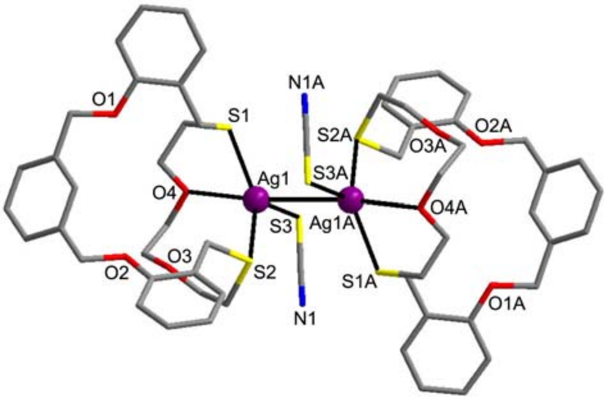


Figure 2. Crystal structure of **2**, $[\mathrm{Ag_2}(\mathbf{L}^3)_2(\mathrm{SCN})_2]$.

Colorless crystalline complex **2** suitable for X-ray analysis was obtained by slow evaporation of the reaction mixture of silver(I) thiocyanate and $\mathbf{L}^3$ in methanol/dichloromethane at

Table 3. Selected bond lengths (Å) and bond angles (°) for **2**, $[\mathrm{Ag}(\mathbf{L}^3)\mathrm{SCN}]$

Ag1-S1	2.533(1)	Ag1-S2	2.552(1)
Ag1-S3	2.503(1)	Ag1-Ag1A	3.209(1)
Ag1-O4	2.721(1)		
S1-Ag1-S2	126.0(1)	S1-Ag1-S3	122.0(2)
S1-Ag1-Ag1A	106.3(1)	S2-Ag1-S3	111.8(2)
S2-Ag1-Ag1A	82.3(1)	S3-Ag1-Ag1A	75.0(1)
S1-Ag1-O4	73.7(3)	S2-Ag1-O4	111.6(3)
S3-Ag1-O4	90.6(3)	O4-Ag1-Ag1A	163.2(3)

symmetry operations: (A) $-x+1$, $-y+1$, $-z+1$

room temperature. The structure of **2** is shown in Figure 2, with selected geometric parameters presented in Table 3. Again, the crystallographic analysis confirms that **2** is a 2:2 stoichiometric complex with the formula being [Ag_2(**L**^{3})$_2$-(SCN)$_2$]. Asymmetric unit of **2** contains one **L**^{3}, one Ag atom, and one thiocyanato ligand. Each Ag center is facially coordinated by S_2O donors from **L**^{3} in a bent conformation and one thiocyanato ligand bound in a monodentate manner with a bond distance [Ag1-S3, 2.503(1) Å] that falls within the range observed for other monodentate thiocyanato complexes of silver(I).[9] The coordination sphere is completed by an Ag1-Ag1A contact with a distance of 3.209(1) Å. Some *d*^{10} metal ions show a tendency to form metal-metal bonds and the Ag-Ag contacts in the range 2.80-3.30 Å have been reviewed.[8] The three macrocyclic O atoms (O1-O3) remain uncoordinated.

Addison *et al.*[10] introduced the distortion parameter τ, which provides a measure of the degree of square pyramid (SP) versus trigonal bipyramid (TBP) geometry adopted by the five-coordinate complexes. According to its definition [$\tau = (\theta_1 - \theta_2)/60$], where θ_1 is the largest and θ_2 is the second largest basal angle in the coordination sphere, an ideal SP is characterized by $\tau = 0$, while $\tau = 1$ means an ideal TBP. The experimental τ value for the Ag1 atom in **2** is 0.62. Thus, the coordination geometry around the Ag atom in **2** can be described as a distorted trigonal bipyramid. Around Ag1 atom, for example, S1, S2, and Ag1A atoms form the trigonal plane and O4 and Ag1A occupy the axial position [O4-Ag1-Ag1A 163.2(3)°]. The Ag-S bond distances [2.503(1)-2.552(1) Å] are similar to those in **1** and also typical. The preference for the dinuclear complex formation may be associated with the greater anion coordination ability toward the metal center and also the flexibility of **L**^{3} which allows the metal coordination to S_2O donors.

Preparation and Structures of the Mercury(II) Complexes (3 and 4). On complexation with mercury(II) salts (thiocyanate and chloride), two supramolecular complexes (**3** and **4**) were obtained for **L**^{1} and **L**^{2}. The preparation of the corresponding mercury(II) complexes with **L**^{3} was not possible.

First, the colorless crystalline complex **3** suitable for X-ray analysis was obtained by slow evaporation of the reaction mixture of mercury(II) thiocyanate and **L**^{1} in methanol/dichloromethane at room temperature. As shown in Figure 3(a), the crystal structure of **3** has a mononuclear arrangement with the formula being [Hg(**L**^{1})(SCN)$_2$]. The selected geometric parameters are presented in Table 4. In this structure, the Hg center is facially coordinated by consecutive S_2O donors from **L**^{1} and the coordination sphere is completed by two S atoms from two thiocyanato-ligands bound in a monodentate manner with bond distances [Hg1-S3 2.555(1), Hg1-S4 2.471(1) Å] that fall within the range observed for other monodentate thiocyanato complexes of mercury(II).[11] Thus, the Hg atom is effectively five-coordinate. Unlike **2**, the experimental τ value for the Hg atom in **3** is 0.26, suggesting that the metal coordination can be described as a distorted square pyramid, where S1, S2, S3, and O3 atoms form the basal square plane while S4 atom occupies the apex position. The Hg atom is defected out of the square plane by 1.040 Å toward S4. Again, the two oxygen donors (O1 and O2) lying between the aromatic units remain uncoordinated.

Table 4. Selected bond lengths (Å) and bond angles (°) for **3**, [Hg(**L**^{1})(SCN)$_2$]

Hg1-S1	2.614(1)	Hg1-S2	2.623(1)
Hg1-S3	2.555(1)	Hg1-S4	2.471(1)
Hg1-O3	2.816(2)		
S1-Hg1-S2	125.0(1)	S1-Hg1-S3	94.4(1)
S1-Hg1-S4	114.9(1)	S1-Hg1-O3	68.6(1)
S2-Hg1-S3	96.5(1)	S2-Hg1-S4	104.0(1)
S2-Hg1-O3	69.1(1)	S3-Hg1-S4	122.0(1)
S3-Hg1-O3	140.5(1)	S4-Hg1-O3	97.5(1)

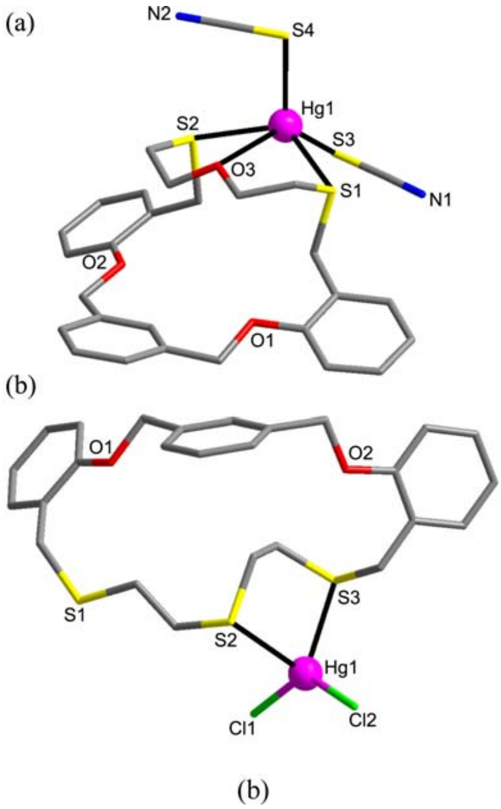


Figure 3. Crystal structures of (a) **3**, [Hg(**L**^{1})(SCN)$_2$] and (b) **4**, [Hg(**L**^{2})Cl_2].

Table 5. Selected bond lengths (Å) and bond angles (°) for **4**, [Hg(**L**^{2})Cl_2]

Hg1-S2	2.793(1)	Hg1-S3	2.585(1)
Hg1-Cl1	2.362(1)	Hg1-Cl2	2.415(1)
S3-Hg1-S2	83.1(1)	Cl1-Hg1-S2	101.7(1)
Cl1-Hg1-S3	114.8(1)	Cl1-Hg1-Cl2	132.9(1)
Cl2-Hg1-S2	96.3(1)	Cl2-Hg1-S3	110.3(1)

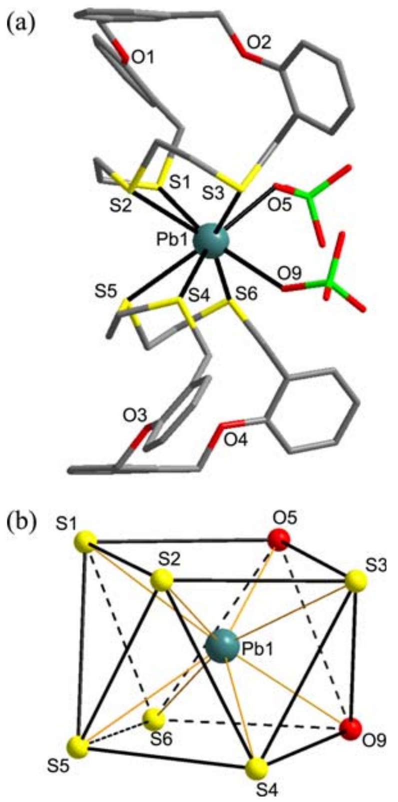


Figure 4. Crystal structure of **5**, [Pb($\mathbf{L}^2$)$_2$(ClO$_4$)$_2$]: (a) general view and (b) coordination environment of Pb1 in **5** showing a square antiprism arrangement.

As mentioned above, the reaction of mercury(II) chloride with $\mathbf{L}^2$ in methanol/dichloromethane yielded a colorless crystalline product **4**. The X-ray analysis revealed that **4** is a mononuclear complex with the formula being [Hg($\mathbf{L}^2$)Cl$_2$] (Figure 3(b)). The selected geometric parameters are presented in Table 5. The Hg atom is outside the cavity in a 'tetrahedral' arrangement coordinated by two sulfur atoms from $\mathbf{L}^2$. Two chlorine atoms are occupying the rest of two binding sites. Two ether oxygen atoms between two aromatic rings are remaining uncoordinated. Normally, Hg-S(thioether) bond distances are found in the range of 2.5-2.8 Å.[12] Thus, the Hg1-S3 [2.585(1) Å] is consist with the strong bond, whereas the Hg1-S2 [2.793(1) Å] indicates weaker bond. The Hg-Cl bond distances [2.362(1), 2.415(1) Å] are comparable with those reported previously.[13]

Table 6. Selected Bond Lengths (Å) and Bond Angles (°) for **5**, [Pb($\mathbf{L}^2$)$_2$(ClO$_4$)$_2$]

Pb1-S1	2.997(1)	Pb1-S2	3.007(1)
Pb1-S3	3.102(1)	Pb1-S4	3.088(1)
Pb1-S5	3.078(1)	Pb1-S6	3.146(1)
Pb1-O5	2.661(2)	Pb1-O9	2.698(2)
S1-Pb1-S2	69.9(2)	S1-Pb1-S6	78.3(2)
S2-Pb1-S3	68.2(2)	S4-Pb1-S3	72.6(2)
S5-Pb1-S4	68.7(2)	S5-Pb1-S6	68.0(2)
O5-Pb1-S1	76.5(1)	O5-Pb1-S2	114.4(1)
O5-Pb1-S3	81.4(1)	O5-Pb1-S4	147.7(1)
O5-Pb1-S5	142.6(1)	O5-Pb1-S6	83.1(1)
O5-Pb1-O9	84.9(1)	O9-Pb1-S1	155.4(1)
O9-Pb1-S2	133.6(1)	O9-Pb1-S3	74.2(1)
O9-Pb1-S4	70.0(1)	O9-Pb1-S5	113.7(1)
O9-Pb1-S6	83.7(1)		

Notably, one sulfur atom (S1) is remaining uncoordinated reflecting, in part, the repulsive interaction between the two sulfur donors in the three consecutive sulfur donors upon complexation. Also the high affinity of the Cl atoms seems to be the reason for the formation of an exo-coordinated 'tetrahedral' geometry. The 'tetrahedral' bond angles around the Hg atom vary from 83.1(1)° (S3-Hg1-S2) to 132.9(1)° (Cl1-Hg1-Cl2). The large deviations are due to the formation of a pentagonal ring *via* two Hg-S bonds.

Preparation and Structure of the Lead(II) Complex (5). Colorless crystalline complex **5** suitable for X-ray analysis was obtained by slow evaporation of the reaction mixture of lead(II) perchlorate and $\mathbf{L}^2$ in acetonitrile/dichloromethane at room temperature. Interestingly, the X-ray analysis revealed that **5** is a 1:2 type mononuclear complex with the formula being [Pb($\mathbf{L}^2$)$_2$(ClO$_4$)$_2$] (Figure 4). The selected geometric parameters are presented in Table 6. The structure consists of a sandwich arrangement in which two macrocycles are sandwiching one lead atom. The coordination of each $\mathbf{L}^2$ to the lead(II) center is *via* facial arrangement of its three sulfur donors with the ether oxygen donors remaining uncoordinated. The coordination sphere of the lead(II) center is completed by two O atoms from two perchlorato-ligands in a monodentate manner, giving a coordination number eight. The Pb-S bond distances [2.997(2)-3.146(2) Å] is longer than those of Pb-O(perchlorate) [2.661(2), 2.698(2) Å], because these can be considered as weak bonds for the sulfur as a soft base due to the intermediate behavior of the lead(II) between soft and hard acids. The resulting geometry of the lead(II) coordination sphere in **5** can be described as a distorted square antiprism (Figure 4(b)). The two square faces of the square antiprism are defined by S1-S2-S3-O5 and S4-S5-S6-O9. Some examples of eight-coordination in lead(II) complexes with noncyclic ligand system, adopting the square antiprism geometry have been reported.[14] As far as we are aware, complex **5** is the first isolated and structurally characterized macrocyclic lead(II) complex with the square antiprism geometry.

Conclusion

We have described the synthesis and structural characterization of five supramolecular complexes of three oxathia-tribenzo-macrocycles with silver(I), mercury(II), and lead(II) salts. The reactions of the macrocycles with the silver(I) salts employed provide a facile means of generating different metallosupramolecules, including a cyclic and a linear dinuclear complexes. In mercury(II) complexation, two complexes obtained show an exocyclic mononuclear structure with different coordination geometries due to the donor variation as well as the anions used. One lead(II) complex isolated exhibits the sandwich-type structure, adopting a square antiprism arrangement. From these results, it can be concluded that the anion-coordination ability and/or the donor variation act as key roles for the resulting topologies of the soft metal complexes with thia-macrocycles which favor the exocyclic coordination.

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Supplementary Materials. Crystallographic data for the structures reported here have been deposited with CCDC (Deposition No. CCDC-910302 - 910306 (**1-5**).

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