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Research paper

Coordination behaviors of a 23-membered NO₄S₂-macrocycle: Mononuclear silver(I) complex and conformational isomers of tetranuclear bis (macrocycle) mercury(II) complexes exhibiting *exo-* and *endo/exocyclic* coordination modes



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ABSTRACT

A ditopic 23-membered NO₄S₂-macrocycle (L) incorporating both semi-rigid and flexible binding sites was synthesized and its silver(I) and mercury(II) complexes exhibiting different stoichiometries and coordination modes were prepared. First, silver(I) perchlorate reacts with L to afford an *endocyclic* mononuclear complex [Ag (L)]ClO₄ (1) in which the silver(I) ion locates at the semi-rigid binding site in the cavity. The solution study for the silver(I) complexation via the ¹H NMR titration agrees with the corresponding solid state data that show the endo-mode. Interestingly, the reaction of L with HgI₂ led to the isolation of two conformational isomers with a tetranuclear bis(macrocycle) composition, [(^{exo}HgLI₂)₂(µ-Hg₂I₄)] (2a) and [(^{endo}HgLI₂)₂(µ-Hg₂I₄)] (2b), which are dominated by the coordination modes of L toward the mercury(II) complex units (^{exo}HgLI₂)₂ in 2a or two endocyclic complex units [(^{endo}HgLI₂)₂ in 2b are linked by tetraiododimercury(II) core (µ-Hg₂I₄) to give a 4:2 (metal-to-ligand) stoichiometry. Based on the packing structures and high temperature experiment, the intermolecular interactions might be responsible for the formation of 2a and 2b which are kinetically and thermodynamic controlled, respectively.

1. Introduction

Coordination chemistry of the crown ether type macrocycles including heterocrowns are not limited to Group I and II metal ions but extend to diverse ionic and neutral guests [1–5]. Based on the wellestablished cation-to-cavity size ratio for the selectivity of the endocyclic complexations [6], the macrocyclic complexes can be divided by three categories. In the first category, the cavity is too small to fit the metal ion to its inside, and therefore, the metal ion lies above the cavity in a perching mode to form a sandwich [7–13] or a club-sandwich [14–17] type complex. The second category includes the complexes in which the cation fits properly in the cavity to form a stable endocyclic mononuclear species (*optimal spatial fit*). In the last category, when the cavity is larger than the cation it is hard to isolate the solid complexes due to the lower stability.

Generally, the flexible large macrocycle in the last category wraps around the metal ion [18–20] and could act as a receptor in the areas of sensors and carriers [21] when the 'bind-detect' or 'transport-release' process is required. In practice, dibenzo-30-crown-10 offers a bent form accommodating potassium(I) in a 3-D configuration [18,19]. Our group have also reported the silver(I) complexation of a 21-membered dibenzo- O_4S_2 macrocycle with a twist-and-squeeze fashion via a synergic cooperation of multiple contacts [20].

Apart from the oxygen-bearing crown ethers, the sulfur-containing heterocrowns such as thiaoxa- or thiaaza-macrocycles frequently form not only endocyclic complexes but also exocyclic complexes due to the exo-orientation of the sulfur donors [22,23]. A range of the exocyclic complexes based on the thia- and thiaaza macrocycles with from 13- to 24-membered macrocycles have been reported by Schröder [24,25], Sheldrick [26–29], Heller [30], and our groups [31–38]. Thus, the larger macrocycles incorporating aromatic subunits and some sulfur donors with conformational flexibility can provide a potential design tool for engineering new coordination products in terms of stoichiometries, topologies and coordination modes.

In this work, we propose a 23-membered NO_4S_2 -macrocycle L incorporating a semi-rigid binding site and a flexible binding site due to

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Scheme 1. Ditopic macrocycle L with semi-rigid and flexible domains.

three aromatic subunits and an -S-O-O-S- segment, respectively (Scheme 1). Considering the relative metal ion binding affinities of the donor atoms in L, the presence of one pyridine subunit is expected to promote coordination of the metal ion inside the cavity [38].

Herein, we report the synthesis of the ditopic macrocycle L and its silver(I) and mercury(II) complexes. Related solution studies for the silver(I) complexation including ¹H NMR titration is also reported. In the mercury(II) complexations, an interesting feature is the isolation of two tetramercury(II) bis(macrocycle) complex isomers whose coordination modes are exocyclic and endocyclic respect to the macrocyclic ring cavity. The strategies to control the endocyclic and exocyclic coordination modes for the macrocyclic complexes by variation of interdonor (S…S) distance [10], anion [32,39], ring rigidity [37], and ligand isomers with different coordination modes have not encountered in the macrocyclic complexes so far.

2. Experimental

2.1. General considerations

All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. Mass (ESI) spectra were obtained employing a Thermo Scientific LCQ Fleet spectrometer. The FT-IR spectra were measured using a Thermo Fisher Scientific Nicolet iS 10 FT-IR spectrometer. The elemental analysis was carried out using a Thermo Scientific Flash 2000 Series elemental analyzer. NMR spectra were recorded on a Bruker 300 spectrometer (300 MHz). PXRD experiments were performed with a Bruker GADDS diffractometer equipped with graphite-monochromated Cu K α radiation.

Caution! The perchlorate-containing complexes are potentially explosive and should be handled with great care.

2.2. Synthesis and characterization of L

Cs₂CO₃ (6.4 g, 18.1 mmol) was dissolved in DMF (2 L) in a 3 L round-bottom flask. 3,6-Dioxa-1,8-octane-dithiol (2.3 g, 12.8 mmol) and dichloride 6 (5.1 g, 13.1 mmol) were dissolved in DMF (1.0 L) and placed in a dropping funnel. The contents of the dropping funnel were added dropwise into the DMF solution under a nitrogen atmosphere at 50-60 °C for 12 h. After being cooled to room temperature, the reaction mixture was filtered and the solvent evaporated. Water was added, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous sodium sulfate and filtered and the solvent was removed to give a yellow crude mixture. Flash column chromatography (SiO₂, n-hexane/ethyl acetate = 7:3) afforded the product as a white solid in 20% yield. Mp: 120-121 °C. IR (KBr, pellet) 2923, 2859, 2362, 2343, 1654, 1597, 1493, 1449, 1246, 1105, 1091, 1047, 1020, 781, 749 cm⁻¹. Anal. Calcd for [C₂₇H₃₁NO₄S₂]: C, 65.16; H, 6.28; N, 2.81; S, 12.88. Found: C, 65.22; H, 6.24; N, 2.85; S, 13.27. ¹H NMR (see Fig. S1a, 300 MHz, CDCl₃, δ): 7.88–6.96 (11H, aromatic), 5.22 (s, 4H, PyCH₂O), 3.87 (s, 4H, OCH₂CH₂O), 3.37 (t, 4H, OCH₂CH₂S), 3.22 (s, 4H, ArCH₂S), 2.56 (t, 4H, SCH₂CH₂O); ¹³C NMR (see Fig. S1b, 75 MHz, CDCl₃, δ) 156.6, 155.9, 139.9, 131.7, 129.8, 125.4, 125.1, 121.7, 113.0,

70.3 69.6, 69.0, 33.7, 33.6. MS (ESI) m/z: 520.25 [L·Na]⁺.

2.3. Preparation of complexes

2.3.1. $[Ag(L)]ClO_4$ [1]

AgClO₄ (4.3 mg, 0.021 mmol) in methanol (1 mL) was added to a solution of L (9.9 mg, 0.019 mmol) in dichloromethane (1 mL). Slow evaporation of the solution afforded colorless crystalline product 1 suitable for X-ray analysis (yield 60%). IR (KBr pellet): 2921, 2845, 1592, 1490, 1451, 1411, 1367, 1286, 1237, 1187, 1129 (ClO₄⁻), 1095, 1045, 1024, 780, 747 cm⁻¹. Anal. Calcd for $[C_{27}H_{31}AgClNO_8S_2]$: C, 45.65; H, 4.48; N, 1.97; S, 9.03. Found: C, 45.66; H, 4.33; N, 1.99; S, 8.86. ¹H NMR (see Fig. S3a, 300 MHz, CDCl₃, δ): 8.12–7.83 (11H, aromatic), 5.32 (s, 4H, PyCH₂O), 4.05 (s, 4H, OCH₂CH₂O), 3.56 (t, 4H, OCH₂CH₂S), 3.42 (s, 4H, ArCH₂S), 2.84(t, 4H, SCH₂CH₂O); ¹³C NMR (see Fig. S3a, 75 MHz, CDCl₃, δ) 156.5, 156.2, 137.6, 130.8, 128.4, 127.7, 121.6, 121.4, 110.9, 71.1, 70.7, 69.6, 30.6, 30.0. MS (ESI) *m/z*: 604.08 [AgL]⁺.

2.3.2. $[(^{exo}HgLI_2)_2(\mu-Hg_2I_4)]$ [2a] and $[(^{endo}HgLI_2)_2(\mu-Hg_2I_4)]$ [2b]

A solution of HgI₂ (8.9 mg, 0.020 mmol) in methanol (1 mL) was layered onto a solution of L (10.3 mg, 0.021 mmol) in dichloromethane (1 mL). Slow evaporation of the solution in the capillary tube afforded a lump of the needle-shaped pale yellow crystals of **2a** (below 2% yield) suitable for the X-ray analysis. No further analysis were possible due to the extremely low yield.

A solution of HgI₂ (8.7 mg, 0.019 mmol) in methanol (1 mL) was added to the stirred solution of **L** (10.7 mg, 0.022 mmol) in dichloromethane (1 mL). Slow evaporation of the solution in the vial for two days afforded needle-shaped pale yellow crystals of **2b** (60% yield) suitable for the X-ray analysis. For **2b**: Mp: 135–136 °C. Anal. Calcd for $[C_{54}H_{62}Hg_4I_8N_2O_8S_4]$: C, 23.06; H, 2.22; N, 1.00; S, 4.56. Found: C, 23.23; H, 2.14; N, 1.24; S, 4.84. ¹H NMR (see Fig. S4a, 300 MHz, CDCl₃, δ): 7.98–6.96 (11H, aromatic), 5.20 (s, 4H, PyCH₂O), 3.83 (s, 4H, OCH₂CH₂O), 3.29 (t, 4H, OCH₂CH₂S), 3.14 (s, 4H, ArCH₂S), 2.47 (t, 4H, SCH₂CH₂O); ¹³C NMR (see Fig. S4a, 75 MHz, CDCl₃, δ) 156.6, 156.5, 138.3, 131.1, 128.9, 127.9, 122.0, 121.6, 112.9, 71.2, 70.3, 69.4, 30.9, 29.9.

2.4. X-ray crystallography

All data were collected on a Bruker SMART APEX2 ULTRA diffractometer equipped with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) generated by a rotating anode. Data collection, data reduction, and semiempirical absorption correction were carried out using the software package APEX2 [41]. All of the calculations for the structure determination were carried out using the SHELXTL package [42]. Relevant crystal data collection and refinement data for the crystal structures are summarized in Table. S1.

3. Results and discussion

3.1. Synthesis of macrocycle L

Synthesis of the target macrocycle L involves four steps starting from ditosylate **3** (Scheme 2). Dichloride 6 was prepared from dialdehyde **4** and dialcohol **5** using known procedures [43–45]. L was obtained by a coupling cyclization reaction between dichloride **6** and dithiol in the presence of CS_2CO_3 under high dilution condition in dimethylformamide (DMF) (20% yield). The ¹H and ¹³C NMR spectra (Fig. S1) together with the microanalysis and the mass spectra were all in clear agreement with the proposed structures.

For the complexation of L, AgClO₄ was used. In this reaction, a dichloromethane solution of L was allowed to diffuse slowly into a methanol solution of one equivalent of AgClO₄. Slow evaporation of the solution afforded a colorless crystalline product 1 suitable for single



Scheme 2. Synthesis of L.

crystal X-ray diffraction (SC-XRD) analysis. The SC-XRD analysis revealed that 1 crystallizes in the monoclinic space group $P2_1/n$ and adopts a typical endocyclic mononuclear structure of the type [Ag (L)]ClO₄ (Fig. 1). In the macrocyclic complex cation, the silver(I) center binds to NO_2S_2 donors at the semi-rigid site of L (Scheme 1) in a twisted conformation, preventing coordination from the anion or solvent. The coordination sphere adopts a distorted square pyramidal coordination geometry ($\tau = 0.1$) [46] with the S1, S2, N1 and O2 atoms defining a square plane, and the O1 atom as an apex. The bond lengths of Ag-O [2.710(2), 2.718(2) Å] and Ag-S [2.481(8), 2.519(9) Å] are typical. Two oxygen donors in the flexible site remain uncoordinated (Ag1...O3 3.821(3) Å and Ag1...O4 4.315(3) Å) due to the stronger affinity of pyridine toward the silver(I) center (Ag1-N1 2.325(3) Å). Hence, the metal center in 1 is effectively shielded by the bound macrocycle from the anion and solvent. Consequently, the preferred formation of the endocyclic structure of 1 is in keeping with the coordination ability of the NO₂S₂ donors in the semi-rigid domain which provide a favorable conformation in the aids of the flexible domain of L.

3.2. NMR titration of L with silver(I) perchlorate

¹H NMR titration of L with AgClO₄ was performed to obtain further information on the complexation behavior in solution (Fig. 2a). On stepwise addition of AgClO₄ to the ligand solution, the signals for all aliphatic protons (H₁ – H₅) shift downfield, in keeping with the complex formation with a fast ligand exchange rate. The titration shows that the plots for all proton signals exhibit no further shifts above a mole ratio of 1.0 (Fig. 2b), indicating that the complex formed has a stable 1:1 metalto-ligand species. The silver(I)-induced shifts for the aliphatic protons follow the order H₃ (Δδ 0.35 ppm) > H_{2,4} (0.27 ppm) > H₅ (0.19 ppm) > H₁ (0.09 ppm). The largest downfield shift for H₃ adjacent to the S donor is due to the silver(I) being strongly bound to the S donors, whereas the smaller downfield shifts for H_1 and H_5 near the O donors indicate a weaker contribution of the O donors to the coordination to the silver(I) center. The downfield shifts of the pyridyl protons ($\Delta\delta$: 0.13 ppm for H_a and 0.06 ppm for H_b) also show the contribution of the hetero N donor to the coordination, reflecting the metal ion position inside the cavity similar to its endocyclic mononuclear complex in the solid state shown in Fig. 2. From the titration data in Fig. 2b, the stability constant (at 23 °C) for the 1:1 complexation between silver(I) and L was obtained by using HyperNMR2008 software [47] and this yields the log *K* value of 8.9, suggesting the formation of a stable endocyclic mononuclear complex due to the collective effect of Ag-S, Ag-N and Ag-O bonds in solution.

3.3. Mercury(II) iodide complexes: kinetic product (2a) and thermodynamic product (2b)

As depicted in Scheme 3, we found that a reaction of L with mercury (II) iodide at room temperature afforded a kinetically controlled (see later) tetranuclear bis(macrocycle) complex 2a; this was followed by formation of a thermodynamically stable product 2b whose formula is identical but its conformation is different. Since, 2a and 2b seem to be interconvertible via a flip-flop, they could be considered *conformational isomers*. Furthermore, 2a and 2b show exocyclic and endocyclic coordination modes, respectively. Details of the two isomers are described below mainly in terms of the coordination modes. We also provide some evidences for the two isomers as the kinetic and thermodynamic products.

Slow diffusion of HgI_2 in methanol to L in dichloromethane and allowing the solution to evaporate afforded a small amount of **2a** as a pale yellow crystalline product (Route I in Scheme 3). The SC-XRD analysis revealed that **2a** has a tetranuclear bis(macrocycle) arrangement with the formula [($^{exo}HgLI_2$)₂(μ -Hg₂I₄)] in which two *exo*-type macrocyclic complex units, ($^{exo}HgLI_2$), are bridged by tetraiododimercury(II) core, (μ -Hg₂I₄) (Fig. 3). In CCDC [48], 155 hits for the (Hg₂I₄) unit have been found, however, only two examples of such core bridging two thiamacrocycles via Hg-S bonds have been reported so far [32,49]. Since an inversion center locates in the middle of **2a**, the asymmetric unit contains one L, two Hg atoms (Hg1 and Hg2) and four iodide atoms.

As mentioned above, we found that the *exo*-mode of the Hg1 atom (exo Hg) in **2a** was converted to the endo-mode (endo Hg) in **2b** (Fig. 4). When the reaction solution was left undisturbed for 5 days; at the end of this period only crystals of **2b** were left, and these had formed in much higher yield (60%) than occurred initially for **2a**.

Some modified approaches were also carried out, affording isolation

Fig. 1. Crystal structure of 1, [Ag(L)]ClO₄. Selected bond lengths (Å) and bond angles (°): Ag1-S1 2.481(8), Ag1-S2 2.519(9), Ag1-N1 2.325(3), Ag1-O1 2.710(2), Ag1-O2 2.718(2), S1-Ag1-S2 118.68(3), S1-Ag1-O1 135.94(6), S1-Ag1-O2 78.69(5), S2-Ag1-O1 76.94(5), S2-Ag1-O2 123.16(5), N1-Ag1-S1 125.70(7), N1-Ag1-S2 114.77(7), N1-Ag1-O1 65.12(8), N1-Ag1-O2 64.70(8), O1-Ag1-O2 129.77(7).





Fig. 2. (a) ¹H NMR spectra of L $(1.0 \times 10^{-2} \text{ M})$ following the stepwise addition of AgClO₄ in CD₃CN and (b) their titration curves for each proton in L.



2a (Kinetic product)





Fig. 3. Crystal structure of 2a, $[({}^{exo}\text{HgLI}_2)_2(\mu\text{-Hg}_2\text{I}_4)]$ showing an exocyclic coordination mode of the ^{exo}Hg1 atom.

of **2b** both in crystal and powder form directly. For example, under the identical reaction condition but with stirring at 50 °C for 10 min (Route II in Scheme 3), a pale yellow precipitate was obtained. The powder Xray diffraction (PXRD) pattern confirmed that this solid is a pure product 2b (Fig. S2). When a mixture of HgI2 and L in dichloromethane/



Fig. 4. Crystal structure of 2b, $[({}^{\textit{endo}}\text{HgLI}_2)_2(\mu\text{-Hg}_2\text{I}_4)]$ showing an endocyclic coordination mode of the endoHg1 atom.

methanol was allowed on standing at 50 °C and was cooled down to room temperature to evaporate, a pale yellow crystalline product 2b was afforded. Considering the above results, the conversion of 2a to 2b at the room temperature is in accord with the exocyclic product 2a being a kinetic product, while the endocyclic product 2b being a thermodynamic product. The selected geometric parameters of 2a and 2b are presented in Table 1. The structural characteristics of both products are compared and discussed below

Table 1

Comparison of the selected bond lengths (Å) and bond angles (°) for 2a and 2b.

	2a	2b
Hg1-O3	2.741(4)	2.740(3)
Hg1-S1	2.671(14)	2.799(13)
Hg1-I1	2.647(5)	2.615(5)
Hg1-I2	2.626(5)	2.596(5)
Hg2-S2	2.564(14)	2.573(12)
Hg2-I3	2.728(5)	2.760(6)
Hg2-I3A	3.397(5)	3.158(5)
Hg2-I4	2.635(5)	2.664(5)
S1-Hg1-O3	71.74(8)	69.11(8)
S1-Hg1-I1	96.16(3)	99.94(3)
S1-Hg1-I2	114.92(3)	101.86(3)
O3-Hg1-I1	93.74(9)	89.65(7)
O3-Hg1-I2	96.21(8)	104.50(7)
I1-Hg1-I2	148.92(16)	157.13(16)
S2-Hg2-I3	104.79(3)	114.24(3)
S2-Hg2-I4	124.58(3)	123.60(3)
S2-Hg2-I3A	90.40(3)	88.45(3)
I3-Hg2-I3A	93.69(12)	96.97(13)
I4-Hg2-I3	129.82(15)	117.98(15)
I4-Hg2-I3A	94.29(13)	104.63(15)

2a and 2b both of which crystallize in the triclinic space group P-1 also share structural similarities featuring a tetranuclear bis(macrocycle) arrangement. Each Hg1 atom in both products is four-coordinate, being bound to one sulfur atom, one oxygen atom from L in a highly twisted and bent conformation. The coordination sphere is completed by two iodide atoms adopting a distorted tetrahedral geometry with the tetrahedral angles falling in the range 71.74(8)° (S1-Hg1-O3) to 148.92(16)° (I1-Hg1-I2) in 2a and 69.11(8)° (S1-Hg1-O3) to 157.13(16)° (I1-Hg1-I2) in 2b. The large deviations are due to the formation of the pentagonal ring via Hg1-S1 and Hg1-O3 chelation as well as the repulsive interaction between two spacious iodo ligands. The ^{exo}Hg1-S1 in **2a** [2.671(14) Å] is typical, while that of ^{endo}Hg1-S1 in **2b** [2.799(13) Å] falls on the longer end of the reported values in literatures for such bonds (2.5-2.8 Å) [50,51]. Oppositely, the exoHg1-I bond distances in 2a [2.647(5), 2.626(5) Å] are slightly longer than those of endoHg1-I in 2b [2.615(5), 2.596(5)Å] but all values are comparable with those reported previously [32,49].

On complexation, the flexible domain (S1-O3-O4-S2) incorporating an S1-C-C-O3 fragment shows a larger conformational change than the semi-rigid domain (Fig. 5). The associated difference of the intermetallic distance between e^{xo} Hg1...Hg2 (9.64Å) in **2a** and e^{n-do} Hg1...Hg2 (4.78Å) in **2b** is also remarkable. In the overlapped top views of the macrocyclic complex units (Fig. 5a), the inward form of the e^{ndo} Hg1 atom in **2b** (dark green) could be occurred not by hindered rotation about a particular bond but rather hindered rotation through the flipping of an S1-C-C-O3 fragment bound to the e^{xo} Hg1 atom in **2a** (light blue) or by the packing stability via the intermolecular interactions (Fig. 5b).

In practice, the packing structures confirmed that both products feature pseudo polymeric arrangements with different connectivity and dimensions (Fig. 6). In 2a, the complex molecules interact via face-toface type aromatic π - π stacking (orange dashed lines in Fig. 6a, centroid…centroid 4.04 Å) to form a pseudo 1D polymeric chain and no further interactions exist between the chains. In 2b, the intermolecular edge-to-face type π - π interactions (yellow dashed lines in Fig. 6b, 3.16 Å) form pseudo 1D chains which are further cross-linked by C-H…O hydrogen bonds between the chains (red dashed lines, 2.46 Å), resulting in the pseudo 2-D network. Thus, unlike 2a, the compact network structure of **2b** is reinforced by π - π interactions as well as by hydrogen bonds. As a consequence, the packing for 2b is more favorable because of (i) a minimization of the steric repulsion between adjacent two molecules and (ii) maximization of their attraction via the edge-to-face π - π interactions as well as van der Walls interactions. Although the origin of the formations of two conformers associated with the different coordination modes is not clear, the close packing of 2b may play a role in forming a more stable thermodynamic product incorporating the endocyclic conformation of the S1-C-C-O3 segment toward Hg1 atom.

Since **2a** was obtained in a very low yield under the layered condition, the reversibility test between **2a** and **2b** was not possible. Sometimes mole-ratio of the reactants for the complexation could be a controlling factor to give different topological products (supramolecular isomers or polymorph) with an identical composition [52]. In order to examine the mole-ratio effect on the resulting complexes, the concentration of HgI₂ was varied (2–5 equiv.) relative to the ligand concentration under the homogenous condition. According to the PXRD patterns for these products (Fig. 7), all the reactions solely yielded **2b**, suggesting that no mole-ratio dependency was observed in this case. Consequently, the results from the mole-ratio experiments also support that **2b** is a thermodynamically stable.



Fig. 5. Structural comparison of ^{exo}Hg1 complex unit (2a, light blue) and ^{endo}Hg1 complex (2b, dark green): (a) top views (overlapped) and (b) side views. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



(a)

Fig. 6. Packing arrangement of (a) **2a** showing intermolecular face-to-face π - π interactions (orange dashed lines, centroid-to-centroid distance = 4.036 Å) and (b) **2b** showing intermolecular edgeto-face π - π interactions (yellow dashed lines) and interchain hydrogen bonds (red dashed lines). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 7. PXRD patterns for the two mercury(II) iodide complexes showing no mole-ratio dependency: data from simulated (2a and 2b, black color) and synthesized (2-5 equiv. of HgI₂) ones.

4. Concluding remarks

In summary, the synthesis of a ditopic 23-membered NO_4S_2 -macrocycle (L) incorporating a semi-rigid and a flexible binding sites are described. The structural characteristics of its endocyclic mononuclear silver(I) complexation both in solid and solution states are discussed. Depending on the reaction conditions with HgI₂, L yields two isomers in which mercury(II) exist inside and outside the macrocyclic cavity. As supported by their relative abundances in functions of reaction time and temperature, the minor exocyclic complex is the kinetically favored product, and the major endocyclic complex is the thermodynamically favored product. The results serve to exemplify the rich and diverse coordination modes documented so far for the formation of conformational isomers incorporating the endocyclic and exocyclic coordination.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.ica.2018.07.012.

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