

Discrete and Continuous Soft Metal Complexes of O₂S₂ and NO₂S₂ Macrocycles with Endo- or Exo-Coordination Mode

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Coordination chemistry of thioxa- and thioxaaza-macrocycles is an intensive area of investigation, and a number of related macrocycles and their soft and heavy metal ion complexes are reported.¹ These macrocycles show the remarkable ability to form stable complexes with *d*-block metal ions, in many cases forcing the metal ion to adopt unusual position. In particular, the versatility of sulfur-containing macrocycles makes them useful for a range of *d*¹⁰-metal complexes as products because the sulfur donor is expected to favor binding toward soft metals such as silver(I), copper(I) and mercury(II) in either exo-² or endocyclic mode. Some complexes with the exocyclic mode have been investigated by us³ and others.⁴ Recently, we have reported the fact that the influence of the ring rigidity of the small thioxa-macrocycles in complexation alters the ligand

behavior and has important consequences for ligand bonding.^{3a} As a part of ongoing efforts, we herein report our investigation of mercury(II) and copper(I) complexes for the medium or larger macrocycles (**L**¹ and **L**²) with sulfur donors and aromatic-subunits simultaneously exhibiting different coordination modes and topologies.

Results and Discussion

Synthesis of Macrocylic Ligands. The bimolecular cyclization of dichloride-dithiol enables the preparation of dithia-macrocycles *via* C-S bond formation.⁵ Thus, **L**¹ was synthesized by coupling reaction between dichloride (**6**) and 1,2-ethanedithiol in the presence of Cs₂CO₃ in moderate yield (20%) (Figure 1). **L**² was prepared with the method reported by us previously.⁶ Compounds **4-6** were prepared using known procedures.⁷ The ¹H and ¹³C NMR spectra together with elemental analyses and mass spectra are clearly in agreement with the proposed structures.

Preparation and Crystal Structure of [Hg(L**¹)Cl₂] (**1**).** Reaction of **L**¹ in dichloromethane and HgCl₂ in methanol afforded a colorless complex precipitate, and single crystals of **1** suitable for X-ray analysis were obtained by vapor diffusion of diethyl ether into an acetonitrile solution of this complex. The FAB mass spectrum of **1** showed a peak at *m/z* 645.2 corresponding to [Hg(**L**¹)Cl]⁺. The single crystal X-

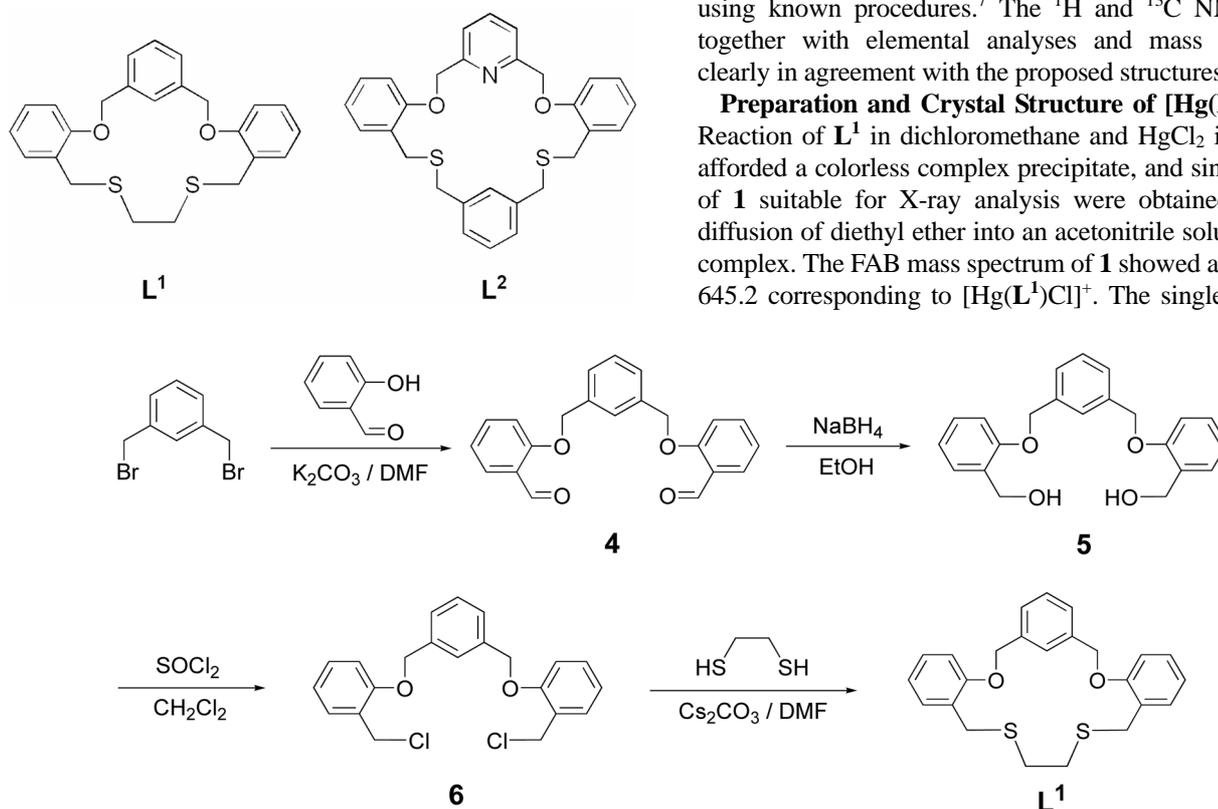


Figure 1. Synthesis of **L**¹.

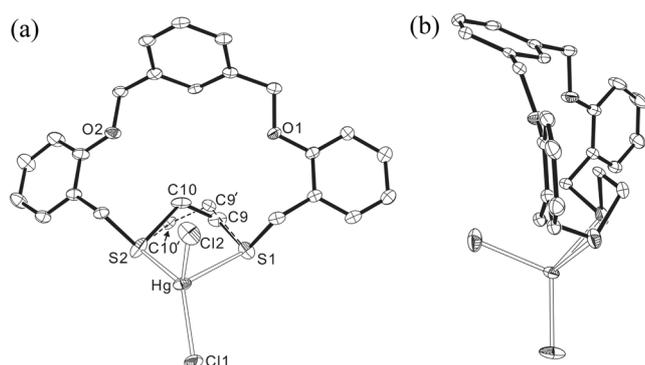


Figure 2. Crystal structure of $[\text{Hg}(\text{L}^1)\text{Cl}_2]$, **1**. (a) front view and (b) side view. Hydrogen atoms are omitted. Selected bond lengths (Å), bond angles ($^\circ$) and torsion angles ($^\circ$): Hg-S1 2.818(1), Hg-S2 2.504(1), Hg-Cl1 2.381(1), Hg-Cl2 2.454(1), S1-Hg-S2 80.3(1), S1-Hg-Cl1 112.2(1), S1-Hg-Cl2 99.9(1), Cl1-Hg-Cl2 114.0(1), S2-Hg-Cl2 109.0(1), S2-Hg-Cl1 131.5(1), S1-C9-C10-S2 -64.9(8), S1-C9'-C10'-S2 73.5(9).

ray analysis⁸ reveals that **1** is an exo-coordinated complex of formula $[\text{Hg}(\text{L}^1)\text{Cl}_2]$ (Figure 2). The Hg atom is outside the macrocyclic cavity in a tetrahedral arrangement coordinated by two S atoms from L^1 in a bent form. Two Cl atoms are occupying the rest of two binding sites. Two ether O atoms are remaining uncoordinated. Typically, Hg(II)-S(thioether) bond lengths are found in the range of 2.5–2.8 Å.⁹ Thus, the Hg-S2 [2.504(1) Å] interaction is consistent with strong coordination to the Hg center, whereas the Hg-S1 bond length [2.818(1) Å] indicates a weaker bond. The Hg-Cl bond lengths [Hg-Cl1 2.381(1) and Hg-Cl2 2.454(1) Å] are comparable with those reported previously for such bonds.⁹ The unusual exo-coordinated complex **1** seems to be obtained because of higher affinity of the Cl atoms toward the Hg atom than that of the ether O donors in the ring cavity. The bond angles around the Hg atom, (S,Cl)-Hg-(S,Cl), vary from 80.3(1) (S1-Hg-S2) to 131.6(1) $^\circ$ (S2-Hg-Cl1). These large deviations are due to formation of the pentagonal ring via Hg-S bonds. The ethylene unit between S1 and S2 is disordered over two positions with occupancies of 0.54 [C9-C10] and 0.46 [C9'-C10'] (dashed-lines).

Preparation and Crystal Structure of $[\{\text{Hg}(\text{L}^2)\text{Cl}_2\}\cdot\text{CH}_3\text{OH}]_n$ (2**).** The reaction of L^2 with HgCl_2 in dichloro-

methane and methanol afforded colorless crystals of **2** that were of X-ray quality. Unlike the case of **1**, complex **2** features a polymeric arrangement. It is clear from the X-ray structure⁸ that **2** crystallizes to yield an interesting single-stranded 1-D coordination framework consisting of L^2 and HgCl_2 with $-\text{L}^2\text{-Hg-L}^2\text{-Hg-}$ pattern. Thus, the asymmetric unit contains one mercury atom, two chloride atoms, and one macrocycle. The Hg atom which links two macrocycles via Hg-S bonds shows distorted tetrahedral coordination composed of two S donor atoms from two L^2 and two Cl atoms. Bond lengths for Hg-S [Hg-S1 2.581(3), Hg-S2A 2.549(3) Å] and Hg-Cl [Hg-Cl1 2.448(3), Hg-Cl2 2.437(3) Å] are within the normal literature range for these bond types.⁹ The pyridine ring is vertically tilted to the ring cavity, and there is no indication that the pyridine nitrogen atom is involved in bonding. The bond angles around the Hg atom vary from 100.6(1) (S1-Hg-Cl2) to 121.9(1) $^\circ$ (S1-Hg-S2A). These deviations from the ideal tetrahedral geometry are due to the repulsive interaction between two adjacent macrocycles linked *via* Hg-S bonds. In complex **2**, the sulfur-to-sulfur distance in the macrocycle [7.232(4) Å] is much far from that of complex **1** [3.439(2) Å] because of the insertion of one benzo-unit between two sulfur donors. Consequently, the longer sulfur-to-sulfur distance in the macrocycle induces the bridging type $-\text{L}^2\text{-Hg-L}^2\text{-Hg-}$ chain to produce the polymeric scaffold.

Preparation and Crystal Structure of $[\text{Cu}(\text{L}^2)\text{Br}]$ (3**).** CuBr in acetonitrile was layered above a dichloromethane solution of L^2 and on standing afforded pale yellow crystalline product **3** suitable for X-ray analysis.⁸ The FAB mass spectrum of complex **3** showed a peak at m/z 548.1 corresponding to $[\text{CuL}^2]^+$. Unlike above two complexes, complex **3** was revealed as an endo-type 1:1 complex. The copper ion in the cavity is bound to one S (S2) and one N atom from one macrocyclic ring that exhibits a bent arrangement; the S1 atom is not bound [$\text{Cu}\cdots\text{S1}$ 5.574(1) Å]. One bromide ion completes the third coordination shell. Accordingly, the copper center is three-coordinate and the overall coordination geometry around the copper ion can be considered as a distorted trigonal plane. The deviation of the angles [from 113.4(1) $^\circ$ S2-Cu-Br to 129.6(1) $^\circ$ N-Cu-Br] from the ideal trigonal planar geometry may reflect the presence of addi-

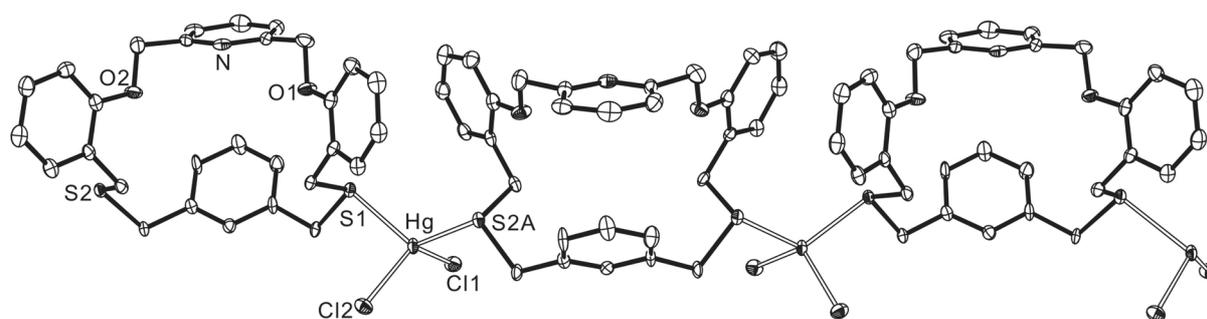


Figure 3. Crystal structure of $[\{\text{Hg}(\text{L}^2)\text{Cl}_2\}\cdot\text{CH}_3\text{OH}]_n$, **2**. Hydrogen atoms and solvent molecules are omitted. Selected bond lengths (Å) and bond angles ($^\circ$): Hg-S1 2.581(3), Hg-S2A 2.549(3), Hg-Cl1 2.448(3), Hg-Cl2 2.437(3), S1-Hg-S2A 121.9(1), S1-Hg-Cl2 100.6(1), S2A-Hg-Cl1 105.2(1), Cl1-Hg-Cl2 119.4(1), S1-Hg-Cl1 101.7(1), Cl2-Hg-S2A 109.0(1). Symmetry codes A: $x+1/2$, $-y+3/2$, $z-1/2$.

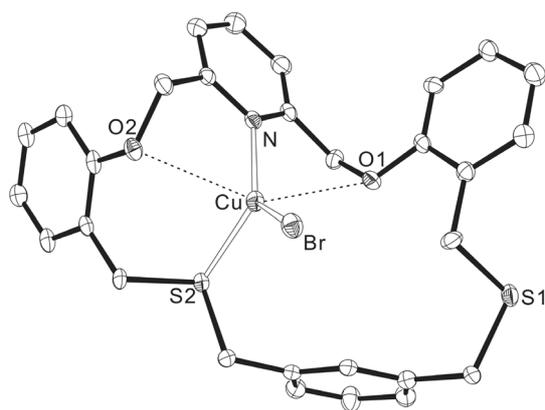


Figure 4. Crystal structure of $[\text{Cu}(\text{L}^2)\text{Br}]$, **3**. Hydrogen atoms are omitted. Selected bond lengths (Å), bond angles ($^\circ$), torsion angles ($^\circ$) and interatomic distances (Å): Cu-N 1.999(3), Cu-S2 2.298(1), Cu-Br 2.348(1), N-Cu-S2 115.9(1), N-Cu-Br 129.6(1), S2-Cu-Br 113.4(1), O1-C1-C29-N -44.6(4), O2-C25-C24-N 55.5(3), Cu...O1 2.850(2), Cu...O2 2.716(2).

tional interactions between copper and O-donors of the rings (dotted lines), which are slightly shorter than the sum of Cu and O van der Waals radii (2.90 \AA)¹⁰ [Cu...O1 2.850(2) and Cu...O2 2.716(2) Å].

In summary, two macrocycles L^1 (17-membered with O_2S_2 donors) and L^2 (20-membered with NO_2S_2 donors) were employed and their complexes with different types of coordination modes and topologies were presented. The tendency to adopt these respective arrangements shows the possibility that metal coordination modes and/or topologies can be controlled by tuning the inter-donor distances in larger thia-macrocycles as well as the smaller ones.

Experimental Section

Materials. Dichloride **6** (1.00 g, 2.58 mmol) and Cs_2CO_3 (2.50 g, 7.67 mmol) were dissolved in DMF (100 mL) in a 500 mL round-bottom flask. Under nitrogen atmosphere a solution of 1,2-ethanedithiol (0.29 g, 3.08 mmol) in DMF (30 mL) was added dropwise at the constant rate to the DMF solution of dichloride **6** and Cs_2CO_3 for 6 h at 70–75 $^\circ\text{C}$. The mixture was kept for a further 24 h. After cooling to room temperature, the reaction mixture was filtered and the solvent was evaporated. Water (100 mL) was added, and the mixture was extracted with CH_2Cl_2 . The column chromatography on silica gel (25% ethyl acetate/*n*-hexane) gave L^1 as colorless solid. Yield: 20%. Mp. 145–147 $^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3): δ 6.93–7.92 (m, 12 H, Ar), 5.08 (s, 4 H, ArCH_2O), 3.83 (s, 4 H, ArCH_2S), 2.71 (s, 4 H, SCH_2CH_2), $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 156.4, 137.7, 130.9, 128.4, 128.3, 127.4, 127.2, 127.1, 121.3, 111.9, 70.4, 31.7, 30.1. IR (KBr, cm^{-1}): 3030, 2920, 1595, 1495, 1450, 1240, 1144, 1030, 752. Found: C, 70.80; H, 6.10%. Calc for $\text{C}_{24}\text{H}_{24}\text{O}_2\text{S}_2$: C, 70.55; H, 5.92%. EI-MS: m/z 408 ($[\text{M}]^+$).

Preparation of $[\text{Hg}(\text{L}^1)\text{Cl}_2]$, **1.** Equimolar amount of HgCl_2 in methanol was added to the solution of L^1 in dichloromethane. The colorless precipitates were formed after

1h and filtered off. The single crystals of suitable for X-ray analysis were obtained by slow evaporation of its solution in acetonitrile. Mp. 210–212 $^\circ\text{C}$ (decomp). IR (KBr disc, cm^{-1}) 3063, 2922, 2365, 1595, 1493, 1452, 1244, 1161, 1047, 1009, 752. Found: C, 42.63; H, 3.75%. Calc for $\text{C}_{24}\text{H}_{24}\text{O}_2\text{Cl}_2\text{HgS}_2$: C, 42.39; H, 3.56%. FAB-MS: m/z 645.2 ($[\text{Hg}(\text{L}^1)\text{Cl}]^+$).

Preparation of $[\text{Hg}(\text{L}^2)\text{Cl}_2][\text{CH}_3\text{OH}]_n$, **2.** Equimolar amount of HgCl_2 in methanol was added to the solution of L^2 in dichloromethane. The reaction mixture was stirred for 30 min. The single crystals suitable for X-ray analysis were obtained by slow evaporation of the reaction mixture. Mp. 268–270 $^\circ\text{C}$ (decomp). IR (KBr disc, cm^{-1}) 3022, 2924, 2353, 1599, 1493, 1250, 1018, 750. Found: C, 46.21; H, 3.80; N, 2.04%. Calc for $\text{C}_{29}\text{H}_{27}\text{N}_2\text{O}_5\text{S}_2\text{HgCl}_2$: C, 46.00; H, 3.59; N, 1.85%.

Preparation of $[\text{Cu}(\text{L}^2)\text{Br}]$, **3.** Equimolar amount of CuBr in acetonitrile was layered above a dichloromethane solution of L^2 and on standing afforded pale yellow crystalline product **3** suitable for X-ray analysis. Mp. 180–182 $^\circ\text{C}$ (decomp). IR (KBr disc, cm^{-1}) 3038, 2924, 2363, 1601, 1491, 1221, 1101, 754. Found: C, 55.45; H, 4.55; N, 2.30%. Calc for $\text{C}_{29}\text{H}_{27}\text{N}_2\text{O}_5\text{S}_2\text{CuBr}$: C, 55.37; H, 4.33; N, 2.23%. MS-FAB: m/z 548.1 ($[\text{CuL}^2]^+$).

Supplementary materials. CCDC 662725, 662726 and 662727 contain the supplementary crystallographic data, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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8. A crystal was mounted on a Bruker SMART diffractometer equipped with a graphite monochromated Mo K α ($\lambda = 0.71073$ Å) radiation source and a CCD detector. The frame data were processed to give structure factors using the program SAINT. The intensity data were corrected for Lorentz and polarization effects. Empirical absorption corrections were also applied for complexes using the program SADABS. The structure was solved by direct method and refined by full matrix least squares against F^2 for all data using SHELXTL software. All non-H atoms were refined with anisotropic displacement parameters. Crystal data for **1**: C₂₄H₂₄Cl₂HgO₂S₂, $M = 680.04$, Monoclinic, $a = 11.0144(4)$ Å, $b = 7.8393(3)$ Å, $c = 28.2461(11)$ Å, $\beta = 98.608(1)^\circ$, $V = 2411.44(16)$ Å³, $T = 173(2)$ K, space group $P2_1/n$, $Z = 4$, $\nu(\text{Mo K}\alpha) = 6.797$ mm⁻¹, 14500 reflections measured, 5468 unique ($R_{\text{int}} = 0.0580$) which were used in all calculations. Refinement converged as a final $R = 0.0366$ ($wR_2 = 0.0923$) for 5468 independent reflections [$I > 2\sigma(I)$]. Crystal data for **2**: C₃₀H₃₁Cl₂HgNO₃S₂, $M = 789.17$, Monoclinic, $a = 14.429(2)$ Å, $b = 14.182(2)$ Å, $c = 15.115(2)$ Å, $\beta = 97.350(3)^\circ$, $V = 3067.7(8)$ Å³, $T = 173(2)$ K, space group $P2_1/n$, $Z = 4$, $\nu(\text{Mo K}\alpha) = 5.359$ mm⁻¹, 17778 reflections measured, 6616 unique ($R_{\text{int}} = 0.0471$) which were used in all calculations. Refinement converged as a final $R = 0.0813$ ($wR_2 = 0.2230$) for 6616 independent reflections [$I > 2\sigma(I)$]. Crystal data for **3**: C₂₉H₂₇BrCuNO₂S₂, $M = 629.09$, Monoclinic, $a = 12.8796(14)$ Å, $b = 9.9634(11)$ Å, $c = 21.521(2)$ Å, $\beta = 102.098(2)^\circ$, $V = 2700.4(5)$ Å³, $T = 173(2)$ K, space group $P2_1/n$, $Z = 4$, $\nu(\text{Mo K}\alpha) = 2.471$ mm⁻¹, 16166 reflections measured, 5883 unique ($R_{\text{int}} = 0.0405$) which were used in all calculations. Refinement converged as a final $R = 0.0370$ ($wR_2 = 0.0727$) for 5883 independent reflections [$I > 2\sigma(I)$].
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