

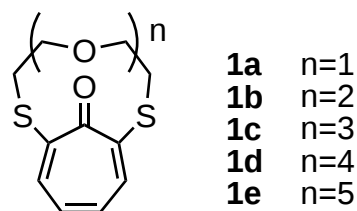
**CRYSTAL STRUCTURES OF MERCURY(II) DICHLORIDE
COMPLEXES OF 5,8-DIOXA-2,11-DITHIABICYCLO[10.4.1]-
HEPTADECA-1(16),12,14-TRIEN-17-ONE AND 5,8,11-TRIOXA-
2,14-DITHIABICYCLO[13.4.1]ICOSA-1(19),15,17-TRIEN-20-
ONE**

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Abstract—5,8-Dioxa-2,11-dithiabicyclo[10.4.1]heptadeca-1(16),12,14-trien-17-one (**1b**) and 5,8,11-trioxa-2,14-dithiabicyclo[13.4.1]icosa-1(19),15,17-trien-20-one (**1c**) formed **1b**-2HgCl₂ and **1c**-2.5HgCl₂-H₂O complex with HgCl₂ and H₂O, respectively. The Hg(II) ions were coordinated to both the tropone carbonyl group and the thioether sulfur atom to form a side-on complex.

Recently, we have been interested in synthesizing dithio-crown ethers having a tropone pendant (**1**), since these molecules are excellent carriers of Hg(II) ion through a liquid membrane.^{1,2} The order of Hg(II) transport rate of **1** was **1d** > **1e** > **1b** > **1a** > **1c**.² The efficiency of transport of Hg(II) with **1** was dependent on the size of the cavity of the crown ethers. This was confirmed by the X-Ray diffraction studies of the HgCl₂ complexes of **1a**³ and **1d**;⁴ there are two kinds of coordination modes, in which one is a side-on complex and another is a normal penetrated complex. In the shortest homologue (**1a**) whose crown ring is not large enough to provide a cavity to include Hg(II) ion, its X-Ray structural analysis showed that the Hg(II) ion is coordinated with both the tropone carbonyl group and the thioether sulfur atom to form a side-on complex. While the most effective mercurophile was **1d**, having four ethereal heteroatoms with the fitted cavity size, the X-Ray diffraction study of its HgCl₂ complex showed that the Hg(II) ion is at the center of dithiocrown ring to form a normal penetrated complex. Here, we report the structures of HgCl₂ complexes of **1b** and **1c** investigated by X-Ray crystallographic analyses.



The single crystals of **1b**-2HgCl₂⁵ and **1c**-2.5HgCl₂-H₂O⁶ were obtained by recrystallization of mixtures of a large amount of HgCl₂ and **1** in CH₃CN. The molecular structure of **1b**-Hg(3)Cl₂-0.5Hg(2)Cl₂-0.5Hg(1)Cl₂ is shown in Figure 1.

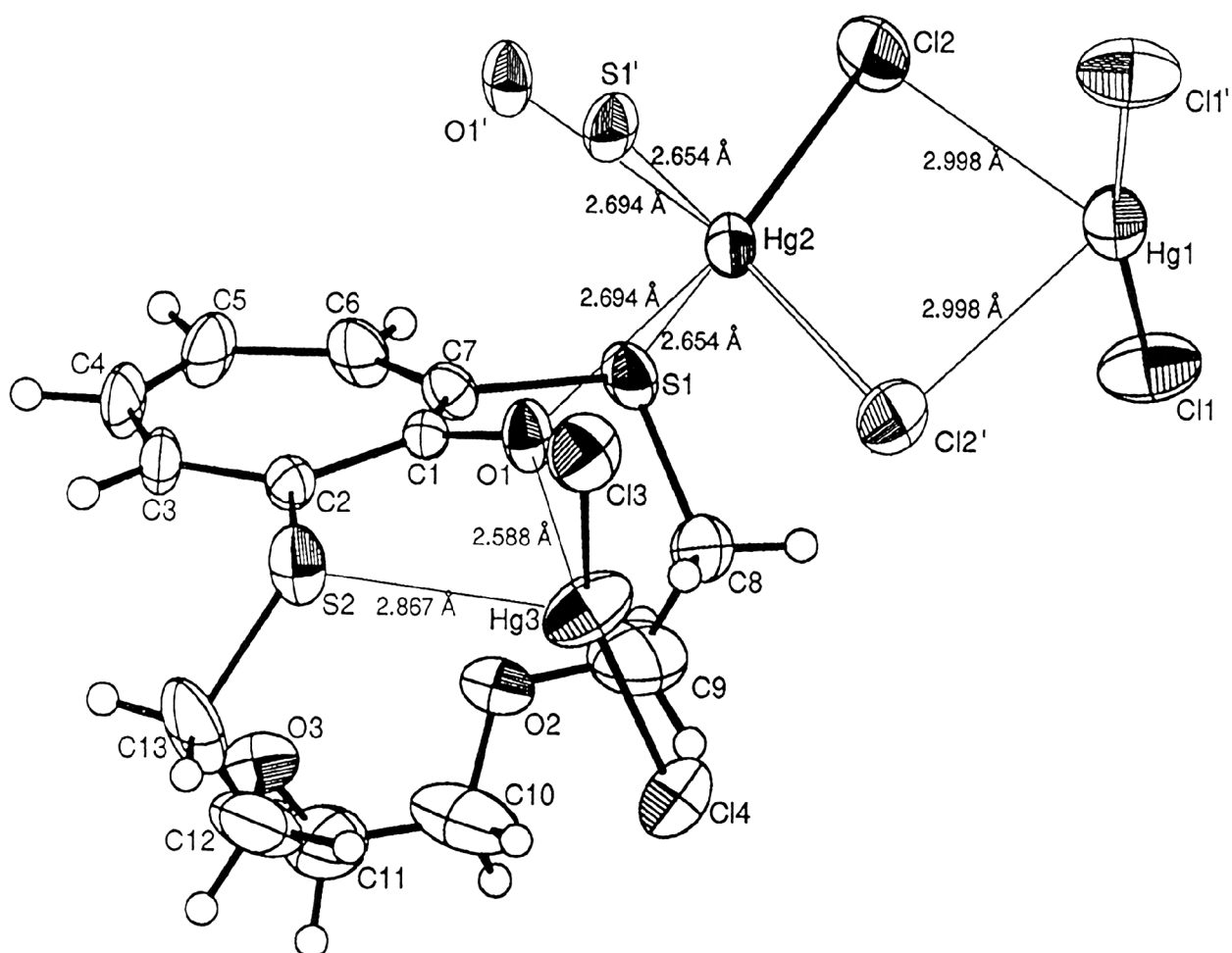


Figure 1. An ORTEP drawing of **1b**-2HgCl₂ with thermal ellipsoids to enclose 50% probability.

The oxygen atoms of the ethereal moiety are intact on the formation of the Hg complex in the crystal state. The Hg(3) was coordinated by S(2), O(1), Cl(3), and Cl(4) in a distorted tetrahedral coordination. The Hg(2) was coordinated by each one of the sulfur and oxygen atoms of intermolecular tropone part, Cl(2) and Cl(2') in an octahedral coordination. The Hg(1) was coordinated by Cl(1), Cl(1'), Cl(2), and Cl(2') in a distorted tetrahedral coordination.

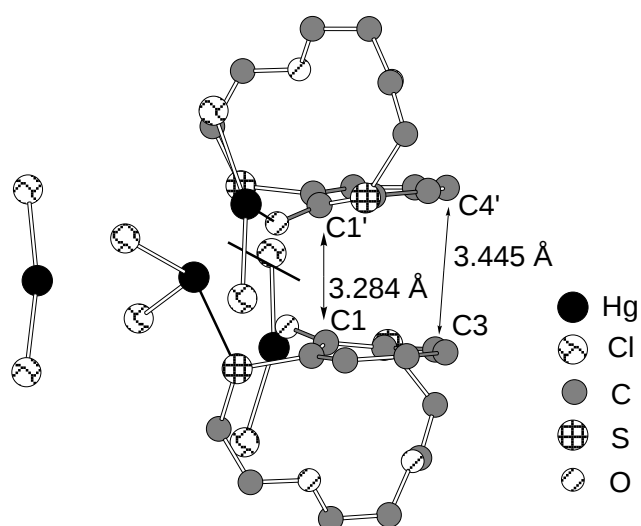


Figure 2. A segment of the molecular packing of **1b**-2HgCl₂.

Interestingly, it is clear from Figure 2 that the distances between two tropone rings are 3.28-3.45 Å (C(1)-C(1'): 3.284, C(3)-C(4'): 3.445 Å) which are shorter than that (3.53 Å)⁸ between two pyrenes of pyrene crystal. These distances are within the range associated with p-p interactions (3.3-3.8 Å)⁷.

An ORTEP view of **1c**-Hg(3)Cl₂-Hg(2)Cl₂-0.5Hg(1)Cl₂-H₂O is illustrated in Figure 3. Any Hg(II) atom in the complexation was not in the cavity of the crown system; they were in the side-on positions. The Hg(3) was coordinated by O(3), O(4), Cl(4), and Cl(5) to form a tetrahedral coordination, and the Hg(2) was coordinated by Cl(2), Cl(3), S(2), and O(1) of the tropone moiety and O(5) of H₂O to form a distorted trigonal bipyramidal coordination. The Hg(1) was coordinated by Cl(1), Cl(1'), each one of the sulfur and ethereal oxygen atoms on two tropone moieties to form an octahedral coordination.

The conformations of the ethereal moiety in the complex were: S(g)C(g)C(t)O(t)C(g)C(g)O(t)C(g)C(t)O(g)C(g)C(g)S, where *t* and *g* denote trans and gauche forms, respectively.

Interestingly, the planarity of the seven-membered ring of **1c**-2.5HgCl₂-H₂O is better than those of **1a**, **1a**-2HgCl₂, **1b**-2HgCl₂, **1c**, **1c**-2.5HgCl₂-H₂O, and **1d**-HgCl₂. The magnitude of the angle of intersection between the least-squares plane defined by C(1), C(2), and C(7) and the plane defined by C(2), C(3), C(6), and C(7) is **1a** (33.8°)³ > **1a**-2HgCl₂ (29.5°)³ > **1c** (20.7°) > **1d**-HgCl₂ (20.4°)⁴ > **1b**-2HgCl₂ (14.7°) > **1c**-2.5HgCl₂-H₂O (7.5°). This means that the complexation with Hg(II) and the large etheral ring reduced the planarity of seven-membered ring of **1c**.

Consequently, in complexation of troponoid dithiocrown derivatives having a smaller cavity size than **1d** with Hg(II) chloride, the Hg (II) ions were not in the cavity of crown system and coordinated with the tropone carbonyl and the thioether sulfur atoms (side-on complex).

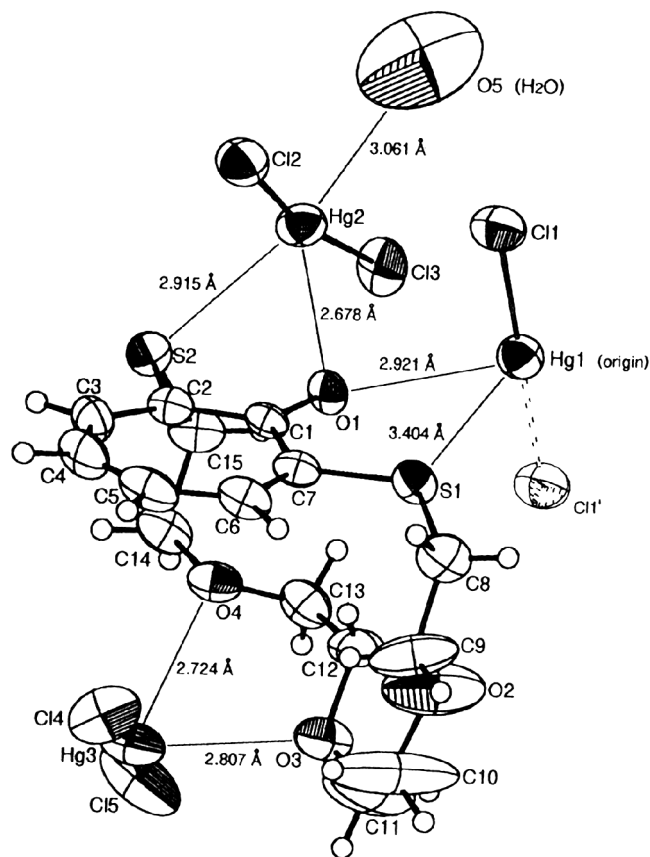


Figure 3. An ORTEP drawing of **1c**-2.5HgCl₂-H₂O with thermal ellipsoids to enclose 50% probability.

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 5. Crystal data of **1b**-HgCl₂-0.5HgCl₂-0.5HgCl₂, mp 195-197 °C (in a sealed tube), C₁₃H₁₆O₃Cl₄Hg₂S₂ (M=827.39), monoclinic, *A2/n*, *a*=20.481 (2), *b*=14.172 (2), *c*=14.550 (1) Å, *b*=107.93 (1)°, *V*=4018.1 (7) Å³, *Z*=4, *D_x*=2.74 gcm⁻³, *wR*=0.096, *R*=0.081. The structure was solved by direct method (*SIR88*)⁹ and difference Fourier syntheses. All calculations were performed on a MicroVAX 3100 computer using *MolEN*.¹⁰
 6. Crystal data of **1c**-HgCl₂-HgCl₂-0.5HgCl₂-H₂O), mp <155 °C (in a sealed tube), C₁₅H₂₂O₅Cl₅Hg_{2.5}S₂ (M=1025.21), triclinic, *P1*, *a*=10.662 (1), *b*=11.700 (2), *c*=10.404 (2) Å, *a*=102.03 (1)°, *b*=94.63 (1)°, *g*=84.83 (1)°, *V*=1261.7 (3) Å³, *Z*=2 and *D_x*=2.70 gcm⁻³, *wR*=0.062, *R*=0.048.
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