HETEROCYCLES, Vol. 53, No. 3, 2000, pp. 535 - 538, Received, 10th November, 1999

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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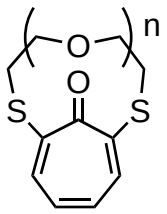
Abstract—5,8-Dioxa-2,11-dithiabicyclo[10.4.1]heptadeca-1(16),12,14-trien-17-one (**1b**) and 5,8,11-trioxa-2,14-dithiabicyclo[13.4.1]icosa-1(19),15,17-trien-20-one (**1c**) formed **1b**-2$HgCl_2$ and **1c**-2.5$HgCl_2$-H_2O complex with $HgCl_2$ and H_2O, respectively. The Hg(II) ions were coordinated 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 troponoid 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 $HgCl_2$ 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 $HgCl_2$ 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 $HgCl_2$ complexes of **1b** and **1c** investigated by X-Ray crystallographic analyses.



1a n=1
1b n=2
1c n=3
1d n=4
1e n=5

The single crystals of **1b**-2$HgCl_2$[5] and **1c**-2.5$HgCl_2$-H_2O[6] were obtained by recrystallization of mixtures of a large amount of $HgCl_2$ and **1** in CH_3CN. The molecular structure of **1b**-Hg(3)Cl_2-0.5Hg(2)Cl_2-0.5Hg(1)Cl_2 is shown in Figure 1.

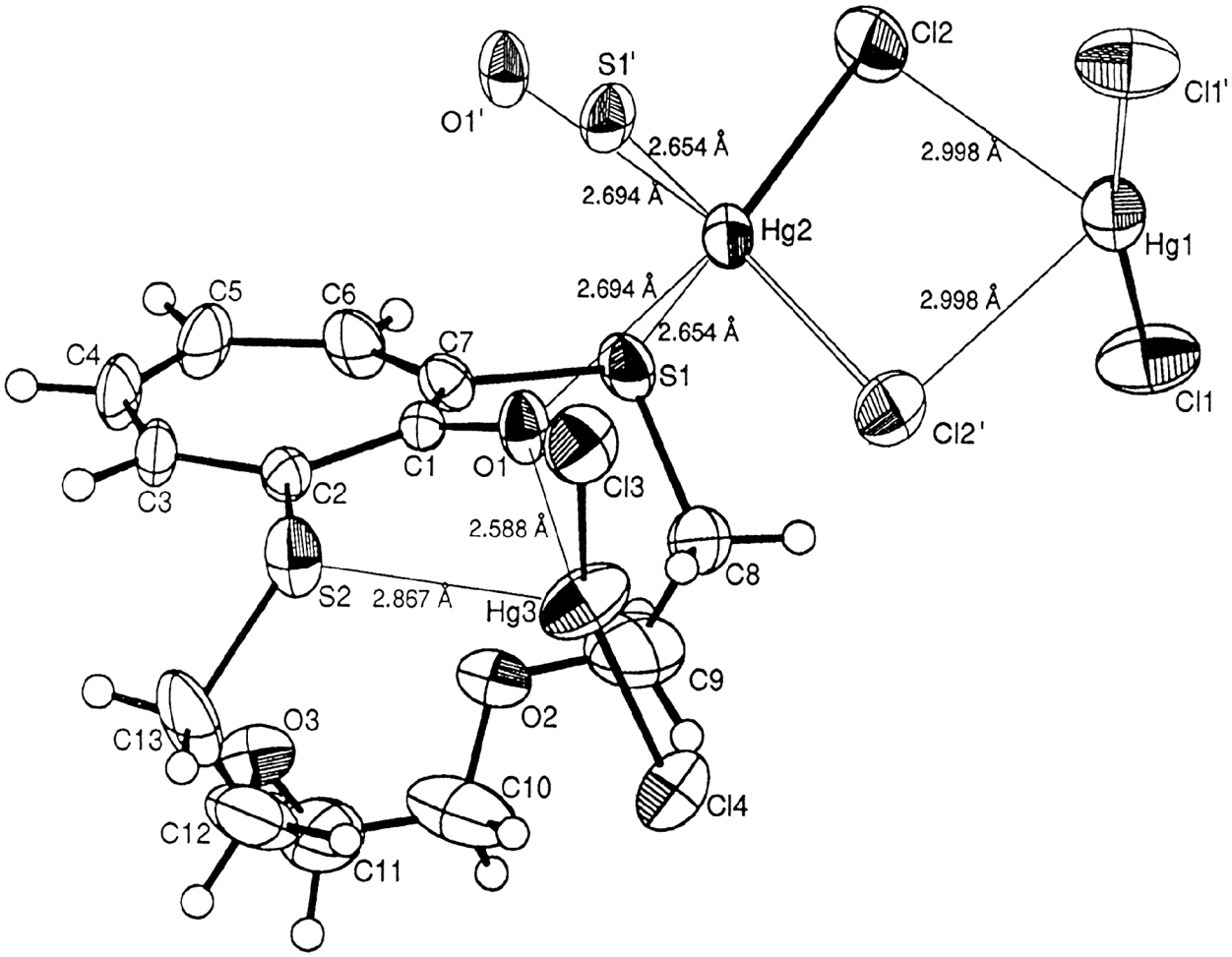


Figure 1. An ORTEP drawing of **1b**-2$HgCl_2$ with thermal ellipsoids to enclose 50% probability.

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.

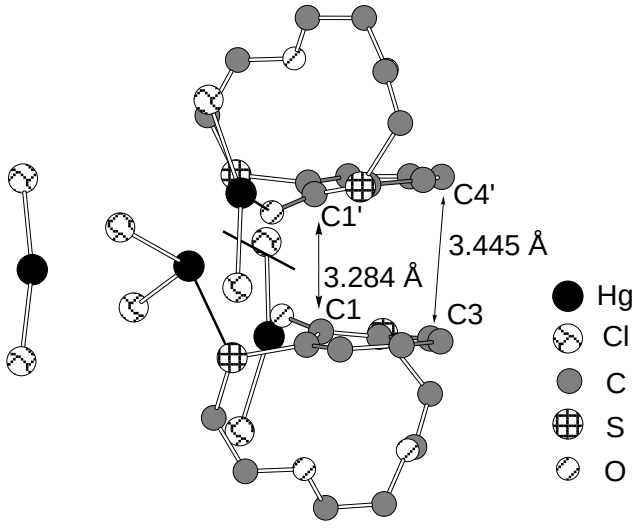


Figure 2. A segment of the molecular packing of **1b**-2$HgCl_2$.

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 π-π interactions (3.3-3.8 Å)[7].

An ORTEP view of **1c**-Hg(3)Cl_2-Hg(2)Cl_2-0.5Hg(1)Cl_2-H_2O 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 H_2O 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.

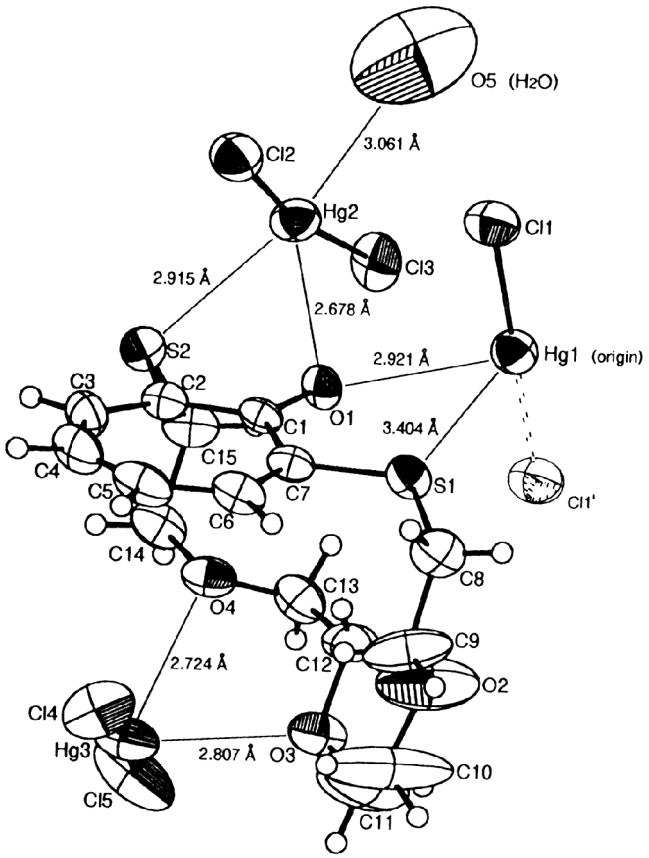


Figure 3. An ORTEP drawing of **1c**-2.5$HgCl_2$-H_2O with thermal ellipsoids to enclose 50% probability.

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**-2.5$HgCl_2$-H_2O is better than those of **1a**, **1a**-2$HgCl_2$, **1b**-2$HgCl_2$, **1c**, **1c**-2.5$HgCl_2$-H_2O, and **1d**-$HgCl_2$. 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**-2$HgCl_2$ (29.5°)[3] > **1c** (20.7°) > **1d**-$HgCl_2$ (20.4°)[4] > **1b**-2$HgCl_2$ (14.7°) > **1c**-2.5$HgCl_2$-H_2O (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 conplextaion 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).

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5. Crystal data of **1b**-$HgCl_2$-0.5$HgCl_2$-0.5$HgCl_2$, mp 195-197 ℃ (in a sealed tube), $C_{13}H_{16}O_3Cl_4Hg_2S_2$ (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) $Å^3$, *Z*=4, *Dx*=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**-$HgCl_2$-$HgCl_2$-0.5$HgCl_2$-H_2O), mp <155 ℃ (in a sealed tube), $C_{15}H_{22}O_5Cl_5Hg_{2.5}S_2$ (M=1025.21), triclinic, *P*1, *a*=10.662 (1), *b*=11.700 (2), *c*=10.404 (2) Å, α=102.03 (1)°, β=94.63 (1)°, γ=84.83 (1)°, *V*=1261.7 (3) $Å^3$, *Z*=2 and *Dx*=2.70 gcm^{-3}, *wR*=0.062, *R*=0.048.
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