

PREPARATION AND X-RAY CRYSTAL STRUCTURE OF A UNIQUE 2:1-COMPLEX OF MERCURY(II) CHLORIDE AND 5-OXA-2,8-DITHIA-BICYCLO[7.4.1]TETRADECA-9,11,13-TRIEN-14-ONE, A TROPONOID DITHIO-CROWN ETHER†

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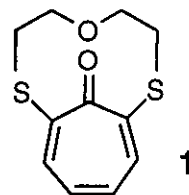
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Abstract—5-Oxa-2,8-dithiabicyclo[7.4.1]tetradeca-9,11,13-trien-14-one formed a unique 1:2 complex with HgCl₂, in which each HgCl₂ molecule coordinates to a sulfur atom and the carbonyl group to form a pseudo C_s structure while the free crown ether forms a spiral crystal packing.

It has been known that cyclic thioethers are superior ligands for the complexation of heavy and soft ions.^{1,2} Recently, we have reported the synthesis and the complexation of mercuriphilic dithio-crown ethers with 2,4,6-cycloheptatrien-1-one (tropone)³ and heptafulvene⁴ chromophores, in which the carbonyl or dicyanomethylene groups played an important role on the selective complexation and transport of Hg(II) ion. The efficiency of transport of Hg(II) ion was dependent on the size of the cavity of the crown ethers.

Interestingly, 5-oxa-2,8-dithiabicyclo[7.4.1]tetradeca-9,11,13-trien-14-one (**1**),^{3a} a troponoid dithio-crown ether, with a smaller hydrophobic cavity than the diameter of Hg(II) ion was also effective in extracting and transporting Hg(II) ion. In this paper, we report the preparation and the crystal structure of the complex between **1** and HgCl₂.

When an aqueous solution of HgCl₂ and a CHCl₃ solution of **1** were mixed, an initial complex with stoichiometry of (HgCl₂)_{0.3-0.4}·**1** was obtained. By repeated recrystallizations of the initial complex



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†Dedicated to Professor Koji Nakanishi on the occasion of his 75th birthday.

from CHCl_3 , a single crystal was obtained. The single crystal structure is representative in Figure 1, which shows that the complex has stoichiometry of $(\text{HgCl}_2)_2 \cdot \mathbf{1}$.⁵

The crown ether part of the complex is in a chair conformation as like as cyclodecane and the tropone moiety is not planar. The carbonyl group is out of the plane defined by C(2), C(3), C(6), and C(7) carbons as much as $28(1)^\circ$. Two HgCl_2 molecules are incorporated between the carbonyl group and a sulfur atom, respectively. The Hg atoms of the complex $(\text{HgCl}_2)_2 \cdot \mathbf{1}$ are four-coordinate. The shape of the complex is near to a C_s symmetrical structure.

The angles of Cl(1)-Hg(1)-Cl(2) and Cl(3)-Hg(2)-Cl(4) of the complex $(\text{HgCl}_2)_2 \cdot \mathbf{1}$ are $168.9(1)$ and $168.2(1)^\circ$. They are bent as much as *ca.* 10° from the reported angle of HgCl_2 , $178.9(5)^\circ$.⁶ The average length (2.317 Å) of the Hg-Cl bonds of the complex is longer than that of 2.291(9) Å of HgCl_2 ⁶ and similar to the value of $[(\text{HgCl}_2)_3(\text{DMSO})_2]$.⁷ The angles and the bond lengths of the complex are different from the Cl-Hg-Cl angle (110.6°) and the Hg-Cl bond length (2.427(6) Å) of a distorted tetrahedral geometry of $[\text{Hg}(\text{C}_{12}\text{H}_{24}\text{O}_4\text{S}_2)\text{Cl}_2]\text{HgCl}_2$.^{1a} The lengths of S(1)-Hg(1) and S(2)-Hg(2) of the complex $(\text{HgCl}_2)_2 \cdot \mathbf{1}$ are 2.899(3) and 2.976(3) Å, respectively. They are about 0.4 Å longer than the Hg-S bond length of a tetrahedrally coordinated Hg(II) atom⁸ and about 0.2 Å longer than the Hg-S lengths of $\text{HgI}_2(\text{C}_{10}\text{H}_{20}\text{S}_4)$ ^{1b} and $(\text{HgBr}_2)_2(\text{C}_{12}\text{H}_{24}\text{S}_6)$.^{1c} The angles of S(1)-Hg(1)-O(1) and S(2)-Hg(2)-O(1) are $63.8(2)$ and $62.8(2)^\circ$, which are similar to the O-Hg-O bond angles of the HgCl_2 complex of 1,4,7,10-tetraoxa-13,16-dithiacyclooctadec-14-en-14,15-dicarbonitrile.^{1g} The Hg(1)-O(1) and Hg(2)-O(1) bond lengths are 2.719(8) and 2.720(7) Å, which are shorter than the mean distance of the Hg-O bond length of $\text{HgCl}_2(\text{dibenzo-18-crown-6})$.⁹

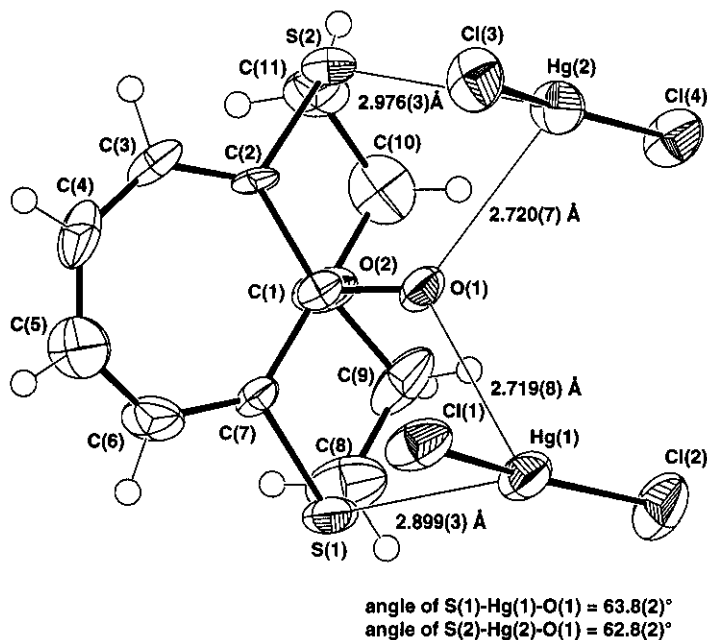


Figure 1. ORTEP Drawing of $(\text{HgCl}_2)_2 \cdot \mathbf{1}$ with thermal ellipsoids to enclose 50% probability.

Hydrogen atoms are shown as spheres with their arbitrary radii of 0.15 Å.

The X-Ray structure of **1**^{10,11} in Figure 2 shows that the seven-membered ring is not planar and the carbonyl group derived from the plane defined by C(2), C(3), C(6), and C(7) carbons as much as 34.6(7)°, which is larger than that of the complex (HgCl₂)₂·**1**. Since the carbonyl group donates electrons to the mercury atom, a tropylium ion contributes to increase the planarity of the seven-membered ring of the complex. The crown ether part of **1** is twisted and the dihedral angles of C(6)-C(7)-S(1)-C(8) and C(3)-C(2)-S(2)-C(11) are observed to be 91.1(7) and 145.0(7)°, respectively. The crystal packing of **1** reveals that eight sets of two independent molecules are present in a unit cell to form a spiral crystal packing.

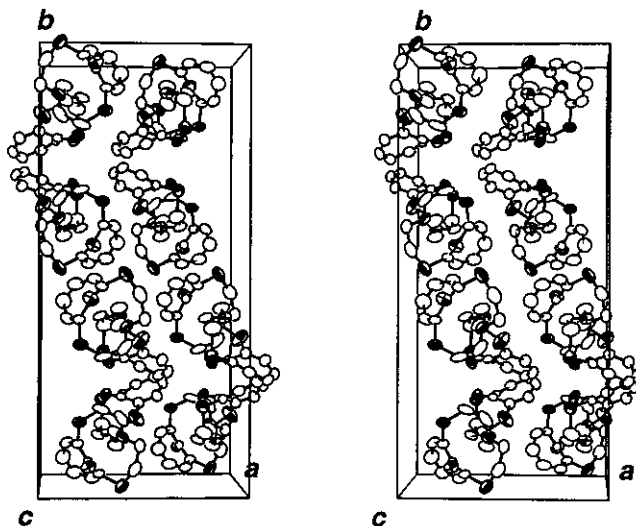


Figure 2. ORTEP Drawing of **1** with thermal ellipsoids to enclose 50% probability. Packing diagram viewed down the *c* axis. Hydrogens are omitted for clarity.

Thus, the HgCl₂ molecule is surrounded by the carbonyl and a sulfur atom in the crystal. This complexation could make transport of Hg(II) possible in solutions.

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