FORMATION OF A DIMERIC COMPLEX OF 14-DICYANOMETHYLENE-5,8,21,24-TETRAOXA-2,11,18,27-TETRATHIATRICYCLO-[26.4.1.1^{12,17}]TETRATRIACONTA-12,15,17(34),28,30,32-HEXAEN-33-ONE WITH MERCURY(II) CHLORIDE

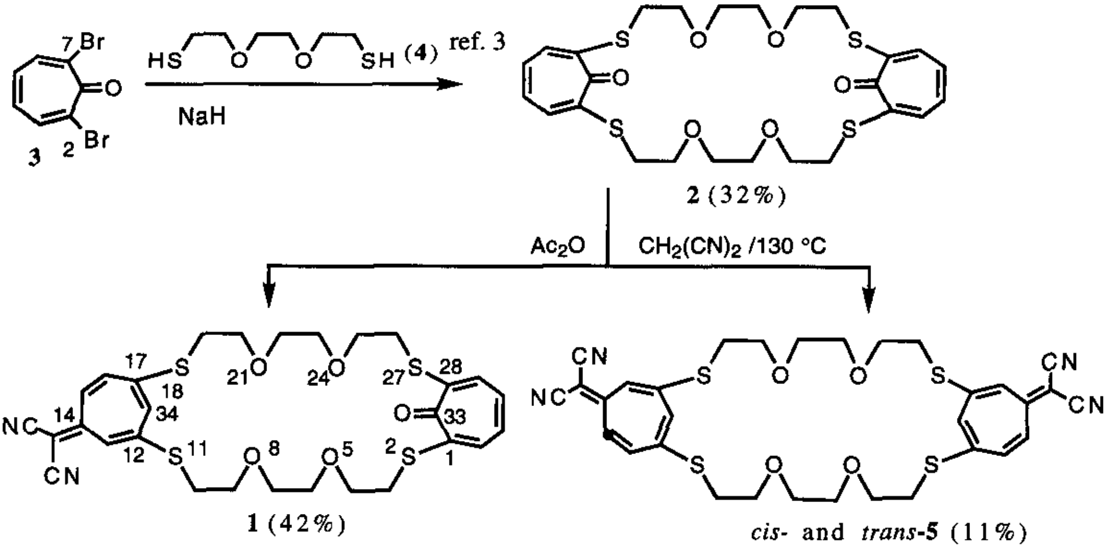
Nobuo Kato, Kanji Kubo,† Akira Mori, and Hitoshi Takeshita*

Institute of Advanced Material Study, 86, Kyushu University, Kasuga-koen,
Kasuga, Fukuoka, 816, Japan
†Graduate School of Engineering Sciences, 39, Kyushu University, Kasuga-koen,
Kasuga, Fukuoka, 816, Japan

Abstract—14-Dicyanomethylene-5,8,21,24-tetraoxa-2,11,18,27-tetrathiatricyclo-[26.4.1.1^{12,17}]tetratriaconta-12,15,17(34),28,30,32-hexaen-33-one, a thiocrown ether, having a large cavity for complexation, formed a 1:2-complex with $HgCl_2$. The X-ray structural analysis revealed that two aromatic rings were almost planar and, of the eight heteroatoms of the ethereal ring, each set of the consecutive two oxygen atoms and one sulfur atom on the tropone ring coordinated to one Hg^{2+} ion, but two sulfur atoms on the heptafulvene part were free from the coordination. The interatomic distance of two Hg^{2+} was 4.248 Å.

Currently, we have been interested in the pronounced mercurophilic properties of dithio-crown ethers incorporated into troponoid frameworks.[1,2] Particularly, the exclusive transportation of Hg^{2+} ion by means of a U-type cell with a water-$CHCl_3$ system was remarkable. Since the transportation is facilitated by liberation of Hg^{2+} ions by Coulomb repulsion against the protonated non-alternant conjugated systems, it is worth investigating the complex formation with crown ethers having both tropone and dicyanoheptafulvene rings in order to evaluate a role of seven-membered units to transport Hg^{2+} ion. Herein described is the preferential complexation of thioether sulfurs on the tropone unit over those on the heptafulvene unit on the basis of the X-ray evidence for a 1:2 complex with Hg^{2+}.

A thiocrown ether carrying two non-alternant aromatic systems, 23-dicyanomethylene-5,8,21,24-tetraoxa-2,11,18,27-tetrathiatricyclo[26.4.1.$1^{12,17}$]tetratriaconta-12,15,17(34),28,30,32-hexaen-33-one (**1**), was prepared by heating an Ac_2O solution of malononitrile and 5,8,21,24-tetraoxa-2,11,18,27-tetrathiatricyclo-[26.4.1.$1^{12,17}$]tetratriaconta-12,15,17,28,30,32-hexaene-33,34-dione (**2**), which is a 2:2-condensate obtained from 2,7-dibromotropone (**3**) and ethylene glycol bis(2-mercaptoethyl) ether (**4**),[3] *via* a remote substitution reaction in 42% yield together with two *cis*- and *trans*-disubstituted products (**5a** and **5b**).[4] The remote substitution is rather common in this heptafulvene synthesis.[3]



Four sulfur atoms of this tetraoxatetrathia-crown derivative(**1**)are in the structurally similar positions and expected to be nearly equivalent as the sites for complexation; therefore, determination of the structure of the complex formed should provide an information on the mercurophilic properties of two seven-membered aromatic systems. Thus, the complex of **1** with $HgCl_2$ was prepared and its single crystals were obtained after intensive recrystallizations from acetonitrile as dark red prisms, mp 206-208 °C. The composition revealed it to be a 1:2-complex, and the X-ray diffraction analysis was carried out.[5]

The ORTEP diagram at the final stage, R=0.043 and Rw=0.052, showed that the two molecules of $HgCl_2$ were included in the large crown ethereal cavity (Figure 1); two Hg^{2+} were hemi-circularly surrounded respectively by three heteroatoms within the cavity, and there might be a mutual interaction between two Hg^{2+} units.

Each Hg^{2+} retains two chloride ion intact; and each one of them made a bridge with another Hg^{2+} in a parallel square geometry.

The interatomic distance of two Hg^{2+} was 4.248 Å; previously, the figure, 3.93 Å, was recorded for a similar guest Hg_2Cl_4 unit complexed to hexaethylene glycol diethyl ether.[6] Of the heteroatoms, all of the four ethereal oxygens are coordinated to Hg^{2+}, but sulfurs are not; only those on the tropone ring are coordinated. In addition, two *anti*-oriented aromatic rings were nearly perpendicular to the large crown ring, and the both seven-membered rings were almost planar.

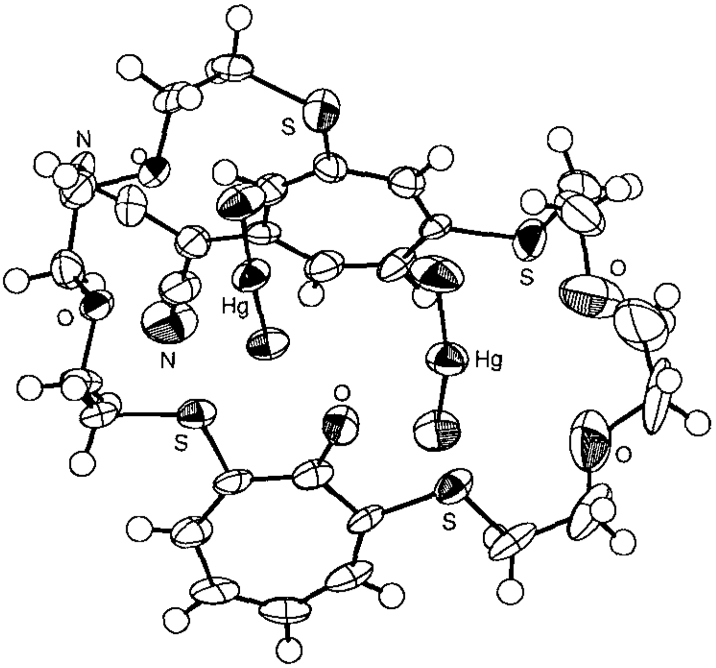


Figure 1. The ORTEP diagram of 2($HgCl_2$) complex of **1**.

Figure 2 indicates short contacts with less than 3.5 Å; two Hg^{2+} were surrounded hemi-circularly by each coordinating heteroatoms, one sulfur and two ethereal oxygens, together with three of four chlorines, form a dimeric hexagonal bipyramidal structure. This was different from the monomeric Hg^{2+} complexes generally observed in the troponoid dithiocrown derivatives, i.e., pentagonal bipyramidal one.[7]

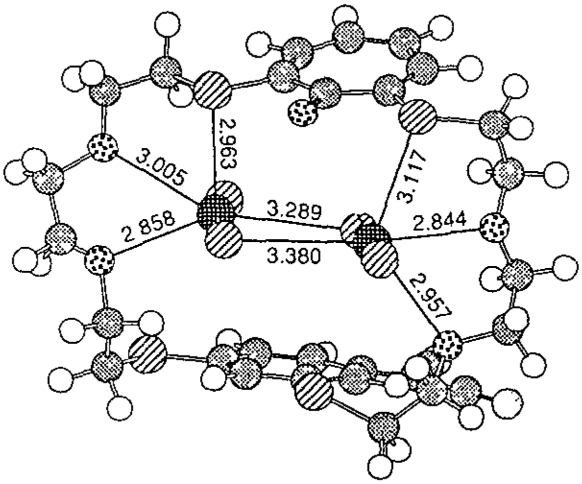


Figure 2. Interatomic distances of coordinating heteroatoms and Hg^{2+} in the complex.

To our knowledge, this is the first case that two Hg^{2+} salts are penetrated in a single cavity.

Previously, we ourselves have already observed a 1:2-complex formation with a troponoid thiocrown ether, 5-oxa-2,8-dithiabicyclo[7.4.1]tetradeca-1(12),9,11-trien-14-one (**6**), but it is a the side-on type.

As has been already described,[3] $HgCl_2$ was transported quite efficiently by means of a U-type cell with **1**. It was selective with Hg^{2+}, and the coexisted Cu^{2+} salt did not interfere the transportation. This is particularly interesting since the large flexible cavity of **1** could take suitable conformations for other metals. No involvement of sulfur atoms attached on the heptafulvene for complexation should suggest that the 6π-polarization is stronger in the dicyanoheptafulvene system than the tropone system.

References

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5. Monoclinic crystal of $2(HgCl_2)$-complex of **1**, $C_{29}H_{32}N_2O_4S_4 \cdot 2HgCl_2$ (M.W.= 933.96), belong to a space group of $Pna2_1$ with cell dimensions, a=17.101(2) Å, b=12.158(2) Å, c=17.678(1) Å, β= 112.66(1)°, and V=3675(1) Å^3 with d=2.10 g/cm^3 and Z=4. Data collection was performed with Cu $K\alpha$ radiation on an Enraf-Nonius FR590 computer controlled equipment. Structure was solved by direct method direct method (Multan, 11/82, P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. DeClercq, andM. M. Woolfson, 1982) and differential Fourier syntheses. Using the 2839 reflections having intensities greater than 3.0 times their standard deviation, for 415 variable parameters, the structure was refined in full-matrix least squares. Hydrogen atoms were located at calculated positions and were included in the refinement with fixed isotope thermal factors (5.0 Å^2), bur restrained to ride on the atom to which they are bonded.
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