MERCUROPHILIC PROPERTY OF 23-DICYANOMETHYLENE-5,8,11,14,17-PENTAOXA-2,20-DITHIABICYCLO[19.4.1]-HEXACOSA-1(26),21,24-TRIENE

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Abstract—23-Dicyanomethylene-5,8,11,14,17-pentaoxa-2,20-dithiabicyclo-[19.4.1]hexacosa-1(26),21,24-triene (**1**) showed selective transport of mercury(II) ion through a liquid membrane. The effective transport of mercury(II) ions was likely to correspond to association constants. Both the association constant and the transport rate of **1** were greater than the troponoid dithiocrown ether, 5,8,11,14-tetraoxa-2,17-dithiabicyclo[16.4.1]tricosa-18,20,22-trien-23-one (**2**). In the crystal structure of the mercury(II) chloride complex of **1**, the mercury(II) atom was surrounded by only the five oxygen donor atoms in a pentagonal bipyramidal coordination. The sulfur atoms of **1** are far from the coordination to the mercury(II) ion.

The development of selective ion recognition systems has been of much concern because of a solution to environmental pollution.[1-3] Macrocyclic ligands are of great interest both because they are able to impose unusual coordination numbers and geometries on metal ions[2] and because they serve as models for metal ion transport through a membrane.[3] Bacon[4] has reported transport of heavy metal ions such as Hg^{2+} and Pb^{2+} through a liquid membrane. Izatt[5] and Gokel[6] have elucidated that the metal ion transport rates by the 18-crown-6 and azacrown ethers in a chloroform membrane bulk correlated with both the association constants and the picrate extraction constants.

The metallophilic properties of crown ethers having sulfur and oxygen atoms differ from crown ethers or thiocrowns. As a mercury(II) chloride complex of thiocrown derivatives, Dalley and Larson[7] reported a mercury(II) chloride complex of dithio-18-crown-6, $[HgCl_2C_{12}H_{24}O_4S_2]\cdot HgCl_2$, in which only two sulfur atoms of the crown ether coordinate to one of the mercury atoms, forming a distorted tetrahedral geometry and the other $HgCl_2$ unit is free from coordination of the crown ether. Hoffman *et al.*[8] reported the mercury(II) chloride complex of 1,4,7,10-tetraoxa-13,16-dithiacyclooctadec-14-ene-14,15-dicarbonitrile, in which the Hg(II) atom was surrounded by six donor atoms (four oxygen and two sulfur atoms) in a hexagonal bipyramidal coordination with long Hg-S distances.

While the structure of 8,8-dicyanoheptafulvene was elucidated by Shimanouchi *et al.*,[9] the exocyclic double bond of 8,8-dicyanoheptafulvene has single bond character (1.422 Å). We also reported the structures and the effect of 1,4-dithiine ring on the crystal structure of 5- and 7-dicyanomethylene-1,2-ethylenedithiocycloheptatriene.[10] The planarity of the latter was fairly good. However, the former was not planar because of the steric repulsion between the 1,4-dithiine ring and the dicyanomethylene group.

Recently, we have synthesized some remarkably efficient mercurophilic dithiocrown ether derivatives to which the tropone[11] and heptafulvene[12] systems are incorporated. Their carbonyl or dicyanomethylene groups played an important role on the selective complexation and transport of the mercury(II) ion. The efficiency of transport of mercury(II) ion was dependent on the size of the cavity of the crown ethers. In the mercury(II) chloride complex of troponoid dithiocrown ethers, each $HgCl_2$ molecule of the [$(HgCl_2)_2$(5-oxa-2,8-dithiabicyclo[7.4.1]tetradeca-9,11,13-trien-14-one)] complex coordinates to a sulfur atom and the carbonyl group to form a pseudo *Cs* structure.[13]

Interestingly, 23-dicyanomethylene-5,8,11,14,17-pentaoxa-2,20-dithiabicyclo[19.4.1]hexacosa-1(26),21,24-triene (**1**) showed the most effective extraction and excellent transport of the mercury(II) ion over the all other dithiocrown derivatives.[12] In this paper, we describe the association constant, selective transport of mercury(II) chloride through a liquid membrane, and the molecular structure of the mercury(II) complex of **1**.

^{1}H NMR Titration and Determination of Association Constants (K). Binding interaction of the crown ether and mercury(II) ion was examined using NMR spectrometry. ^{1}H-NMR spectral changes are shown in Figure 1, where a $Hg(SCN)_2$ solution is successively added to an CD_3CN solution.

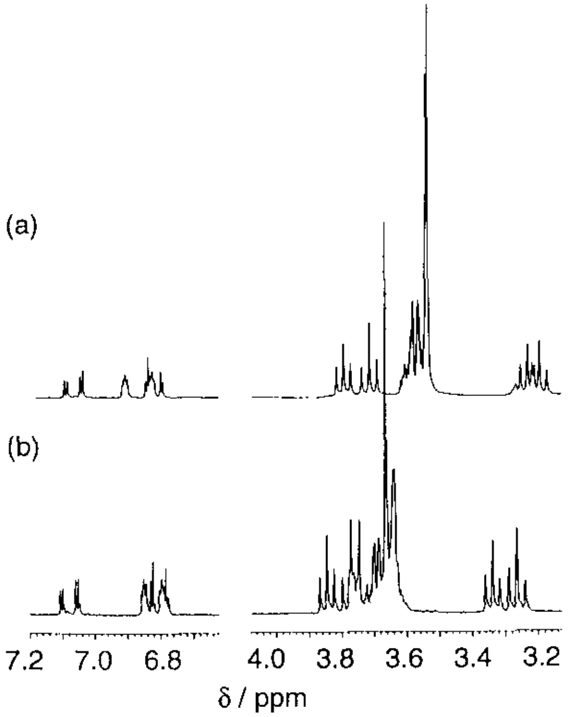
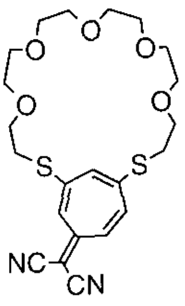
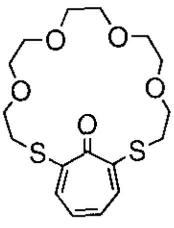


Figure 1. ^{1}H NMR spectral changes of **1** (1.66×10^{-3} M) with $Hg(SCN)_2$ in CD_3CN. Concentration of $Hg(SCN)_2$: (a) 0 and (b) 1.03×10^{-1} M.



1



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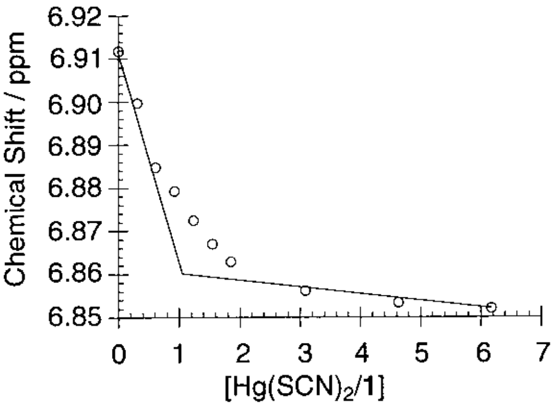

Figure 2. Determination of molar composition of **1**·$Hg(SCN)_2$. [Concentration of **1**; 1.67 x 10^{-3} M, $Hg(SCN)_2$; 0–1.03 x 10^{-1} M].

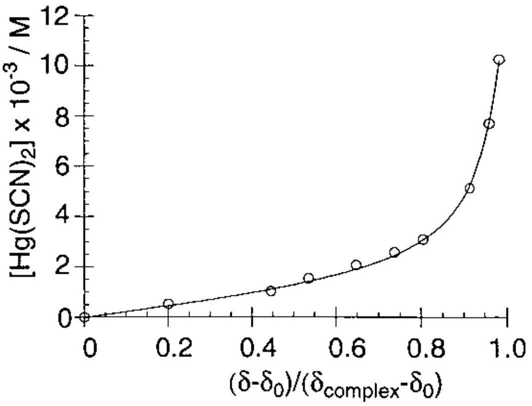

Figure 3. ^{1}H NMR titration curve of **1** for $Hg(SCN)_2$. [Concentration of **1**; 1.67 x 10^{-3} M, $Hg(SCN)_2$; 0–1.03 x 10^{-1} M].

The resonance peaks shifted gradually downfield or upfield as $Hg(SCN)_2$ is added. This indicates that the exchange process between a free host and its complex is rapid when compared with the NMR time scale. This result suggests that **1** has an observable binding ability with Hg^{2+}. The stoichiometry of the complex was determined as **1**·$Hg(SCN)_2$ by the molar ratio method (Figure 2). On the other hand, association constants were determined by the non-linear curve fitting method[14] from the chemical shift change of ^{1}H-NMR (CD_3CN) spectra with the mercury(II) thiocyanate titration at 298 K. Figure 3 shows the curve-fitting plot by ^{1}H NMR titration of $Hg(SCN)_2$. The association constant (1910 M^{-1}) of **1** was larger than that (1090 M^{-1}) of 5,8,11,14-tetraoxa-2,7-dithiabicyclo[16.4.1]tricosa-1(22),18,20-trien-23-one (**2**).[11]

Transport Experiments. Transport experiments of **1** and **2**,[11] which were carried out under the same conditions, are shown in Figure 4. Compared in the transport rates, **1** was larger than **2**.[11] This result was consistent with the observation of the association constant as shown in Table 1.

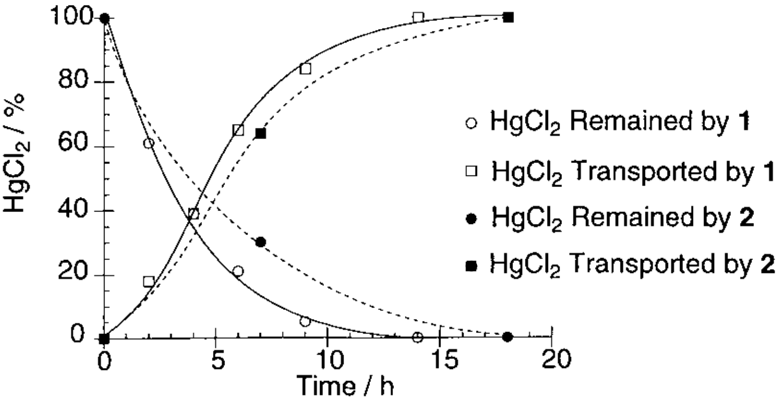

Figure 4. Transport of $HgCl_2$ (5.0 x 10^{-5} M) with **1** and **2** using 2 M HCl.

The following conclusion can be drawn from this experiment: Mercury(II) ion is transported more effectively by **1**. The association constant (1910 M^{-1}) of **1** for the mercury(II) thiocyanate was larger than those (1090 and 516 M^{-1}) of other dithiocrown ethers (**2** and 1,3-benzo-19-dithiocrown-6 ether).[12] This result is parallel to the results of the transport.

Table 1. Transport rates and association constants (K) of **1** and **2**

	K (M^{-1})	Transport Rate (μM / hr)
1	1910	5.42
2	1090	4.83

X-Ray Crystallographic Analysis. A single crystal of the $HgCl_2$ complex of **1** was obtained by prolonged standing to remove off the solvent from an equimolar mixture of mercury(II) chloride and **1** in CH_3CN. The color of the complex obtained was dark red. Figure 5 shows the stereoscopic view of the unit cell and the packing diagram of **1**·$HgCl_2$.

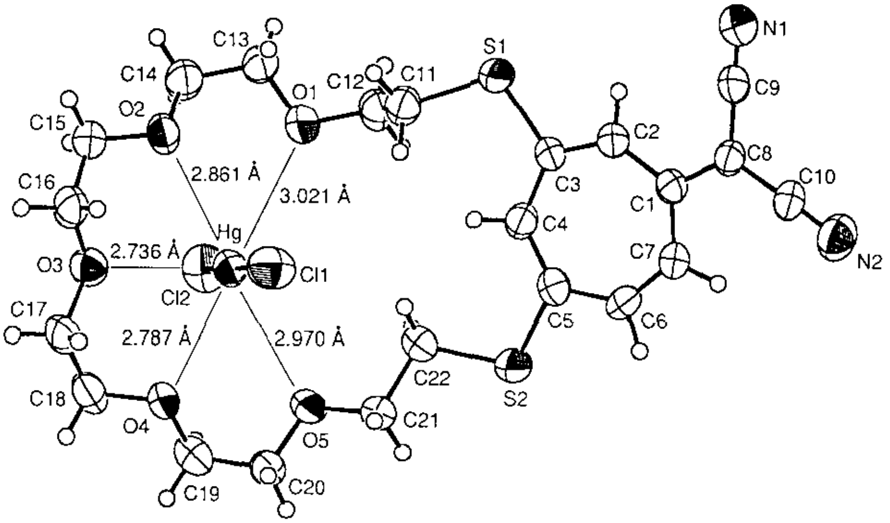

Figure 5a. ORTEP Drawing of **1**·$HgCl_2$ with thermal ellipsoids scaled to enclose 50% probability.

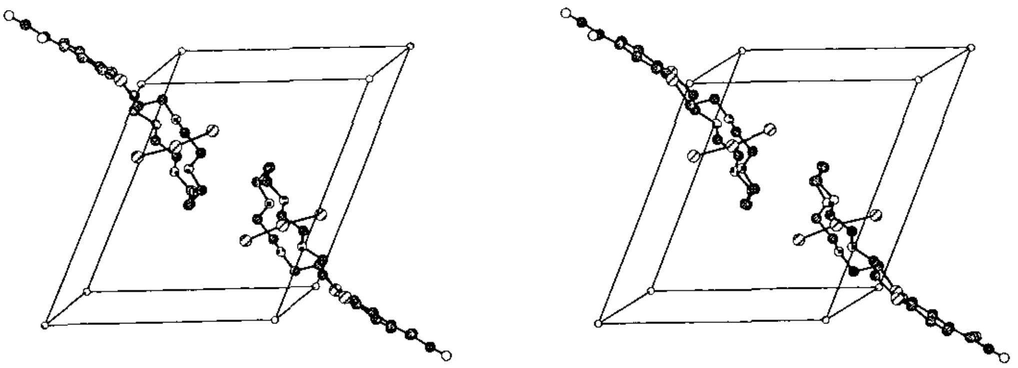

Figure 5b. Packing diagram of **1**·$HgCl_2$ viewed down the *c* axis.

The ORTEP drawing (Figure 5a) at the final stage of R=0.074 and wR=0.094 showed that the five oxygen atoms are endodentate, whereas the two sulfur atoms have the exo orientation. The Hg(II) atom was surrounded by the five donor oxygen atoms in a pentagonal bipyramidal coordination. The dicyanomethylene group is outside the crown ether ring.

Table 2. Selected bond lengths (Å) and angles (°) for the heptafulvene moiety of **1**·$HgCl_2$

N1—C9	1.14(2)	C4—C5—C6	127(1)
N2—C10	1.18(1)	C5—C6—C7	131(1)
C1—C2	1.42(1)	C1—C7—C6	130(1)
C1—C7	1.43(2)	C2—C1—C7	124(1)
C1—C8	1.39(2)	C9—C8—C10	114(1)
C2—C3	1.36(2)	C1—C2—C3	131(1)
C3—C4	1.44(2)	C2—C3—C4	129.4(9)
C4—C5	1.37(1)	C3—C4—C5	127(1)
C5—C6	1.41(1)		
C6—C7	1.36(2)		
C8—C9	1.42(2)		
C8—C10	1.42(1)		

Table 2 shows that the length of the exocyclic bond of **1**·$HgCl_2$ is between the typical C-C and C=C bonds, which indicates the contribution of the cycloheptatrienylium ion. The value (1.39(2) Å) is similar to those (1.389(3) and 1.392(5) Å) for 5- and 7-dicyanomethylene-1,2-ethylenedithiocycloheptatriene.[11]

The crown ether part of the complex is in the following conformation: S(t)C(t)C(t)O(t)C(g)C(t) O(t)C(g)C(t)O(t)C(g)C(t)O(t)C(g)C(t)O(t)C(t)C(t)S, where t and g indicate *trans* and gauche forms, respectively. All the CH_2-O and CH_2-S bonds are in *trans* conformation.

Table 3 shows the bond distances and angles of the $HgCl_2$. The bond angle of Cl-Hg-Cl of the complex **1**·$HgCl_2$ is 171.9°, which is smaller by *ca.* 7° than the reported angle of $HgCl_2$, 178.9°. The average bond length (2.295 Å) of Hg-Cl bond is similar to that of 2.291(9) Å of $HgCl_2$.[15]

Table 3. Interatomic distances (Å) and angles (°) of **1**·$HgCl_2$

Hg—Cl1	2.288(5)	Cl1—Hg—Cl2	171.9(1)
Hg—Cl2	2.301(5)	O1—Hg—O2	57.2
Hg—O1	3.021	O2—Hg—O3	61.0
Hg—O2	2.861	O3—Hg—O4	62.0
Hg—O3	2.736	O4—Hg—O5	58.9
Hg—O4	2.787		
Hg—O5	2.970		
Hg—S1	6.242		
Hg—S2	5.600		

The Hg-O bond distances are 2.736-3.021 Å. The coordination of the Hg(II) atom of the complex is similar to that of the mercury(II) chloride complexes of open chain polyethers such as tetraethylene glycol dimethyl ether[16] and 1,15-bis(2-bromophenyl)-2,5,8,11,14-pentaoxapentadecane.[17] The Hg-O bond distances are 2.78-2.96 Å *in the former complex and* 2.718-3.059 Å in the latter. The Hg-O bond distances of **1**·$HgCl_2$ are shorter than those of $HgCl_2$(18-crown-6)[18] and $HgCl_2$(dibenzo-18-crown-6).[19]

Interestingly, the distances between Hg and S of **1**·$HgCl_2$ are 5.600 and 6.242 Å, which are far longer than those of the mercury(II) chloride complex of 1,4,7,10-tetraoxa-13,16-dithiacyclooctadec-14-ene-14,15-dicarbonitrile.[8]

The crystal structure of **1**·$HgCl_2$ would suggest that the affinity of the sulfur atoms towards the mercury(II) ion was reduced by electron-withdrawing effect of the 8,8-dicyanoheptafulvene ring. As the result, the decreased electron density of the sulfur atoms allowed the sulfur atoms to take the exodentate conformation to become reluctant and only the ethereal oxygens interacted.

EXPERIMENTAL

Melting points were obtained with a Yanagimoto Micro Melting Point Apparatus and are uncorrected. NMR spectra were measured on a JEOL GSX 270H Model spectrometer in CD$_3$CN; the chemical shifts are expressed by an δ unit using tetramethylsilane as an internal standard. UV spectra were measured using a Hitachi Model U-3200 and U-3410 spectrophotometers.

^{1}H NMR Titration and Determination of Association Constants (K)

The ^{1}H NMR titrations were conducted by adding a crown ether solution (1.67 x 10^{-3} M) for **1** in CD$_3$CN a progressive concentration of excess metal salt, using a 0.25 cm^3 syringe, to a cuvette containing 1 cm^3 of the crown ether solution (1.67 x 10^{-3} M in CD$_3$CN). The solutions were kept for 30 min. The spectrum was recorded after each addition. The added equivalents of the cation were then plotted against the chemical shift change, as shown Figure 2. The association constants (K) were calculated by the non-linear curve-fitting method.[14]

Transport Experiments of Metal Ions by Means of a U-Type Cell

The apparatus is the same as one used in the previous study.[11,12] The solutions of metal ions in water (10 cm^3, Aq I) and 2 M-HCl (10 cm^3, Aq II) were connected with the CHCl$_3$ layer (10 cm^3) containing crown ether and the latter was stirred with a magnetic bar. Occasionally, aliquots of Aq I and Aq II were taken for the UV spectrophotometry measurement.

X-Ray Crystallographic Analysis of the Complex

A dark red crystal of HgCl$_2$·C$_{22}$H$_{28}$N$_2$O$_5$S$_2$ having approximate dimensions of 0.20 x 0.18 x 0.08 mm was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Cu *Kα* radiation (λ = 1.54184 Å) on an Enraf-Nonius FR590 computer-controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochrometer. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $18 < \theta < 42°$, measured by the computer controlled diagonal slit method of centering. There were no systematic absences and the space group was determined to be $P\bar{1}$. The data were collected at a temperature of 23 ℃ using the ω-2θ scan technique. A total of 4893 reflections were collected, of which 4536 were unique. A spherical absorption correction was applied and the radius of the crystal was estimated to be 0.09 mm (μr = 1.3). The structure was solved by direct method (*SIR88*)[20] and difference Fourier syntheses.

Table 4. Crystallographic data of **1**·HgCl$_2$

mp 193–195 °C
C$_{22}$H$_{28}$O$_5$N$_2$S$_2$·HgCl$_2$
M_r = 736.10
Triclinic
$P\bar{1}$
a = 12.874(1) Å
b = 14.649(2) Å
c = 8.081(1) Å
α=101.56(1)°
β = 107.27(1)°
γ= 67.45(1)°
V = 1337.6(3) Å^3
Z = 2
D_x = 1.83 Mg m^{-3}
R = 0.079
wR = 0.094

Using the 3940 reflections having intensities greater than 3.0 times their standard deviation, the structure was refined in full-matrix least-squares for 308 variable parameters. Hydrogen atoms were located at the calculated positions and included in the refinement with fixed isotropic thermal factors (5.0 Å), but restrained to ride on the atom to which they are bonded. Atomic scattering factors were taken from International Tables for X-Ray Crystallography.

The highest peak in the final difference Fourier had a height of 4.82 e/Å^3 which was located near to the Hg atom and the minimum negative peak had a height of -0.45 e/Å^3. All calculations were performed on a MicroVAX 3100 computer using *MolEN.*[21]

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