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Formation and Structures of Mercury Complexes of 18-Membered Unsaturated and Saturated Thiacrown Ethers

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The complexation of 18-membered unsaturated thiacrown ether, 18-UT-6, with 1 equiv of $HgCl_2$ in acetone afforded mercury complex Hg^{II}(18-UT-6)Cl_2. The complexations of 18-membered saturated thiacrown ether, 18S6, with 1 equiv each of $HgCl_2$ and $CdCl_2$ in acetone afforded Hg^{II}(18S6)Cl_2 and Cd^{II}(18S6)Cl_2, respectively. The crystal structure of Hg^{II}(18-UT-6)Cl_2 revealed that the mercury atom was inside the cavity of the macrocycle and the geometry around the mercury atom was an eight-coordinate hexagonal bipyramidal arrangement. ORTEP drawing of Hg^{II}(18S6)Cl_2 revealed the existence of the mercury atom outside the cavity of the ring, as well as a polymeric chain structure. ^{1}H NMR study of Hg^{II}(18-UT-6)Cl_2 in acetone-d_6 indicated that the interconversion between free 18-UT-6 and pure complex was slower than the NMR time scale. The titration experiment by ^{1}H NMR revealed that 18-UT-6 had inclusion selectivity for the number of mercury atoms. The electrochemical behavior of complexes Hg^{II}(18-UT-6)Cl_2 and Hg^{II}(18S6)Cl_2 was also examined.

Introduction

Recently, much attention has been given to the chemistry of thiacrown ethers.[1,2] Thiacrown ethers are known to coordinate with “soft” transition metals[1,3] and are of interest as possible metal-delivering agents.[1,4] We have recently reported the synthesis of unsaturated thiacrown ethers with cis geometry across the carbon−carbon double bonds[5] and the complexation of 15-, 18-, and 21-membered unsaturated thiacrown ethers [15-UT-5 (**1**), 18-UT-6 (**2**), and 21-UT-7 (**3**)] with CF_3COOAg.[6] As a result, it was found that the unsaturated thiacrown ether had higher selectivity for the inclusion number of silver atoms than the corresponding saturated system. The introduction of the “soft” sulfur atom into 18-crown-6 is known to enhance its binding strength to mercury over silver.[7] Sevdić and co-workers reported that the complexations of 18-membered saturated thiacrown ether, 1,4,7,10,13,16-hexathiacyclooctadecane (18S6), with 1 and 2 equiv of $HgCl_2$ afforded 1:1 and 1:2 macrocycle/metal complexes, respectively.[8] This phenomenon of forming complexes, of which the macrocycle/metal ratio depends on the amount of $HgCl_2$ added, may be due to the flexible structure of 18S6. On the other hand, unsaturated thiacrown ethers are expected to exhibit high selectivity for the inclusion number of mercury atoms in their complexation since they are more conformationally restricted than the corresponding saturated compounds. In this paper, we report the complexations of unsaturated and saturated thiacrown ethers with group XII metals

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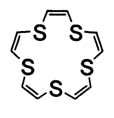
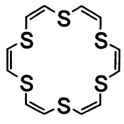
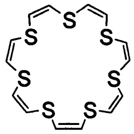
and the crystal structures of the mercury complexes of **2** and 18S6. Differences between **2** and 18S6 in terms of their complexation behavior with $HgCl_2$ were also clarified.



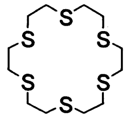
1: 15-UT-5



2: 18-UT-6



3: 21-UT-7

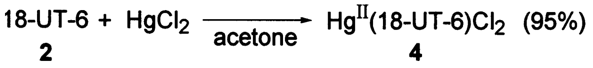


18S6

Results and Discussion

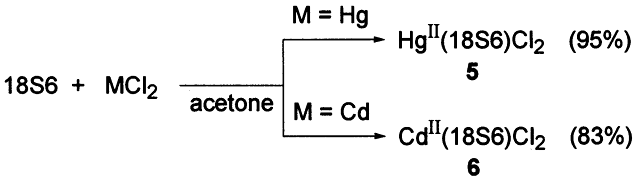
Complexation of Unsaturated and Saturated Thiacrown Ethers with Group XII Metals. The complexation of 18-membered unsaturated thiacrown ether **2** with 1 equiv of $HgCl_2$ in acetone at ambient temperature gave a white precipitate. Mercury complex Hg^{II}(18-UT-6)Cl_2·Me_2CO (**4**) was obtained as colorless prisms in 95% yield by recrystallization of the precipitate from acetone (Scheme 1). The complexation of **2** with 2 equiv of $HgCl_2$ also gave the 1:1 complex **4** as crystals in 98% yield, and no formation of the 1:2 complex was observed. As mentioned before, the complexation of 18S6 with $HgCl_2$ is known to form 1:1 and 1:2 macrocycle/mercury complexes depending on the amount of $HgCl_2$ added.[8] These results indicate that **2** has selectivity for the inclusion number of mercury atoms in the complexation. The complexation reactions of **2** with 1 equiv of other group XII metal chlorides, $CdCl_2$ and $ZnCl_2$, were also examined. However, cadmium and zinc complexes were not obtained by the reactions, and starting material **2** was recovered as crystals in 93 and 86% yields, respectively. These reactions were also examined by ^1H NMR measurement of the mixtures in acetone-d_6, and only one singlet of **2** was observed, indicating no formation of metal complexes even in solution. Two reasons are proposed for the lack of formation of complexes with $ZnCl_2$ and $CdCl_2$: One is that the cavity size of **2** better matches the diameter of Hg than those of Cd and Zn. The other reason is that Hg^{2+} is the most "soft" acid among these group XII metal ions,[9] and therefore, **2**, having soft sulfur atoms, has an affinity for $HgCl_2$. The reaction of **2** with a 1:1:1 mixture of $HgCl_2$, $CdCl_2$, and $ZnCl_2$ was carried out to confirm whether **2** could selectively form a complex with $HgCl_2$ in the mixture of group XII metal chlorides. As a result, the reaction selectively afforded only mercury complex **4** as crystals in 74% yield.

SCHEME 1



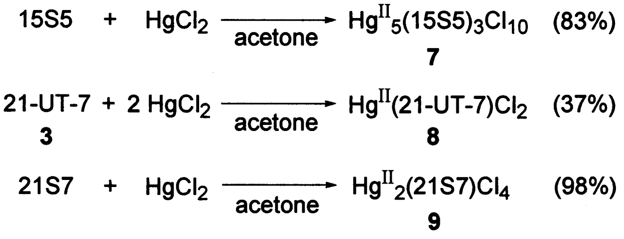
To clarify the difference in the complexation behavior with group XII metals between unsaturated thiacrown ether and the saturated system, the complexations of 18S6 with $HgCl_2$, $CdCl_2$, and $ZnCl_2$ were also examined. The complexation of 18S6 with 1 equiv of $HgCl_2$ in acetone afforded a white precipitate, and the mercury complex Hg^{II}(18S6)Cl_2 (**5**) was obtained as colorless prisms in 95% yield by recrystallization of the precipitate from dimethyl sulfoxide–acetone (Scheme 2). Complex **5** was previously prepared by Sevdić and co-workers, but the crystal structure was not clarified.[8] The complexation of 18S6 with 1 equiv of $CdCl_2$ in acetone also afforded a white powder. Elemental analysis and FAB mass spectra indicated that the molecular formula of the powder is Cd^{II}(18S6)Cl_2 (**6**) (83% yield), although it could not be recrystallized. However, the reaction of 18S6 with $ZnCl_2$ under similar conditions did not afford the zinc complex, and starting material 18S6 was recovered.

SCHEME 2



The complexations of 15- and 21-membered unsaturated and saturated thiacrown ethers with group XII metal chlorides were also examined. The reactions of 15-membered unsaturated thiacrown ether **1** with 1 and 2 equiv of $HgCl_2$, $CdCl_2$, and $ZnCl_2$ were carried out in acetone and tetrahydrofuran. However, the reactions did not afford any metal complexes, and starting material **1** was recovered as crystals. On the other hand, the complexation of the corresponding 15-membered saturated thiacrown ether, 15S5, with 1 equiv of $HgCl_2$ in acetone afforded a white precipitate. Elemental analysis supported the stoichiometry of the precipitate as a 3:5 macrocycle/metal complex, and indicated the molecular formula Hg^{II}_5(15S5)$_3Cl_{10}$ (**7**) (83% yield) (Scheme 3). The reactions of 15S5 with 1 equiv of other group XII metal chlorides, $CdCl_2$ and $ZnCl_2$, did not afford any metal complexes. In the complexation of the larger unsaturated thiacrown ether **3** with 2 equiv of $HgCl_2$, 1:1 complex Hg^{II}(21-UT-7)Cl_2 (**8**) was obtained although the yield was low (37%), whereas no mercury complex was obtained by the reaction of **3** with 1 equiv of $HgCl_2$. The reactions of **3** with 1 and 2 equiv of $CdCl_2$ and $ZnCl_2$ did not afford any complexes. In contrast, the complexation of the corresponding saturated thiacrown ether, 21S7, with 1 equiv of $HgCl_2$ in acetone afforded Hg^{II}_2(21S7)Cl_4 (**9**) in 98% yield as a white precipitate, the molecular formula of which was confirmed by elemental analysis. Cadmium and zinc complexes were not obtained by the reactions of 21S7 with $CdCl_2$ and $ZnCl_2$. The reason 15-membered unsaturated thiacrown ether **1** did not afford any complex

SCHEME 3



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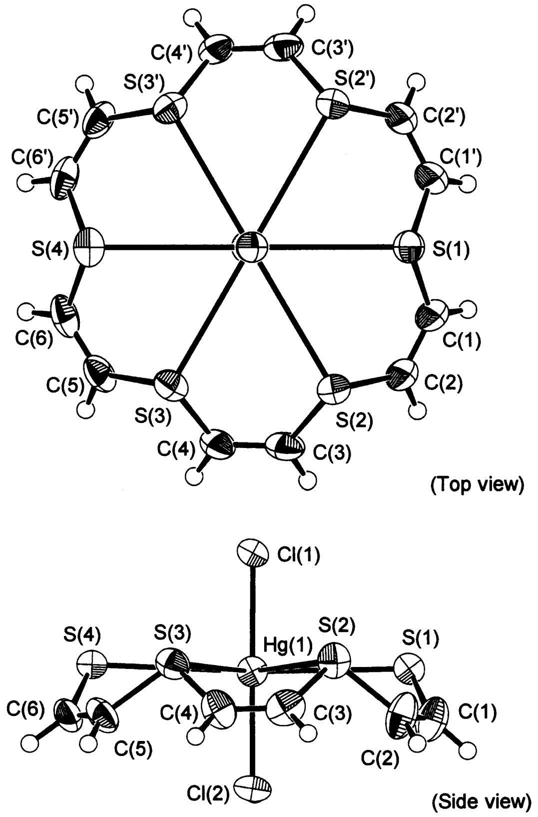

FIGURE 1. ORTEP drawing of Hg^{II}(18-UT-6)Cl$_2$·Me$_2$CO (**4**) showing thermal ellipsoids at the 50% probability level. The acetone molecule is omitted for clarity.

on reaction with group XII metal chlorides, and 15-, 18-, and 21-membered saturated thiacrown ethers formed the mercury complexes lies in the difference in the flexibility of the ring.

Crystal Structures of Mercury Complexes 4 and 5. The crystal structure of **4** was determined by X-ray crystallographic analysis (Figure 1). The selected atomic distances and angles are listed in Table 1.

The ORTEP drawing of **4** shows C_s symmetry, the presence of a mercury atom at the center of the macrocycle, and the nearly coplanar arrangement of the mercury atom and all sulfur atoms. The atomic distances between the six sulfur atoms and the mercury atom are 3.11−3.25 Å. The sum of the van der Waals radii of mercury and sulfur atoms is 3.58 Å (Hg, 1.73 Å; S, 1.85 Å),[10] and the usual atomic distances of mercury−sulfur complexes are 2.4−2.8 Å.[11] Therefore, the mercury atom is considered to be coordinated to six sulfur atoms although the coordination is weak. The Cl(1) and Cl(2) atoms coordinate to the mercury atom at the axial position with atomic distances of 2.38 and 2.34 Å, respectively, and the angle of Cl(1)−Hg−Cl(2) is almost linear (179.6°). These Hg−Cl distances are somewhat longer than the value of 2.25 Å observed for HgCl$_2$.[11] The elongation of the Hg−Cl bonds also supports the coordination of sulfur atoms to the mercury atom. These results show that the geometry around the mercury center was an eight-coordinate hexagonal bipyramidal arrangement, which is rare for mercury except for the complexes of crown compounds.[12] For example, Paige and Richardson reported that the complex Hg^{II}(18-crown-6)Cl$_2$ has a hexagonal bipyramidal arrangement in the crystalline state, similar to that of **4**.[13] In the case of **2**, six sulfur atoms are known to orient toward the inside of the ring (endodentate) in the crystalline state.[5] Therefore, the sulfur atoms of **2** are considered to easily coordinate to the mercury atom with endodentate orientation, and as a consequence, the mercury atom can exist in the hole of **2**.

TABLE 1. Selected Atomic Distances and Angles of Mercury Complexes 4 and 5

Hg^{II}(18-UT-6)Cl$_2$·Me$_2$CO (**4**)		Hg^{II}(18S6)Cl$_2$ (**5**)	
distances, Å			
Hg(1)−Cl(1)	2.377(4)	Hg(1)−Cl(1)	2.670(5)
Hg(1)−Cl(2)	2.341(4)	Hg(1)−S(1)	2.680(5)
Hg(1)···S(1)	3.106(4)	Hg(1)−S(2)	2.753(5)
Hg(1)···S(2)	3.247(3)		
Hg(1)···S(3)	3.154(3)		
Hg(1)···S(4)	3.182(5)		
angles, deg			
Cl(1)−Hg(1)−Cl(2)	179.6(2)	Cl(1)−Hg(1)−Cl(1*)	180.0
Cl(1)−Hg(1)···S(1)	88.5(1)	Cl(1)−Hg(1)−S(1)	87.2(2)
Cl(1)−Hg(1)···S(2)	85.97(8)	Cl(1)−Hg(1)−S(1*)	92.8(2)
Cl(1)−Hg(1)···S(3)	87.45(8)	Cl(1)−Hg(1)−S(2)	85.0(2)
Cl(1)−Hg(1)···S(4)	88.1(1)	Cl(1)−Hg(1)−S(2*)	95.0(2)
Cl(2)−Hg(1)···S(1)	91.1(1)	S(1)−Hg(1)−S(1*)	180.0
Cl(2)−Hg(1)···S(2)	93.81(9)	S(1)−Hg(1)−S(2)	82.3(2)
Cl(2)−Hg(1)···S(3)	92.76(8)	S(1)−Hg(1)−S(2*)	97.7(2)
Cl(2)−Hg(1)···S(4)	92.4(1)	S(1*)−Hg(1)−S(2)	97.7(2)
S(1)···Hg(1)···S(2)	59.97(6)	S(1*)−Hg(1)−S(2*)	82.3(2)
S(1)···Hg(1)···S(3)	120.01(6)	S(2)−Hg(1)−S(2*)	180.0
S(1)···Hg(1)···S(4)	176.6(1)		
S(2)···Hg(1)···S(3)	60.04(8)		
S(2)···Hg(1)···S(4)	119.74(6)		
S(3)···Hg(1)···S(4)	59.82(6)		

The crystal structure of **5** was also determined by X-ray crystallographic analysis (Figure 2). The selected atomic distances and angles are listed in Table 1. An ORTEP drawing of the complex shows C_i symmetry, and the mercury atom is coordinated to four sulfur atoms of two different macrocycles with Hg−S distances of 2.63−2.75 Å. The angles of S−Hg−S (cis position) range from 82.3 to 97.7°. Sulfur atoms S(1) and S(2) are engaged in the coordination to the Hg(1) atom that is existing outside the hole of the macrocycle, and sulfur atoms S(1*) and S(2*) coordinate to the Hg(1′) atom. Consequently, the complex forms a polymeric chain structure. Each mercury atom is also coordinated to two chlorine atoms by a distance of 2.67 Å, and the angle of Cl−Hg−Cl is 180.0°. Therefore, the mercury atom has a distorted six-coordinated square-bipyramidal arrangement. Thiacrown ether 18S6 is known to have four exodentate sulfur atoms in the crystalline state.[14] Therefore, in the complexation with HgCl$_2$, 18S6 can easily form a complex with mercury that exists outside the macrocycle.

Complexation Behavior of 2 with HgCl$_2$ in Solution. The ^{1}H NMR spectrum of complex **4** in acetone-d_6

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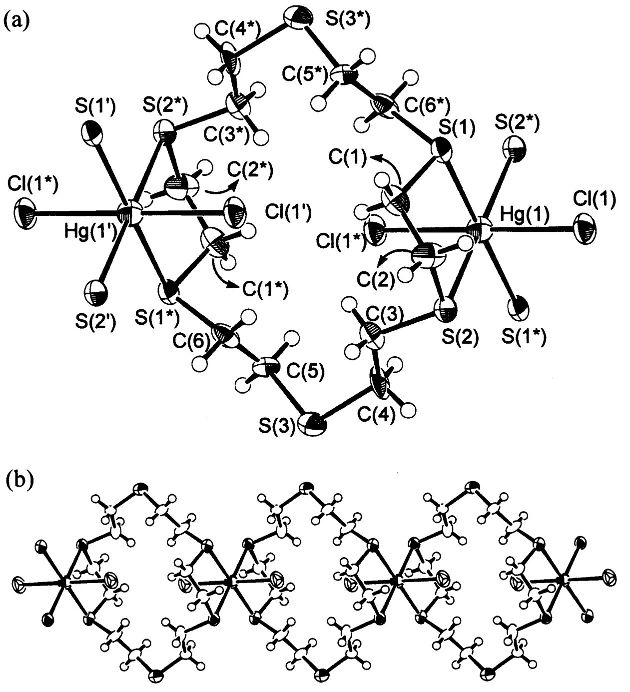


FIGURE 2. (a) ORTEP drawing of $Hg^{II}(18S6)Cl_2$ (**5**) showing thermal ellipsoids at the 50% probability level. (b) Packing diagram showing one of the arrangements of the polymeric chain structure.

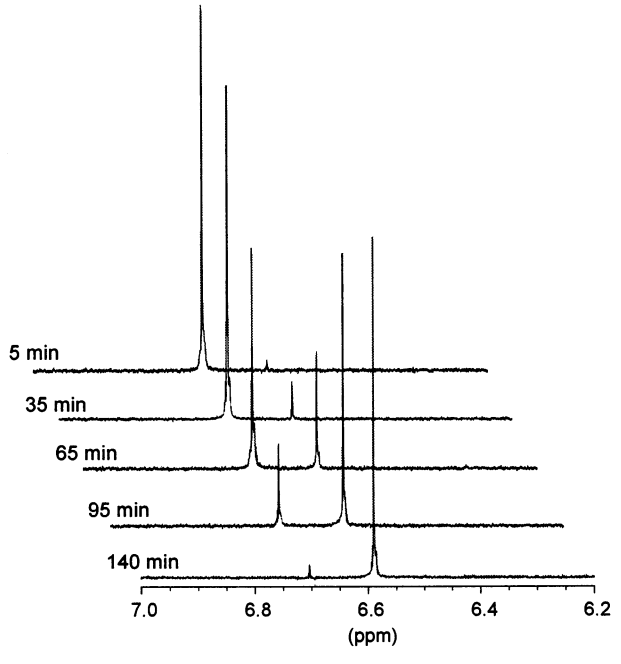


FIGURE 3. Time-course study of the ^{1}H NMR spectrum of $Hg^{II}(18\text{-}UT\text{-}6)Cl_2{\cdot}Me_2CO$ (**4**) in acetone-d_6 at 27 °C. Initial concentration of **4**: 4.0×10^{-3} M.

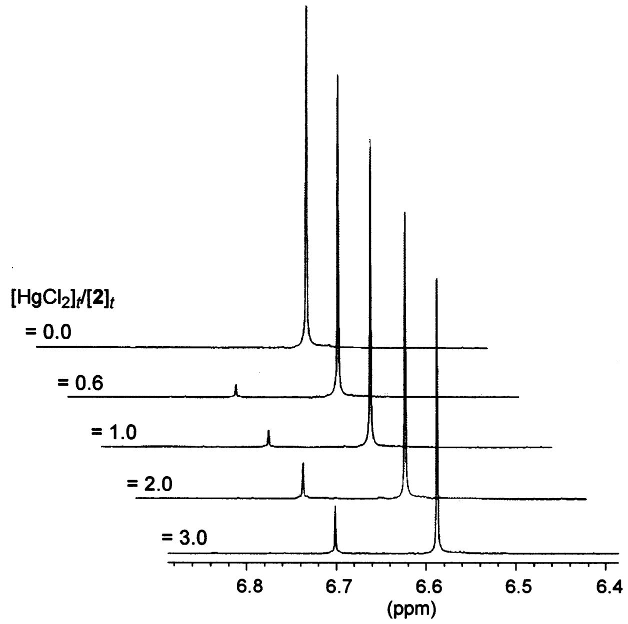
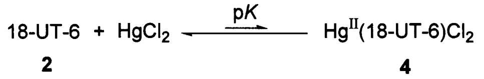


FIGURE 4. ^{1}H NMR spectra in the titration experiment of **2** with $HgCl_2$ in acetone-d_6 at 27 °C. Initial concentration of **2**: 4.0×10^{-3} M.

at 27 °C showed only one singlet at 6.70 ppm, which was found in a lower field than that of **2** (6.59 ppm). The intensity of this signal decreased with time, and concurrently a singlet of **2**, which was due to the dissociation of the complex, appeared and increased in intensity (Figure 3). Such separate signal of free ligand **2** and pure complex was not observed in the case of the silver complex of **2**, and only one singlet was observed at the weighted mean value between their signals.[6] These phenomena reveal that the interconversion between free ligand **2** and the pure mercury complex is slower than the NMR time scale ($1/\Delta\nu = 18$ ms) whereas the interconversion between **2** and the silver complex is relatively facile.[6] The ratio of the integral values of the two signals became constant after 140 min; the **2**:**4** ratio was 145:1 in the equilibrium state. The dissociation constant of **4** in acetone-d_6 was determined to be pK 1.4 from the integral values of the ^{1}H NMR signals in the equilibrium state, which shows that the equilibrium lies to the left (Scheme 4). However, the equilibrium may shift to the right since the complex is deposited owing to its poor solubility in acetone.

SCHEME 4



The titration experiment of **2** with $HgCl_2$ in acetone-d_6 was performed by ^{1}H NMR measurement of the dilute solutions to prevent precipitation of the resulting complex. ^{1}H NMR samples of **2** containing 0−3 equiv of $HgCl_2$ were prepared independently, and measurements were carried out in the equilibrium state at 27 °C (Figure 4). The intensity of the signal at 6.70 ppm of the 1:1 complex **4** increased with increasing amounts of $HgCl_2$, whereas that of **2** at 6.59 ppm decreased. Except for the signals of **2** and **4**, no other signal was observed even at $[HgCl_2]_t/[\mathbf{2}]_t = 3$. If **2** forms a complex with more than 1 equiv of $HgCl_2$ in acetone-d_6, other signals must be observed in the lower field. Therefore, the result confirms that **2** selectively forms a 1:1 macrocycle/metal complex with $HgCl_2$ in solution.

Electrochemical Behavior of Mercury Complexes 4 and 5. The electrochemical behavior of complexes **4** and **5** was examined by the cyclic voltammetric technique with a scanning potential range of +1.2 to −1.2 V vs Ag/Ag^+ at a scan rate of 100 mV s^{-1}. Measurements were carried out immediately after dissolving the complexes in 0.1 M tetra-*n*-butylammonium perchlorate solution. Dimethyl sulfoxide was used as the solvent since **5** was slightly soluble in dichloromethane, ethyl acetate, acetone, acetonitrile, nitromethane, and *N*,*N*-dimethylformamide, but soluble in dimethyl sulfoxide. Cyclic voltammograms of $HgCl_2$, **2**, and 18S6 were also measured for comparison with those of **4** and **5**. The cyclic voltammogram of $HgCl_2$ showed a quasireversible wave for the Hg(II/I) redox couple at $E_{1/2} = -0.43$ V with $\Delta E_p(E_{pa} - E_{pc}) = 90$ mV and an irreversible reduction wave from Hg(I) to Hg(0) at $E_{pc} = -0.80$ V. In the cases of **2** and 18S6, no oxidation and reduction peaks appeared, whereas irreversible oxidation peaks were observed at 0.84 and 1.13 V, respectively, in acetonitrile.[5] This may be due to the oxidation of dimethyl sulfoxide in preference to the macrocycles. On the other hand, the cyclic voltammogram of complex **5** showed a reversible wave for the redox couple of Hg(II/I) at $E_{1/2} = -0.43$ V ($\Delta E_p = 28$ mV), and an irreversible reduction wave from Hg(I) to Hg(0) at $E_{pc} = -0.72$ V. In contrast, the cyclic voltammogram of **4** showed neither an oxidation peak of the macrocycle nor a reduction wave of $HgCl_2$ in the present scanning potential range. These results show that $HgCl_2$ becomes difficult to be reduced by complexing with **2**. The following two reasons are considered: One is that **2** has electron-donating ability to the metal center. The other reason is that **2** renders reduction of $HgCl_2$ more difficult by sterically hindering dimerization ($2HgCl_2 + 2e^- \rightarrow Hg_2Cl_2 + 2Cl^-$).

Conclusions

The complexation of 18-membered unsaturated thiacrown ether **2** with $HgCl_2$ in acetone afforded mercury complex **4**, whereas **2** did not react with $CdCl_2$ and $ZnCl_2$ in acetone. The complexations of 18S6 with $HgCl_2$ and $CdCl_2$ in acetone afforded mercury and cadmium complexes **5** and **6**, respectively, although the zinc complex was not obtained by the reaction of 18-UT-6 with $ZnCl_2$. The crystal structure of **4** showed that the mercury atom was inside the cavity of the macrocycle and the geometry around the mercury atom was an eight-coordinate hexagonal bipyramidal arrangement. An ORTEP drawing of complex **5** showed that the macrocyclic ligand formed a complex with mercury atoms that is existing outside the ring, and a polymeric chain structure. ^1H NMR study of **4** showed that the interconversion between free ligand **2** and the pure complex was slower than the NMR time scale. The titration experiment by ^1H NMR measurement of **2** with $HgCl_2$ in acetone-d_6 revealed that **2** showed selectivity for the inclusion number of mercury atoms.

Experimental Section

General. Acetone and dimethyl sulfoxide were distilled from $CaSO_4$ prior to use. Preparation and purification of **1**−**3** have been previously described.[5] Preparation and purification of 15S5, 18S6, and 21S7 were carried out according to the literature.[15]

Typical Example of Complexation of Saturated and Unsaturated Thiacrown Ethers with Metal Dichlorides. An acetone solution (2 mL) of metal dichlorides (0.12 mmol) was added to an acetone solution (10 mL) of unsaturated thiacrown ethers (0.12 or 0.24 mmol) under nitrogen. The reaction mixture was stirred at room temperature for 3 h. Crystallization by slow evaporation of acetone or recrystallization of the precipitate from DMSO−acetone or DMSO−AcOEt was carried out.

Hg^{II}(18-UT-6)Cl_2·Me_2CO (4). A solution of mercury(II) chloride (32 mg, 0.12 mmol) in acetone (2 mL) was added to a solution of **2** (42 mg, 0.12 mmol) in acetone (10 mL) under nitrogen. The reaction mixture was stirred at room temperature for 3 h. Crystallization by slow evaporation of acetone yielded colorless crystals of Hg^{II}(18-UT-6)Cl·Me_2CO (77 mg, 95%). Anal. Calcd for $C_{15}H_{18}Cl_2OS_6Hg$: C, 26.56; H, 2.68. Found: C, 26.16; H, 2.51. Mp 167.0−168.5 °C (colorless prisms, dec); ^1H NMR (500 MHz, DMSO-d_6) δ 6.82 (12H, s); ^{13}C NMR (125 MHz, DMSO-d_6) δ 123.0; MS (EI) *m*/*z* 348 ($C_{12}H_{12}S_6^+$, 2%), 116 ($C_4H_4S_2^+$, 100%); IR (KBr) ν_{max} 3017, 1561, 1280, 1172, 880, 814, 721, 670 cm^{-1}.

Hg^{II}(18S6)Cl_2 (5). A solution of mercury(II) chloride (23 mg, 0.09 mmol) in acetone (2 mL) was added to a solution of 18S6 (30 mg, 0.08 mmol) in acetone (10 mL) under nitrogen. The reaction mixture was stirred at room temperature for 3 h, and the resulting white precipitate was collected by filtration and recrystallized from DMSO−acetone to give colorless crystals of Hg^{II}(18S6)Cl_2 (52 mg, 95%). Anal. Calcd for $C_{12}H_{24}Cl_2HgS_6$: C, 22.80; H, 3.83. Found: C, 22.79; H, 3.60. Mp 149.0−151.5 °C (colorless prisms); ^1H NMR (500 MHz, DMSO-d_6) δ 2.82 (24H, s); ^{13}C NMR (125 MHz, DMSO-d_6) δ 31.6; MS (EI) *m*/*z* 360 ($C_{12}H_{24}S_6^+$, 3%), 120 ($C_4H_8S_2^+$, 100%); IR (KBr) ν_{max} 2961, 2917, 1420, 1208, 928, 896, 861, 743, 717, 691 cm^{-1}.

Cd^{II}(18S6)Cl_2 (6). A solution of cadmium(II) chloride (17 mg, 0.09 mmol) in acetone (2 mL) was added to a solution of 18S6 (30 mg, 0.08 mmol) in acetone (10 mL) under nitrogen. The reaction mixture was stirred at room temperature for 3 h, and the resulting white precipitate was collected by filtration and dried in vacuo. Yield: 36 mg, 83%. Anal. Calcd for $C_{12}H_{24}CdCl_2S_6$: C, 26.49; H, 4.45. Found: C, 26.42; H, 4.11. Mp 243.5−255.0 °C (white powder, dec); ^1H NMR (500 MHz, DMSO-d_6) δ 2.72 (24H, s); ^{13}C NMR (125 MHz, DMSO-d_6) δ 31.6; FAB mass spectrum *m*/*z* 509 ($C_{12}H_{24}{}^{114}CdClS_6^+$), 361 ($C_{12}H_{24}S_6^+ + 1$); IR (KBr) ν_{max} 2962, 2920, 1423, 1261, 1207, 1159, 929, 896, 864, 745, 718, 692 cm^{-1}.

$Hg^{II}_5(15S5)_3Cl_{10}$ (7). A solution of mercury(II) chloride (41 mg, 0.15 mmol) in acetone (3 mL) was added to a solution of 15S5 (45 mg, 0.15 mmol) in acetone (15 mL) under nitrogen. The reaction mixture was stirred at room temperature for 3 h, and the resulting white precipitate was collected by filtration and dried in vacuo. Yield: 56 mg, 83%. Anal. Calcd for $C_{30}H_{60}Hg_5Cl_{10}S_{15}$: C, 15.95; H, 2.68. Found: C, 15.69; H, 2.58. Mp 113.0−114.0 °C (white powder); ^1H NMR (500 MHz, DMSO-d_6) δ 2.78 (20H, s); ^{13}C NMR (125 MHz, DMSO-d_6) δ 31.9; FAB mass spectrum *m*/*z* 535 ($C_{10}H_{20}Cl^{200}HgS_5^+$); IR (KBr) ν_{max} 2914, 1408, 1260, 1206, 1121, 1018, 915, 868, 823, 704, 679 cm^{-1}.

Hg^{II}(21-UT-7)Cl_2 (8). A solution of mercury(II) chloride (55 mg, 0.20 mmol) in acetone (2 mL) was added to a solution of **3** (41 mg, 0.10 mmol) in acetone (10 mL) under nitrogen. The reaction mixture was stirred at room temperature for 3 h, and the resulting white precipitate was collected by filtration and dried in vacuo. Yield: 25 mg, 37%. Anal. Calcd for $C_{14}H_{14}Cl_2HgS_7$: C, 24.79; H, 2.08. Found: C, 24.80; H, 2.07. Mp 137.0−138.5 °C (colorless prisms, dec); ^1H NMR (500 MHz, acetone-d_6) δ 6.59 (14H, s); ^{13}C NMR (125 MHz, acetone-d_6) δ 123.5; FAB mass spectrum *m*/*z* 641 ($C_{14}H_{14}Cl^{200}Hg\ S_7^+$), 406 ($C_{14}H_{14}S_7^+$); IR (KBr) ν_{max} 3023, 1653, 1278, 810, 721, 654, 537 cm^{-1}.

Hg^{II}_2(21S7)Cl_4 (9). A solution of mercury(II) chloride (27 mg, 0.10 mmol) in acetone (2 mL) was added to a solution of 21S7 (42 mg, 0.10 mmol) in acetone (10 mL) under nitrogen. The reaction mixture was stirred at room temperature for 3

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[15] Diaddario, L. L.; Zimmer, L. L.; Jones, T. E.; Sokol, L. S. W. L.; Cruz, R. B.; Yee, E. L.; Ochrymowycz, L. A.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1979**, *101*, 3511.

h, and the resulting white precipitate was collected by filtration and dried in vacuo. Yield: 47 mg, 98%. Anal. Calcd for $C_{14}H_{28}Cl_4Hg_2S_7$: C, 17.45; H, 2.93. Found: C, 17.52; H, 2.78. Mp 139.5−140.5 °C (colorless needles); ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.82 (28H, s); ^{13}C NMR (125 MHz, DMSO-d_6) δ 31.5; FAB mass spectrum m/z 657 ($C_{14}H_{28}Cl^{202}HgS_7^+$); IR (KBr) ν_{max} 2965, 2918, 1421, 1404, 1267, 1201, 921, 894, 871, 853, 735, 709, 692, 657 cm^{-1}.

X-ray Structure Determination. X-ray diffraction data were collected with use of a Rigaku RAXIS-RAPID imaging plate two-dimensional area detector, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71070$ Å) to 2θ max of 55.0°. All of the crystallographic calculations were performed by using the teXan software package from the Molecular Structure Corporation. The crystal structure was solved by direct methods and refined by full-matrix least squares. All non-hydrogen atoms were refined anisotropically. The experimental details including data collection, data reduction, and structure solution and refinement, as well as the atomic coordinates and B_{iso}/B_{eq} anisotropic displacement parameters, have been deposited in the Supporting Infomation.

Crystal Data for 4. $C_{15}H_{18}HgCl_2OS_6$, $f_w = 678.16$, orthorhombic, space group $Pnma$ (no. 62), $a = 16.746(5)$ Å, $b = 12.028(8)$ Å, $c = 11.574(9)$ Å, $V = 2331(3)$ Å^3, $Z = 4$, $D_{calc} = 1.932$ g cm^{-3}, μ(Mo Kα) = 73.89 cm^{-1}. A colorless crystal with dimensions of 0.30 × 0.35 × 0.40 mm^3 was used for data collection. A total of 3032 unique reflections were obtained, and 2067 observed reflections [$I > 0.00\sigma(I)$] were used for refinement to give $R = 0.099$, $R_w = 0.243$, and R1 = 0.070.

Crystal Data for 5. $C_{12}H_{24}HgCl_2S_6$, $f_w = 632.18$, triclinic, space group $P\bar{1}$ (no. 2), $a = 7.552(1)$ Å, $b = 7.923(1)$ Å, $c = 17.271(2)$ Å, $\alpha = 95.464(6)°$, $\beta = 97.418(7)°$, $\gamma = 93.576(7)°$, $V = 1017.2(2)$ Å^3, $Z = 2$, $D_{calc} = 2.064$ g cm^{-3}, μ(Mo Kα) = 84.55 cm^{-1}. A colorless crystal with dimensions of 0.20 × 0.20 × 0.30 mm^3 was used for data collection. A total of 10061 unique reflections were obtained, and 2889 observed reflections [$I > 3.00\sigma(I)$] were used for refinement to give $R = 0.127$, $R_w = 0.218$, and R1 = 0.088.

Cyclic Voltammetry. Cyclic voltammograms were measured in dimethyl sulfoxide, using a platinum working electrode at 24 °C under an atmospheric pressure of nitrogen. The counter electrode was a platinum wire. The measured potentials were recorded with respect to an Ag/AgNO$_3$ (0.01 M) reference electrode. A 0.1 M solution of tetra-n-butylammonium perchlorate was used as supporting electrolyte solution. The solid samples were added and dissolved to this solution to yield 1.5 mM concentrations of the respective materials.

Typical Procedure for ^{1}H NMR Shift Titration. To acetone-d_6 solutions of **2** (1×10^{-2} M, 200 μL) in an NMR tube were added individually the required amounts of an acetone-d_6 solution of HgCl$_2$ (4×10^{-2} M, 0−350 μL). The volume of the samples was prepared to 550 μL by addition of acetone-d_6 (concentration of macrocycle = 4×10^{-3} M). ^{1}H NMR measurement of the samples was carried out at 27 °C.

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Supporting Information Available: X-Ray crystallographic files (CIF) for **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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