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Structures of 1,4,13,16-Tetraoxa-7,10-dithia[16](1,1′)ruthenocenophane and Its 1 : 2 $HgCl_2$ Complex

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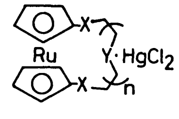
The reaction of 1,1′-bis(6-chloro-1,4-dioxahexyl)ruthenocene with disodium 1,2-ethanedithiolate gave 1,4,13,16-tetraoxa-7,9-dithia[16](1,1′)ruthenocenophane (**5**) in 63% yield. The reaction of **5** with $HgCl_2$ in acetonitrile gave a 1 : 2 complex (**6**) in 47% yield. The crystal structure of complex **6** and its metal free ligand **5** were determined by an X-ray method. Crystal data: **5**, triclinic, $a=11.128(2)$, $b=12.720(2)$, $c=10.196(2)$ Å, $\alpha=113.55(1)$, $\beta=64.13(1)$, $\gamma=122.01(1)°$, $U=1074.1$ Å^3. $P\bar{1}$, $Z=2$, $D_c=1.54$ Mg m^{-3}, μ(Mo $K\alpha$)=9 mm^{-1}. $R=0.028$. **6**, triclinic, $a=16.595(4)$, $b=12.645(3)$, $c=7.401(1)$ Å, $\alpha=104.92(1)$, $\beta=92.37(1)$, $\gamma=69.38(2)°$, $U=1402.4$ Å^3, $P\bar{1}$, $Z=2$, $D_c=2.46$ Mg m^{-3}, μ(Mo $K\alpha$)=12.2 mm^{-1}, $R=0.081$. The X-ray analysis of **6** revealed that one Hg atom was bonded to the Ru atom of the ruthenocene nucleus with a distorted trigonal-planar configuration and another Hg atom was bonded to the two sulfur atoms of the macrocycle. This result is completely different from that obtained regarding complex 4,7,10,13-tetraoxa-1,16-dithia[16](1,1′)ruthenocenophane with $HgCl_2$.

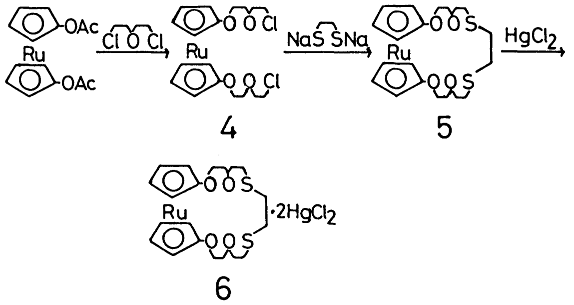
It is well-known that mercury forms a very wide range of complexes with thioethers and cyclic thioethers. Mercury halides readily form 1 : 1, 1 : 2, and 2 : 3 complexes with thioethers when the metal and ligands are mixed in aqueous alcoholic solution.[1–4] The 1 : 1 complexes[5] involve essentially linear mercury(II) coordination $[R_2SHgCl]Cl$ (type 1) and the 1 : 2 complexes[5,6] are thought to involve HgX_2 and $[R_2SHgX]X$ units held together by weak chloride bridges (type II), while 2 : 3 complexes[3] appear to be a mixture of 1 : 1 and 1 : 2 complexes. In contrast with the above, the reaction of mercury(II) halide with polyethylene glycols gives complexes of type 1 only.[7–9] Pedersen[10] has reported that mercury(II) chloride does not form a complex with dibenzo-18-crown-6 in methanol. Recently, Kawasaki et al.,[11] however, reported the formation of a mercury(II) chloride complex of dibenzo-18-crown-6 in acetonitrile or toluene. In this complex a linear Cl-Hg-Cl moiety (type 1) was found by X-ray analysis to be held perpendicularly to a quasi-planar ring of O_6. It has also been reported that the reaction of the metallocene with HgX_2 gives various adducts.[12] For example, the complex of ruthenocene with $HgBr_2$ is essentially a simple adduct complicated by the presence of halide bridging. In connection with the above-mentioned viewpoints we have been interested in the complexing manner of the metallocenocrown ethers with $HgCl_2$.



1; X=S, Y=O, n=4
2; X=Y=O, n=3
3; X=S, Y=O, n=3

In previous papers,[13,14] we reported on the molecular structures of a 1 : 1 complexes (**1**, **2**, and **3**) of 4,7,10,13-tetraoxa-1,16-dithia[16](1,1′)ruthenocenophane, 1,4,7,10,13-pentaoxa- and 1,13-dioxa-4,7,10-trithia[13](1,1′) ruthenocenophanes with $HgCl_2$. In this paper we report on the molecular structure of a 1 : 2 complex (**6**) of 1,4,13,16-tetraoxa-7,10-dithia[16](1,1′)ruthenocenophane (**5**) with $HgCl_2$ in order to clarify the manner of the complexing.

Syntheses. The following reactions were carried out to obtain complex **6**. The reaction of 1,1′-diacetoxyruthenocene with bis(2-chloroethyl) ether in ethanol in the presence of potassium hydroxide gave **4** in 73% yield. The reaction of **4** with dipotassium 1,2-ethanedithiolate in ethanol gave **5** in 63% yield. A solution of $HgCl_2$ in 1 ml of acetonitrile was added, dropwise, to a solution of 1 ml of acetonitrile containing **5**. The resulting precipitates were filtered and washed with a small amount of acetonitrile to give a 1 : 2 complex (**6**) in 47% yield. In spite of the many attempts to prepare the 1 : 1 complex of **5** with $HgCl_2$ it could not be obtained.



^{1}H NMR spectra of **5** and its mercury(II) complex (**6**) were measured in DMSO-d_6 as the solvent. Upon comparing the ^{1}H NMR spectra of **6** with **5**, the signals of the β-protons of the Cp-rings in **6** were shifted further down field (3.0 ppm) than the α-protons (2.1 ppm). The signals of the methylene protons attached to the sulfur atoms of **6** were also shifted down field (0.05—0.06 ppm), although the change in the chemical shifts of the methylene protons attached to the oxygen atoms was negligible. These results sug-

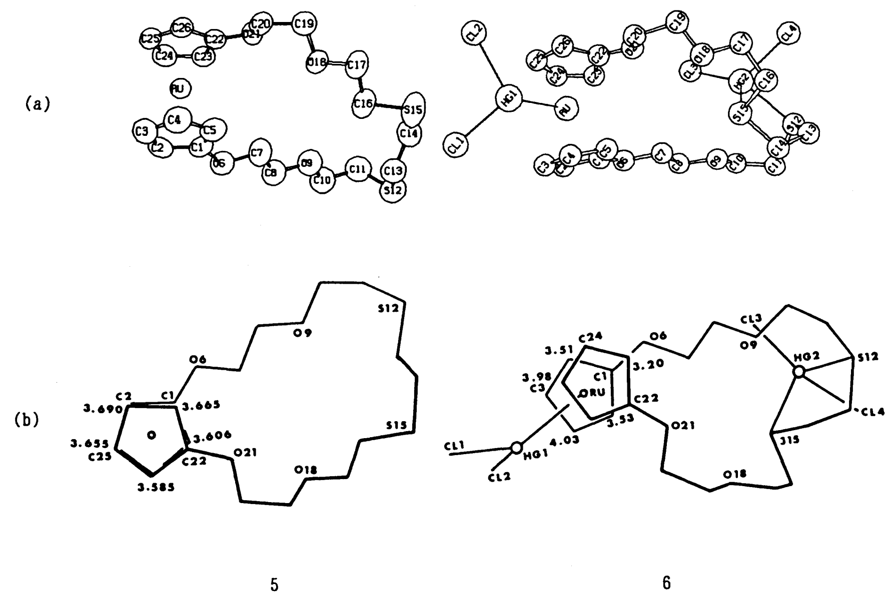


Fig. 1. ORTEP (Johnson, 1965) drawings of the molecules **5** and **6** with atom numbering scheme. (b) Projections of the molecules on the Cp rings containing the C(1) atom with the C···C distances (The mean standard deviations are 0.005 and 0.04 Å for **5** and **6**, respectively).

Table 1. Fractional Atomic Coordinates (×10^4) and Thermal Parameters, with Estimated Standard Deviations in Parentheses of **5**

Atom	*x*	*y*	*z*	$B_{eq}$$^{a)}$/Å^2
Ru	2432.1(3)	4457.0(2)	2551.6(3)	3.34
C(1)	1289(3)	2686(3)	1095(3)	4.1
C(2)	1283(3)	3713(3)	866(3)	4.4
C(3)	478(3)	4247(3)	2272(4)	4.7
C(4)	37(3)	3560(3)	3324(4)	4.3
C(5)	544(3)	2582(3)	2607(4)	4.2
O(6)	1845(2)	1888(2)	−80(2)	5.4
C(7)	2206(4)	1138(3)	289(4)	6.0
C(8)	2803(4)	393(3)	−1181(4)	5.8
O(9)	3237(3)	−350(2)	−910(2)	5.8
C(10)	3837(4)	−1066(3)	−2275(4)	6.0
C(11)	4309(4)	−1821(3)	−1942(4)	5.7
S(12)	2862(1)	−3312(1)	−1434(1)	6.1
C(13)	1860(4)	−2847(3)	472(4)	5.2
C(14)	2722(4)	−2440(3)	1536(4)	5.2
O(15)	1755(1)	−2038(1)	3470(1)	6.6
C(16)	1732(4)	−620(3)	3495(4)	5.4
C(17)	2011(4)	353(3)	4900(4)	5.2
O(18)	1971(2)	1423(2)	4831(2)	5.0
C(19)	2519(4)	2524(3)	5923(4)	4.8
C(20)	2656(3)	3627(3)	5585(3)	4.1
O(21)	3792(2)	3849(2)	4214(2)	4.1
C(22)	3919(3)	4727(3)	3655(3)	3.7
C(23)	4722(3)	4855(3)	2157(3)	3.6
C(24)	4706(3)	5906(3)	1995(3)	4.2
C(25)	3876(3)	6407(3)	3380(4)	4.4
C(26)	3360(3)	5676(3)	4432(3)	3.8

a) W.C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).

gest that the mercury atoms were coordinated to the ruthenium atom of the ruthenocene nucleus and the sulfur atoms of the macrocyclic moiety.

X-Ray Analyses. The molecular structures of **5**

Table 2. Fractional Atomic Coordinates (×10^4) and Thermal Parameters, with Estimated Standard Deviations in Parentheses of **6**

Atom	*x*	*y*	*z*	$B_{eq}$$^{a)}$/Å^2
Hg(1)	4082.2(7)	−47.0(9)	3352.9(13)	3.63
Hg(2)	1333.1(8)	7795.3(10)	5112.1(15)	5.28
Ru	2747.7(12)	1923.7(16)	3271.4(24)	3.08
Cl(1)	4621(4)	−1943(5)	974(9)	4.5
Cl(2)	4510(4)	−694(5)	6373(8)	4.1
Cl(3)	534(5)	6782(7)	6013(9)	7.0
Cl(4)	1731(5)	9327(6)	7454(9)	6.1
C(1)	2227(15)	2741(20)	894(28)	3.7
C(2)	2216(16)	1580(19)	477(30)	3.9
C(3)	3030(17)	831(20)	348(29)	4.0
C(4)	3623(16)	1444(23)	738(31)	4.6
C(5)	3100(16)	2645(21)	1124(28)	4.2
O(6)	1526(10)	3669(12)	929(22)	4.1
C(7)	1666(17)	4774(21)	1232(36)	5.0
C(8)	833(18)	5591(18)	910(36)	5.0
O(9)	951(11)	6694(12)	1120(22)	4.3
C(10)	182(16)	7607(22)	1055(33)	4.8
C(11)	379(16)	8642(21)	898(33)	4.5
S(12)	833(5)	9295(6)	3001(10)	5.1
C(13)	1912(19)	8989(23)	2259(39)	6.0
C(14)	2486(17)	7732(23)	1372(31)	5.0
S(15)	2728(4)	6780(6)	2995(9)	4.4
C(16)	3544(18)	7230(23)	4330(35)	5.4
C(17)	3692(21)	6761(24)	6041(38)	6.9
O(18)	3821(14)	5590(17)	5520(28)	8.0
C(19)	3981(20)	5057(24)	6994(40)	6.7
C(20)	3824(18)	3902(23)	6449(36)	5.7
O(21)	2894(12)	4183(14)	6271(23)	5.2
C(22)	2634(16)	3252(20)	5973(32)	4.1
C(23)	1805(16)	3314(20)	5296(32)	4.2
C(24)	1705(16)	2232(23)	5290(35)	4.8
C(25)	2490(18)	1507(23)	5813(35)	5.7
C(26)	3114(16)	2114(19)	6281(31)	3.8

a) W.C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).

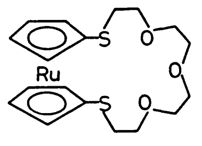
Table 3. Bond Lengths (*l*) and Bond Angles (*θ*) and Torsion Angles (*τ*) in the Organic Ligand of **5**

1	2	3	4	1–2 *l*/Å	1–2–3 *θ*/°	1–2–3–4 *τ*/°
Tetraoxa-dithia-crown moiety						
O(6)	C(1)	C(2)	C(3)	1.377(5)	121.1(3)	173.3(3)
O(6)	C(1)	C(5)	C(4)		128.6(3)	173.0(3)
C(2)	C(1)	O(6)	C(7)			162.1(3)
C(5)	C(1)	O(6)	C(7)			−24.3(5)
C(1)	O(6)	C(7)	C(8)		116.6(3)	−179.0(3)
O(6)	C(7)	C(8)	O(9)	1.428(5)	105.2(3)	178.1(3)
C(7)	C(8)	O(9)	C(10)	1.500(6)	108.7(3)	−179.1(3)
C(8)	O(9)	C(10)	C(11)	1.420(5)	111.1(3)	178.9(3)
O(9)	C(10)	C(11)	S(12)	1.426(5)	109.5(3)	82.4(4)
C(10)	C(11)	S(12)	C(13)	1.505(6)	116.0(3)	−76.1(3)
C(11)	S(12)	C(13)	C(14)	1.810(4)	103.1(2)	−75.3(3)
S(12)	C(13)	C(14)	S(15)	1.806(4)	111.0(3)	−177.1(1)
C(13)	C(14)	S(15)	C(16)	1.516(6)	113.7(3)	−67.2(3)
C(14)	S(15)	C(16)	C(17)	1.798(4)	100.2(2)	−140.0(3)
S(15)	C(16)	C(17)	O(18)	1.807(5)	110.0(3)	−179.9(1)
C(16)	C(17)	O(18)	C(19)	1.498(6)	106.3(3)	−167.6(3)
C(17)	O(18)	C(19)	C(20)	1.415(5)	113.0(3)	170.8(3)
O(18)	C(19)	C(20)	O(21)	1.419(5)	108.1(3)	−67.1(4)
C(19)	C(20)	O(21)	C(22)	1.491(6)	107.7(3)	171.9(3)
C(20)	O(21)	C(22)	C(23)	1.424(5)	114.6(3)	−164.5(3)
C(20)	O(21)	O(22)	C(26)			18.4(5)
O(21)	C(22)	C(23)	C(24)	1.365(4)	122.5(3)	−176.1(3)
O(21)	C(22)	C(26)	C(25)		128.1(3)	175.9(3)
Cyclopentadienyl ring						
C(1)	C(2)	C(3)	C(4)	1.420(5)	106.6(3)	1.1(4)
C(2)	C(3)	C(4)	C(5)	1.437(3)	108.1(3)	−0.3(4)
C(3)	C(4)	C(5)	C(1)	1.411(5)	109.1(3)	−0.5(4)
C(4)	C(5)	C(1)	C(2)	1.434(5)	106.2(3)	1.2(4)
C(5)	C(1)	C(2)	C(3)	1.418(5)	110.1(3)	−1.4(4)
C(22)	C(23)	C(24)	C(25)	1.418(5)	107.2(3)	−1.0(4)
C(23)	C(24)	C(25)	C(26)	1.421(5)	108.4(3)	0.0(4)
C(24)	C(25)	C(26)	C(22)	1.422(5)	108.9(3)	0.9(4)
C(25)	C(26)	C(22)	C(23)	1.427(5)	106.0(5)	−1.5(4)
C(26)	C(22)	C(23)	C(24)	1.440(5)	109.4(3)	1.6(4)

Table 4. Bond Lengths (*l*) and Bond Angles (*θ*) and Torsion Angles (*τ*) in the Organic Ligand of **6**

1	2	3	4	1–2 *l*/Å	1–2–3 *θ*/°	1–2–3–4 *τ*/°
Hexaoxa-crown moiety						
O(6)	C(1)	C(2)	C(3)	1.32(3)	123(2)	173(2)
O(6)	C(1)	C(5)	C(4)		131(2)	−173(3)
C(2)	C(1)	O(6)	C(7)			−175(2)
C(5)	C(1)	O(6)	C(7)			1(4)
C(1)	O(6)	C(7)	C(8)		115.5(19)	171(2)
O(6)	C(7)	C(8)	O(9)	1.46(3)	104(2)	−177.6(17)
C(7)	C(8)	O(9)	C(10)	1.46(3)	106(2)	−173(2)
C(8)	O(9)	C(10)	C(11)	1.44(3)	113(2)	−168.8(19)
O(9)	C(10)	C(11)	S(12)	1.40(3)	109(2)	−67(3)
C(10)	C(11)	S(12)	C(13)	1.49(4)	113.1(19)	112(2)
C(11)	S(12)	C(13)	C(14)	1.83(3)	103.7(14)	−55(3)
S(12)	C(13)	C(14)	S(15)	1.77(3)	120(2)	−66(3)
C(13)	C(14)	S(15)	C(16)	1.52(4)	114(2)	−78(2)
C(14)	S(15)	C(16)	C(17)	1.85(3)	100.3(13)	167.1(19)
S(15)	C(16)	C(17)	O(18)	1.81(3)	109(2)	50(3)
C(16)	C(17)	O(18)	C(19)	1.51(5)	109(3)	179(2)
C(17)	O(18)	C(19)	C(20)	1.37(4)	114(3)	161(2)
O(18)	C(19)	C(20)	O(21)	1.39(4)	111(3)	−69(3)
C(19)	C(20)	O(21)	C(22)	1.52(4)	107(2)	−174(2)
C(20)	O(21)	C(22)	C(23)	1.46(3)	114(2)	−164(2)
C(20)	O(21)	O(22)	C(26)			17(4)
O(21)	C(22)	C(23)	C(24)	1.36(3)	121(2)	−175(12)
O(21)	C(22)	C(26)	C(25)		127(2)	177(2)
Cyclopentadienyl ring						
C(1)	C(2)	C(3)	C(4)	1.43(4)	109(2)	2(3)
C(2)	C(3)	C(4)	C(5)	1.34(4)	111(2)	0(3)
C(3)	C(4)	C(5)	C(1)	1.43(4)	105(2)	−2(3)
C(4)	C(5)	C(1)	C(2)	1.42(4)	109(2)	4(3)
C(5)	C(1)	C(2)	C(3)	1.42(3)	106(2)	−4(2)
C(22)	C(23)	C(24)	C(25)	1.43(4)	107(2)	−5(3)
C(23)	C(24)	C(25)	C(26)	1.43(4)	107(2)	3(3)
C(24)	C(25)	C(26)	C(22)	1.41(4)	112(2)	−1(3)
C(25)	C(26)	C(22)	C(23)	1.47(4)	102(2)	−2(3)
C(26)	C(22)	C(23)	C(24)	1.45(4)	112(2)	4(3)
Hg coordination						
Ru	HG1	Cl(1)		2.701(2)	129.7(2)	Cl(2′): 1−*x*, −*y*, 1−*z*
Ru	HG1	Cl(2)			122.6(2)	
Ru	HG1	Cl(2′)			102.4(2)	
Cl(1)	HG1	Cl(2)		2.470(7)	101.1(2)	
Cl(2′)	HG1	Cl(1)		2.792(7)	102.5(2)	
Cl(2)	HG1	Cl(2′)		2.564(7)	88.5(2)	
S(12)	HG2	S(15)		2.576(8)	87.0(2)	
S(12)	HG2	Cl(3)			123.6(3)	
S(12)	HG2	Cl(4)			100.3(3)	
S(15)	HG2	Cl(3)		2.654(8)	127.3(3)	
Cl(3)	HG2	Cl(4)		2.356(9)	121.5(3)	
Cl(4)	HG2	S(15)		2.504(9)	87.2(3)	

and **6** are illustrated in Fig. 1. The final atomic parameters for **5** and **6** are listed in Tables 1 and 2, and bond lengths as well as bond and torsion angles are given in Tables 3 and 4 for **5** and **6**, respectively. The structure of complex **6** differs completely from that of **1** in which the Hg atom of $HgCl_2$ incorporated in the central cavity of the crown ether moiety forms a distorted hexagonal-bipyramidal geometry with an angle of 172.7(2)° (type 1), even though **1** has the same number of crown moieties as **6** and the positions of the two sulfur atoms in **1** and **6** are the only difference between them. Surprisingly, the one Hg(1) atom of $HgCl_2$ in complex **6** is bonded directly to the Ru atom of the ruthenocene nucleus from the opposite side of the crown ether moiety with a distorted trigonal-planar configuration and one Cl(2)′ atom of the adjacent complex also linked by a weak bond to the Hg atom. Therefore, the Hg(1) atom forms a distorted trigonal-pyramidal geometry. The Ru-Hg(1) interatomic distance in **6** is 2.701 Å, which essentially equals the sums (2.68 Å) of the covalent radii of Ru and Hg atoms.[15] However, the value is intermediate between those (2.65 and 2.74 Å) found in the 2 : 3 $HgCl_2$ complex[16] and the 1 : 1 $HgBr_2$ complex[16] of ruthenocene. The sum of the three bond angles about the Hg(1) atom is 353.3° and the deviation of the Hg atom from the Cl(1)-Ru-Cl(2) plane is 0.381°. These values are similar to those found in the 1 : 1 mercury complexes **2** and **3**.[14] The values (2.470(7) and 2.564(7) Å of the Hg-Cl(1) and Hg-Cl(2) bonds are even smaller than those (2.55 and 2.60 Å) of the corresponding Hg-Cl bonds in the 2 : 3 complex[16] of ruthenocene with $HgCl_2$. It may be attributed to the difference in the complexing ratios between ruthenocene and $HgCl_2$. Another Hg(2) atom of $HgCl_2$ is also bonded to the two sulfur atoms of the macrocyclic moiety with a distorted tetrahedral geometry. The lengths (2.576(8) and 2.654(8) Å) of S(12)-Hg(2) and S(15)-Hg(2) bonds and the dihedral angle (62.3(2)°) between the planes defined by S(12)-Hg(2)-S(15) and Cl(3)-Hg(2)-Cl(4) is smaller than those found in μ-(1,4,8,11-tetrathiacyclotetradecane-S^1S^4;S^8S^{11})bis[dichloromercury(II)].[17] It is noteworthy that the Cp ring in **6** deviates from planarity, and its tilting angle is 21.1(1)°, although that in the corresponding metal free ligand **5** is only 2.5(2)°. The large tilting in **6** is attributed to the metal-metal (Ru-Hg(1)) bond formation followed by the steric repulsion between the two Cp-rings and Hg(1)Cl_2 units. Finally, the difference in the complexing manner of **6** and **3** with $HgCl_2$ seems to be attributable to: (I) the Hg(2) atom is more easily bonded to the S(12) and S(15) atoms in **5** compared to the two sulfur atoms in the metal free ligand **7** of the corresponding complex **3**, because the directions of the lobes of lone pair electrons of the two sulfur atoms in **5** are more suitable for S-Hg-S bonding compared with those in **7**; (II) the differences of the ring sizes and tilting angles of the two Cp-rings in **5** and **7** are also effected by the complexing manner of the metal free ligands (**5** and **7**) with $HgCl_2$. Therefore, the Hg(2) atom is selectively bonded to the two sulfur atoms in **5** without incorporation into the central cavity of the macrocycle as the linear Cl-Hg-Cl form.



7

Experimental

Melting points are uncorrected. The ^{1}H NMR spectra were measured on a JEOL GX400 spectrometer with TMS as the internal standard.

Materials. 1,1′-Diacetoxyruthenocene was prepared according to a method mentioned in a previous paper.[18] The other reagents employed were either commercial or prepared by the usual methods. The solvents were purified by distillation.

1,1′-Bis(6-chloro-1,4-dioxahexyl)ruthenocene (4). 1,1′-Diacetoxyruthenocene (471 mg, 1.36 mmol) was added to 10 ml of potassium hydroxide solution (619 mg, 15.4 mmol) containing catalytic amounts of 18-crown-6 under nitrogen. After the mixture was stirred at reflux temperature, bis(3-chloropropyl) ether (5.488 g, 38.1 mmol) in 10 ml of ethanol was added to the mixture at once. The stirring was continued for 6 h under reflux. The solution was cooled to room temperature, and extracted with three 100 ml portions of ether. The extracts were combined, washed with water, and concentrated in vacuo. The residual oil was chromatographed on silica-gel TLC (hexane : acetone=4 : 1 as eluent). The second band was extracted with acetone at room temperature, followed by filtration and evaporation of the solvent to give **4** as a pale-yellow oil. 73% yield. Found: C, 45.21; H, 5.10%. Calcd for $C_{18}H_{24}Cl_2O_4Ru$: C, 45.38; H, 5.04%. MS(M^+) 476.

1,4,13,16-Tetraoxa-7,10-dithia[16](1,1′)ruthenocenophane (5). A solution of **4** (1.63 g, 3.42 mmol) in THF (120 ml) and a mixture of 1,2-ethanedithiol (1.68 g, 17.8 mmol) and potassium hydroxide (1.46 g, 36.5 mmol) in 120 ml of aqueous ethanol were added to 100 ml of ethanol-THF (1 : 1) solution over 3 h under reflux. The refluxing was continued for 12 h with stirring. The mixture was cooled to room temperature and concentrated in vacuo. The residual oil was chromatographed on silica gel (hexane : acetone=4 : 1 as eluent). The main band was extracted with acetone, and the solution was evaporated in vacuo. Recrystallization of the residue from hexane gave **5** as white needles in 13% yield. Mp 93.0—94.0 °C. Found: C, 48.35; H, 5.55%. Calcd for $C_{20}H_{28}O_4S_2Ru$: C, 48.29; H, 5.63%. ^{1}H NMR (in DMSO-d_6) δ=4.66 (t, J=1.8 Hz, 4H), 4.27 (t, J=1.8 Hz, 4H), 3.79—3.40 (m, 8H), 3.63 (t, J=6.2 Hz, 4H), 2.80 (s, 4H), 2.70 (t, J=6.2 Hz, 4H). MS (M^+) 497.

Isolation of 1 : 2 Complex of 5 with $HgCl_2$. A solution of **5** (38 mg, 7.6×10^{-2} mmol) in ether (5 ml) was added to a solution containing mercury(II) chloride (26 mg, 9.6×10^{-2} mmol) in 15 ml of ether. As the mixture was concentrated to 10 ml in vacuo, a yellow solid precipitated. Recrystallization of the solid from acetonitrile (2 ml) gave pure mercury complex (**6**) in 47% yield. Mp 159.5—160.5 °C. Found: C, 23.28; H, 2.80%. Calcd for $C_{20}H_{28}O_4S_2Ru(HgCl_2)_2$: C, 23.10; H, 2.69%. ^{1}H NMR (in DMSO-d_6) δ=4.87 (broad s, 4H), 4.57 (broad s, 4H), 3.78 (t, J=4.6 Hz, 4H), 3.64 (t, J=4.6 Hz, 4H), 3.62 (t, J=6.2 Hz, 4H), 2.86 (s, 4H), 2.75 (t, J=6.2 Hz, 4H).

X-Ray Crystallography of 5 and 6. Crystals of dimensions 0.3×0.3×0.3 mm for **5** and 0.4×0.2×0.1 mm for **6** were used for X-ray crystallography. Lattice constants were determined by a least-squares fit of angular settings of 2θ reflections within the range $15<2\theta<30°$. Intensity data were obtained on a Rigaku AFC-5R diffractometer equipped with graphite-monochromatized Mo $K\alpha$ (λ=0.71069 Å) radiation and using the θ-2θ scan technique ($2\theta<50°$). During data collection, three standards (measured before every 200 reflections) indicated no systematic variation of the intensity with time. Of 3781 and 4928 independent reflections measured, only 3573 and 3999 for **5** and **6**, respectively, were considered as observed on the basis of the criterion $F_o<2\sigma(F_o)$. All intensities were corrected for Lorentz and polarization effects, but not for absorption. Crystal data: **5**, $C_{20}H_{28}O_4S_2Ru$, Mw=497.7. Triclinic, space group $P\bar{1}$, a=11.128(2), b=12.720(2), c=10.196(2) Å, α=113.55(1), β=64.13(1), γ=122.01(1)°, U=1074.1 Å^3, Z=2, D_c=1.54 Mg m^{-3}, μ(Mo $K\alpha$)=0.9 mm^{-1}. **6**, $C_{20}H_{28}O_4S_2RuHg_2Cl_4$, Mw=1040.7. Triclinic, space group $P\bar{1}$, a=16.595(4), b=12.645(3), c=7.401(1) Å, α=104.92(1), β=92.37(1), γ=69.38(2)°, U=1402.4 Å^3, Z=2, D_c=2.46 Mg m^{-3}, μ(Mo $K\alpha$)=12.2 mm^{-1}. The structures of **5** and **6** were solved by the heavy-atom methods, and refined by the block-diagonal least-squares method. The positions of the hydrogen atoms were estimated using standard geometry. The final refinements with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms lowered the R values to 0.028 (R_w=0.025, $w=1/\sigma^2(F_o)$) and 0.081 (R_w=0.070, $w=1/\sigma(F_o)$) for **5** and **6**, respectively.[19] Anomalous dispersion corrections were applied to the scattering factors of Hg, Ru, Cl, and S.[20] The complete F_o-F_c data are deposited as Document No. 8904 at the office of the Bull. Chem. Soc. Jpn.

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