Novel Structures of 1 : 1 Complexes of 1,4,7,10,13-Pentaoxa-, 1,13-Dioxa-4,7,10-trithia[13]- and 1,4,7,10,13,16-Hexaoxa[16](1,1′)-ruthenocenophanes with $HgCl_2$: Metal-Metal (Ru-Hg) Bond Formation

Sadao SATO,† Masaru SATO,†† and Sadatoshi AKABORI*
Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274
†Analytical and Metabolic Research Laboratories, Sankyo Co., Hiromachi, Shinagawa-ku, Tokyo 140
††Chemical Analysis Center, Saitama University, Urawa, Saitama 338
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The structures of 1 : 1 complexes (**3b**, **4b**, and **5b**) of 1.4,7,10,13-pentaoxa-, 1,13-dioxa-4,7,10-trithia[13]- and 1,4,7,10,13,16-hexaoxa[16](1,1′)ruthenocenophanes (**3a**, **4a**, and **5a**) with $HgCl_2$, and **3a** have been determined by the single-crystal X-ray diffraction method. The complexing forms of the three complexes are quite similar to each other. Crystal data: **3b**, triclinic, space group $P\bar{1}$, a=12.043(3), b=10.759(2), c=8.529(2) Å, α=98.76(2), β=101.22(2), γ=77.03(2)°, U=1049.5 Å^3, Z=2, D_c=2.19 g cm^{-3}, μ(Mo $K\alpha$)=84 cm^{-1}. **4b**, triclinic, space group $P\bar{1}$ a=17.100(3), b=8.986(1), c=8.618(2) Å, α=105.17(1), β=62.24(1), γ=100.54(1)°, U=1128.1 Å^3, Z=2, D_c=2.18 g cm^{-3}, μ(Mo $K\alpha$)=81 cm^{-1}. **5b**, monoclinic, a space group $P2_1/a$, a=26.881(7), b=10.344(3), c=8.414(2), β=96.97(2)°, U=2322.2 Å^3, Z=4, D_c=2.11 g cm^{-3}, μ(Mo $K\alpha$)=76 cm^{-1}. **3a**, triclinic, space group $P\bar{1}$, a=11.107(1), b=8.816(1), c=9.788(1) Å, α=70.48(1), β=99.76(1), γ=101.31(1)°, U=877.6(2) Å^3, Z=2, D_c=1.59 g cm^{-3}, μ(Mo $K\alpha$)=9 cm^{-1}. Only the Ru atom of the ruthenocene nucleus of these complexes was coordinated to $HgCl_2$ with a slightly distorted trigonal-planar configuration. The distances between the Ru and the Hg atoms are 2.683(3), 2.704(1), and 2.696(2) Å, respectively.

Many research groups have recently attempted to investigate modified crown ethers in order to develop a new functionality for them.[1] For example, the syntheses of many kinds of macrocyclic compounds containing aza, thia, phosphorus, arsenic, and/or other coordinatable atoms have been reported. In this connection, several research groups have reported new-type crown ethers, thiacrown ethers, and oxathiacrown ethers which contain a ferrocene unit as an integral part of a ring member.[2] However, the complexes of crown ethers,[3] thiacrown ethers[4] and azacrown ethers[5] with $HgCl_2$ are rare, although a number of the complexes of crown ethers including ferrocenocrown ethers have already been reported.[2] In connection with this viewpoint, we have studied the preparation and structures of the complexes of metallocenocrown ethers with an interest in the electron-transfer interaction between the complexed cation and the metal atom of the metallocene nucleus.[6] In a previous paper,[7] we reported on the molecular structure of a 1 : 1 complex (**1b**) of 4,7,10,13-tetraoxa-1,16-dithia[16](1,1′)ruthenocenophane (**1a**) with $HgCl_2$, in which the linear Cl-Hg-Cl moiety was found to be held perpendicularly in the central cavity of the macrocyclic moiety. The distance between the Ru atom and the Hg atom is longer than 3.6 Å, which is too long for a direct Ru-Hg interaction. We have also previously reported[8] on the complexes (**2b—4b**) of polyoxa- and 1,n-dioxathia[n]ruthenocenophanes (**2a—4a**) with $HgCl_2$ (or $AgNO_3$) (**2—4**) and the presence of a strong electron-transfer interaction between the Ru atom and the Hg atom in **3a** and **4a** from the ^{1}H NMR and UV spectral data. The Ru-Hg interaction may be explained by two possible complexing manners: i) the Hg atom incorporated into the crown ether moiety interacts with the Ru atom; ii) the Hg atom is directly coordinated to the Ru atom from the opposite side of the macrocyclic ring. The result is very different from that of the 1:1 silver complex **2b** in which the Ag atom incorporated in the crown ether cavity of the host molecule does not interact with the Ru atom of the ruthenocene. In this paper,[9] we report on the molecular structures of **3b**, **4b** and the 1 : 1 complex **5b** of 1,4,7,10,13,16-hexaoxa[16](1,1′)ruthenocenophane (**5a**) in order to clarify the nature of the Ru-Hg interaction. An X-ray analysis of ruthenocenophane (**3a**) was also carried out in order to compare the structural change of the organic moiety by complexing.

Complexes **3b**, **4b**, and **5b** were prepared by the same method as mentioned in a previous paper.[8]

The molecular structures of **3a** and its $HgCl_2$ complex **3b** are illustrated in Fig. 1. Also, the molecular structures of **4b** and **5b** are also illustrated in Fig. 2. The final atomic parameters for **3b**, **4b**, **5b**, and **3a** are listed in Tables 1—4, and the bond lengths as well as the bond and torsion angles are given in Tables 5—8 for **3b**, **4b**, **5b**, and **3a**, respectively. In the complexes (**3b—5b**) the Hg atom is coordinated directly to the Ru atom of the ruthenocene nucleus from the opposite side of the crown ether moiety, with a slightly distorted trigonal-planar configuration. The Ru-Hg interatomic distances in **3b**, **4b**, and **5b** are 2.683(3), 2.704(1), and 2.696(2) Å, respectively, which essentially equal the sum (2.68 Å) of the covalent radii of Ru and Hg atoms.[10] The results differ completely from that of **1b** in which the Hg atom incorporated in the central cavity of the macrocyclic moiety forms a distorted hexagonal-bipyramidal geometry with the two chlo-

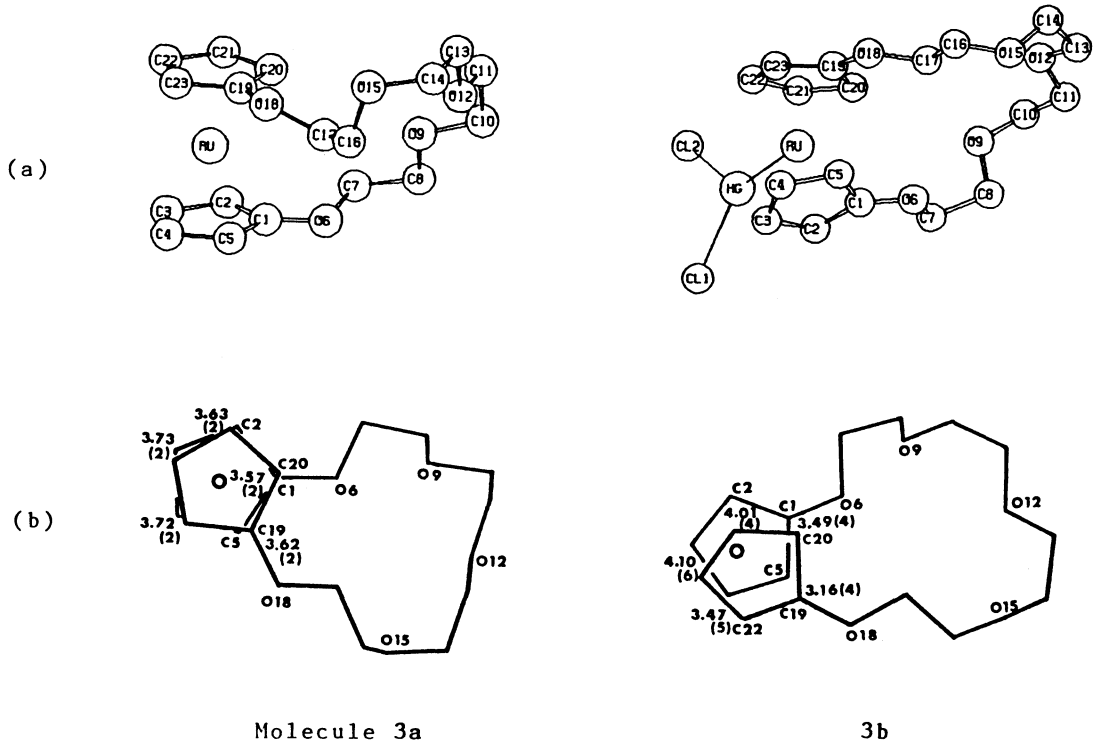

Fig. 1. (a) A perspective view of the molecules with atom numbering. (b) Projection of the organic ligand moiety on the Cp ring containing the C(1) atom are also given with the C·····C distances (Å) between the rings. An open circle denotes the Ru atom.

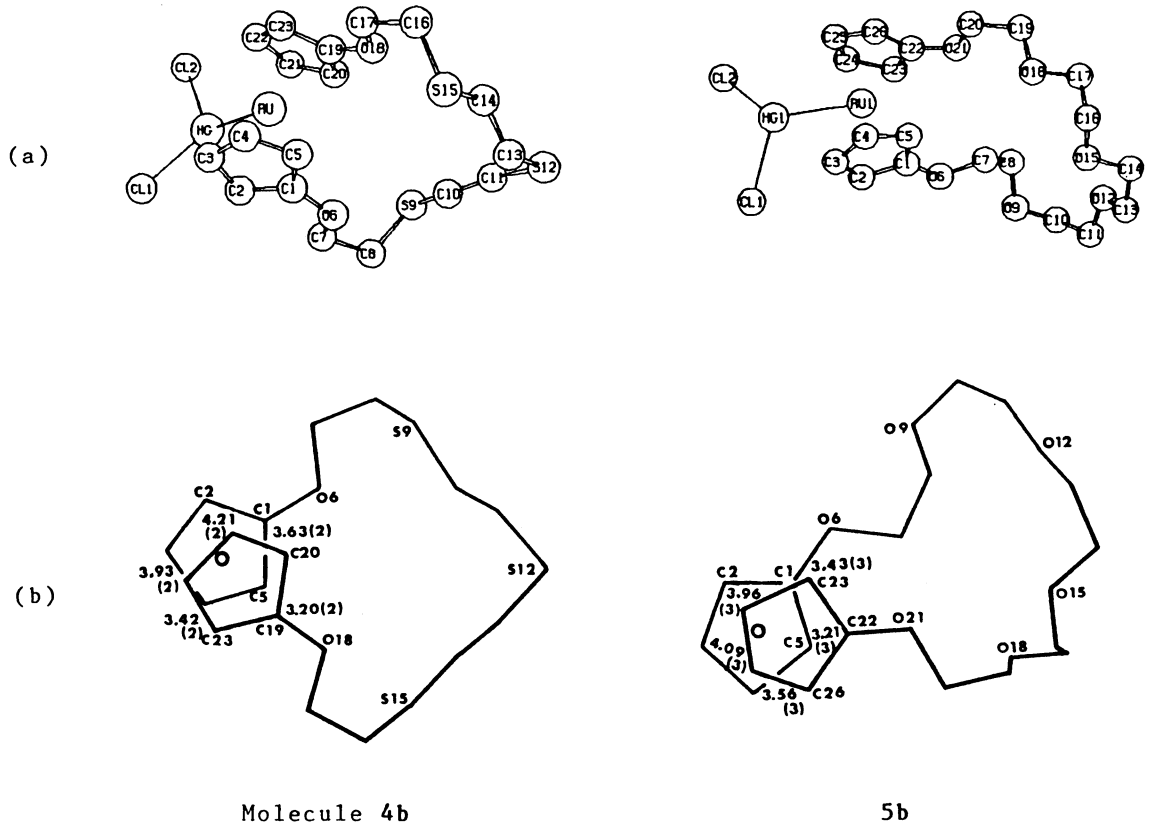

Fig. 2. (a) A perspective view of the molecules with atom numbering. (b) Projection of the organic ligand moiety on the Cp ring containing the C(1) atom are also given with the C·····C distances (Å) between the rings. An open circle denotes the Ru atom.

Table 1. Fractional Atomic Coordinates ($\times 10^4$; $\times 10^3$ for C, O) and Thermal Parameters (Å^2), with Estimated Standard Deviations in Parentheses of **3b**

Atom	x	y	z	B_{eq}[19]
Hg	−190.6(11)	9352.4(12)	2731.8(15)	4.8
Ru	1476(2)	7572(2)	1546(3)	3.9
Cl(1)	5(7)	11559(6)	4126(8)	5.0
Cl(2)	−2284(7)	9481(8)	2101(10)	5.8
C(1)	310(2)	752(3)	333(3)	3.9(0.5)
C(2)	235(2)	871(3)	359(3)	4.3(0.5)
C(3)	225(4)	934(4)	218(5)	7.7(0.9)
C(4)	280(3)	847(3)	101(4)	6.2(0.7)
C(5)	331(3)	733(3)	176(4)	5.0(0.6)
O(6)	358(2)	659(2)	421(3)	5.4(0.4)
C(7)	306(3)	665(3)	567(4)	5.8(0.7)
C(8)	333(3)	532(4)	626(5)	7.1(0.9)
O(9)	258(3)	458(3)	515(3)	8.5(0.7)
C(10)	251(5)	339(5)	565(6)	10.4(1.3)
C(11)	342(4)	241(5)	538(6)	9.6(1.2)
O(12)	341(2)	211(3)	361(3)	8.2(0.7)
C(13)	442(3)	131(4)	335(5)	7.1(0.9)
C(14)	460(3)	127(4)	166(5)	7.0(0.8)
O(15)	487(2)	242(2)	134(3)	6.9(0.6)
C(16)	409(3)	318(4)	35(4)	6.7(0.8)
C(17)	306(3)	395(3)	104(4)	5.4(0.6)
O(18)	243(2)	478(2)	−12(3)	5.6(0.5)
C(19)	149(2)	561(3)	17(3)	4.0(0.5)
C(20)	98(2)	571(3)	177(3)	4.0(0.5)
C(21)	−2(3)	667(3)	136(4)	4.7(0.6)
C(22)	−14(3)	720(3)	−4(4)	5.5(0.7)
C(23)	82(3)	654(3)	−71(4)	4.8(0.6)

Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters (Å^2), with Estimated Standard Deviations in Parentheses of **4b**

Atom	x	y	z	B_{eq}[19]
Hg	650.9(4)	−296.7(7)	1322.7(9)	3.7
Ru	1529.0(7)	2072.4(7)	2677.1(12)	2.4
Cl(1)	911(3)	−3026(4)	455(6)	5.4
Cl(2)	−992(2)	−242(4)	2101(5)	3.7
C(1)	2930(8)	1564(15)	847(17)	2.9
C(2)	2425(8)	117(15)	1028(20)	3.4
C(3)	2023(9)	85(17)	2921(19)	3.7
C(4)	2313(9)	1464(18)	3776(19)	4.2
C(5)	2850(9)	2416(17)	2541(18)	3.5
O(6)	3469(6)	2079(11)	−702(12)	3.3
C(7)	3332(11)	1204(17)	−2247(18)	4.1
C(8)	3837(11)	2127(20)	−3702(20)	5.0
S(9)	3366(4)	3908(6)	−3303(8)	8.5
C(10)	3905(27)	5219(25)	−2067(36)	18.4
C(11)	4059(19)	6613(31)	−2094(33)	13.8
S(12)	4644(3)	8135(5)	−1267(6)	5.3
C(13)	4582(10)	7545(19)	659(21)	4.9
C(14)	3690(10)	7717(18)	2186(21)	4.7
S(15)	3695(3)	7038(6)	4015(6)	5.1
C(16)	2585(10)	7339(18)	5698(20)	4.3
C(17)	1925(9)	6009(17)	5664(18)	3.4
O(18)	1892(6)	5744(10)	3945(12)	3.4
C(19)	1298(8)	4580(15)	3699(18)	2.9
C(20)	1236(9)	4129(14)	2052(17)	3.0
C(21)	514(9)	3021(14)	2309(19)	3.5
C(22)	146(9)	2707(16)	4054(20)	3.6
C(23)	629(9)	3707(16)	4963(18)	3.2

Table 3. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters (Å^2), with Estimated Standard Deviations in Parentheses of **5b**

Atom	x	y	z	B_{eq}[19]
Hg	5062.3(3)	3336.8(9)	3958.7(9)	3.5
Ru	5636(1)	2818(2)	1621(2)	2.6
Cl(1)	5528(2)	4556(5)	6515(6)	3.1
Cl(2)	4495(2)	1931(6)	5278(6)	3.8
C(1)	6419(7)	3637(22)	1876(24)	3.0
C(2)	6159(7)	4113(19)	3101(20)	4.7
C(3)	5752(8)	4863(19)	2389(22)	5.6
C(4)	5752(8)	4740(20)	736(23)	7.3
C(5)	6151(7)	3969(21)	399(21)	9.0
O(6)	6848(5)	2975(18)	2195(15)	6.6
C(7)	7078(8)	2521(29)	841(26)	5.7
C(8)	7404(9)	1457(35)	1378(34)	6.1
O(9)	7794(7)	1902(26)	2564(21)	6.0
C(10)	8263(9)	1336(32)	2555(28)	5.6
C(11)	8570(9)	2030(28)	1479(29)	5.5
O(12)	8357(6)	1846(19)	−84(17)	4.8
C(13)	8529(9)	2731(28)	−1182(31)	5.0
C(14)	8214(9)	2583(28)	−2763(25)	4.4
O(15)	7736(6)	3122(19)	−2596(17)	4.6
C(16)	7400(9)	3006(26)	−4017(25)	4.1
C(17)	7101(9)	1786(27)	−4133(24)	3.6
O(18)	6706(5)	1895(16)	−3184(16)	2.9
C(19)	6328(9)	906(23)	−3514(23)	3.2
C(20)	5900(8)	1180(21)	−2608(22)	4.3
O(21)	6042(5)	865(14)	−973(14)	4.0
C(22)	5693(7)	1100(19)	0(20)	2.9
C(23)	5793(8)	739(18)	1670(21)	3.2
C(24)	5331(9)	958(19)	2305(22)	2.3
C(25)	4978(8)	1541(22)	1110(26)	4.3
C(26)	5211(8)	1672(18)	−301(20)	3.5

Table 4. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters (Å^2), with Estimated Standard Deviations in Parentheses of **3a**

Atom	x	y	z	B_{eq}[19]
Ru	607.5(10)	2464.0(14)	2467.7(12)	2.0
C(1)	985(13)	1321(16)	961(15)	2.7
C(2)	−10(13)	297(17)	1718(15)	2.8
C(3)	−984(13)	1171(19)	1386(17)	3.5
C(4)	−623(13)	2767(20)	409(16)	3.5
C(5)	637(14)	2876(19)	129(15)	3.2
O(6)	2109(8)	1002(12)	869(9)	2.7
C(7)	2493(14)	−397(17)	2038(16)	3.3
C(8)	3847(14)	−286(19)	2049(18)	3.8
O(9)	4446(9)	891(13)	2748(12)	4.1
C(10)	5813(14)	966(21)	2928(21)	4.9
C(11)	6397(16)	2159(22)	3670(19)	4.8
O(12)	6336(10)	3733(13)	2722(11)	4.0
C(13)	6873(17)	5015(23)	3344(20)	5.2
C(14)	6736(14)	6632(21)	2360(19)	4.4
O(15)	5480(9)	6990(13)	2163(12)	4.4
C(16)	4636(14)	6417(18)	1125(17)	3.6
C(17)	3702(15)	4968(20)	1729(21)	5.1
O(18)	2851(8)	5492(11)	2425(11)	2.8
C(19)	2044(12)	4243(17)	3214(16)	2.8
C(20)	2269(14)	2612(18)	4068(16)	3.1
C(21)	1153(14)	1821(20)	4788(15)	3.5
C(22)	308(14)	2958(20)	4381(16)	3.8
C(23)	836(13)	4434(18)	3428(16)	3.3

Table 5. Bond Lengths (Å) and Bond and Torsion Angles (°) in the Organic Ligand of **3b**

1	2	3	4	1-2	1-2-3	1-2-3-4
Pentaoxa-crown moiety						
O(6)	C(1)	C(2)	C(3)	1.30(4)	134(3)	174(3)
O(6)	C(1)	C(5)	C(4)		116(3)	−176(3)
C(2)	C(1)	O(6)	C(7)			15(5)
C(5)	C(1)	O(6)	C(7)			−163(3)
C(1)	O(6)	C(7)	C(8)		114(2)	159(3)
O(6)	C(7)	C(8)	O(9)	1.48(4)	110(3)	−75(4)
C(7)	C(8)	O(9)	C(10)	1.53(5)	106(3)	−168(3)
C(8)	O(9)	C(10)	C(11)	1.45(5)	116(3)	−80(5)
O(9)	C(10)	C(11)	O(12)	1.43(6)	114(5)	−65(6)
C(10)	C(11)	O(12)	C(13)	1.37(8)	109(4)	169(4)
C(11)	O(12)	C(13)	C(14)	1.50(6)	109(3)	−164(3)
O(12)	C(13)	C(14)	O(15)	1.36(5)	111(3)	72(4)
C(13)	C(14)	O(15)	C(16)	1.49(6)	113(3)	−112(4)
C(14)	O(15)	C(16)	C(17)	1.42(5)	119(3)	75(4)
O(15)	C(16)	C(17)	O(18)	1.35(5)	116(3)	174(3)
C(16)	C(17)	O(18)	C(19)	1.50(5)	107(3)	−178(3)
C(17)	O(18)	C(19)	C(20)	1.43(4)	121(2)	2(4)
C(17)	O(18)	C(19)	C(23)			175(3)
O(18)	C(19)	C(20)	C(21)	1.32(4)	123(2)	−177(3)
O(18)	C(19)	C(23)	C(22)		130(3)	177(3)
Cyclopentadienyl ring						
C(1)	C(2)	C(3)	C(4)	1.41(4)	105(3)	8(4)
C(2)	C(3)	C(4)	C(5)	1.45(5)	109(3)	−5(5)
C(3)	C(4)	C(5)	C(1)	1.41(6)	106(3)	−1(4)
C(4)	C(5)	C(1)	C(2)	1.43(5)	109(3)	6(4)
C(5)	C(1)	C(2)	C(3)	1.39(4)	110(3)	−9(4)
C(19)	C(20)	C(21)	C(22)	1.59(4)	97(2)	−5(4)
C(20)	C(21)	C(22)	C(23)	1.44(4)	118(3)	2(4)
C(21)	C(22)	C(23)	C(19)	1.37(5)	104(3)	3(4)
C(22)	C(23)	C(19)	C(20)	1.39(5)	113(3)	−6(4)
C(23)	C(19)	C(20)	C(21)	1.37(4)	108(2)	6(3)
Hg coordination						
Ru		Hg	Cl(1)		2.683(3)	126.3(2)
Ru		Hg	Cl(2)			1281(2)
Ru		Hg	Cl(1′)			99.4(2)
Cl(1)		Hg	Cl(2)		2.528(9)	103.7(3)
Cl(1′)		Hg	Cl(1)		2.943(9)	89.9(3)
Cl(2)		Hg	Cl(1′)		2.451(9)	93.0(3)
Cl(1′)		−x, 2−y, 1−z.				

Table 6. Bond Lengths (Å) and Bond and Torsion Angles (°) in the Organic Ligand of **4b**

1	2	3	4	1-2	1-2-3	1-2-3-4
Trithia-crown moiety						
O(6)	C(1)	C(2)	C(3)	1.367(18)	127.4(14)	175.8(13)
O(6)	C(1)	C(5)	C(4)		122.4(13)	−174.4(12)
C(2)	C(1)	O(6)	C(7)			16(2)
C(5)	C(1)	O(6)	C(7)			−168.5(14)
C(1)	O(6)	C(7)	C(8)		114.1(12)	168.6(12)
O(6)	C(7)	C(8)	S(9)	1.46(2)	106.0(14)	−70.0(16)
C(7)	C(8)	S(9)	C(10)	1.51(3)	114.5(13)	89(2)
C(8)	S(9)	C(10)	C(11)	1.80(2)	100.8(16)	151(3)
S(9)	C(10)	C(11)	S(12)	1.80(5)	123(4)	−172.6(14)
C(10)	C(11)	S(12)	C(13)	1.24(6)	135(3)	−28(5)
C(11)	S(12)	C(13)	C(14)	1.74(3)	103.1(13)	−74.3(17)
S(12)	C(13)	C(14)	S(15)	1.823(19)	111.6(13)	178.3(2)
C(13)	C(14)	S(15)	C(16)	1.48(3)	107.8(13)	179.9(12)
C(14)	S(15)	C(16)	C(17)	1.837(19)	101.0(8)	89.7(13)
S(15)	C(16)	C(17)	O(18)	1.789(18)	115.2(12)	−62.4(16)
C(16)	C(17)	O(18)	C(19)	1.49(2)	107.2(12)	−178.3(12)
C(17)	O(18)	C(19)	C(20)	1.464(18)	115.3(11)	−175.8(11)
C(17)	O(18)	C(19)	C(23)			8(2)
O(18)	C(19)	C(20)	C(21)	1.366(19)	121.4(14)	−174.6(13)
O(18)	C(19)	C(23)	C(22)		129.1(14)	175.9(15)
Cyclopetadienyl ring						
C(1)	C(2)	C(3)	C(4)	1.43(2)	105.9(14)	−1.3(19)
C(2)	C(3)	C(4)	C(5)	1.45(2)	107.2(14)	3(2)
C(3)	C(4)	C(5)	C(1)	1.40(2)	110.6(15)	−2.9(19)
C(4)	C(5)	C(1)	C(2)	1.41(2)	106.1(14)	2.0(19)
C(5)	C(1)	C(2)	C(3)	1.42(2)	110.1(14)	−0.4(19)
C(19)	C(20)	C(21)	C(22)	1.42(2)	106.6(14)	−2.9(19)
C(20)	C(21)	C(22)	C(23)	1.41(2)	1103(14)	3(2)
C(21)	C(22)	C(23)	C(19)	1.42(2)	107.2(14)	−1.4(19)
C(22)	C(23)	C(19)	C(20)	1.44(2)	106.4(14)	−0.3(19)
C(23)	C(19)	C(20)	C(21)	1.44(2)	109.5(13)	1.9(19)
Hg coordination						
Ru		Hg	Cl(1)	2.704(1)	128.0(1)	
Ru		Hg	Cl(2)		122.1(1)	
Ru		Hg	Cl(2′)		106.0(1)	
Cl(1)		Hg	Cl(2)	2.430(5)	104.6(2)	
Cl(2)		Hg	Cl(2′)	2.574(4)	85.0(1)	
Cl(2′)		Hg	Cl(1)	2.885(4)	99.2(2)	
Cl(2′)		−x, −y, −z.				

rine atoms coordinated axially and the Cl-Hg-Cl skelton is almost linear with an angle of 172.7(2)°.[7] The complexing manner is very similar to that of the 1 : 1 complex[3] of dibenzo-18-crown-6 with $HgCl_2$.

In the ^1H NMR spectra of the ruthenocenophanes (**3a** and **4a**), the chemical shift differences between α- and β-protons of the Cp rings are only 0.41 and 0.38 ppm, respectively.[8] The results suggest that the two Cp rings are nearly parallel[11] to each other. Furthermore, CPK model inspections suggest that cavity sizes of **3a** and **4a** are sufficient to encapsule the Hg atom. Also, if the Hg atom is incorporated into the crown ether part of **3b** and **4b**, the Hg atom has to take a distorted pentagonal-bipyramidal geometry with two Cl atoms coordinated axially. However, interestingly, the Hg atom in **3b** and **4b** is directly bonded to the Ru atom of the ruthenocene nucleus from the opposite side of the crown ether moiety. The result suggests that, in the complexes **3b** and **4b**, the pentagonal-bipyramidal geometry of the Hg atom is unstable compared with its hexagonal-bipyramidal geometry in **1b**, although some other factors can not be ruled out. It is noteworthy that the Hg atom in **5b**, which has the same ring number of the crown ether moiety as **1b**, is directly bonded to the Ru atom from the opposite site of the crown ether moiety with a slightly distorted trigonal-planar configuration, although the Hg atom in **1b** is incorporated into the macrocyclic moiety with a distorted hexagonal-bipyramidal geometry (as described above). The difference in the complexing mode of **5b** and **1b** is attributed to the presence of the two sulfur atoms in the crown ether moiety in **1b**, since the sulfur atom coordinates more strongly with the Hg atom than does the oxygen atom. In the complexes (**3b**, **4b**, and **5b**), the sums of the three bond angles about each Hg atom are 358.1, 354.7, and 345.7°, and

Table 7. Bond Lengths (Å) and Bond and Torsion Angles (°) in the Organic Ligand of **5b**

1	2	3	4	1-2	1-2-3	1-2-3-4
Hexaoxa-crown moiety						
O(6)	C(1)	C(2)	C(3)	1.40(3)	122(2)	173.7(19)
O(6)	C(1)	C(5)	C(4)		130(2)	−176(2)
C(2)	C(1)	O(6)	C(7)			179(2)
C(5)	C(1)	O(6)	C(7)			0(4)
C(1)	O(6)	C(7)	C(8)		117(2)	−158(2)
O(6)	C(7)	C(8)	O(9)	1.44(4)	108(3)	−63(3)
C(7)	C(8)	O(9)	C(10)	1.44(5)	110(3)	−144(3)
C(8)	O(9)	C(10)	C(11)	1.43(4)	117(3)	88(3)
O(9)	C(10)	C(11)	O(12)	1.39(4)	112(3)	−68(3)
C(10)	C(11)	O(12)	C(13)	1.48(4)	109(2)	164(2)
C(11)	O(12)	C(13)	C(14)	1.38(3)	114(2)	−171(2)
O(12)	C(13)	C(14)	O(15)	1.42(3)	109(2)	72(3)
C(13)	C(14)	O(15)	C(16)	1.50(4)	107(2)	−178(2)
C(14)	O(15)	C(16)	C(17)	1.42(3)	112(2)	90(3)
O(15)	C(16)	C(17)	O(18)	1.41(3)	114(2)	78(3)
C(16)	C(17)	O(18)	C(19)	1.49(4)	109(2)	165.9(19)
C(17)	O(18)	C(19)	C(20)	1.41(3)	113.3(18)	−173.3(18)
O(18)	C(19)	C(20)	O(21)	1.44(3)	109.7(19)	−75(2)
C(19)	C(20)	O(21)	C(22)	1.48(3)	108.6(18)	178.3(16)
C(20)	O(21)	C(22)	C(23)	1.42(4)	115.1(16)	176.4(16)
C(20)	O(21)	O(22)	C(26)			−4(3)
O(21)	C(22)	C(23)	C(24)	1.34(2)	119.0(17)	−172.7(17)
O(21)	C(22)	C(26)	C(25)		131.2(19)	173.2(2)
Cyclopentadienyl ring						
C(1)	C(2)	C(3)	C(4)	1.40(3)	108.0(18)	5(2)
C(2)	C(3)	C(4)	C(5)	1.41(3)	106.2(18)	−1(3)
C(3)	C(4)	C(5)	C(1)	1.40(3)	110.3(19)	−2(3)
C(4)	C(5)	C(1)	C(2)	1.39(3)	106.6(19)	5(3)
C(5)	C(1)	C(2)	C(3)	1.40(3)	108.5(19)	−6(3)
C(22)	C(23)	C(24)	C(25)	1.45(3)	104.7(18)	−5(3)
C(23)	C(24)	C(25)	C(26)	1.43(3)	110(2)	1(3)
C(24)	C(25)	C(26)	C(22)	1.43(3)	108(2)	3(3)
C(25)	C(26)	C(22)	C(23)	1.41(3)	107.3(18)	−7(2)
C(26)	C(22)	C(23)	C(24)	1.42(3)	109.9(19)	7(2)
Hg coordination						
Ru	Hg	Cl(1)		2.696(2)	115.3(1)	
Ru	Hg	Cl(2)			130.6(1)	
Ru	Hg	Cl(1′)			115.5(1)	
Cl(1)	Hg	Cl(2)		2.670(6)	99.8(2)	
Cl(1′)	Hg	Cl(1)		2.697(6)	87.0(1)	
Cl(2)	Hg	Cl(1′)		2.466(6)	99.1(2)	
Cl(1′)	1−x, 1−y, 1−z.					

Table 8. Bond Lengths (Å) and Bond and Torsion Angles (°) in the Organic Ligand of **3a**

1	2	3	4	1-2	1-2-3	1-2-3-4
Pentaoxa-crown moiety						
O(6)	C(1)	C(2)	C(3)	1.355(14)	130.4(13)	−176.0(15)
O(6)	C(1)	C(5)	C(4)		119.3(13)	176.6(12)
C(2)	C(1)	O(6)	C(7)			−21(2)
C(5)	C(1)	O(6)	C(7)			−163.8(13)
C(1)	O(6)	C(7)	C(8)		113.9(11)	−163.1(11)
O(6)	C(7)	C(8)	O(9)	1.454(19)	107.0(13)	78.2(15)
C(7)	C(8)	O(9)	C(10)	1.486(19)	107.6(10)	174.8(13)
C(8)	O(9)	C(10)	C(11)	1.428(17)	111.0(8)	−178.9(13)
O(9)	C(10)	C(11)	O(12)	1.489(16)	109.7(11)	−73.4(19)
C(10)	C(11)	O(12)	C(13)	1.46(2)	110.1(16)	179.3(15)
C(11)	O(12)	C(13)	C(14)	1.39(2)	115.0(11)	−176.8(14)
O(12)	C(13)	C(14)	O(15)	1.440(18)	113.7(17)	74(2)
C(13)	C(14)	O(15)	C(16)	1.45(3)	112.9(16)	−82.9(19)
C(14)	O(15)	C(16)	C(17)	1.457(16)	116.5(9)	105.4(17)
O(15)	C(16)	C(17)	O(18)	1.414(16)	116.1(17)	68.6(19)
C(16)	C(17)	O(18)	C(19)	1.50(2)	107.5(14)	−171.1(13)
C(17)	O(18)	C(19)	C(20)	1.473(16)	114.4(13)	35(2)
C(17)	O(18)	C(19)	C(23)			−151.3(14)
O(18)	C(19)	C(20)	C(21)	1.375(12)	127.9(14)	175.0(14)
O(18)	C(19)	C(23)	C(22)		123.4(14)	175.2(14)
Cyclopentadienyl ring						
C(1)	C(2)	C(3)	C(4)	1.42(2)	107.8(14)	0.1(19)
C(2)	C(3)	C(4)	C(5)	1.38(2)	104.0(15)	0(2)
C(3)	C(4)	C(5)	C(1)	1.44(2)	108.2(15)	−0.1(19)
C(4)	C(5)	C(1)	C(2)	1.45(2)	104.8(14)	0.2(19)
C(5)	C(1)	C(2)	C(3)	1.43(2)	110.2(13)	−0.2(19)
C(19)	C(20)	C(21)	C(22)	1.45(2)	105.9(14)	−0.6(19)
C(20)	C(21)	C(22)	C(23)	1.46(2)	108.4(15)	0(2)
C(21)	C(22)	C(23)	C(19)	1.42(2)	109.1(15)	0(2)
C(22)	C(23)	C(19)	C(20)	1.41(2)	108.2(14)	−0.5(19)
C(23)	C(19)	C(20)	C(21)	1.44(2)	108.4(13)	0.7(19)

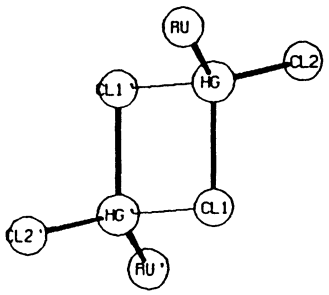

Fig. 3.

the deviations of the Hg atom from the Cl(1)-Ru-Cl(2) plane are 0.201, 0.340, and 0.562 Å, respectively. The deviation of the Hg atom from the Cl(1)-Ru-Cl(2) plane in **5b** is larger than those found in **3b** and **4b**. These values mean that the coordination of the Hg atom found in the present complexes is very close to trigonal, and that most probably those bonds are formed by sp^2 hybridization. This configuration of the Hg atom is very similar to those of $N(CH_3)_4HBr_3$[12] and $[(C_5H_5)_2Ru]_23HgCl_2$.[13] A slight distortion from sp^2 hybridization which would require an exactly planar configuration is due to the interaction with the adjacent molecule as described below. Furthermore, one Cl atom of the complex, which is the atom with the longer distance in the two Hg-Cl bonds, is linked by a weak bond to the Hg atom of the adjacent complex, as shown in Fig. 3. The bond length between Hg-Cl(2) (1−x, 1−y, 1−z) in **5b** which is responsible for the dimer formation is 2.697(6) Å, and the value is shorter than those (2.943 and 2.885 Å) for **3b** and **4b**, respectively. These distances for **3b**, **4b**, and **5b** are about 0.35—0.6 Å shorter than the sum of the van der Waals radii[10] of Hg and Cl atoms. These results indicate that the complexes (**3b**, **4b**, and **5b**) consist of a dimer of the Hg-Cl′ bond in crystals. Therefore, the total coordination sphere of the Hg atom can be described as a trigonal pyramid with the chlorine of the adjacent molecule in the apex.

The deviations of the dihedral angle between the plane of Cl(1)-Ru-Cl(2) and the average plane of the Cp rings in **5b**, 69.4(6) and 75.2(7)°, respectively, were also smaller than those (90.2 and 89.0°, 84.5 and 91.4°) for **3b** and **4b**, respectively. These results are thought to be due to differences in the ring numbers of the crown ether moieties in **3b**, **4b**, and **5b**.

^{13}C NMR Spectra. The ^{13}C NMR spectra of complex **5b** and the ruthenocenophane (**5a**) in DMSO-d_6 were obtained. The bridge-head carbon signal of **5b** is shifted up-field (10.40 ppm) and the α- and β-ring carbon signals down-field (1.0 and 1.1 ppm) compared with those of the ruthenocenophane (**5a**), although the methylene carbon signals are slightly shifted up-field (0.2 ppm). In the ^{13}C NMR spectra of **3b** and **4b**, however, the signals of the bridge-head carbon are shifted only 2.0 and 1.9 ppm up-field compared with those in the corresponding metal free ligands. Seyferth et al.[14] reported that the signal of the bridge-head carbon in (1,1′-ferrocenediyl)phenylphosphine, in which the Cp rings are highly tilted, is shifted up-field about 58 ppm compared with that of the corresponding acyclic compound (diphenylphosphinoferrocene). Also Osborne et al.[15] observed similar results in [1]ferrocenophanes. As shown in Fig. 2, the Cp rings of **5b** are tilted back to allow an interaction of the Hg atom to the ruthenium atom. The angles between the Cp ring planes in **5b** (22.1(9)°), **3b** (23.1(4)°), and **4b** (22.5(7)°) are larger than those found in **3a** (3.8(7)°) and **5a** (2.5°).[16] The angles of **5b** are comparable to those obtained for **3b** (23.1(4)°) and **4b** (22.5(7)°), and the differences in the tilt angles between **3a** and **3b**, **5a** and **5b** are nearly the same. However, the main conformational change in **5b** is reflected in the overlapping pattern between the two Cp rings compared with **3b** and **4b**. The torsion angle C(1)-Cp(1)-Cp(2)-C(22) (Cp1 and Cp2 are centroids of the Cp rings) in **5b** is 53.4°, although those of **3b** and **4b** are 69.3 and 75.9°, respectively. Therefore, the large shift of the bridge-head carbon in **5b** is not attributed only to the tilting of the Cp rings. The distances between the bridge-head carbon atom and C(22) and/or C(23) carbon atoms in the opposite Cp ring in **5b** are also nearly equal to those in **3b** and **4b**. Therefore, the large shift of the bridge-head carbon in **5b** is also not attributed to a steric compression.[17]

At present the reason is not clear.

Experimental

^{13}C NMR spectra were obtained on a JEOL FX-90Q spectrometer with TMS as internal standard.

Materials. 1,4,7,10,13-Pentaoxa[13](1,1′)ruthenocenophane (**3a**), 1,13-dioxa-4,7,10-trithia[13](1,1′)ruthenocenophane (**4a**), dichloro(1,4,7,10,13-pentaoxa[13](1,1′)ruthenocenophane)mercury(II) (**3b**), dichloro(1,13-dioxa-4,7,10-trithia[13](1,1′)ruthenocenophane)mercury(II) (**4b**), and dichloro(1,4,7,10,13,16-hexaoxa[16](1,1′)ruthenocenophane)-mercury(II) (**5b**) were prepared by the same manner as in described in the previous paper. Mercury(II) chloride used was reagent grade. Solvents were dried in appropriate methods and then purified by distillation under nitrogen.

^{13}C NMR Spectra (in DMSO-d_6). **3a**, 128.3(Cb), 60.2(C_β), 64.8(C_α), 71.2, 70.4, 69.8, 69.1(CH_2). **3b**, 130.3(Cb), 64.4(C_α), 61.5(C_β), 72.0, 66.5(CH_2). **4a**, 128.1(Cb), 60.2(C_β), 65.2(C_α), 72.5, 33.7, 32.5, 31.6(CH_2). **4b**, 130.0(Cb), 66.0(C_α), 61.4(C_β), 71.2, 70.3, 69.8, 69.0(CH_2). **5a**, 128.2(Cb), 60.1(C_β), 64.9(C_α), 71.0, 70.3, 70.0, 69.9, 69.1(CH_2). **5b**, 117.8(Cb), 65.9(C_α), 61.2(C_β), 71.0, 70.3, 69.9, 69.1(CH_2).

X-Ray Crystallography. Crystals of dimensions 0.5×0.5×0.2 mm, 0.5×0.2×0.1 mm, 0.4×0.2×0.2 mm, and 0.5×0.2×0.05 mm for the metal free ligand **3a**, complexes **3b**, **4b**, and **5b** were used for X-ray crystallography. Crystal data are as follows: **3a**, $C_{18}H_{24}O_5Ru$, Mw=421.5, triclinic, space group $P\bar{1}$, a=11.107(1), b=8.816(1), c=9.788(1) Å, α=70.48(1), β=99.76(1), γ=101.31(1)°, U=877.6(2) Å^3, Z=2, D_x=1.59 g cm^{-3}, μ(Mo $K\alpha$)=9 cm^{-1}. **3b**, $C_{18}H_{24}O_5RuHgCl_2$, Mw=693.0, triclinic, space group $P\bar{1}$, a=12.043(3), b=10.759(2), c=8.529(2) Å, α=98.76(2), β=101.22(2), γ=77.03(2)°, U=1049.5 Å^3, Z=2, D_x=2.19 g cm^{-3}, μ(Mo $K\alpha$)=84 cm^{-1}. **4b**, $C_{18}H_{24}O_2S_3RuHgCl_2$, Mw=741.2, triclinic, space group $P\bar{1}$, a=17.100(3), b=8.986(1), c=8.618(2) Å, α=105.17(1), β=62.24(1), γ=100.54(1)°, U=1128.1 Å^3, Z=2, D_x=2.18 g cm^{-3}, μ(Mo $K\alpha$)=81 cm^{-1}. **5b**, $C_{20}H_{28}O_6RuHgCl_2$, Mw=737.04, monoclinic, space group $P2_1/a$, a=26.881(7), b=10.334(3), c=8.414(2) Å, β=96.97(2)°, U=2322.2 Å^3, Z=4, D_x=2.11 g cm^{-3}, μ(Mo $K\alpha$)=76 cm^{-1}.

Intensity data for $2\theta \leq 50°$ were recorded on a Rigaku AF C-5R with graphite-monochromatized Mo $K\alpha$ radiation. Among totals of 3084 (**3a**), 3689 (**3b**), 3946 (**4b**), and 4070 (**5b**) independent reflections collected, 2996, 3244, 3394, and 3142 were considered to be observed at the 2.0σ (F_o) level and were corrected for Lorentz and polarization factors, but not for absorption. The structures of **3a**, **3b**, **4b**, and **5b** were solved by the heavy-atom method, and refined by a block-diagonal least-squares method. The positions of the hydrogen atoms could be estimated by using standard geometry. The final refinements with anisotropic temperature factors for the nonhydrogen atoms and isotropic temperature factors for the hydrogen atoms lowered the R values to 0.097 (R_w=0.123, $w=1/\sigma^2(F_o)$), 0.107 (R_w=0.128, w=1.0), 0.055 (R_w=0.057, $w=1/\sigma(F_o)$), and 0.067 (R_w=0.056, $w=1/\sigma^2(F_o)$) for **3a**, **3b**, **4b**, and **5b**, respectively. But, for **3b** the isotropic temperature factors were used for the O and C atoms because of the negative values of several atoms on the anisotropic refinements for the nonhydrogen atoms. Anomalous dispersion corrections were applied to the scattering factors of Hg, Ru, Cl, and S.[18]

Lists of structural factors, anisotropic thermal parameters, and H-atom coordination are being kept at the Chemical Society of Japan (Document No. 8853).

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