Preparation of Polyoxa-1,*n*-dithia[*n*](1,1′)ruthenocenophanes and the Structural Studies of Their Metal Complexes

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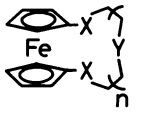
Polyoxa-1,*n*-dithia[*n*](1,1′)ruthenocenophanes were prepared by treatment of 1,1′-ruthenocenedithiol with α, ω-dibromo polyethers. The ruthenocenophanes formed efficiently complexes with soft ions, but not with hard and borderline cations. The ^{1}H- and ^{13}C-NMR spectral data of the silver(I) ion-complexed ruthenocenophanes suggested a partial electron-transfer interaction between the ruthenium atom of the ruthenocene nucleus and the incapsulated silver(I) ion. The crystal structure of the 1:1 complex of 4,7,10,13-tetraoxa-1,16-dithia[16](1,1′)ruthenocenophane with mercury(II) chloride was determined by the X-ray method. The crystals are triclinic, space group $P\bar{1}$, with a=13.722 (3), b=11.678 (4), c=8.179 (2) Å, α=102.69 (3), β=72.82 (2), γ=100.73 (2)°, Z=2, D_x=2.11 g cm^{-3}. The mercury(II) cation and the two chloride ions are situated in the central cavity of the macrocyclic moiety and at the apexes, respectively. The distance between the ruthenium atom of a ruthenocene nucleus and the incapsulated mercury(II) ion is 4.846 (2) Å which is too long for direct metal–metal interaction.

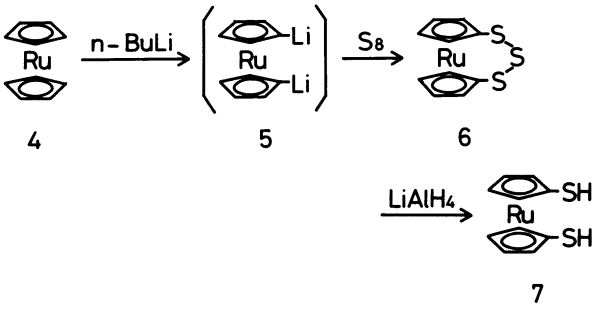
Preparation of a number of crown ethers was first reported by Pedersen twenty years ago.[1] Since that time, a large number and variety of crown, thiacrown and oxathiacrown ethers have been prepared and their complexes with various metal cations and/or organic ammonium cations have been extensively studied.[2] Recently, in order to develop a new functionality, many research groups have attempted to investigate the modified crown ethers.[2] For example, the syntheses of



1 : X=Y=S
2 : X=Y=O
3a: X=S, Y=O
3b: X=O, Y=S

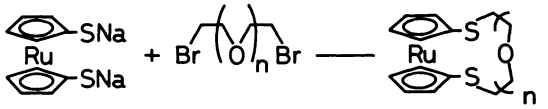
many kinds of macrocyclic compounds containing phosphorus, arsenic, and/or other coordinatable atoms have been reported[2] and in this connection, several research groups[3] have reported new-type crown ethers, thiacrown ethers, and oxathiacrown ethers which contain a ferrocene unit as an integral part of a ring member. Although a number of ferroceno crown ethers have already been reported, a crown ether containing a ruthenocene unit is rare.[4,5] Therefore, we wish to report the syntheses of polyoxa-1,*n*-dithia[*n*](1,1′)-ruthenocenophanes, their ability for forming complexes with various metal cations including transition metals, and the crystal structure of the complex of 4,7,-10,13-tetraoxa-1,16-dithia[16](1,1′)ruthenocenophane with mercury(II) chloride.

Syntheses and Spectral Studies. The reaction of 1,1′-dilithioruthenocene (**5**), which was prepared from ruthenocene (**4**) and butyllithium in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), with sulfur gave 1,2,3-trithia[3](1,1′)ruthenocenophane (**6**) in a 43% yield. The ^{1}H-NMR spectrum of **6** showed the cyclopentadienyl (Cp) ring protons as a AA′BX pattern at δ 4.05—4.83, supporting the assigned structure. Reduction of **6** with lithium aluminum hydride in boiling ether afforded a 94% yield of ruthenocene-1,1′-dithiol (**7**) as colorless crystals. The ^{1}H-NMR spectrum of **7** showed the Cp ring protons as A_2B_2 pattern at δ 4.47 (t, 4H, J=3.5 Hz) and 4.66 (t, 4H, J=3.5 Hz), and SH protons as a singlet at 2.25 (s, 2H). Also the IR spectrum of **7** showed C–H absorption bands of the Cp rings at 1485 and 3097 cm^{-1} and S–H absorption band at 2500 cm^{-1}. Disodium ruthenocene-1,1′-dithiolate (**8**), which was prepared from the reaction of **7** with aqueous sodium hydroxide in ethanol, was allowed to react with dihalide (**9a**) in aqueous ethanol using highly diluted conditions to give 4,7,10,13-tetraoxa-1,16-dithia[16](1,1′)ruthenocenophane (**10a**) as pale yellow crystals in a 17% yield. In the same manner, the reaction of **8** with dihalide (**9b**) and (**9c**) also gave 4,7,10-trioxa-1,13-dithia[13](1,1′)ruthenocenophane (**10b**) and 4,7-dioxa-1,10-dithia[10](1,1′)-ruthenocenophane (**10c**) in 48 and 23% yields, respectively. The structures of **10a—c** were confirmed as follows. For example, the molecular formula of **10a** was deduced to be $C_{20}H_{18}O_4S_2Ru$ by elemental analysis and mass spectroscopy (M$^+$, m/z 498). In the ^{1}H-NMR spectrum of **10a**, the resonance for the methylene protons



4 5 6 7

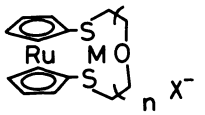
attached to the sulfur atom appeared as a triplet (J= 6.3 Hz, 4H) at δ 2.86, in addition to a singlet (12H, OCH_2CH_2) at δ 3.51 and a triplet (J=6.3 Hz, 4H, OCH_2CH_2S) and a pair of triplets (each 4H, J=1.7 Hz, Cp-H, Cp-H) at δ 4.74 and 4.61. The IR spectrum of **10a** displayed absorptions of the ruthenocene ring and ether linkage at 3090, 1470, and 1102 cm^{-1} respectively, but there was no band arising from the S-H group. The electronic spectra of **10a** (λ_{max} 310 nm in CH_3CN) suggest the presence of a ruthenocene nucleus. The structures of other new ruthenoceno crown ethers (**10b**



8 9a : n=4 10a : n=4
b : n=3 b : n=3
c : n=2 c : n=2

and **10c**) were also determined by a method similar to that described above.

Complexing Ability. The complexing ability of the crown ether with metal cations depends on several factors. These include cavity size of the ligand, cation diameter, spacial distribution of the ring binding sites, the character of the heteroatoms, and other causes.[6] The complexation of polyoxa-1,*n*-dithia[*n*](1,1′)ferrocenophanes (**3a**) with a variety of metal cations has already been reported in the previous paper.[7] The ferrocenophanes (**3a**) showed a highly complexing ability with silver(I) and thallium(I) ions, while little or negligible with alkali metal, calcium, strontium, and lead cations. These results suggest that the character of the heteroatom is the most important factor in the complexation ability. In order to compare the complexing ability of **10** with that of the corresponding ferrocenophanes (**3a**), the extraction ability of **10** with a variety of metal cations was measured by the method described by Pedersen[8] and the results are summarized in Table 1. The complexing ability of **10** was little or negligible for hard cations (K^+, Cs^+, Rb^+, Li^+, Na^+,



11a : n=4, M=Hg^{2+}
X=Cl_2
11b : n=3, M=Ag^+
X=NO_3

Ca^{2+}, Ba^{2+}, and Sr^{2+}) and borderline cations (Cu^{2+}, Co^{2+}, and Ni^{2+}), but excellent for soft cations (Ag^+, Hg^{2+}, and Tl^+). The results of the extraction ability may be explained by the HSAB rule.[9] That is, the successive displacement of an oxygen atom in the macrocyclic ring of the ruthenocenophane by a sulfur atom, which is softer compared with an oxygen atom, increases the affinity to soft ions. The highly complexing ability of **10** with soft ions compared with the corresponding ferrocenophanes (**3a**) suggests some participation of the ruthenium atom of the ruthenocene nucleus in the process of complexation. It is also interesting that the extraction ability of thallium(I) ion showed a remarkable dependence on the cavity size in the macrocycle of **10**.

The ^{1}H-NMR spectrum of **10** in acetonitrile-d_3 was compared with that measured in the presence of an equivalent amount of silver nitrate. The chemical shift of the ligands (**10**) and the difference in the chemical shift between the free ligands and the complexes are shown in Table 2. The change of chemical shifts of the

Table 1. Percentage of metal picrates extracted from the aqueous to the organic phase[a]

Compd	Ag^+	Hg^{2+}	Tl^+	K^+	Cs^+	Rb^+	Cu^{2+}	Cd^{2+}	Li^+ Sr^{2+}	Na^+ Co^{2+}	Ca^{2+} Ni^{2+}	Ba^{2+}
10a	99	95[b]	2	0	0	0	2	1		0		
10b	99	95[b]	33	0	0	0	2	1		0		
10c	99	30[b]	87	5	3	9	3	1		0		

a) Solvent: Water and dichloromethane (1:1). Concentration of ruthenocenocrown ether: 7×10^{-4} M(1M=1 mol dm^{-3}). Concentration of picric acid: 7×10^{-5} M. Concentration of metal nitrates: 0.1 M. b) Mercury dichloride was used instead of nitrate.

Table 2. Low-field shift of ^{1}H-NMR spectra on addition of silver nitrate to a solution of **10** in acetonitrile-d_3

Compd	Chemical shift/δ				
	Cp-H_α	Cp-H_β	SCH_2	OCH_2	
10a	4.74	4.61	2.86	3.51	3.63
10a+$AgNO_3$	(0.23)[a]	(0.21)	(0.32)	(0.03)	(0.17)
10b	4.76	4.61	2.87	3.61	3.59
10b+$AgNO_3$	(0.15)	(0.16)	(0.21)	(0.11)	(0.09)
10c	4.79	4.62	2.87	3.73	3.65
10c+$AgNO_3$	(0.16)	(0.16)	(0.21)	(0.10)	(0.10)

a) Shift changes are presented in parentheses.

ruthenocenophanes (**10**) on complexation with metal cations seems to be attributable to (i) an electronic field effect caused by a incorporated metal cation, (ii) perturbation of the electron density on the carbon atom through Ag-Ru-ring and/or through Ag-S-ring, and (iii) a factor due to the conformational change on complexation. In the case of the complexes of polyoxa[n](1,1′)ferrocenophanes (**2**) with the alkali metal thiocyanates, the differences of the chemical shift between the α- and β-protons of Cp rings depends on the ring size of ligands and the diameter of the incapsulated metal cations.[10] On the contrary, in the ^{1}H-NMR spectrum of the free ligands (**10**) and their silver complexes the chemical shift differences of the α- and β-ring protons were approximately the same, although these signals were remarkably shifted (0.15—0.23 ppm) to down field. If the down field shift is caused by perturbation of the inductive and conjugative effect of the sulfur substituent on coordination to a silver cation through a sulfur atom, the α-protons would be expected to resonate at a lower-field than the β-protons. Therefore, a relatively large down-field shift of the Cp ring protons seems partially to be due to the perturbation of the electron density on the Cp rings by charge transfer from the Ru atom to the Ag(I) ion,

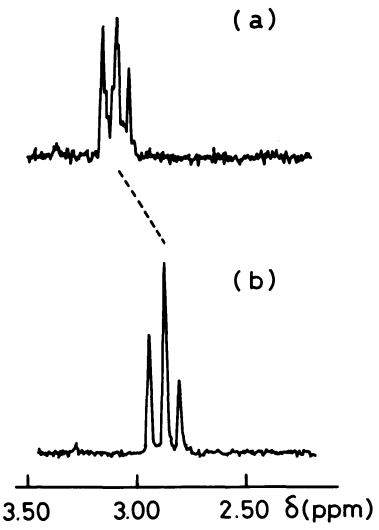


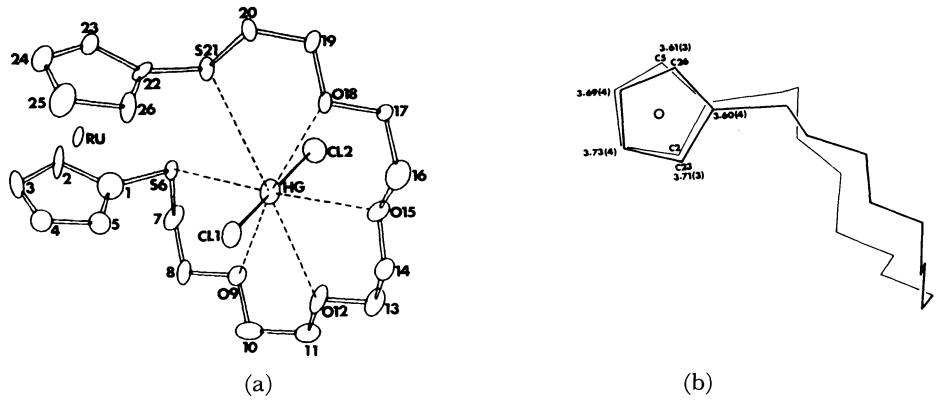
Fig. 1. ^{1}H-NMR Spectra of 10b (b) and the Ag^+ complex of 10b (a).

although other effects could not be ruled out. In the ^{1}H-NMR spectra of **10**, the methylene protons attached to the sulfur atom showed a large down-field shift (0.21—0.32 ppm), but those attached to the oxygen atom showed a small down-field shift (0.03—0.17 ppm). This finding is in good accord with the HSAB rule,[9] and indicates the presence of a strong coordination of the sulfur atom and a weak coordination of the oxygen atom to the central metal cation. Furthermore, the following finding in the ^{1}H-NMR spectra of **10** is also interesting. The protons of the methylene groups in the free ligands appeared as a triplet (J=*ca.* 6.5 Hz), while the methylene protons in the complexes were shifted to down-field and better resolved as shown in Fig. 1. This result suggests that in the complexes, the silver(I) ion is incapsulated by both sulfur and oxygen atoms in the macrocycle and the complexes takes a more rigid conformation. Similar conclusions were also obtained in the ^{13}C-NMR spectra of the free ligands and their silver complexes of **10** (Table 3). In the spectrum of **10a**, the bridgehead carbon, α-, and β-carbons of the Cp rings and the methylene carbons attached to a sulfur atom showed their resonances at δ 88.1, 77.3, 72.6, and 39.6 ppm, respectively, together with the methylene carbons, which were not rigorously assigned, at δ 71.5, 71.3, and 70.9 ppm. However, when an equimolar amount of silver(I) nitrate were added to an acetonitrile-d_3 solution of **10a**, the ^{13}C-NMR spectrum showed resonances at δ 83.1, 78.7, 74.5, and 40.4 ppm (C_b, C_α, C_β, and CH_2S), together with the resonances of other methylene carbons attached to oxygen atoms at δ 71.2, 71.0, 70.8, and 68.0 ppm. The signal of the bridgehead carbon in **10a** shifted to up-field but those of α- and β-carbons of a ruthenocene nucleus shifted to down-field. These results would be explained by the following effects: (i) The direct electron transfer from the ruthenium atom to the complexed silver(I) ion, (ii) the electron transfer *via* the sulfur atom from the Cp ring to the silver(I) ion, and (iii) a conformational change of the ruthenocenophane on complexation. When silver(I) nitrate was added to a solution of **10a**, the peaks of methylene carbons shifted and became more resolved (four peaks→five peaks). This result is also explained on the basis of the rigid conformation of the macrocycle in the ruthenocenophane (**10a**) as described in the

Table 3. Low-field shift of ^{13}C-NMR spectra on addition of silver nitrate to a solution of **10** in acetonitrile-d_3

Compd	Chemical shift/ppm[a]						
	C_b	Cp-H_α	Cp-H_β	SCH_2		OCH_2	
10a	88.1	77.3	72.6	39.6	71.5	71.3	70.9
10a+$AgNO_3$	(−0.50)[b]	(+1.4)	(+1.9)	(+0.8)		(−0.3 —	−1.1)
10b	89.2	77.0	72.3	39.0	71.4	71.2	70.0
10b+$AgNO_3$	(−8.4)	(+2.4)	(+2.5)	(+1.6)		(−0.1 —	−0.15)
10c	90.4	77.1	72.0	39.6	71.5	70.8	
10c+$AgNO_3$	(−3.6)	(+0.6)	(+2.1)	(+1.1)		(−0.7 —	−3.9)

a) Chemical shifts as δ values. A downfield shift is denoted as a positive value. b) Shift changes are presented in parentheses.



(a) (b)

Fig. 2. (a) ORTEP[20] drawing of the complex with atom numbering scheme. (b) Projection of the organic ligand moiety on the Cp ring containing the C(1) atom. The C·····C distances (Å) between the rings are also given. An open circle denotes the Ru atom.

description of ^{1}H-NMR spectra.

Isolation of Complexes. The 1:1 complexes of **10** with $HgCl_2$ and $AgNO_3$, (**11a**) and (**11b**), respectively, were isolated. In the ^{1}H-NMR spectrum (in CD_3CN) of **11a**, the signals of methylene protons next to a sulfur atom, α-, and β-ring protons of ruthenocene nucleus were shifted down-field only +0.19, +0.03, −0.03 ppm, compared with those of **10a**, respectively. On the other hand, the ^{1}H-NMR spectrum of the complex $Cp_2Ru \cdot HgCl_2$ (**12**) in CD_3CN showed a signal at δ 5.31 corresponding to the Cp-ring protons.[11] The down-field shift of the Cp-ring protons of **12**, compared with those of ruthenocene (**4**), is about +0.7 ppm. Hence, the difference in the chemical shift between the free ligand (**10a**) and the complex (**11a**) seems to be attributable to the inductive and field effects *via* the coordinated sulfur atom by complexation of mercury(II) ion into the crown ether part of the ligand, although a possibility of the weak coordination of the incorporated mercury(II) ion to the Ru atom of ruthenocene nucleus cannot be ruled out. The above explanation was supported by the X-ray crystallographic analysis of **11a** as described below.

Crystal Structure of 11a. The conformation of the complex (**11a**) is illustrated in Fig. 2, which also shows the atom labels used. The positional parameters for non-hydrogen atoms are listed in Table 4. Also, the bond lengths, bond angles and torsion angles are listed in Table 5.

The complex can be divided into two parts: The complexing unit containing dithia-18-crown-6 like moiety which is defined by S(6) to S(21), and the ruthenocene unit. In the complexing unit, the mercury(II) ion and the two chloride ions are situated in the central cavity and at the apexes, respectively. The six heteroatoms (two S and four O atoms) take a slightly distorted half chair form in which O(12) and O(15) deviate by 0.61 and −0.16 Å, respectively, to the side of Cl(1) from the mean plane of the remaining four atoms, S(1), O(9), O(18), and S(21), with a maximum deviation of 0.06 Å at O(9). The mercury(II) ion is situated in the same plane with a deviation of 0.17 Å. The intramolecular atomic distances between the mercury(II) ion and the six heteroatoms are 3.034(6), 3.120(18), 2.888(17), 2.838(17), 3.048(17), 3.330(6) Å with S(6), O(9), O(12), O(15), O(18), and S(21), respectively. These values are longer than the sum of the ionic radius of a mercury(II) ion (1.10 Å) and the van der Waals radius of a sulfur atom (1.85 Å) or O (1.40 Å).[12]

Table 4. Fractional atomic coordinates (×10^4), with estimated standard deviations in parentheses

Atom	x	y	z	B_{eq}(Å^2)[a]
HG	2782(1)	1604(1)	3616(1)	2.7
RU	2091(1)	5675(1)	5521(2)	1.4
CL(1)	1408(4)	2014(5)	2814(8)	2.8
CL(2)	4010(5)	984(6)	4506(8)	3.6
C(1)	3477(19)	5165(18)	3624(30)	2.5
C(2)	3684(18)	6405(18)	4268(31)	2.4
C(3)	3014(21)	6981(20)	3846(34)	3.3
C(4)	2405(19)	6173(22)	2956(30)	2.7
C(5)	2685(17)	5017(20)	2751(29)	2.3
S(6)	4059(4)	4021(4)	3920(7)	1.7
C(7)	5188(18)	3956(20)	2040(33)	2.7
C(8)	4907(18)	3430(20)	421(30)	2.4
O(9)	4549(13)	2171(14)	371(21)	2.7
C(10)	4269(21)	1589(25)	−1192(34)	3.6
C(11)	4014(19)	323(23)	−1199(31)	2.9
O(12)	3085(12)	116(14)	230(21)	2.5
C(13)	2785(20)	−1098(20)	260(32)	2.8
C(14)	1765(21)	−1217(20)	1589(30)	2.9
O(15)	1954(12)	−824(13)	3253(20)	2.4
C(16)	1026(17)	−1118(19)	4613(33)	2.6
C(17)	1270(18)	−562(18)	6316(27)	2.1
O(18)	1186(12)	656(12)	6656(20)	2.2
C(19)	1303(19)	1184(19)	8368(29)	2.3
C(20)	1123(17)	2472(19)	8762(28)	2.1
S(21)	2184(4)	3360(5)	7474(7)	2.2
C(22)	1577(18)	4543(19)	7539(28)	2.1
C(23)	1770(18)	5749(19)	8327(29)	2.2
C(24)	1110(19)	6435(20)	8011(34)	2.9
C(25)	472(18)	5666(22)	7052(34)	3.1
C(26)	769(18)	4497(19)	6717(31)	2.4

a) W.C.Hamilton, Atca Cryst., **12**, 609 (1959).

TABLE 5. BOND LENGTHS (l/Å) AND BOND AND TORSION ANGLES (ϕ/°) IN THE ORGANIC LIGAND

1	2	3	4	1-2	1-2-3	1-2-3-4
Dithia-crown moiety						
C(2)	C(1)	S(6)	C(7)	1.43(3)	126(2)	−89(2)
C(5)	C(1)	S(6)	C(7)	1.43(4)	126.3(18)	93(2)
C(1)	S(6)	C(7)	C(8)	1.77(2)	101.8(12)	−73(2)
S(6)	C(7)	C(8)	O(9)	1.83(2)	111.8(19)	−70(2)
C(7)	C(8)	O(9)	C(10)	1.46(4)	110.6(19)	−179(2)
C(8)	O(9)	C(10)	C(11)	1.46(3)	113.8(18)	174.8(17)
O(9)	C(10)	C(11)	O(12)	1.44(4)	110(2)	65(3)
C(10)	C(11)	O(12)	C(13)	1.45(4)	109(2)	179(2)
C(11)	O(12)	C(13)	C(14)	1.48(3)	111.3(17)	−172.5(18)
O(12)	C(13)	C(14)	O(15)	1.41(3)	107(2)	−73(3)
C(13)	C(14)	O(15)	C(16)	1.50(4)	107(2)	−169.5(19)
C(14)	O(15)	C(16)	C(17)	1.42(3)	110.1(14)	−174.5(18)
O(15)	C(16)	C(17)	O(18)	1.46(3)	106.0(17)	79(2)
C(16)	C(17)	O(18)	C(19)	1.51(4)	109.3(16)	173.6(18)
C(17)	O(18)	C(19)	C(20)	1.41(2)	110.4(13)	−175.4(17)
O(18)	C(19)	C(20)	S(21)	1.44(3)	109.4(16)	−71(2)
C(19)	C(20)	S(21)	C(22)	1.52(3)	111.0(17)	158.3(17)
C(20)	S(21)	C(22)	C(23)	1.82(2)	100.0(11)	115(2)
C(20)	S(21)	C(22)	C(26)			−68(2)
S(21)	C(22)	C(23)		1.73(2)	129(2)	
S(21)	C(22)	C(26)			125(2)	
Cyclopentadienyl moiety						
C(1)	C(2)	C(3)	C(4)	1.43(3)	108(2)	−1(3)
C(2)	C(3)	C(4)	C(5)	1.39(3)	110(2)	−1(3)
C(3)	C(4)	C(5)	C(1)	1.37(4)	109.1(18)	2(3)
C(4)	C(5)	C(1)	C(2)	1.43(3)	106.1(19)	−2(3)
C(5)	C(1)	C(2)	C(3)	1.43(4)	107.4(15)	2(3)
C(22)	C(23)	C(24)	C(25)	1.43(3)	110(2)	1(3)
C(23)	C(24)	C(25)	C(26)	1.42(4)	107.9(19)	−2(3)
C(24)	C(25)	C(26)	C(22)	1.41(4)	107.7(18)	2(3)
C(25)	C(26)	C(22)	C(23)	1.44(3)	109(3)	−1(3)
C(26)	C(22)	C(23)	C(24)	1.44(4)	105.7(15)	0(3)

The Cl-Hg-Cl angle is 172.7 (2)° which slightly deviates from the expected 180°. The Hg-Cl bond lengths of 2.327(7) and 2.304(7)Å are in agreement with reported values for the linear Hg-Cl bond.[13] Thus, the mercury(I) ion forms a distorted hexagonal-bipyramidal geometry with the two chloride ions coordinated axially. The organic ligand moiety in present complexing unit has structural similarity compared with that in the complex of $HgCl_2$:1,4-dithia-18-crown-6 (HGDTC).[14] The 13 torsion angles about the chemically corresponding bonds between the both complexes agree well, and the average difference is about 5°. However, in the case of HGDTC the mercury(II) ion interacts with the two sulfur atoms from the outside of the macrocyclic ring because the C-C bridge joining the sulfur atoms directs into the interior of the ring. The Cp rings take an eclipsed conformation to each other and the dihedral angle between the rings is 3.4°. The Ru···C and inter-ring C···C distances of the ruthenocene unit are in the ranges of 2.18(3) to 2.23(3)Å and 3.60(4) to 3.73(4)Å with the average values of 2.21 and 3.67Å, respectively, and the distances from the Ru atom to the best plane of the Cp rings are 1.84(3) and 1.83(3)Å. These values agree well with those of ruthenocene[15] and [4](1,1')ruthenocenophane.[16] The distance between the Ru atom of the ruthenocene nucleus and the mercury(II) ion incorporated is 4.846(2)Å which is too long for direct metal-metal interaction, because the sum of the van der Waals radius of the Ru atom and the ionic radius of the Hg^{2+} ion is 3.15Å[12].

The crystal packings are formed with van der Waals forces; the short intermolecular distances are 3.36(3), 3.49(3), and 3.707(8)Å for C(3)···O(15) (x,1+y,z), Cl(1)···C(16) (−x,−y,1−z), and S(6)···S(6) (1−x,1−y,1−z), respectively.

Experimental

The melting points are uncorrected. The electronic spectra were measured on a Hitachi 340 Spectrometer. The ^{1}H-NMR and ^{13}C-NMR spectra were obtained on a JEOL FX-90Q Spectrometer, TMS being chosen as an internal standard. The mass spectra were taken by using a Hitachi M-80 Spectrometer. The IR spectra were measured on a JASCO DS-701G Diffraction Grating Infrared Spectrophotometer.

Material. All solvents and reagents were used as purchased unless otherwise specified. Ruthenocene, 1,8-dibromo-3,6-dioxaoctane, 1,11-dibromo-3,6,9-trioxaundecane, and 1,14-dibromo-3,6,9,12-tetraoxatetradecane were prepared according to the literatures. Silica gel for thinlayer chromatography utilized Wakogel B-5F.

1,2,3-Trithia[3](1,1')ruthenocenophane (6). To a mixture

of hexane (3.5 cm³) and TMEDA (3.0 cm³, 0.019 mol) was added a solution of butyllithium (0.024 mol) in hexane (18 cm³) and then a solution of ruthenocene (2.0 g, 8.65 mmol) in hexane (35 cm³) under nitrogen. The mixture was then further stirred for 8 h at room temperature. To the mixture was added 1,2-dimethoxyethane (90 cm³, 0.86 mol) and sulfur (1.72 g, 0.05 mol) and the mixture was then stirred for 12 h at refluxing temperature. After the mixture had been cooled to room temperature, the precipitates were filtered and washed with ether. The filtrate and the washings were combined, washed with 10% aq sodium hydroxide solution and water, and concentrated *in vacuo*. Sublimation of the residue at 130°/1.5 mmHg (1 mmHg=133.322 Pa) gave crude **6**. Recrystallization of the crude material from hexane gave pure **6** as yellow flat plates, mp 183.5—184°C, in 42.7% yield. Found: C, 36.76; H, 2.55%. Calcd for $C_{10}H_8S_3Ru$: C, 36.91; H, 2.48%. MS (70 eV): *m/z* 326 (M^+). ^{1}H-NMR ($CDCl_3$): δ=4.05—4.83 (m, 8H). IR (KBr): 3097 and 1401 cm^{-1}.

Ruthenocene-1,1'-dithiol (7). **6** (1.78 g, 5.47 mmol) was added to ether (107 cm³) containing lithium aluminum hydride (0.05 g, 0.013 mol) under nitrogen. Stirring was continued at refluxing temperature for 3 h, and the mixture was then cooled to ice-water temperature. To the mixture was added dropwise 1.5% aq potassium hydroxide solution (142 cm³) and an aq layer was separated. The aq solution was extracted with three 20 cm³ portions of ether. The aq solution was acidified with concd hydrochloric acid until it became weakly acidic, and then extracted with four 20 cm³ portions of ether. The combined extracts were dried and concentrated to give pure **7** as colorless crystals, mp 116—117°C, in 94% yield. Found: C, 40.54; H, 3.59%. Calcd for $C_{10}H_{10}S_2Ru$: C, 40.66; H, 3.42%. MS (70 eV): *m/z* 296 (M^+). ^{1}H-NMR ($CDCl_3$): δ=2.25 (s, 2H, -SH), 4.47 (t, *J*=3.5 Hz, 4H, Cp-H), and 4.66 (t, *J*=3.5 Hz, Cp-H). IR (KBr): 3097, 2500, and 1419 cm^{-1}.

*General Procedure for Polyoxa-1,*n*-dithia[*n*](1,1')ruthenocenophanes. 4,7-Dioxa-1,10-dithia[10](1,1')ruthenocenophane (10c).* A solution of **7** (1.51 g, 5.12 mmol) in 20% aq sodium hydroxide solution (100 cm³) and a solution of 1,8-dibromo-3,6-dioxaoctane (1.76 g, 6.38 mmol) in 60% ethanol (100 cm³) were added dropwise at the same rate to 60% ethanol (200 cm³) for a period of 3.5 h at refluxing temperature under nitrogen, and then further stirred for 3 h. After the solution had been cooled to room temprerature, 100 cm³ of water was added to the reaction mixture. The solution was extracted with four 30 cm³ portions of ether. The ether extracts were combined, washed with water, and concentrated *in vacuo*. The residual oil was chromatographed by silica gel TLC (using benzene–acetone 10:1 as eluent). The third fraction was eluted with acetone at room temperature, followed by filtration. The evaporation of the solvent gave pale yellow oil which solidified on standing. Recrystallization of the crude material from hexane gave a pure **10c** as yellow needles, mp 101.0—101.5°C, in 23.4%. Found: C, 46.66; H, 5.12%. Calcd for $C_{16}H_{20}O_2S_2Ru$: C, 46.92 ; H, 4.93%. MS (70 eV): *m/z* 410 (M^+). IR (KBr): 3075, 2850, 1410, and 1127 cm^{-1}. UV (MeOH:H_2O=1:1): λ_{max} 320 nm (ε=472).

4,7,10-Trioxa-1,13-dithia[13](1,1')ruthenocenophane (10b). Pale yellow flat plates, 48% yield. Found: C, 47.96; H, 5.48%. Calcd for $C_{18}H_{24}O_3S_2Ru$: C, 47.66; H, 5.68%. MS (70 eV): *m/z* 454 (M^+). IR (KBr): 3090, 2860, 1470, 1416, 1352, 1282, 1115, and 807 cm^{-1}. UV (MeOH:H_2O=1:1): λ_{max} 320 nm (ε=472).

4,7,10,13-Tetraoxa-1,16-dithia[16](1,1')ruthenocenophane (10a). Pale yellow flat plates, mp 46.2—48.0°C, 17% yield. Found: C, 48.48; H, 5.81%. Calcd for $C_{20}H_{28}O_4S_2Ru$: C, 48.26; H, 5.68%. MS (70 eV): *m/z* 498 (M^+). IR (KBr): 3090, 2860, 1480, 1418, 1353, 1286, 1136, and 811 cm^{-1}. UV (MeOH:H_2O=1:1): λ_{max} 320 nm (ε=472).

Complex of 4,7,10,13-Tetraoxa-1,16-dithia[16](1,1')ruthenocenophane (10a) with Mercury(II) Chloride. A solution of **10a** (41 mg, 0.082 mmol) in acetonitrile (1 cm³) was added dropwise to a solution of mercury(II) chloride (22 mg, 0.081 mmol) in acetonitrile (1 cm³). The resulting precipitates were filtered and washed with a small amount of acetonitrile to give a pure 1:1 complex (**11a**), mp 172.0—173.0°C, in 69% yield. Found: C, 31.44; H, 3.75%. Calcd for $C_{20}H_{28}O_2S_2Ru$: C, 31.23; H, 3.68%. IR (KBr): 3090, 2910, 1470, 1411, 1355, 1298, 1102, and 810 cm^{-1}. UV (CH_3CN): λ_{max} 310 nm (ε=455).

Complex of 4,7,10-Trioxa-1,13-dithia[13](1,1')ruthenocenophane (10b) with Silver(I) Nitrate. To a solution of **11b** (30 mg, 0.066 mmol) in acetonitrile was added a solution silver(I) nitrate (11 mg, 0.065 mmol) in acetonitrile (1 cm³). To the mixture was added dropwise 3 cm³ of ether to give colorless precipitates. The precipitates were washed with a small amount of acetonitrile and then ether to give a pure 1:1 complex (**11b**), mp 157.0—157.5°C, in 84% yield. Found: C, 34.51; H, 3.78; N, 2.22%. Calcd for $C_{18}H_{24}NO_5S_2AgRu$: C, 34.67; H, 3.89; N, 2.25%. IR (KBr): 3190, 2920, 2870, 1470, 1450, 1384, 1110, 1025, and 810 cm^{-1}. UV (CH_3CN): λ_{max} 310 nm (ε=403).

Extraction Ability. Extraction ability of the ruthenocenophanes with metal picrate was examined by the method described in the previous paper.[17] The results are summarized in Table 1.

X-Ray Crystal Determination of 11a. A crystal of dimensions 0.5×0.3×0.2 mm obtained from methanol, was used for the intensity measurement. Intensity data were obtained on a Rigaku AFC5 apparatus equipped with a rotating-anode X-ray generator and using a graphite monochrometer (λ(Cu$K\alpha$)=1.5418 Å, $2\theta \geq 128°$) was used. The data were corrected for Lorentz and polarization effects but not for absorption. Among the 3749 unique reflections collected, 3352 were considered to be observed at the 2.0σ (F_o) level.

Crystal Data. $C_{20}H_{28}O_4S_2Cl_2RuHg$, M=769.2. Triclinic, *a*=13.722(3), *b*=11.678(4), *c*=8.179(2) Å, α=102.69(3), β=72.82(2), γ=100.73(2)°, *Z*=2, D_x=2.11 g cm^{-3}, space group $P\bar{1}$.

The structure was solved by the combination of the heavy atom technique and direct methods using MULTAN[18] and refined by block-diagonal least-squares methods. Positions of the hydrogen atoms were estimated from standard geometry. The final refinements with anisotropic temperature factors for the non-hydrogen atoms were reduced the R to 0.089. The anomalous dispersion corrections were applied to the scattering factors of Hg, Ru and Cl.[19]

Thermal parameters for non-hydrogen atoms and observed and calculated structure factors are kept at the Chemical Society of Japan (Document No. 8530).

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