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Preparation of Polyoxa- and Dioxapolythia[*n*](1,1′)-ruthenocenophanes and Their Metal Complexes

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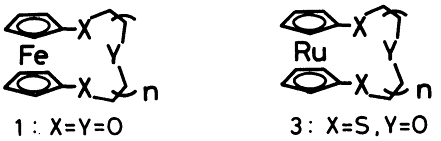
Polyoxa- and dioxapolythia[*n*]ruthenocenophanes were prepared by the reaction of 1,1′-diacetoxyruthenocene with α-(2-bromoethyl)-ω-bromopoly(oxyethylene) in the presence of alkali metal hydroxides and by the reaction of 1,1′-bis(2-chloroethoxy)ruthenocene with dithiolate in the presence of sodium hydroxide, respectively. The extraction ability of their compounds was excellent for mercury(II) and thallium(I) ions. The ruthenocenophanes with oxygen atoms attached to the ruthenocene nucleus showed excellent extraction ability for a silver(I) ion, although the corresponding ferrocenophane analogs decomposed in similar reaction conditions. The ruthenocenophanes formed 1 : 1 complexes with mercury(II) and silver(I) ions. ^{1}H-NMR, electronic, and IR spectral data of their complexes showed the presence of direct electronic interaction between the mercury(II) or silver(I) ion and the ruthenium atom of ruthenocenophanes.

For the purpose of syntheses of crown compounds possessing specific properties, several research groups to date have reported on the syntheses and complexing ability of crown ether typed compounds containing a ferrocene nucleus in their macrocyclic skeleton.[1—5)] Morrison *et al.* reported on the Ru–Hg and the Fe–Hg interaction in the mercury adducts of ruthenocene and ferrocene.[6)] However, Biernat *et al.* suggested that the interaction between the iron atom of the ferrocene nucleus and the complexed rubidium ion was not present from their electronic spectral data.[1b)] Our X-ray analysis elucidated no interaction between the iron atom of 1,4,7,10,13-pentaoxa[13](1,1′)ferrocenophane and the complexed sodium cation in the solid state.[5b)] The above results suggest that the soft mercury(II) and silver(I) ions which were incorporated by the crown site of the ferroceno-crown ethers might cause the strong interaction with the iron atom of the ferrocene nucleus. Although the compound 2 with sulfur atoms at the 1,*n*-position of the ferrocenophane was not decomposed by treating with silver(I) and mercury(II) ions, the compound 1 with oxygen atoms at the 1,*n*-position of the ferrocene nucleus, decomposed by their metal ions.



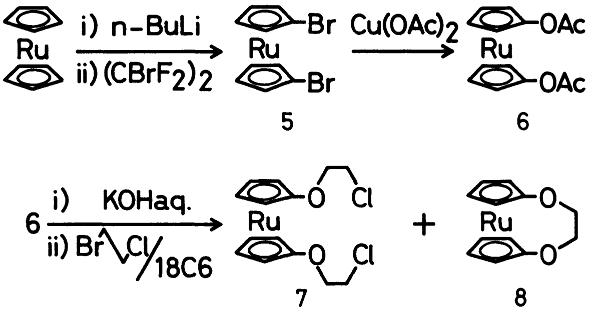
1 : X=Y=O
2 : X=S, Y=O or S
3 : X=S, Y=O
4 : X=Y=S

a : n=1, b : n=2, c : n=3, d : n=4

The enhanced stability of the silver complexes of **2** may be attributed to the pπ-dπ interaction of sulfur and iron atoms of the ferrocene nucleus of **2**.[2d)] It is well-known[7)] that ruthenocene is more stable for oxidation compared with ferrocene as seen by the reduction potential of both metallocene. Therefore, in this paper, we wish to report on the synthesis of polyoxa- and dioxapolythia[*n*]-(1,1′)ruthenocenophanes and their complexing ability with transition metal ions, along with alkali and alkaline earth metal ions.[8)]

Results and Discussion

Syntheses of Polyoxa[n](1,1′)- (10) and Oxathia[n]-(1,1′)ruthenocenophanes (11). In order to obtain the starting material of **10**, 1,1′-diacetoxyruthenocene **6** was prepared according to the method of the synthesis of 1,1′-diacetoxyferrocene.[5b)] 1,1′-Dilithioruthenocene which was prepared by the reaction of ruthenocene with butyllithium in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), was reacted with 1,2-dibromo-1,1,2,2-tetrafluoroethane to give 1,1′-dibromoruthenocene **5** in 53% yield. Compound **5** was reacted with copper(II) acetate to give **6** in 53% yield. After **6** had been hydrolyzed by alkali metal hydroxide, α-(2-bromoethyl)-ω-bromopoly(oxyethylene) (**9**) was immediately added to the hydrolyzate. The stirring was



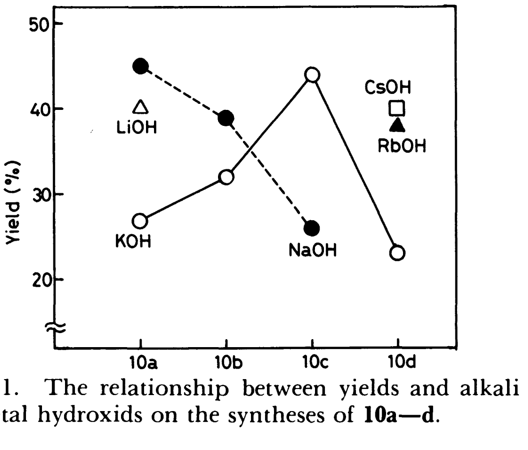


Fig. 1. The relationship between yields and alkali metal hydroxids on the syntheses of **10a—d**.

continued for 5 h at reflux temperature under nitrogen. The reaction mixture was treated by the usual method and subsequently separated by Silica-gel TLC to give 10. In the above reactions several kinds of alkali metal hydroxide were used for hydrolysis. As shown in Fig. 1, the use of sodium and potassium hydroxides resulted maximum yield of **10a** and **10c**, respectively. In the synthesis of **10d**, the use of cesium hydroxide was most favorable. This result is correlated to the cavity size of metallocenophanes.[9,10] Compound **7**, the starting material for dioxapolythia[n](1,1′)ruthenocenophanes, was synthesized by the reaction of **6** with 1-bromo-2-chloroethane in the presence of a catalytic amount of 18-crown-6. To prepare **11a**, a mixture of **7** and sodium sulfide in *N*,*N*-dimethylformamide (DMF) was stirred at reflux temperature for 9 h. The reaction mixture was treated by the usual method and separated by silica-gel TLC to give **11a** in 11% yield. The compound **7** was reacted with disodium 1,2-ethanedithiolate in ethanolic tetrahydrofuran (THF) to give **11b** and **11c** in 25 and 5% yields, respectively. The possible mechanism of the formation of **11c** in the above reaction may be the same as that for ferrocene analogues.[5f] Similarly, **7** was reacted with disodium 2,2′-thiobis(ethanethiolate) in ethanolic THF to give only **11c** in 63% yield.

The ^{1}H-NMR and ^{13}C-NMR spectra of **10—11** are summarized in Table 1. The structures of the new compounds were determined on the basis of ^{1}H-NMR, ^{13}C-NMR, mass spectra and elemental analyses. For example, the molecular formula of **10c** was deduced to be $C_{18}H_{24}O_5$ Ru by the elemental analysis and mass spectroscopy (M^+ 422). As the ^{1}H-NMR spectrum of **10c** showed α- and β-protons of the ruthenocene nucleus appeared as two triplets (J=1.8 Hz) at δ 4.63 and 4.24, respectively and the methylene protons appeared as a multiplet of the A_2B_2 type at δ 3.89—3.49 and a singlet at δ 3.58. In the completely decoupled ^{13}C-NMR spectrum of **10c**, bridge-head, α-, and β-carbons of the ruthenocene nucleus appeared at δ 128.3, 60.2, and 64.8 ppm, respectively. Furthermore, eight methylene carbons appeared as four signals at δ 71.2, 70.4, 69.8, and 69.1 ppm. The structures of the new other compounds were also determined by a similar method described above.

The Extraction Ability. The measurement of extraction ability was carried out by the method

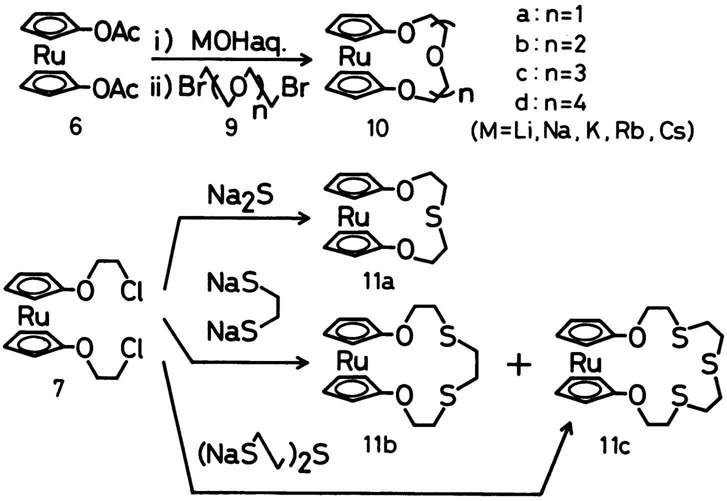


TABLE 1. ^{1}H- AND ^{13}C-NMR SPECTRAL DATA OF **10** AND **11**

Compd	^{1}H-NMR Spectra (chemical shift/ppm)[a)]	^{13}C-NMR Spectra (chemical shift/ppm)[b)]
10a	4.68 (J=1.8Hz, 4H), 4.21 (J=1.8Hz, 4H), 4.04—3.63 (m, 8H)	126.7 (Cb), 59.7 (Cα), 64.3 (Cβ), 71.7, 67.7 (CH$_2$)
10b	4.65 (t, J=1.8Hz, 4H), 4.23 (t, J=1.8Hz, 4H), 3.95—3.52 (m, 8H), 3.60 (s, 4H)	128.4 (Cb), 60.2 (Cα), 64.6 (Cβ), 71.1, 71.0, 69.1 (CH$_2$)
10c	4.63 (t, J=1.8Hz, 4H), 4.25 (t, J=1.8Hz, 4H), 3.87—3.56 (m, 8H), 3.58 (s, 8H)	128.3 (Cb), 60.2 (Cα), 64.8 (Cβ), 71.2, 70.4, 69.8, 69.1 (CH$_2$)
10d	4.62 (t, J=1.8Hz), 4.25 (t, J=1.8Hz, 4H), 3.89—3.49 (m, 8H), 3.58 (s, 12H)	128.2 (Cb), 60.1 (Cα), 64.9 (Cβ), 71.0, 70.3, 70.0, 69.9, 69.1 (CH$_2$)
11a	4.91 (t, J=1.8Hz, 4H), 4.44 (t, J=1.8Hz, 4H), 4.22 (t, J=6.2Hz, 4H), 3.06 (t, J=6.2Hz, 4H)	126.8(Cb), 60.2 (Cα), 64.5 (Cβ), 72.4, 30.8 (CH$_2$)
11b	4.64 (t, J=1.8Hz, 4H), 4.29 (t, J=1.8Hz, 4H), 3.95 (t, J=6.2Hz, 4H), 2.90 (s, 4H), 2.82 (t, J=6.2Hz, 4H)	128.4 (Cb), 60.5 (Cα), 65.0 (Cβ), 73.7, 33.3, 31.3 (CH$_2$)
11c	4.72 (t, J=1.8Hz, 4H), 4.31 (t, J=1.8Hz, 4H), 3.88 (t, J=6.2Hz, 4H), 2.86 (s, 8H), 2.81 (t, J=6.2Hz, 4H)	128.1 (Cb), 60.2 (Cα), 65.2 (Cβ), 72.5, 33.7, 32.5, 31.6 (CH$_2$)

a) Compounds **10** and **11** were measured in CD_3CN and DMSO-d_6, respectively. b) Compounds **10** and **11** were measured in $CDCl_3$.

Table 2. Percentage of metal picrates extracted from the aqueous to organic phase[a,b)]

Compd	**3b**	**3c**	**3d**	**4a**	**4b**	**4c**	**10a**	**10b**	**10c**	**10d**	**11a**	**11b**	**11c**
Ag^+	99	99	99	96	98	100	13	11	60	53	53	94	82
Hg^{2+}	95	95	99	12	20	20	12	80	85	20	20	22	34
Tl^+	2	33	87	0	1	2	2	37	37	0	0	0	0

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

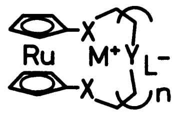
Table 3. Electronic and IR spectral data of compounds **10**—**15**

Compd	Electronic spectral data [nm (ε)][a)]	Infrared spectral data (cm^{-1})[b)]
10c	321(300)	3080, 3060, 1475, 440, 385
12c	287(2500, sh)	3070, 1475, 435, 385
10d	321(300)	3100, 3080, 1480, 430, 384
12d	287(2500, sh)	3090, 1480, 430, 385
14d	269(7400, sh), 299(7700), 357(750, sh), 459(310)	3100, 3030, 1510, 450, 460, 470, 380
11b	309(310)	3080, 1480, 434, 370
13b	330(2100), 429(200)	3080, 1475, 435, 375
15b	318(370)	3085, 1484, 439, 390
11c	315(310)	3080, 1480, 435, 380
13c	307(5500)	3090, 1494, 446, 375
15c	313(380)	3090, 1484, 437, 383

a) in CH_3CN. b) CsI disk.

described in a previous paper.[5f)] Their results are summarized in Table 2. The extraction ability of their compounds toward alkali and alkaline earth metal ions was very low and/or negligible in value and this tendency was the same for the ferrocene analogues.[5b,f)] However, the extraction ability of **10** and **11** toward silver(I), mercury(II), and thallium(I) ions was excellent and showed ionic selectivity. Although ferrocenophanes bearing oxygen atoms at the 1,1′-positions were decomposed by the attack of silver(I) ion, **10** and **11** showed excellent extraction ability without decomposition. This result is explicable by means of the higher stability of ruthenocene nucleus than that of the ferrocene nucleus for oxidation by silver(I) nitrate, because the oxidation potential of ruthenocene (0.693 eV) is higher than that of ferrocene (0.307 eV).[7)] The compounds **10c** and **11b** showed the highest extraction ability toward silver(I) ion due to the fitness of the diameter of the guest ion on the hole size of the host molecule. Furthermore, the extraction ability of the ruthenocenophanes containing soft sulfur atoms for silver(I) ions as shown in **3**, **4**, and **11** was higher than that of polyoxa[*n*]ruthenocenophanes **10** containing no sulfur atoms. This result is in accord with the HSAB rule.[11)] However, the extraction ability of the ruthenocenophanes containing sulfur atoms except **3** toward mercury(II) and thallium(I) ions was lower than that of **10**. These results show that the extraction ability also depends on the hetero-atom (Y); *i.e.* compounds **3** and **10** (Y=O) showed the good extraction ability toward mercury(II) and thallium(I) ions, while compounds **4** and **11** (Y=S) showed low or negligible extraction ability. Consequently, in the ruthenoceno crown ethers, the selectivity toward a metal cation can be controlled not only by the kind and number of heteroatoms and cavity size, but also the position of the heteroatoms.

*Isolation of Silver(I) and Mercury(II) Complexes of **10** and **11**.* A solution of ruthenoceno-crown ethers (**10** and **11**) in ether was reacted with an equimolar of silver(I) nitrate or mercury(II) chloride in acetonitrile solution to give 1:1 complexes in good yield. The melting or decomposition points of their silver and mercury complexes were higher than those of the metal free ligands, respectively.



12 : $X=Y=O, ML=HgCl_2$
13 : $X=O, Y=S, ML=HgCl_2$
14 : $X=Y=O, ML=AgNO_3$
15 : $X=O, Y=S, ML=AgNO_3$

a: n=1, b: n=2, c: n=3, d: n=4

*Electronic, Infrared, and ^{1}H-NMR Spectral Change of Compounds **10** and **11** to Their Mercury(II) and Silver(I) Complexes.* The electronic and infrared spectral data of the title compounds are summarized in Table 3. In the electronic spectra of mercury(II) complexes (**12** and **13**), the wavelength of maximum absorption showed a blue shift about 8—34 nm and their molecular coefficient increased when compared with those of the free ligands (**10** and **11**). Only the **12b** showed red shift about 11 nm, but ε increased to the same extent as the other mercury(II) complexes. Derisovich *et al.*[12)] described the electronic spectra of ruthenocene–$HgCl_2$ adduct as showing an intense band at 280 nm, which is absence in ruthenocene itself. This fact suggests that mercury(II) complexes (**12** and **13**) have the interaction between the ruthenium atom of ruthenoceno-crown

TABLE 4. ^{1}H-NMR SPECTRAL DATA OF COMPOUNDS **12**—**15**

(chemical shift/ppm)$^{a)}$

Compd	Cp-ring protons		Methylene protons			
	Hα	Hβ	-OCH$_2$		-SCH$_2$	
12c	4.87(t, *J*=1.8Hz, 4H), (+0.22)	4.53(t, *J*=1.8Hz, 4H), (+0.28)	3.57(s, 8H), (+0.02)	3.91—3.57(m, 8H) (+0.03)		
12d	4.85(t, *J*=1.8Hz, 4H), (+0.19)	4.51(t, *J*=1.8Hz, 4H), (+0.26)	3.56(s, 8H), (+0.01)	3.90—3.55(m, 8H) (0.05—+0.01)		
13b	4.83(t, *J*=1.8Hz, 4H), (+0.15)	4.43(t, *J*=1.8Hz, 4H), (+0.15)	3.88(t, *J*=6.2Hz, 4H), (+0.01)		2.82(s, 8H), (0.00)	2.81(t, *J*=6.2Hz, 4H) (−0.01)
13c	4.87(t, *J*=1.8Hz, 4H), (+0.19)	4.54(t, *J*=1.8Hz, 4H), (+0.26)	3.85(t, *J*=6.2Hz, 4H), (+0.04)		2.82(s, 8H), (0.00)	2.81(t, *J*=6.2Hz, 4H) (+0.02)
14d	6.06(t, *J*=2.5Hz, 4H), (+1.43)	5.72(t, *J*=2.5Hz, 4H), (+1.47)	4.55(t, *J*=4.0Hz, 4H), (+0.85)	3.80(t, *J*=4.0Hz, 4H), (−0.08)	3.50(s, 4H), (−0.08)	3.55—3.45(m, 8H) (+0.01—−0.08)
15b	4.75(t, *J*=1.8Hz, 4H), (+0.07)	4.28(t, *J*=1.8Hz, 4H), (+0.00)	3.88(t, *J*=6.2Hz, 4H), (+0.01)		2.96(s, 4H), (+0.14)	2.96(t, *J*=6.2Hz, 4H) (+0.14)
15c	4.75(t, *J*=1.8Hz, 4H), (+0.07)	4.43(t, *J*=1.8Hz, 4H), (+0.02)	3.89(t, *J*=6.2Hz, 4H), (+0.07)		3.02(s, 8H), (+0.22)	3.06(t, *J*=6.2Hz, 4H) (+0.25)

a) Compound **14** was measured in CD$_3$CN. Compounds **12**, **13**, and **15** were measured in DMSO-d_6. A downfield shift is denoted as a positive value. Shift changes are presented in parentheses.

ethers and mercury(II) chloride. The maximum absorption of **13**, containing sulfur atoms, was in a longer wavelength range than that of **12** containing no sulfur atom. This result may be explained by a difference in the coordination ability between the sulfur and oxygen atoms toward the mercury(II) ion.[11] That is, the sulfur atoms of **11** are so strongly coordinated to the mercury(II) ion that the interaction between Ru and Hg(II) is weakend.

On comparison of the IR spectra of mercury(II) complexes with their free ligands, slight differences were observed at the C–H and C–C streching bands and Cp–Ru–Cp ring tilting band of the ruthenocene nucleus. Morrison *et al.*[6] reported that the antisymmetric C–C streching band at 1400 cm^{-1} region of the mercury(II) adduct of ruthenocene was split into two absorption bands because of ring tilting derived from the HgCl$_2$ interaction. However, the absorption band at *1400 cm^{-1} of the mercury(II) complexes* (**12** and **13**) did not show the spliting in the IR spectra. Therefore, the bridging between the two Cp rings by the crown moiety of the ruthenocenophanes may be inhibit the tilting of the Cp rings. As the ^{1}H-NMR spectral changes showed the β-protons of the ruthenocene nucleus of all mercury complexes (**12** and **13**) were more shifted downfield than the. α-protons, whereas the ethylene protons were only little downfield shifted by 0.01—0.05 ppm. From their spectral data of the mercury complexes (as shown in Table 4), two types of complexing form are anticipated as follows: (i) the mercury ion incorporated into the crown cavity has an interaction with the ruthenium atom of the ruthenocene nucleus. (ii) the mercury(II) ion is coordinated to the ruthenium atom from the opposite site of the macrocyclic ring. On the other hand, **14d** showed characteristic spectral data in contrast to other silver complexes. For example, in the electronic spectra of **14d**, new and very intense absorption appeared at 299 (ε 7700), 357 (sh), and 459 nm (310), whereas **15** showed merely a little increase of ε (+60—+70) and a slight shifting of the d-d transition band of the ruthenocene nucleus. As early as 1952, Wilkinson reported[13] that the electronic spectra of the ruthenicinium cation which was prepared from ruthenocene and perchloric acid employing controlled potential anodes showed characteristic bands at 320 (ε *ca.* 10000), 400(sh), and 450 nm (sh). This tendency was very similar to that of **14d**. In the complex **14d** the silver(I) cation is incorporated into the cavity of macrocyclic polyether and coordinated weakly toward the six oxygen atoms although the complexed silver(I) cation in the complex **15** is coordinated more strongly toward the sulfur atoms. Therefore, the distance between the silver(I) cation and the ruthenium atom in the complex **14d** is shorter than that in the complex **15**. So, it is suggested that the electron transfer from the ruthenium atom to the complexed silver(I) ion in **14d** leads to the change of the ruthenocene nucleus to the ruthenicinium cation form. A similar phenomenon was also observed in the mercury complex **13b** and **13c**. Some remarkable *differences were also observed in the* IR *spectrum of* **14d**. Apparently, the C–H stretching band at the 3080 cm^{-1} region shifted to low frequency by about 50 cm^{-1} and the Cp–Ru–Cp ring tilting band at 430 cm^{-1} was split into three bands at 450, 460, and 470 cm^{-1}. Complexes **15b** and **15a** showed no characteristic change in the IR spectrum as **14d** did. Furtheremore, the ^{1}H-NMR spectrum of **14d** changed dramatically as shown in Fig. 2. The α- and β-protons of the Cp rings were shifted downfield by 1.43 and 1.47 ppm, respectively. The methylene protons near the ruthenocene nucleus were more shifted downfield (0.85—0.10 ppm) than other methylene protons. However, in **15c** carrying sulfur atoms as donor atoms, only the methylene protons attached to sulfur atoms were shifted (+0.22 ppm), and the Cp ring protons and the methylene protons attached to oxygen atoms were shifted slightly. This result suggests that the silver(I) ion of **14d** is coordinated with the crown site near the ruthenocene nucleus and then interacts with the ruthenium atom, while **15b** and **15c** has no interaction between ruthenium atom of ruthenocene and the incapsulated silver(I) ion.

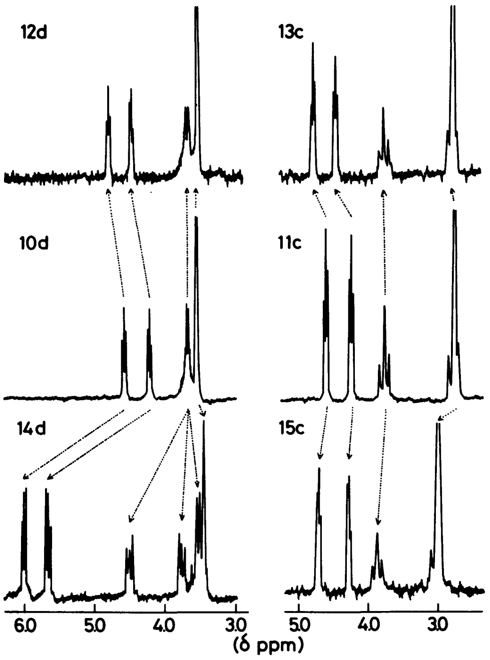


Fig. 2. ^{1}H-NMR Spectra of **10d**, **11c**, **12d**, **13c**, **14d**, and **15c**.

Experimental

The melting points are uncorrected. The mass spectra were taken on a Hitachi M 80 mass spectrometer. The ^{1}H-NMR (90 MHz) and the ^{13}C-NMR (22.5 MHz) were obtained on a JEOL-FX-90Q spectrometer, with TMS as an internal standard. The electronic spectra were obtained on a Hitachi Model 330 spectrometer. The IR spectra were measured on a JASCO DS-701G Diffraction Grating Infrared Spectrometer.

Materials. The silica-gel used for thin-layer chromatography was Wako gel B-5F. Ruthenocene,[13] 1,5-dibromo-3-oxapentane (**9a**),[14] and 1,8-dibromo-3,6-dioxaoctane (**9b**)[15] were prepared according to the procedure described in the literature. Compounds **9c** and **9d** were prepared by the same manner as described for **9a**.

1,1′-Dibromoruthenocene (5). To a solution of butyllithium in hexane (100 cm^3, 144 mmol) and TMEDA (30 cm^3, 199 mmol) in hexane (15 cm^3) was added ruthenocene in hexane (300 cm^3) under nitrogen. After mixture had been stirred for 5 h at room temperature, 1,2-dibromo-1,1,2,2-tetrafluoroethane (26.8 cm^3, 103 mmol) was added dropwise for 1 h at −60 °C. The stirring was continued overnight at −60 °C. After the solution had been warmed to room temperature, water (15 cm^3) was added to the reaction mixture. The aqueous solution was extracted with three 300 cm^3 portions of hexane. The hexane extracts were combined, washed with water, and concentrated *in vacuo*. The yellow solid was sublimed at 130 °C/0.3 mmHg. The pure product was obtained as pale yellow needles by recrystallization from hexane in 53% yield. Mp 117—118 °C, ^{1}H-NMR ($CDCl_3$) δ=4.51 (t, J=1.8 Hz, 4H), 4.86 (t, J=1.8 Hz, 4H). Found: C, 30.87; H, 2.22%. Calcd for $C_{10}H_8Br_2Ru$: C, 30.87; H, 2.08%. MS (60 eV): m/z 389 (M$^+$).

1,1′-Diacetoxyruthenocene (6). Compound **5** (16.7 g, 83 mmol) and copper(II) acetate (92 g, 460 mmol) in 50% aqueous ethanol (600 cm^3) were refluxed for 1.5 h under nitrogen. After the mixture had been cooled to room temperature, the resulting solid was removed by filtration. The solid was washed with ether (20 cm^3) three times. The ethereal layer combined was dried over anhydrous magnesium sulfate and the ether was removed *in vacuo*. The residue was chromatographed on silica-gel (benzene–ethyl acetate as eluent). The pure product was obtained as pale yellow needles by recrystallization from hexane in 53% yield. Mp 74.5—75 °C. ^{1}H-NMR ($CDCl_3$) δ=4.94 (t, J=1.8 Hz, 4H), 4.42 (t, J=1.8 Hz, 4H), 2.12 (s, 6H). Found: C, 48.69; H, 4.07%. Calcd for $C_{14}H_{14}O_4Ru$: C, 48.41; H, 4.06%. MS (60 eV): m/z 348 (M$^+$).

*Polyoxa[n](1,1′)ruthenocenophanes (**10a—d**).* As a typical example, preparation of 1,4,7,10,13-pentaoxa[13](1,1′)ruthenocenophane (**10c**) is described here. After a mixture of **6** (452 mg, 1.30 mmol) and potassium hydroxide (423 mg, 7.55 mmol) in water (15 cm^3) was stirred for 30 min under nitrogen, 1,11-dibromo-3,6,9-trioxaundecane (**9c**) (510 mg, 1.59 mmol) in 60% aqueous ethanol (60 cm^3) was added to the mixture at once. The stirring was continued for 5 h. The reaction mixture was cooled and extracted with three 30 cm^3 portions of ether. The ethereal extract was washed with water (30 cm^3), and was evaporated. The resulting solid was chromatographed on silca-gel TLC (hexane–acetone as eluent). The main fraction was extracted with acetone and the solution was evaporated *in vacuo*. Recrystallization of the resulting solid from hexane (10 cm^3) gave **10c** as pale yellow crystals in 44% yield. Mp 94.5—95 °C. Found: C, 51.42; H, 5.54%. Calcd for $C_{18}H_{24}O_5Ru$: C, 51.29; H, 5.75%. MS (60 eV): m/z 422 (M$^+$).

*1,4,7-Trioxa[7](1,1′)ruthenocenophane (**10a**).* Mp 97.5—98 °C. Found: C, 50.26; H, 4.80%. Calcd for $C_{14}H_{16}O_3Ru$: C, 50.44; H, 4.85%. MS (60 eV): m/z 334 (M$^+$).

*1,4,7,10-Tetraoxa[10](1,1′)ruthenocenophane (**10b**).* Mp 70—70.5 °C. Found: C, 50.71; H, 5.40%. Calcd for $C_{16}H_{20}O_4Ru$: C, 50.89; H, 5.35%. MS (60 eV): m/z 378 (M$^+$).

*1,4,7,10,13,16-Hexaoxa[16](1,1′)ruthenocenophane (**10d**).* Mp 29—30 °C. Found: C, 51.37; H, 5.80%. Calcd for $C_{20}H_{28}O_6Ru$: C, 51.59; H, 6.07%. MS (60 eV): m/z 465 (M$^+$).

1,1′-Bis(2-chloroethoxy)(1,1′)ruthenocene (7). After **6** (2.164 g, 6.21 mmol) had been reacted with sodium hydroxide (1.558 g, 38.9 mmol) in water (10 cm^3) for 30 min in the presence of 18-crown-6 (438 mg, 1.83 mmol) under nitrogen, 1-bromo-2-chloroethane (28.4 g, 198 mmol) was added to the mixture at once. The stirring was continued for 5 h at a reflux temperature. The reaction mixture was cooled, and extracted with three 300 cm^3 portions of ether. The extracts were combined, washed with water, and concentrated *in vacuo*. The residual solid was chromatographed on silica gel (benzene as eluent). The first fraction was extracted with acetone and the solution was evaporated *in vacuo*. Recrystallization of the residue from hexane gave **8** as white needles in 1% yield, mp 120—121.0 °C. ^{1}H-NMR ($CDCl_3$) δ=4.84 (t, J=1.8 Hz, 4H), 4.31 (t, J=1.8 Hz, 4H), 4.00 (s, 4H). MS (60 eV): m/z 289 (M$^+$). Found: C, 49.53; H, 4.14%. Calcd for $C_{12}H_{12}O_2Ru$: C, 49.81; H, 4.18%. The second fraction was extracted with acetone and the product was recrystallized from hexane to gave **7** as a white amorphous solid in 40% yield, mp 78.5—79.0 °C. MS (60 eV): m/z 388 (M$^+$). Found: C, 43.16; H, 4.14%. Calcd for $C_{14}H_{16}O_2Cl_2Ru$: C, 43.30%; H, 4.16%.

*1,7-Dioxa-4-thia[7](1,1′)ruthenocenophane (**11a**).* To sodium sulfide nonahydrate (328 mg, 1.37 mmol) in refluxing DMF (30 cm^3) was added **7** (251 mg, 0.65 mmol) in DMF (30 cm^3). After the mixture had been cooled to room temperature, water (60 cm^3) was added and the resulting mixture was extracted with three 30 cm^3 portions of chloroform. The extracts were combined and concentrated *in vacuo*. The residue was chromatographed on silica-gel TLC (benzene as eluent). The main fraction was extracted with acetone and the solvent was removed. Recrystallization of the crude product from hexane gave **11a** as white needles in 17% yield, mp 117—117.5 °C. Found: C, 48.14; H, 4.68%. Calcd for $C_{14}H_{16}O_2SRu$: C, 48.12; H, 4.62%. MS (60 eV): *m/z* 350 (M$^+$).

1,10-Dioxa-4,7-dithia[10](1,1′)ruthenocenophane (11b). A solution of **7** (282 mg, 0.73 mmol) in THF (50 cm^3) and a mixture of 1,2-ethanedithiol (300 mg, 3.19 mmol) and sodium hydroxide (230 mg, 5.95 mmol) in ethanol (50 cm^3) were added dropwise to ethanolic THF (ethanol:THF=1:1) (240 cm^3) over a 2.5 h under reflux. The refluxing was continued for 14 h with stirring and then the reaction mixture was cooled and concentrated *in vacuo*. The residual oil was separated by alumina column chromatography (benzene as eluent) and then TLC (silica gel, benzene as eluent). The first fraction in TLC was extracted with acetone and recrystallized from hexane to give **11b** as white needles in 25% yield, mp 116.5—117.0 °C. MS (60 eV): *m/z* 409 (M$^+$). Found: C, 46.94; H, 4.86%. Calcd for $C_{16}H_{20}O_2S_2Ru$: C, 46.92; H, 4.93%. The second fraction in TLC was extracted with acetone and recrystallized from hexane to give **11c** as white needles in 5% yield, mp 113—113.5 °C. MS (60 eV): *m/z* 469 (M$^+$). Found: C, 46.03; H, 5.05%. Calcd for $C_{18}H_{24}O_2S_3Ru$: C, 46.03; H, 5.15%.

1,13-Dioxa-4,7,10-trithia[13](1,1′)ruthenocenophane (11c). A solution of **7** (314 mg, 0.91 mmol) in THF (50 cm^3) and a solution of bis(2-mercaptoethyl) sulfide (640 mg, 4.16 mmol) and sodium hydroxide (330 mg, 8.25 mmol) in ethanol (50 cm^3) were added dropwise to refluxing ethanolic THF (ethanol:THF=1:1) (300 cm^3) at the same rate for 2.5 h. The stirring was continued for 14 h at a refluxing temperature. The reaction mixture was cooled and concentrated *in vacuo*. The residual oil was chromatographed on alumina column (benzene as eluent). The main fraction was combined and concentrated. Recrystallization of the crude product from hexane gave **11c** as white needles in 63% yield. The pure **11c** obtained by this reaction was identified by comparison with the melting point, R_f value of TLC and the spectal data of the authentic sample.

Method of Solvent Extraction. Extraction ability of ruthenoceno-crown ethers toward alkali, alkaline earth, and some non-transition and transition metal ions was examined by the extraction method described in the previous paper.[5f] All metals used were metal nitrates, except for mercury(II) chloride.

Mercury(II) Chloride Complexes (12 and 13). A solution of ruthenoceno-crown ether (**10** or **11**, 0.06 mmol) in ether (5 cm^3) was added to a solution (15 cm^3) containing mercury(II) chloride (0.06 mmol) in ether (15 cm^3). As the ethereal solution was concentrated to 10 cm^3 *in vacuo*, a yellow solid was precipitated. Recrystallization of the solid from acetonitrile (2 cm^3) gave pure mercury complexes in 80—90% yiled as yellow needles.

12a: Mp 210 °C (decomp). Found: C, 27.77; H, 2.65%. Calcd for $C_{14}H_{16}O_3Ru\ HgCl_2$: C, 27.80; H, 2.67%.

12b: Mp 200 °C (decomp). Found: C, 29.59; H, 3.08%. Calcd for $C_{16}H_{20}O_4Ru\ HgCl_2$: C, 29.61; H, 3.11%.

12c: Mp 160 °C. Found: C, 31.23; H, 3.44%. Calcd for $C_{18}H_{24}O_5Ru\ HgCl_2$: C, 31.20; H, 3.40%.

12d: Mp 150 °C (decomp). Found: C, 32.29; H, 3.67%. Calcd for $C_{20}H_{28}O_6Ru\ HgCl_2$: C, 32.58; H, 3.84%.

13b: Mp 184—185.5 °C. Found: C, 28.11; H, 2.91%. Calcd for $C_{16}H_{20}O_2S_2Ru\ HgCl_2$: C, 28.22; H, 2.97%.

13c: Mp 166—167 °C. Found: C, 28.97; H, 3.27%. Calcd for $C_{18}H_{24}O_2S_3Ru\ HgCl_2$: C, 29.17; H, 3.27%.

Silver(I) Nitrate Complex (14d). A solution of **10d** (129 mg, 0.28 mmol) in acetonitrile (2 cm^3) was added to a solution of silver(I) nitrate (55 mg, 0.32 mmol) in acetonitrile (2 cm^3) at one time. After 1.5 h, the resulting precipitate was filtered and then a small amount of ether was added dropwise to the filtrate to give orange crystals in 19% yield. Mp 113—115 °C. Found: C, 40.54; H, 4.64; N, 6.71%. Calcd for $C_{25.5}H_{35.5}N_{3.5}RuAg$: C, 40.67; H, 4.86; N, 6.64%.

Silver(I) Nitrate Complexes (15). A solution of ruthenoceno-crown ether (0.06 mmol) in acetonitrile (2 cm^3) was added to silver(I) nitrate (0.06 mmol) in acetonitrile (2 cm^3). The resulting crystals were collected by filtration and washed with small portions of acetonitrile to give **15** in 76% yield as white needles.

15b: Mp 170 °C (decomp). Found: C, 33.02; H, 3.48; N, 2.50%. Calcd for $C_{16}H_{20}NO_5S_2RuAg$: C, 33.16; H, 3.49; N, 2.42%.

15c: Mp 167—169 °C (decomp). Found: C, 33.64 ; H, 3.66; N, 2.13%. Calcd for $C_{18}H_{24}NO_5S_3RuAg$: C, 33.80; H, 3.79; N, 2.19%.

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