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SYNTHESIS AND PHYSICOCHEMICAL PROPERTIES OF POLYOXA[n]FERROCENOPHANES

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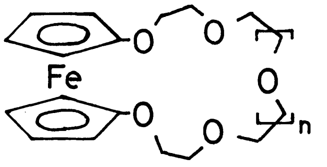
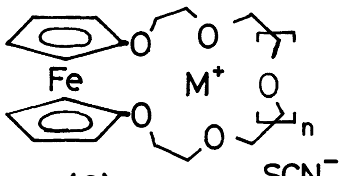
Three mononuclear polyoxa[n]ferrocenophanes (**5**) and binuclear polyoxa[n,n]ferrocenophanes (**6**) derived from 1,1'-bis(hydroxymethyl)ferrocene were synthesized and complexing ability of **5** with alkali and transition metal cations was measured by a solvent extraction method. Their complexing abilities were excellent with silver cation, although polyoxa[n]ferrocenophanes (**1**) derived from 1,1'-dihydroxyferrocene were decomposed by oxidation.

Recently crown-ethers containing ferrocene subunit in macrocyclic skelton have received much attention[1-4] because the iron atom may play a role of coordinatable heteroatom. In the preceding paper,[5] we reported isolation of the complexes (**2**) of polyoxa[n]ferrocenophanes (**1**) with MSCN, and indicated that there may be a possibility of some kinds of interaction between the iron atom of ferrocene nucleus and the incorporated metal cation. The distance between the iron atom of ferrocene nucleus and the incorporated metal cation in the complexes **2** is supposed to be one of the important factors influencing their metal complexing ability. This distance can be easily adjusted by changing the ring size and by insertion of methylene groups between the ferrocene ring and the adjacent oxygen atom, like in polyoxaferrocenophanes (**5**). In connection with the above standpoint, we wish to report the synthesis of polyoxa[n]ferrocenophanes (**5**) derived from 1,1'-bis(hydroxymethyl)ferrocene and the complexing ability of **5** with alkali and transition metal cations.



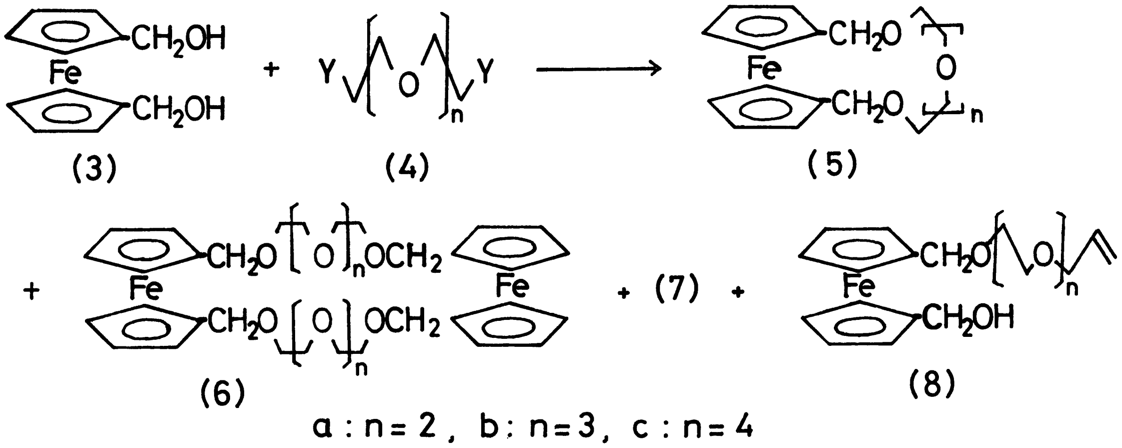
(1) a : n=1, b : n=2



(2)

The reaction of 1,1'-bis(hydroxymethyl)ferrocene (**3**) with the ditosylate (**4a**, y=OTs) of triethylene glycol in benzene in the presence of potassium t-butoxide gave a mixture of mononuclear 2,5,8,11-tetraoxa[12]ferrocenophane (**5a**), binuclear 2,5,8,11,24,27,30,33-octaoxa[12,12]ferrocenophane (**6a**) in 12.9 and 5.3% yields, respectively, along with a trace amount of unexpected 2-oxa[3]ferrocenophane (**7**). In the same manner, the reaction of **3** with the ditosylate of tetraethylene glycol

(**4**b, y=OTs) also gave a mixture of 2,5,8,11,14-pentaoxa[15]ferrocenophane (**5**b), 2,5,8,11,14,27,30,33,36,39-decaoxa[15,15]ferrocenophane (**6**b), and **7** in 3.4, 0.1, and 4.4% yields, respectively. From the reaction of **3** with the ditosylate of pentaethylene glycol (**4**c, y=OTs), 2,5,8,11,14,17-hexaoxa[18]ferrocenophane (**5**c) and **7** were obtained in 3.0% and trace yields, respectively. The unexpected product **7** was obtained in every case, although the yield was extremely low. It is well known that the treatment of **3** with acid gave **7**.[6] However, it is interesting that our reaction condition for the formation of **7** was quite different from that for the acid catalyzed cyclization generally known. Also, the reaction of **3** with the dihalides (**4**, Y=Br or Cl) was carried out in tetrahydrofuran in the presence of a small amount of 18-crown-6. The reaction proceeded smoothly but the pattern of the products was fairly different from that of the reaction described above. Thus, the reaction of **1** with dibromide (**4**a, Y=Br) in tetrahydrofuran, for example, yielded 5a and the vinyl derivative (**8**a) in 13.3 and 10.8% yields, respectively. Dibromide (**4**b,c; Y=Br) and dichlorides (**4**a-c, Y=Cl) reacted in a similar manner.



The structures of the ferrocenophanes (**5**, **6**, and **7**) an **8** were determined on the basis of their IR, ^{1}H-NMR, mass spectra and elemental analyses. The spectral data of these compounds are summarized in Table 1. The molecular formula of **5**a was deduced to be $C_{18}H_{24}O_4Fe$ by means of the mass spectroscopy (M^+, m/e 360) and the elemental analysis. The IR spectrum of **5**a displayed a C-H absorption at 1460 cm^{-1} and ether linkage absorption at 1125 cm^{-1}, but lacked bands arrising from the hydroxyl group. In the ^{1}H-NMR spectrum of **5**a, the resonance for the methylene groups attached to ferrocene ring appeared as a sharp singlet at δ 4.41 (4H), in addition to a multiplet (8H, Fc-H) at δ 4.15, a singlet (4H, CH_2) at δ 3.69, and a singlet (8H, CH_2) at δ 3.71. The molecular formula of **6**a was deduced to be $C_{36}H_{48}O_8Fe_2$ by means of the mass spectroscopy (M^+, m/e 720) and the elemental analysis. The ^{1}H-NMR spectrum of **6**a showed the signal of ferrocene ring protons (m, 16H) at δ 4.11 and the methylene protons attached to ferrocene ring (s, 8H) at δ 4.28, in addition to the signal of methylene protons (m, 16H) at δ 3.49-3.80. The IR spectrum of **6**a displayed a ferrocene ring C-H absorption and ether linkage absorption at 1450 and 1100 cm^{-1}, respectively, but the lack of bands arrising from the hydroxyl groups. The structure of **7** was also determined by the spectral data and the admixture with the authentic sample. The ^{1}H-NMR spectrum of **8**a showed the signals of olefinic (dd, 1H) and hydroxyl protons (s, 1H) at δ 6.48 and 2.77, respectively, in addition to the signals of methylene protons (m, 10H) at δ 3.53-3.98 and ferrocene ring protons (broad s, 8H) at δ 4.15, although the terminal olefinic protons could not be clearly observed because of the overlap of the signals with methylene proton signals. The IR spectrum showed the presence of hydroxyl and olefinic groups at 3400 and 1620 cm^{-1}, respectively. The structures of other new compounds were also determined by a similar method described above.

Table 1. Physical Properties and Spectroscopic Data of Compounds **5**–**8**

Compd.	M.p. (°C)	Mass, M^+ (m/e)	I.R. (cm^{-1})	^{1}H-NMR(60MHz, in $CDCl_3$) (δ, Hz)
5a	28-30	360	3150, 2900, 1480 1460, 1125	3.69(s, 4H, CH_2), 3.71(s, 8H, CH_2) 4.15(m, 8H, Fc-H), 4.41(s, 4H, $FcCH_2$)
5b	oil	404	3050, 2825, 1465 1105	3.69(s, 8H, CH_2), 3.71(s, 8H, CH_2) 4.15(m, 8H, Fc-H), 4.35(s, 4H, $FcCH_2$)
5c	oil	448	3080, 2850, 1465 1110	3.65(s, 8H, CH_2), 3.69(s, 12H, CH_2) 4.13(s, 8H, Fc-H), 4.41(s, 4H, CH_2)
6a	oil	720	3080, 2850, 1465 1100	3.49-3.80(m,24H,CH_2), 4.11(m,16H,Fc-H), 4.28(s, 8H, CH_2)
6b	oil	808	3100, 2959, 1465 1100	3.55-3.76(m,32H,CH_2), 4.14(m,16H,Fc-H) 4.28(s, 8H, CH_2)
8a	oil	360	3400, 3070, 2850 1620, 1450, 1090	2.77(s,1H,OH), 3.53-3.98(m,10H,CH_2), 4.15(s, 8H, Fc-H), 4.28(s, 4H, CH_2), 6.28-6.68(dd, 1H, $-CH=CH_2$)
8b	oil	404	3450, 3070, 2900 2850, 1620, 1450	3.00(s,1H,OH), 3.50-3.95(m,14H,CH_2) 4.31(s,4H,CH_2), 6.25-6.68(dd,1H,$-CH=CH_2$)
8c	oil	448	3400, 3050, 2859 1615, 1090, 1450	3.11(s, 1H, OH), 3.59-3.97(m, 18H) 4.19(s, 8H, Fc-H), 4.21(s, 4H, CH_2) 6.20-6.60(dd, 1H, $-CH=CH_2$)
7	150-0.5[6]	228	3100, 1445, 1045	3.88(s, 4H, CH_2), 4.14(s, 8H, Fc-H)

Table 2. Extraction of Metal Picrates from Aqueous to Organic Phase (%)

Compd.	Li^+	Na^+	K^+	Rb^+	Cs^+	Ba^{2+}	Tl^+	Ag^+
5a	0	0	0	0.51	0	0.68	1.6	59.8
5b	0	0.39	0.79	0.77	0.52	0.27	9.3	59.7
5c	0	0.33	6.81	6.28	4.90	5.87	50.0	71.5
1a	0	1.62	22.7	29.1	18.4	——	79.7	decomp.
1b	0	1.49	4.50	4.56	5.57	——	25.2	"
B18C6		22.3	94.7			——	97.3	84.3
B15C5		23.9	50.1			——	56.0	33.6

Solvent: Water and dichloromethane (1:1). Concentration of Crown ether; $7X10^{-4}M$. Concentration of picric acid: $7X10^{-5}M$. Concentration of metal nitrates: 0.1M.

The complexing ability of polyoxaferrocenophanes (**5** and **1**) with alkali and transition metal cations was measured by the Pedersen's extraction method.[7] The data were summarized in Table 2, along with those of benzocrown ethers. **5a-c** and **1a-b** showed a little or no complexing ability with alkali metal cations. These results indicated that the incorporation of the iron atom of ferrocene nucleus (a soft atom) into macrocyclic unit has an influence on the complexing ability with alkali metal cations (a hard acid). We observed a similar tendency in the extractability of alkali metal cations with polyoxa[n]ferrocenophanes (**1**) prepared from 1,1'-dihydroxyferrocene,[8] although Biernat and Wilczewski reported the reverse and strong complexing ability of **1** with alkali metal cations by the TLC method.[9] Our results are consistent with the prediction from the HSAB principle.[10] Furthermore, in the coincidence with this prediction, **5a-c** showed a high complexing ability with thallium and silver cations. A smaller complexing ability of thallium cation than silver cation may be due to a larger ionic diameter of thallium cation than silver cation. Finally, it is noteworthy that the polyoxaferrocenophanes **5** are able to make stable complex with silver ion without decomposition, because ferrocene itself and polyoxaferrocenophanes **1** decomposed rapidly with silver ion.[8] These facts indicate that the distance between the iron atom of ferrocene nucleus and the incorporated silver cation controlls the oxidation of ferrocene nucleus. Polyoxathiaferrocenophanes similarly showed a high complexing ability with silver ion, although 1,1'-bis(methylthio)ferrocene decomposed rapidly with silver ion. Thus, the silver ion arranged in an appropriate distance by incorporation into crown ether moiety would withdrow an appropriate quantity of electron directly from the iron atom of ferrocene nucleus and lower the electron density on the iron atom. Consequently, the ferrocenophanes **5** may be able to make a stable complex with silver ion. The investigation about the isolation of these compounds is now in progress.

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