Syntheses of Acyclic Polyethers Containing a Ferrocene Nucleus and Its Extraction Ability

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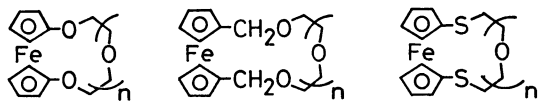
(Received September 13, 1982)

Acyclic polyethers (**7**) (containing a ferrocene nucleus in both terminal sites) were synthesized by a one-pot reaction of 1,1′-diacetoxyferrocene with halide. Also, ferrocene derivatives (**11**) having polyethylene glycols were synthesized by the reaction of potassium salt of hydroxyferrocene with dihalide in DMF. On the addition of alkali metal thiocyanate in methanol, a hypsochromic shift and an increasing intensity of the absorption band at 438 nm were observed in ferrocene-containing polyethers **7**, suggesting the complexing of **7** with cations. However, a similar spectral change could not be observed in **11**. **7a** extracts silver and thallium ions most effectively, the extraction efficiency of several metal cations being in this order: $Ag^+ > Tl^+ > Cs^+ > K^+ > Li^+ > Na^+$.

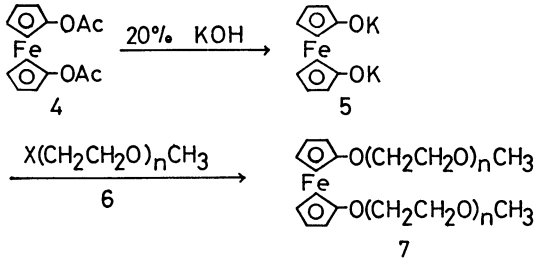
While the investigations of macrocyclic polyether complexes[1] have been steadily gaining popularity during the past several years, it seems that most attention has so far been focused on the syntheses of new types of ligands. During the course of our investigation of polyoxa[*n*]ferrocenophanes **1**, **2**, and **3**,[2–4] we observed



1 **2** **3**

1a n=4 n=2~4 n=1~4
1b n=3

that the incorporation of a ferrocene nucleus into the framework of a crown-ether ring increases the extraction efficiency toward a transition-metal cation. For example, **1** showed a high extraction percentage with the thallium cation, although it showed little or no extractability with alkali-metal cations. Furthermore, **2** similarly showed a high complexing ability with thallium and silver cations, although **1** decomposed rapidly when the silver cation was present. Those results suggest that the distance between the iron atom of the ferrocene nucleus and the incorporated silver cation controls the oxidation of the ferrocene nucleus.[3] In this connection, we wish now to report the syntheses of acyclic polyethers (**7**)(containing a ferrocene nucleus in both terminal sites) and ferrocene derivatives (**11**) having polyethylene glycols and the complexing ability of **7** and **11** with alkali and transition metal cations.

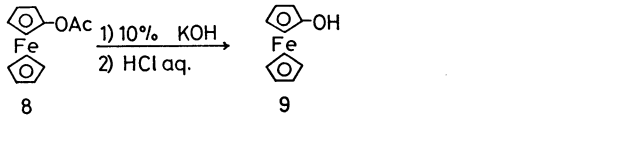


4 **5**

6

7

6a n=3 X=Cl 7a n=3
6b n=2 X=Br 7b n=2
6c n=1 X=Br 7c n=1
6d n=0 X=I 7d n=0



8 **9**

10 **11**

10a n=4 11a n=4
10b n=3 11b n=3
10c n=2 11c n=2

Syntheses. The syntheses of **7a**—**d** were carried out by the following method. The hydrolysis of 1,1′-diacetoxyferrocene (**4**) was carried out under an atmosphere of nitrogen by the usual method. To the resulting alkali solution of the potassium salt of 1,1′-dihydroxyferrocene (**5**) we added at once a solution of halide (**6**) in 60% ethanol at the reflux temperature. Then the mixture was refluxed for 3.5 h. After a usual work-up, the products were chromatographed on silica gel. From the main fraction, pure **7a**—**d** were obtained in moderate to good yields. It is noteworthy that this one-pot preparation of **7** starting directly from **4** avoids the isolation of very air-sensitive 1,1′-dihydroxyferrocene.[5] Compounds **11a**—**c** (containing a ferrocene nucleus in both terminal sites) were prepared by the reaction of hydroxyferrocene (**9**), which had itself been obtained by the hydrolysis of acetoxyferrocene (**8**), with appropriate dihalide (**10**) in DMF in the presence of potassium hydroxide. The molecular formula of **7a** was deduced to be $C_{24}H_{38}O_8Fe$ by means of mass spectroscopy (M^+, *m/e* 510) and the elemental analysis. In the ^{1}H-NMR spectrum of **7a**, the resonance for the α- and β-ring protons of the ferrocene nucleus appeared as the A_2B_2 pattern at δ=4.10 (4H, t, J=2.0 Hz) and 3.84 (4H, t, J=2.0 Hz) respectively, in addition to the signal of methylene protons as a multiplet at δ=3.45—3.90 (m, 24H) and the signal of the methyl group as a singlet at

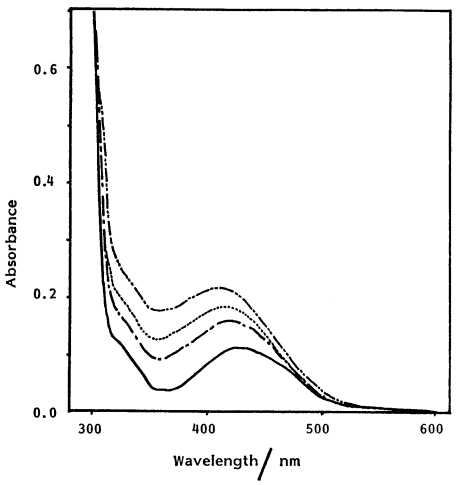


Fig. 1. Spectral change of **7a** by the addition of KSCN. Time: —— 0, ——— 1 h, ---- 2 h, —··— 3 h. Concentration: [**7a**]=1×10^{-3} M, [KSCN]=2.0×10^{-2} M.

δ=3.35 (s, 6H). The IR spectrum of **7a** showed ferrocene ring C–H absorption and ether-linkage absorption near 1480 and 1125 cm^{-1} respectively, but no absorption attributable to hydroxyl and carbonyl groups. The molecular formula of **11a** was deduced to be $C_{30}H_{38}O_6Fe_2$ by means of mass spectroscopy (M^+, *m/e* 608) and elemental analysis. The ^{1}H-NMR spectrum of **11a** showed the signal of unsubstituted ferrocene-ring protons as a singlet at δ=4.14 and the substituted ring protons as the A_2B_2 pattern at δ=4.06 (t, J=2.0 Hz, 4H, H_α) and 3.80 (t, J=2.0 Hz, 4H, H_β), in addition to the signal of the methylene protons at δ=3.72—3.94 (m, 8H) and 3.64 (s, 12H). The IR spectrum of **11** displayed absorptions of the ferrocene ring and ether linkage at 1470 and 1100 cm^{-1} respectively, but the absence of any bands arising from the hydroxyl group. The electronic spectra of **7** and **11** (λ_{max} 434 nm in MeOH) suggest the presence of a ferrocene nucleus. The structures of other new compounds were also determined by a method similar to that described above.

Additive Effect of Metal Salt. At first we examined the electronic spectral change in the ferrocenyl derivatives upon the addition of metal thiocyanate in order to determine the cation complexing ability qualitatively. It is well known[6] that the spectral shapes in the curves for the complexing polyethers are altered by the addition of complexable salts. A typical spectral change in **7a** on the addition of potassium thiocyanate in methanol is shown in Fig. 1. All compounds containing a ferrocene nucleus in the middle of the polyethylene glycol chain show a characteristic absorption maximum at 434 nm in methanol. Upon the addition of potassium thiocyanate, the curve of **7a** shows a remarkable change. Its hypsochromic shift and increase in absorbance suggest the complex formation between **7a** and potassium thiocyanate. These results are listed in Table 1. On the other hand, Compounds **11a**—**c**, which contain a ferrocene nucleus in both terminals, showed no spectral change upon the addition of any given alkali metal salt. In these compounds, no conformational change imposed on complexing with the metal cation takes place, probably because of the steric repulsion between the two ferrocenyl groups. Therefore, **11** could have no complexing ability with the metal cation.

Table 1. Electronic absorption spectral data and their metal complexes in methanol[a)]

Compound	Additive salt λ/nm (ε)			
	None	LiSCN	NaSCN	KSCN
7a	431(112)	434(137)	431(134)	417(159)
7b	434(108)	434(124)	434(122)	432(110)
7c	434(92)	434(112)	434(105)	434(92)
7d	434(142)	434(137)	434(124)	434(112)

a) Measured in the presence of about a 50-fold molar excess of alkali metal thiocyanate at 20 °C.

Extractability. The extraction efficiency of **7** with alkali, alkaline earth, and transition-metal cations was measured according to Pedersen's method;[7] the results are listed in Table 2, together with those for **1a** and **1b**, which were synthesized previously.[2] It was observed that **7** showed only a little complexing ability with alkali and alkaline earth-metal cations, although they showed a relatively high complexing ability with transition metal cations. For the silver cation, Compounds **7a**—**d** have an excellently high complexing ability, as shown in Table 2. When the concentration of **7** was 7×10^{-4} M (1 M=1 mol dm^{-3}), the extractability could not be obtained because a rapid oxidative decomposition of the ferrocene nucleus by the complxed silver cation took place. However, this interaction may be weaker than that of polyoxa-[*n*]ferrocenophanes (**1**) with a closed oxyethylene chain, because, according to a consideration of its molecular model, the complexed silver ion in **7** is situated in a position apart from the iron atom of ferrocene because

Table 2. Extraction of metal picrates from aqueous to organic phase (%)[a,b)]

Compound	Li^+	Na^+	K^+	Cs^+	Ag^+	Tl^+	Ca^{2+}	Ba^{2+}	Cd^{2+}
7a	4.4	4.2	7.7	8.8	51[c)]	25	4.3	2.5	5.6
7b	3.6	3.4	2.9	3.2	40[c)]	5.8	6.0	3.2	7.2
7c	1.9	1.5	1.1	1.9	33[c)]	2.0	2.9	—	4.2
7d	2.5	1.6	1.7	1.3	20[c)]	0.8	2.9	—	3.3
1a	—	1.6	22.7	18.4	28.3[c)]	79.7	—	—	—
1b	—	1.5	4.5	5.6	18.8[c)]	25.2	—	—	—

a) Solvents: Water and dichloromethane (equal volumes). b) Ferrocenyl ether=7.0×10^{-4} M. Picric acid=7.0×10^{-5} M. Metal nitrate=0.1 M. c) Ferrocenyl ether=7.0×10^{-5} M.

of the flexibility of the polyether chain. The extractability of the metal cations by **7a** was in this order: $Na^+ < Li^+ < K^+ < Cs^+ < Tl^+ < Ag^+$.

These phenomena can be explained by the HSAB rule;[8] that is, the incorporation of the iron atom of ferrocene (a soft acid) into the framework of acyclic polyethers decreases the affinity to a hard cation (alkali and alkaline-earth metal ions) and increases the affinity to a soft transition-metal cation. Furthermore, the extraction efficiency of **7** for the several alkali metal cations examined here was in this order: **7a**>**7b**>**7c**≈**7d**. These results suggest that the extraction efficiency of these cations is dependent on the length of the oxyethylene unit of acyclic polyethers (**7**). The above results suggest that there is an appreciable interaction between the incorporated metal ion and the iron atom of the ferrocene nucleus. It is also surprising that **7a** and **7b**, containing many oxygen atoms, showed some extraction efficiency with the lithium ion, although **1a** and **1b** showed no extraction efficiency with the lithium ion. According to a consideration of their molecular models, this was probably because of the nonfitness between the guest ion and the hole size of the host molecule. The extraction efficiency of the lithium ion with **7a** and **7b** suggests that the lithium ion becomes incorporated into the cavity formed by one of the two acyclic polyether arms, while the uptake of the lithium ion into the cavity made by the two side oxyethylene arms seems to be unfavorable because the ion radius of the lithium cation is too small for fitting with the hole size of the host molecule. It is also interesting to note that **7a** and **7b** showed only a little extraction efficiency with alkaline earth-metal ions, although alkaline earth metal ions were not extracted by any of the compounds **1**.

Experimental

The melting points are uncorrected. The mass spectra were taken by using a JEOL-OlSG-2 spectrometer. The ^{1}H-NMR spectra were obtained on a Hitachi R-90 spectrometer, TMS being chosen as the internal standard. The optical spectra were obtained on a Hitachi Model 200-10 spectrometer.

Materials. 1,1′-Diacetoxyferrocene (**4**)[2,5] and acetoxyferrocene (**8**)[5,9] were prepared according to the previously reported method. The other reagents employed were commercial materials or were prepared by the usual methods.

*Syntheses of **7a—d**.* *General Procedure*: **4** (2.14 mmol) was added to a 20% aq potassium hydroxide solution (17 ml) under nitrogen, and the mixture was stirred at 100 °C. After 30 min, a solution of halide (**6**) (4 ml) in ethanol was added all at once, and then the mixture was stirred for 3.5 h at 120 °C. After the solution had been cooled to room temperature, 30 ml of water was added to the reaction mixture. The ether extracts were combined, washed with water, dried over anhydrous magnesium sulfate, and concentrated to give a residue. The residual oil was chromatographed on a silica-gel column, using acetone as the solvent. The crude **7** thus obtained was rechromatographed on a column of silica gel. Elution with chloroform gave pure **7** as a yellow oil.

*1,1′-Bis(1,4,7,10-tetraoxaundecyl)ferrocene (**7a**).* Yellow oil, 53% yield. Found: C, 56.20; H, 7.58%. Calcd for $C_{24}H_{38}O_8Fe$: C, 56.47; H, 7.45%. MS (75 eV): *m/e* 510 (M^+, 81.7%) and 218 ($Fc(OH)_2$, 7.2%). ^{1}H-NMR ($CDCl_3$): δ=4.10 (t, 4H, J=2.0 Hz, H_α), 3.84 (t, 4H, J=2.0 Hz, H_β), 3.45—3.90 (m, 24H, OCH_2CH_2O), 3.35 (s, 6H, OCH_3).

*1,1′-Bis(1,4,7-trioxaoctyl)ferrocene (**7b**).* Yellow oil, 67% yield. Found: C, 57.13; H, 7.29%. Calcd for $C_{20}H_{30}O_6Fe$. C, 56.87; H, 7.11%. MS (75 eV): *m/e* 422 (M^+, 100%) and 218 ($Fc(OH)_2$). ^{1}H-NMR ($CDCl_3$): δ=4.16 (t, 4H, J=2.0 Hz, H_α), 3.93 (t, 4H, J=2.0 Hz, H_β), 3.60—4.01 (m, 16H, OCH_2CH_2O), and 3.43 (s, 6H, OCH_3).

*1,1′-Bis(1,4-dioxapentyl)ferrocene (**7c**).* Yellow oil, 85% yield. Found: C, 57.70; H, 6.87%. Calcd for $C_{16}H_{22}O_4Fe$: C, 57.49; H, 6.59%. MS (75 eV): *m/e* 334 (M^+, 100%) and 218 ($Fc(OH)_2$). ^{1}H-NMR ($CDCl_3$): δ=4.17 (t, 4H, J=2.0 Hz, H_α), 3.92 (t, 4H, J=2.0 Hz, H_β), 3.60—3.90 (m, 8H, OCH_2CH_2O), and 3.40 (s, 6H, OCH_3).

1,1′-Dimethoxyferrocene. Orange crystals, mp 36—37 °C (lit,[5] 35—36 °C), 78% yield. Found: C, 58.32; H, 5.81%. Calcd for $C_{12}H_{14}O_2Fe$: C, 58.54; H, 5.69%. MS (75 eV): *m/e* 246 (M^+, 100%) and 218 ($Fc(OH)_2$, 72.8%). ^{1}H-NMR ($CDCl_3$): δ=4.12 (t, 4H, J=2.0 Hz, H_α), 3.91 (t, 4H, J=2.0 Hz, H_β), and 3.58 (s, 6H, OCH_3).

*Syntheses of **11a—c**.* *General Procedure*: **8** (3.2 mmol) was added to ethanol (16 ml) containing 10% aq potassium hydroxide. The mixture was stirred for 1 h at 100 °C under nitrogen and then evaporated in a vacuum. After the residue had been cooled to room temperature, dilute sulfuric acid (10 ml) was added to the residue, and the resulting yellow precipitates were collected by filtration. The yellow solid was dissolved in *N,N*-dimethylformamide (50 ml). To the solution was added potassium hydroxide (1.0 g), and the resulting solution was stirred at room temperature. After 20 min, dibromide (**10**)(0.98 mmol) was added all at once, and the mixture was stirred for 7 h at 80—100 °C. After the solution had been cooled to room temperature, water (200 ml) was added to the reaction mixture. The solution was extracted with four 100 ml-portions of ether. The ether extracts were combined, washed with water, dried, and concentrated to give dark yellow oil. The residue was chromatographed on a silica-gel column. Elution with chloroform gave yellow crystals except for **11a**.

*Pentaethylene Glycol Diferrocenyl Ether (**11a**).* Yellow oil, 68% yield. Found: C, 59.15; H, 6.48%. Calcd for $C_{30}H_{38}O_6Fe$: C, 59.41; H, 6.27%. MS (75 eV): *m/e* 608 (M^+, 87.8%) and 202 (FcOH, 100%), and 121 ($C_5H_5Fe^+$, 65.4%). ^{1}H-NMR ($CDCl_3$): δ=4.15 (s, 10H, Fc–H), 4.06 (t, 4H, J=2.0 Hz, H_α), 3.80 (t, 4H, J=2.0 Hz, H_β), 3.72—3.94 (m, 8H, OCH_2CH_2O), 3.64 (s, 12H, OCH_2CH_2O).

*Tetraethylene Glycol Diferrocenyl Ether (**11b**).* Yellow crystals, mp 49—51 °C, 86% yield. Found: C, 59.60; H, 6.30%. Calcd for $C_{28}H_{34}O_5Fe$: C, 59.79; H, 6.05%. MS (75 eV): *m/e* 562 (M^+, 100%), 202 (FcOH, 78.2%), and 121 ($C_5H_5Fe^+$, 60.9%). ^{1}H-NMR ($CDCl_3$): δ=4.14 (s, 10H, Fc–H), 4.05 (t, 4H, J=2.0 Hz, H_α), 3.78 (t, 4H, J=2.0 Hz, H_β), 3.72—3.92 (m, 8H, OCH_2CH_2O), and 3.67 (s, 8H, OCH_2CH_2O).

*Triethylene Glycol Diferrocenyl Ether (**11c**).* Yellow crystals, mp 87—89 °C, 68% yield. Found: C, 60.35; H, 5.98%. Calcd for $C_{26}H_{30}O_4Fe$: C, 60.28; H, 5.79%. MS (75 eV): *m/e* 518 (M^+, 100%), 202 (FcOH, 46.9%), 121 ($C_5H_5Fe^+$, 57.7%). ^{1}H-NMR ($CDCl_3$): δ=4.16 (s, 10H, Fc–H), 4.06 (t, 4H, J=2.0 Hz, H_α), 3.80 (t, 4H, J=2.0 Hz, H_β), 3.72—3.95 (m, 8H, OCH_2CH_2), and 3.61 (s, 4H, OCH_2CH_2).

Method of Solvent Extraction. Solvent extraction was carried out by the method described by Pedersen.[7] Equal volumes (5 ml) of dichloromethane containing 7×10^{-4} (or 7×10^{-5}) M of **7** and an aq solution containing 1×10^{-1} M MNO_3 (M: metal cations) and 7×10^{-5} M picric acid were agitated throughly at 25 °C. The solution was then

equilibrated at 25 °C, the aliquot of the upper aq solution was withdrawn, and its electronic spectrum was recorded. A similar extraction was performed with pure dichloromethane. The extractability was determined by means of the difference between two absorbances of picrate in the aq solution and by calculating using by the following equation:

$$\text{Extractability}=\frac{A_0-A}{A_0}\times 100.$$

A_0 is the absorbance in the absence of MNO_3. A is the absorbance in the presence of MNO_3.

The authors wish to acknowledge the assistance given in the experimental work by Mr. Yoichi Habata and Miss Hiroko Ohteki in the experimental work.

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