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Syntheses of Polyoxathia[*n*]ferrocenophanes and Its Extraction Ability with Metal Cations

Sadatoshi AKABORI,* Yoichi HABATA, Masaru SATO,† and Seiji EBINE††
Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274
† *Chemical Analysis Center, Saitama University, Urawa, Saitama 338*
†† *Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338*

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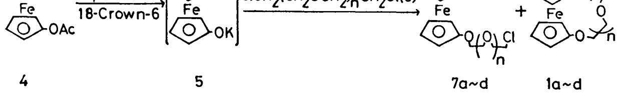
Mononuclear polyoxathia[*n*]ferrocenophanes (**8a**—**d**) and binuclear polyoxadithia[*n,n*]ferrocenophanes were synthesized by the reaction of 1,1′-bis(ω-chloropolyethyleneoxy)ferrocene with sodium sulfide in *N,N*-dimethylformamide and the complexing ability of **8a**—**d** with alkali and transition metal cations was measured by an extraction method. Compound **8d** extracts a thallium ion specifically, the extraction efficiency of several ions being in the order: $Tl^+ \gg Rb^+ > K^+ > Cs^+ > Na^+ > Li^+$.

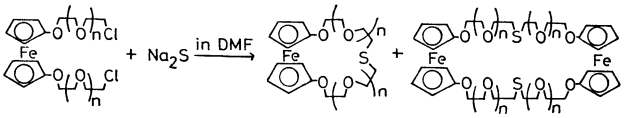
During the past decade, several papers[1)] have described the remarkable interactions between alkali metal ions and crown ethers containing oxygen and heteroatoms. However papers concerned with the complexing ability of transition metal ions by crown ethers are rare.[2)] Recently the syntheses of highly functionalized crown ethers have been reported, and in this connection several research groups[3—6)] have described the preparation of new-type crown ethers containing a ferrocene unit as a ring member, in which the iron atom may play a role of coordinatable heteroatom. We have previously reported that polyoxa[*n*]ferrocenophanes (**1** and **2**)[7,8)] and polyoxathia-[*n*]ferrocenophanes (**3**)[9)] exhibit considerably enhanced transition metal cation binding, compared with the corresponding ring-membered crown ethers. In this paper we discuss the syntheses of polyoxathia[*n*]ferrocenophanes (**8**) and polyoxadithia[*n,n*]ferrocenophanes (**9**) and the complexing behavior of **8a**—**d** with alkali and transition metal picrates.

Syntheses of 8 and 9. It has been reported[7)] that the potassium salt of 1,1′-dihydroxyferrocene (**5**), which is obtained from 1,1′-diacetoxyferrocene (**4**), reacts with the dihalide of polyethylene glycol (**6**) to give polyoxa[*n*]ferrocenophane (**1**). This method has been applied to the syntheses of **7**. We first attempted the reaction of ten molar equivalent of **6** with **5** which was obtained by the hydrolysis of **4**. The product, however, was an intractable mixture of unwanted materials and the yield of the desired **7** was very low. Subsequently, we examined the reaction of **4** with **6** in the presence of 18-crown-6 as phase transfer catalyst[10)] (Scheme 1) and obtained the corresponding **7** in 26—54% yields together with small amounts of **1** which was formed by the reaction of an equivalent molar quantity of **6** with **4**. The structures of **1a**—**1d** were also determined by the spectral data and admixture with authentic samples.[7)] The molecular formula of **7a** was, for example, deduced to be $C_{14}H_{16}Cl_2O_2Fe$ by mass spectroscopy (M^+, *m/e* 342, 344) and elemental analysis. In the ^1H-NMR spectrum of **8a**, the resonances for the α- and β-ring protons of ferrocene nucleus appeared as an A_2B_2 pattern at $\delta=4.05$ (t, $J=2.0$ Hz), and 3.65 (t, $J=2.0$ Hz), respectively, in addition to the signal of the methylene protons as a multiplet at $\delta=3.65$—4.05 (m, 8H). The IR spectrum of **7** showed ferrocene ring C–H absorption and ether linkage absorption near 1470 and 1110 cm^{-1}, respectively, but no absorption attributable to hydroxy and carbonyl groups. A new series of polyoxathia[*n*]ferrocenophanes (**8**) and polyoxadithia[*n,n*]ferrocenophanes (**9**) were synthesized by the reaction of an equimolar amount of sodium sulfide with dichloride (**7**) in several solvents. Best results were achieved when *N,N*-dimethylformamide (DMF) was used as solvent at refluxing temperature. For example, the reaction of **7b** with sodium sulfide in DMF gave a mixture of mononuclear 1,4,10,13-tetraoxa-7-thia[13]ferrocenophane (**8b**) and binuclear 1,4,10,13,24,27,33,36-octaoxa-7,30-dithia[13,13]ferrocenophane (**9b**) in 22% and less than 1% yields, respectively. However, from the reactions of **7a** and **7d** with sodium sulfide the binuclear **9a** and **9d** could not be isolated. Furthermore, the yields of the products were very low when *t*-butyl alcohol or *t*-butyl alcohol–water (1:1) was used as solvent, although the products were similar. The structures of the products **8a**—**d**, **9b**, and **9c** were established by their spectral data and elemental analyses. The structures of **8b** and **9b** were confirmed as follows. The molecular formula of **8b** was deduced to be $C_{18}H_{24}O_4SFe$ by elemental analysis and mass spectroscopy (M^+, *m/e* 392). In the ^1H-NMR spectrum of **8b**, the resonance for the methylene protons attached to the sulfur atom appeared as a triplet (4H, $J=10$ Hz) at $\delta=2.85$, in addition to a multiplet (12H, $-CH_2CH_2OCH_2CH_2S-$) at $\delta=3.65$—4.00 and a pair of triplets (each 4H, $J=2.0$ Hz, Fc–H_α, Fc–H_β) at $\delta=4.10$ and 3.82. The molecular formula of **9b** was also deduced to be $C_{36}H_{48}O_8S_2Fe$ by mass spectroscopy (M^+, *m/e* 748) and elemental analysis. In the ^1H-NMR spectrum of **9b**, the resonance for methylene protons attached



4　5　7a~d　1a~d

a; *n*=0, b; *n*=1, c; *n*=2, d; *n*=3



7a~d　8a~d　9a~d

a; *n*=0, b; *n*=1, c; *n*=2, d; *n*=3

TABLE 1. EXTRACTION OF METAL PICRATES FROM AQUEOUS TO ORGANIC PHASE (%)[a,b]

Compd	Li^+	Na^+	K^+	Rb^+	Cs^+	Tl^+	Ag^+
8a	0.7	0.7	0.5	0.8	0.5	0.8	Decomp
8b	1.2	1.2	1.4	0.8	1.5	8.3	Decomp
8c	0.7	1.4	1.2	3.8	5.1	37.4	Decomp
8d	0.9	2.0	22.5	25.4	20.6	82.1	Decomp
1a	—	1.5	4.5	4.6	5.6	25.2	Decomp
B15C5	1.2	23.9	50.1	27.5	12.8	56.0	33.6

a) Solvents: Water and dichloromethane (equal volumes). b) Ferrocenophane $=7.0\times10^{-4}$ M ($1\ \mathrm{M}=1\ \mathrm{mol\ dm^{-3}}$). Picric acid $=7.0\times10^{-5}$ M. Metal nitrate $=0.1$ M.

to the sulfur atom appeared as triplet (4H, $J=11$ Hz) at $\delta=2.80$, in addition to a multiplet (24H, $-OCH_2CH_2OCH_2CH_2S-$) at $\delta=3.61$—4.00, a pair of triplets (each 8H, $J=2.0$ Hz, Fc–H_α, Fc–H_β) at $\delta=4.09$ and 3.84. The structures of the other new compounds were also determined by similar methods.

Extraction Efficiency of 8a—d. Compounds **8a**—**d** were tested for extractability with metal ions by the Pedersen method.[11] The data are summarized in Table 1, along with those of **1a** and benzo-15-crown-5. Compounds **8** (except **8d**) showed poor extraction efficiency with alkali metal ions. Furthermore, **8b** showed less extraction efficiency than those of the corresponding ring membered polyoxaferrocenophane (**1a**) with all alkali metal cations except lithium. This is not surprising for the ferrocenophanes since Pedersen[12] has shown that the complexing power of crown ethers for alkali metal ions is largely destroyed by substituting –S– for –O– in the macrocyclic polyether ring. From the HSAB rule[13] it is expected that the incorporation of a sulfur atom (a soft atom) into the macrocycle has a strong influence on the complexing ability with transition metal ions (a soft atom). Indeed, the extraction efficiency of **8** toward thallium ion was remarkably higher than those toward alkali metal ions, although the benzo-crown ether showed a similar extraction efficiency toward any of the cations described above. However, it was shown that the extraction efficiency of **8b** with thallium ion is weaker than that of **1a** which has the same ring member. For silver cation, the extraction efficiency of **8**, especially **8d**, could not be measured because of a rapid decomposition in which the iron atom of ferrocene nucleus might be oxidized by the incorporated silver cation. These results are similar to those of the extraction efficiency of **1** with silver ion.[7] Finally, it is noteworthy that **8d** showed high preference toward transition metal ions and the relationship between the hole size of the host molecule and the size of the guest ions was the second factor. The results seem to be reasonable when considering that the macrocyclic polyethers complex with cations within their very larger rings by wrapping themselves completely arround the cation. These results are similar to those of the complexing ability of macrocyclic antibiotics such as nonactin with metal cations.[14]

Experimental

All melting points are not corrected. ^{1}H-NMR spectra were determined in the indicated solvent on a Hitachi R-90 spectrometer. Chemical shifts are expressed in parts par million downfield from an internal tetramethylsilane. Mass spectra were recorded on a JEOL-O1SG-2 spectrometer and Hitachi M-80 spectrometer at 75 and 70 eV, respectively. Optical spectra were obtained on an Hitachi Model 100-10 spectrometer.

Materials. All solvents and reagents were used as purchased unless otherwise specified. 1,1′-diacetoxyferrocene (**4**) was prepared according to the previously reported method. 1,11-dichloro-3,6,9-trioxaundecane (**6c**) and 1,14-dichloro-3,6,9,12-tetraoxatetradecane (**6d**) were prepared according to the usual method. Silica gel for thin layer chromatography utilized Wakogel B-5F.

1,1′-Bis(3-chloro-1-oxapropyl)ferrocene (7a). 1,1′-Diacetoxyferrocene (**4**) (0.8 g, 2.6 mmol) was added to 10% aq potassium hydroxide solution (10 ml) containing 18-crown-6 (0.2 g, 0.075 mmol) under nitrogen and the mixture was stirred under refluxing. After 20 min a large excess of 1,2-dichloroethane (12 g, 80 mmol) was added at once and the mixture was stirred for 6 h at 80 °C. After the solution was cooled to room temperature, the mixture was extracted with three 20 ml portions of ether. The extracts were combined, washed with water, and concentrated *in vacuo*. The residual oil was chromatographed on a silica gel TLC (acetone–hexane 1:9 as eluent). The first band was extracted with acetone at room temperature, followed by filtration and evaporation of the solvent, to give a yellow oil which solidified on standing. The crude material was recrystallized from hexane to give 1,4-dioxa[4]ferrocenophane (**1a**) in 9% yield; mp 129—131 °C (lit,[7] 129—131 °C). The second band was extracted with acetone at room temperature, followed by filtration and evaporation of the solvent, to give yellow crystals. Recrystallization of the crude material from hexane gave **7a**, mp 58—59.5 °C, in 54% yield. ^{1}H-NMR ($CDCl_3$): $\delta=4.05$ (t, $J=2.0$ Hz, 4H, Fc–H_α), 3.65 (t, $J=2.0$ Hz, 4H, Fc–H_β), 3.65—4.05 (m, 8H, $-OCH_2CH_2Cl$). MS (75 eV): *m/e* 342 and 344 (M^+). Found: C, 48.98; H, 4.66%. Calcd for $C_{14}H_{16}Cl_2O_2Fe$: C, 49.27; H, 4.66%.

1,1′-Bis(7-chloro-1,4-dioxahexyl)ferrocene (7b). Reaction of **4** (0.8 g, 2.6 mmol) with **6b** (12 g, 75 mmol) by the method described above gave **1b** (2%) and **7b** (53%). **1b**, mp 120—121 °C (lit,[7] 120—121 °C). **7b**, oil, ^{1}H-NMR ($CDCl_3$): $\delta=4.20$ (t, $J=2.0$ Hz, 4H, Fc–H_α), 3.80 (t, $J=2.0$ Hz, 4H, Fc–H_β), 3.65—4.07 (m, 16H, $-OCH_2CH_2OCH_2CH_2Cl$). MS (75 eV): *m/e* 430 and 432 (M^+). Found: C, 49.93; H, 5.89%. Calcd for $C_{18}H_{24}Cl_2O_4Fe$: C, 50.15; H, 5.61%.

1,1′-Bis(9-chloro-1,4,7-trioxanonyl)ferrocene (7c). Reaction of **4** (0.8 g, 2.6 mmol) with **6c** (12 g, 60 mmol) gave **1c** (0.5%) and **7c** (26%). **1c**, mp 58—59 °C. **7c**, oil, ^{1}H-NMR ($CDCl_3$): $\delta=4.12$ (t, $J=2.0$ Hz, 4H, Fc–H_α), 3.89 (t, $J=2.0$, 4H, Fc–H_β), 3.76 (s, 12H, $-OCH_2CH_2O-$), 3.70—3.98 (m, 12H, $-OCH_2CH_2OCH_2CH_2Cl$). MS (75 eV): *m/e* 518 and 520 (M^+). Found: C, 50.63; H, 6.41%. Calcd for $C_{22}H_{32}Cl_2O_6Fe$: C, 50.89; H, 6.21%.

1,1'-Bis(12-chloro-1,4,7,10-tetraoxadodecyl)ferrocene (**7d**). Reaction of **4** (0.8 g, 2.0 mmol) with **6d** (12 g, 49 mmol) gave **1d** (0.7%) and **7d** (26%). **1d**, mp 60—61 °C (lit,⁷⁾ 60—61 °C). **7d**, oil, ^{1}H-NMR ($CDCl_3$): δ=4.13 (t, J=2.0 Hz, 4H, Fc-H_α), 3.87 (t, J=2.0 Hz, 4H, Fc-H_β), 3.75 (s, 16H, $-OCH_2CH_2O-$), 3.71—4.00 (m, 16H, $-OCH_2CH_2OCH_2CH_2Cl$). MS (75 eV): *m/e* 606 and 608 (M^+). Found: C, 51.57; H, 6.70%. Calcd for $C_{26}H_{40}Cl_2O_8Fe$: C, 51.42; H, 6.64%.

Reaction of **7a** *with Sodium Sulfide in DMF.* To a solution of $Na_2S \cdot 9H_2O$ (0.864 g, 3.6 mmol) in 200 ml of DMF at refluxing temperature was added a solution of **7a** (1.03 g, 3.00 mmol) in 40 ml of DMF under nitrogen. Stirring was continued at refluxing temperature for 20 h, and the reaction mixture was then cooled to room temperature. After evaporation of the solvent, the residue was diluted with water and extracted three times with ether. The combined extracts were washed with water, dried over anhydrous magnesium sulfate, and concentrated. The residual oil was chromatographed on silica gel TLC (dichloromethane: tetrachloromethane 4:1 as eluent). The first band was extracted with acetone at room temperature, followed by filtration and evaporation of the solvent, to give a yellow oil which solidified on standing. The crude material was recrystallized from hexane to give **8a**, mp 104—106 °C, in 66% yield. ^{1}H-NMR ($CDCl_3$): δ=4.20 (t, J=2.0 Hz, 4H, Fc-H_α), 4.14 (t, J=10.0 Hz, 4H, $-SCH_2CH_2O-$), 3.79 (t, J=2.0 Hz, 4H, Fc-H_β), 2.92 (t, J=10 Hz, $-OCH_2CH_2S-$). MS (75 eV): *m/e* 304 (M^+). Found: C, 55.61; H, 5.65%. Calcd for $C_{14}H_{16}O_2SFe$: C, 55.28; H, 5.31%. The second band was extracted with acetone at room temperature, followed by filtration and evaporation of the solvent, to give yellow crystals. Recrystallization of the crude material from hexane gave the starting material, mp 58.5—59.5 °C.

Reaction of **7b** *with Sodium Sulfide in DMF.* Reaction of **7b** (1.29 g, 3.00 mmol) with $Na_2S \cdot 9H_2O$ (0.864 g, 3.60 mmol) in 240 ml of DMF gave a mixture of **1b**, the starting material, and **9b**. After usual work-up, the reaction mixture was chromatographed on silica gel TLC (hexane: acetone 4:1). The first fraction was extracted with acetone, followed by filtration and evaporation of the solvent, to give yellow crystals. Recrystallization of the crude material from hexane gave **8b** as yellow crystals, mp 93—95 °C, in 21% yields. ^{1}H-NMR ($CDCl_3$): δ=4.10 (t, J=2.0 Hz, 4H, Fc-H_α), 3.82 (t, J=2.0 Hz, 4H, Fc-H_β), 3.65—4.00 (m, 12H, $-OCH_2CH_2O-$), and 2.85 (t, J=11 Hz, $-CH_2SCH_2-$, 4H). MS (75 eV): *m/e* 392 (M^+). Found: C, 55.13; H, 6.36%. Calcd for $C_{18}H_{24}O_4SFe$: C, 55.11; H, 6.17%. The second band gave the starting material, oil (8%). The third fraction was extracted with acetone. Evaporation of the solvent gave yellow oil. Crystallization of the crude material from hexane give pure **9b**, mp 108—109 °C, in 0.8% yield. ^{1}H-NMR ($CDCl_3$): δ=4.09 (t, J=2.0 Hz, 8H, Fc-H_α), 3.84 (t, J=2.0 Hz, 8H, Fc-H_β), 3.61—4.00 (m, 24H, $-OCH_2CH_2O-$), 2.80 (t, J=11 Hz, 8H, $-SCH_2CH_2O-$). MS (75 eV): *m/e* 784 (M^+). Found: C, 55.35; H, 6.24%. Calcd for $C_{36}H_{48}O_8S_2Fe$: C, 55.11; H, 6.17%.

Reaction of **7c** *with Sodium Sulfide in DMF.* Reaction of **7c** (1.55 g, 3.00 mmol) with $Na_2S \cdot 9H_2O$ (0.864 g, 3.60 mmol) in 240 ml of DMF gave a mixture of **8c**, **9c**, and the starting material. **8c**, mp 52—53.5 °C, in 30% yield, ^{1}H-NMR ($CDCl_3$): δ=4.09(t, J=2.0 Hz, 4H, Fc-H_α), 3.82 (t, J=2.0 Hz, 4H, Fc-H_β), 3.66 (s, 8H, $-OCH_2CH_2O-$), 3.60—3.95 (m, 12H, $-OCH_2CH_2OCH_2CH_2O-$), 2.79 (t, J=11 Hz, 4H, $-SCH_2CH_2O-$). MS(75 eV): *m/e* 480 (M^+). Found: C, 55.28; H, 6.93%. Calcd for $C_{22}H_{32}O_6SFe$: C, 55.00; H, 6.71%. **9c**, oil, a trace yield, ^{1}H-NMR ($CDCl_3$): δ=4.01 (t, J=2.0 Hz, 8H, Fc-H_α), 3.80 (t, J=2.0 Hz, 8H, Fc-H_β), 3.58 (s, 16H, $-OCH_2CH_2O-$), 3.47—3.80 (m, 24H, $-OCH_2CH_2OCH_2CH_2Cl$), 2.67 (t, J=11 Hz, 8H, $-SCH_2CH_2O-$). MS (75 eV): *m/e* 961 (M^+). Found: C, 55.26; H, 6.90%. Calcd for $C_{44}H_{64}O_{12}S_2Fe$: C, 55.00, H, 6.71%.

Reaction of **7d** *with Sodium Sulfide in DMF.* Reaction of **7d** (1.82 g, 3.00 mmol) with $Na_2S \cdot 9H_2O$ (0.864 g, 3.60 mmol) in 240 ml of DMF gave a mixture of **8d** and the starting material. **8d**, mp 47—48 °C, 38% yield, ^{1}H-NMR ($CDCl_3$): δ=4.10 (t, J=2.0 Hz, 4H, Fc-H_α), 3.83 (t, J=2.0 Hz, 4H, Fc-H_β), 3.69 (s, 16H, $-OCH_2CH_2O-$), 3.56—4.05 (m, 12H, $-OCH_2CH_2O-$), and 2.67 (t, J=11 Hz, 4H, $-SCH_2CH_2O-$). MS (75 eV): *m/e* 568 (M^+). Found: C, 55.23; H, 7.01%. Calcd for $C_{26}H_{40}O_8SFe$: C, 54.94; H, 7.09%.

Extraction Ability. Extraction ability of **8** with metal cations was examined by the method described in the previous paper.⁷⁾

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