  Bull. Chem. Soc. Jpn., 57, 63—67 (1984)

Synthesis and Physicochemical Properties of Dioxathia[*n*]ferrocenophanes

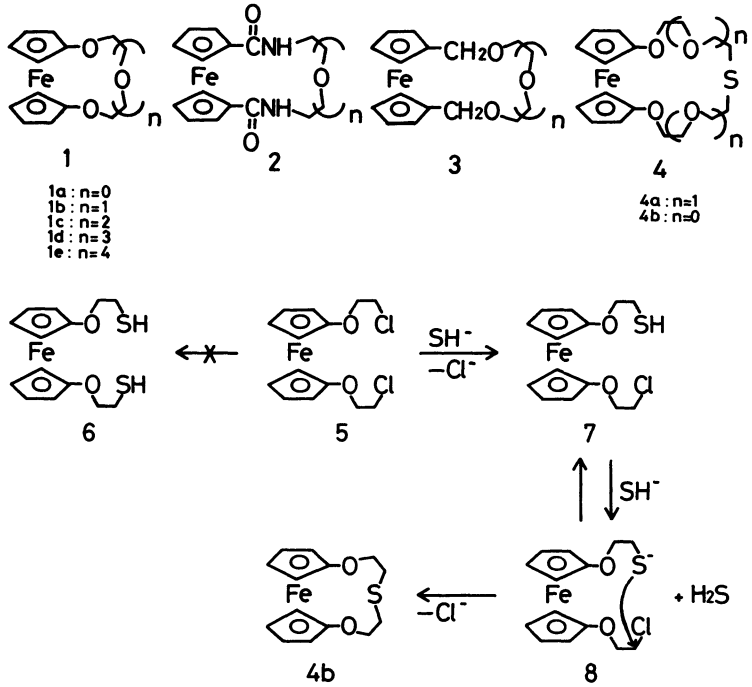
Sadatoshi AKABORI,* Sumio SHIBAHARA, Yoichi HABATA, and Masaru SATO†
Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274
†*Chemical Analysis Center, Saitama University, Urawa, Saitama 338*
(Received April 23, 1983)

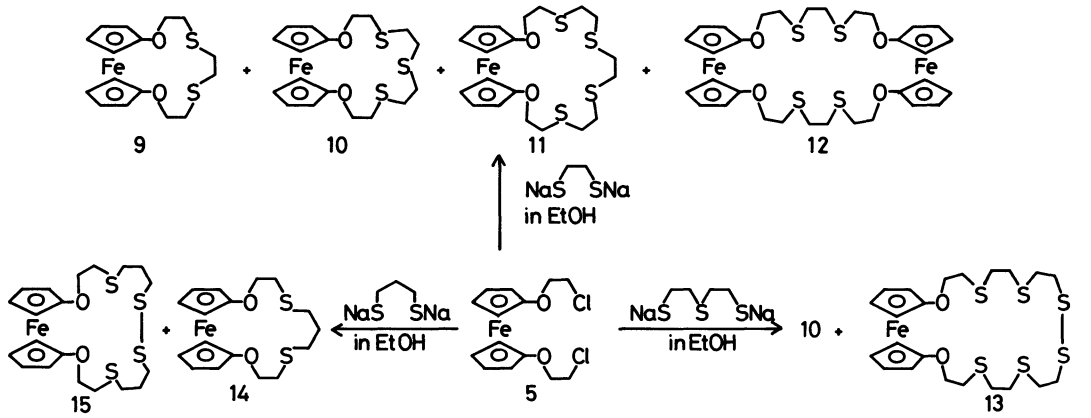
The reaction of 1,1′-bis(2-chloroethoxy)ferrocene with 1,2-ethanedithiolate in absolute ethanol gave mononuclear 1,10-dioxa-4,7-dithia[10]ferrocenophane and binuclear 1,10,21,30-tetraoxa-4,7,24,27-tetrathia-[10,10]ferrocenophane, along with a small amount of unexpected 1,13-dioxa-4,7,10-trithia[13]ferrocenophane and 1,16-dioxa-4,7,10,13-tetrathia[16]ferrocenophane. Extraction of aqueous metal picrates (M; alkali, alkaline earth, Ag^+, Tl^+, Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, and Hg^{2+}) with dioxathia[*n*]ferrocenophanes was examined and also with the corresponding ring membered polyoxa[*n*]ferrocenophanes. Dioxathiaferrocenophanes showed a highly selective extraction ability towards bivalent mercury and copper ions.

While investigations of crown ethers and their cation complexes have been steadily gaining interest during the past decade, most attention has been focused so far on the synthesis of a new type of ligand.[1] The preparation and physicochemical properties of several kinds of polyoxa- and polythia[*n*]ferrocenophanes (**1**—**4**) have been previously reported.[2-7] It was shown that some of these compounds, particularly those containing five and six heteroatoms in the macrocyclic ring, form complexes with alkali-metal, thallium, and silver cations. Many methods for the synthesis of polythiacrown ethers have been reported.[8-11] However, with the exception of thioformaldehyde polymerization,[12] all other methods of thioether ring closure were based on α-mercaptide displacement of ω-halide function. We wish here to report a novel finding concerning the synthesis and extraction ability of dioxathia[*n*]ferrocenophanes.

Synthesis and Structure. The following reactions were carried out in order to obtain 1,1′-bis(2-mercaptoethoxy)ferrocene (**6**) as a starting material. 1,1′-Bis(2-chloroethoxy)ferrocene (**5**) was readily synthesized by reaction of the disodium salt of 1,1′-ferrocenediol, which was prepared by the hydrolysis of 1,1′-diacetoxyferrocene, with large excess of 1-bromo-2-chloroethane. An attempt to convert **5** into the corresponding dithiol (**6**) by a reaction with sodium hydrogensulfide failed. Instead 1,7-dioxa-4-thia[7]ferrocenophane (**4b**) was obtained in 49% yield, doutless by incursion of the cyclization mechanism accompanying an intramolecular attack of the thiolate anion to the halogenated carbon atom.[11] Compound **4b** was found to be identical with an authentic sample[7] prepared by the reaction of **5** with sodium sulfide. Therefore, dioxathia[*n*]ferrocenophanes were prepared according to the following method.

A solution of 5 (1.0 molar equiv) in absolute ethanol was added at once to a solution of disodium 1,2-ethanedithiolate (3.0 molar equiv) in absolute ethanol and the resulting solution was stirred at refluxing temperature for 14 h. After the usual work-up, the reaction mixture was separated by silica-gel thinlayer chromatography. From the reaction mixture, mononuclear 1,10-dioxa-4,7-dithia[10]ferrocenophane (**9**) and





binuclear 1,10,22,31-tetraoxa-4,7,25,28-tetrathia[10.10]ferrocenophane (**12**) were obtained in 38 and 3.2% yields, respectively. Moreover, a small amount of unexpected 1,13-dioxa-4,7,10-trithia[13]ferrocenophane (**10**, 6.1%) and 1,16-dioxa-4,7,10,13-tetrathia-[16]ferrocenophane (**11**, 1.9%) were isolated.[13] When **5** was treated with equimolar of 1,2-ethanedithiol under similar conditions, compounds **9**, **10**, and **12** were obtained, although the yields of those were somewhat low and **11** could not be isolated. Interestingly, the reactions of **5** with bis(2-mercaptoethyl) sulfide did not yield the unexpected ring enlarged dioxathia[*n*]ferrocenophanes, but gave normal mononuclear ferrocenophane (**10**) and disulfide (**13**) in 51 and 2.9% yields, respectively. Such an abnormal reaction was not observed in the reaction of **5** with 1,3-propanedithiol. Isolation of the disulfide (**13** and **15**) suggest that the dithiolate, which was formed by a nucleophilic attack of two molar of 1,2-ethanedithiolate at the halogenated carbons of **5**, was easily oxidized by the trace amount of oxygen in an atmosphere of nitrogen to give the corresponding disulfide in low yield. The results obtained by the reactions of **5** with dithiols are listed in Table 1, along with the physical data of the products.

The possible mechanism of the unexpected formation of compounds **10** and **11** is shown in Scheme. The initial reaction may be a nucleophilic attack of two molar of 1,2-ethanedithiolate on the halogenated carbons of **5** to give the dithiolate **16**. The second step of the reaction is considered to be single proton elimination from the methylene next to the sulfur atom followed by elimination of S^{2-} to give the vinyl sulfide intermediate **17**. Thus, the formation of **10** can be interpreted by an intramolecular attack of $-S^-$ at the double bond followed by addition of a proton to the resulting sulfur-stabilized anion. Moreover, the addition of another disodium 1,2-ethanedithiolate to **17** would form the ferrocenophane **11** by the same mechanism. Support for this mechanism is provided by the following results. The reaction of **5** with disodium 1,3-propanedithiolate gave 1,11-dioxa-4,8-dithia[11]ferrocenophane (**14**) in 64% yield, but no abnormal product corresponding to **10** and **11**, because the dithiolate intermediate corresponding **17** in this reaction have no leaving group (S or SH) for forming a vinyl sulfide group. On the other hand, **5** reacted with the disodium salt of bis(2-mercaptoethyl) sulfide to afford **10** and **13**. This is probably due to the large ring size of the possible cyclization intermediate which would make the template effect impossible, and this can help the intramolecular nucleophilic attack to the cyclization to ferrocenophane. However, many attempts to isolate intermediates such as **17** and **18** from the reaction mixture failed. Thus, the resulting intermediates (**17** and **18**) must be unstable or too reactive and might react easily with an intermediate mercapto group.

Table 1. Yield, Mp, mass spectral data of dioxapolythia[*n*]ferrocenophanes

Compd	Yield %	Mp θ_m/°C	Mass (M^+, *m/e*)
4a	49	104—106 (104—106)[7]	
9	38	115—116.6	364
10	6.1 (51)[a]	114—116	424
11	1.9	69—70	484
12	3.2	129—131	728
13	2.9	79—81	576
14	64	149—150	378
15	8.6	84—86	484

a) The value in parenthesis showed the yield obtained by the reaction of **5** with bis(2-mercaptoethyl) sulfide.

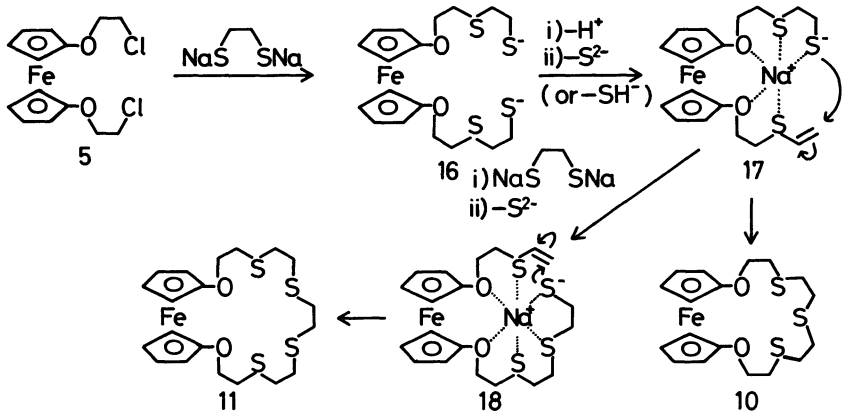
Structural assignment of these ferrocenophanes **9**—**15** and **6** was achieved by their elemental analyses, spectral inspection, and partly on the basis of the unequivocal synthesis. In particular all of their elemental analyses were in good accord with the proposed compositions, and the IR spectra showed a cyclopentadienyl C-H absorption band at near 1485 cm^{-1}, an ether linkage band near 1015 cm^{-1} and a C-S stretching vibration band near 610 cm^{-1}. In addition to the above bands, the IR spectra of compounds **13** and **15** also showed an S-S stretching band near 490 cm^{-1}. In the ^{1}H-NMR spectra of **9**—**11**, the signal for methylene protons next to the oxygen atom appeared as a triplet (4H, *J*=*ca.* 6 Hz) near δ 4.10 and the signal for the methylene protons α to the sulfur atom appeared as a triplet (4H, *J*=*ca.* 6 Hz) near δ 2.9. The signals for the other methylene protons appeared at δ 3.03—2.62, respectively. Furthermore, ferrocene ring protons resonanced as a pair of triplets (each 4H, *J*=*ca.* 1.8 Hz)

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

Compd	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}
4a	1.2	1.2	1.4	0.8	1.5	0.6	0.8	0.7
9	0.5	0.9	0.8	0.3	2.1	0.5	0.1	0.8
10	0.5	1.3	1.3	1.7	2.6	1.4	1.2	0.7
1d	0.5	1.5	4.5	4.6	5.6	1.2	0.5	0.4
B15C5	1.2	23.9	50.1	27.5	12.8	0.3	0.5	0.4

Compd	Ba^{2+}	Cd^{2+}	Hg^{2+}	Tl^+	Pb^{2+}	Ag^+	Cu^{2+}	Co^{2+}	Ni^{2+}
4a	0.4	0.9	30.4	8.3	2.0	Decomp	1.9	1.1	1.1
9	1.3	0.8	38.1	1.4	1.5	Decomp	27.8	0.6	0.5
10	1.6	1.0	76.1	2.1	1.5	Decomp	50.9	2.0	0.7
1d	0.6	0.8	11.7	25.2	3.3	Decomp	17.9	1.3	0.9
B15C5	1.2	1.0	0.5	56.0	2.2	Decomp	0.6	1.2	0.5

a) Solvent: Water and dichloromethane(1 : 1). Concentration of polyether: 7×10^{-4} M. Concentration of picric acid: 7×10^{-5} M. Concentration of metal nitrates: 0.1 M.



at near δ 4.10 (Fc-Hα) and 3.88 (Fc-Hβ). The ^{1}H-NMR spectrum of binuclear ferrocenophane (**12**) and disulfide (**13** and **15**) are similar to those of mononuclear ferrocenophanes.

Extraction Ability. The extraction ability of ferrocenophanes (**4a**, **9**, and **10**) for alkali, alkaline-earth metals, and several other metal cations was measured by Pedersen's method.[15)] The data are summarized in Table 2, along with those of polyoxaferrocenophane (**1d**) and benzo-15-crown-5. The dioxathia[*n*]ferrocenophanes (**4a**, **9**, and **10**) showed little extraction ability toward alkali metal ions (hard cation), although benzo-15-crown-5 showed relatively high extraction ability. The extraction ability of the dioxathiaferrocenophanes toward alkaline-earth metal ions is also low and these result are similar to those of polyoxaferrocenophane (**1d**) and benzo-15-crown-5.

The extraction ability of dioxathiaferrocenophanes (**4a**, **9**, and **10**) toward transition metal cations was more complex. A soft mercury(II) ion was extracted by **9** and **10** very well. The extraction ability of the ferrocenophanes (**1d**, **4a**, and **10**) having the same ring member toward mercury(II) ion in the following order: **10**(76.1)>**4a**(30.4)>**1d**(11.7). The phenomenon may be explained by the HSAB rule.[16)] That is, the successive displacement of an oxygen atom in the macrocyclic ring of the ferrocenophanes by a sulfur atom, which is softer compared with an oxygen atom, increases the affinity to a soft mercury(II) ion. However, the extraction ability of a thallium(I) ion, which is classified in a soft ion, by the ferrocenophanes (**1d**, **4a**, and **10**) rather showed the reverse order: **1d**(25.2)>**4a**(8.3)> **10**(2.1). So, the extraction ability of metal ions by the ferrocenophanes must be influenced by other factors, such as the conformation of the macrocycles, the size of the hole in the macrocycles, and so on, as well as a soft-hard characterization of the metal ions. Interestingly, benzo-15-crown-5 extracted a thallium(I) ion more efficiently than **1d**, while it scarcely extracted a mercury(II) ion. These obsevations indicated that **10** has a specifically high extraction ability toward a mercury(II) ion. A similar trend was observed in the extraction ability of 18-crown-6 and its sulphur analog toward silver(I) ion.[10)] The extraction ability of **4a**, **9**, and **10** toward a silver(I) ion was then examined. However, their extraction ability could not be measured, because of a rapid decomposition, in which the iron atom of ferrocene might be oxidized by the incorporated silver(I) ion. A similar result was also observed in polyoxa[*n*]ferrocenophanes.[3)]

The extraction ability of these ferrocenophanes toward the borderline ions, nickel(II) and cobalt(II) ions,

was very low, while that of a copper(II) ion was relatively high. The remarkable extraction ability of **9** and **10** toward a copper(II) ion is noteworthy, since the extraction ability of a copper(II) ion by a crown-type compound has rarely been reported. In connection with this observation, it is interesting that cyclic polythiaethers formed the complex having a high stability constant with copper(II) ion.[18]

Experimental

The melting points are uncorrected. The mass spectra were taken on a Hitachi M-80 mass spectrometer. The ^{1}H-NMR spectra were obtained on a Hitachi R-90 spectrometer, with TMS as the internal standard. The optical spectra were obtained on a Hitachi Model 200-10 spectrometer. The IR spectra were measured on a JASCO IRA-2 Diffraction Grating Infrared Spectrometer.

Materials and Reagents. 1,1'-Bis(2-chloroethoxy)ferrocene (**5**) is prepared according to the previously reported method. The other reagents employed were commercial materials or were prepared by the usual methods.

Reaction of 5 with Sodium Hydrogensulfide. To a solution of **5** (0.243 g, 0.71 mmol) in *n*-butanol (150 ml) was added sodium hydrogensulfide hydrate (0.7 g, 7.1 mmol) and the mixture was stirred for 13 h at 120 °C under nitrogen. After the solution had been cooled to room temperature, the solvent was evaporated *in vacuo*. The residue was extracted with ether. The extracts were combined and filtered. The filtrate was concentrated and the residue chromatographed on silica gel TLC (hexane:acetone=3:1). The main 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 **4a** as yellow crystals, mp 104—106 °C (lit, 104—106 °C) in 49% yield. Compound **4b** was identified by direct comparison with the spectral data of an authentic sample.

Reaction of 5 with 1,2-Ethanedithiol. 1,2-Ethanedithiol (1.5 ml, 17 mmol) was added to 500 ml of absolute ethanol containing 0.53 g (13.3 mmol) of sodium hydroxide under nitrogen, and the mixture was stirred at room temperature. After 10 min, a solution of **5** (1.43 g, 4.17 mmol) in 100 ml of absolute ethanol was added all at once, and then the mixture was stirred for 13 h at refluxing temperature. After the solution had cooled to room temperature, the solvent was evaporated *in vacuo*. The residue was extracted with ether and chloroform. The extracts were combined, followed by filtration and evaporation of the solvent to give a yellow oil. The residue was chromatographed on silica gel TLC (hexane: acetone: chloroform=6:1:trace). 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 **9** as yellow crystals, mp 115—116 °C, in 38% yields. ^{1}H-NMR (in $CDCl_3$): δ 4.11 (t, J=1.8 Hz, Hα, 4H), 3.89 (t, J=1.8 Hz, Hβ, 4H), 4.12 (t, J=6.3 Hz, -OCH_2, 4H), 3.03 (s, -SCH_2CH_2S-, 4H), 2.91 (t, J=6.3 Hz, -SCH_2, 4H), MS (70 eV): m/e 364 (M^+). IR (KBr): 3100, 2930, 1485, 1275, 1080, and 610 cm^{-1}. Found: C, 52.72; H, 5.58%. Calcd for $C_{16}H_{20}O_2S_2Fe$: C, 52.75; H, 5.53%. The second fraction was extracted with acetone. Evaporation of the solvent gave yellow crystals. Recrystallization of the crude material from hexane gave pure **10**, mp 114—116 °C, in 6.1% yield. ^{1}H-NMR (in $CDCl_3$): δ 4.08 (t, J=2.0 Hz, Hα, 4H), 3.88 (t, J=2.0 Hz, Hβ, 4H), 4.05 (t, J=6.1 Hz, -OCH_2, 4H), 2.62—3.02 (t+m, -SCH_2, 12H). MS (70 eV): m/e 424 (M^+). IR (KBr): 3100, 2940, 1480, 1250, 1085, and 610 cm^{-1}. Found: C, 50.89; H, 5.75%. Calcd for $C_{18}H_{24}O_2S_3Fe$: C, 50,94; H, 5.70%. The third fraction was extracted with acetone. Evaporation of the solvent gave yellow crystals. Recrystallization of the crude material from ethanol gave pure **11**, mp 69—70 °C, in 1.9% yield. ^{1}H-NMR (in $CDCl_3$): δ 4.12 (t, J=1.8 Hz, Hα, 4H), 3.88 (t, J=1.8 Hz, Hβ, 4H), 4.05 (t, J=6.4 Hz, -OCH_2, 4H), 2.80—3.02 (s+m, -SCH_2, 16H). MS (70 eV): m/e 484 (M^+). IR (KBr): 3100, 2930, 1485, 1245, 1050, and 620 cm^{-1}. Found: C, 49.41; H, 5.99%. Calcd for $C_{20}H_{28}O_2S_4Fe$: C, 49.58; H, 5.82%. The fourth fraction was extracted with acetone. Evaporation of the solvent gave a yellow oil which was rechromatographed on silica gel TLC (hexane: acetone: chloroform=3:1:trace). The main band was extracted with acetone. Evaporation of the solvent gave a yellow oil. Recrystallization of the crude material from ethanol gave pure **12**, mp 129—131 °C, in 3.2% yield. ^{1}H-NMR (in $CDCl_3$): δ 4.07 (t, J=1.8 Hz, Hα, 8H), 3.84 (t, J=1.8 Hz, Hβ, 4H), 4.00 (t, J=6.5 Hz, -OCH_2, 8H), 2.77—2.97 (s+t, -SCH_2, 16H). MS (70 eV): m/e 728 (M^+). IR (KBr): 3100, 2920, 1480, 1245, 1085, and 610 cm^{-1}. Found: C, 52.91; H, 5.76%. Calcd for $C_{32}H_{40}O_4S_4Fe$: C, 52.75; H, 5.53%.

Reaction of 5 with Bis(2-mercaptoethyl) Sulfide. Bis(2-mercaptoethyl) sulfide (1.8 ml, 12.4 mmol) was added all at once to 240 ml of absolute ethanol containing sodium hydroxide (0.33 g, 8.2 mmol) under nitrogen and the mixture was stirred at room temperature. After 10 min, a solution of **5** (0.814 g, 2.4 mmol) in 60 ml of absolute ethanol was added all at once, then the mixture was stirred for 15 h at reflux temperature. After the solution had been cooled to room temperature, the solvent was evaporated *in vacuo*. The residue was extracted with chloroform. The extract was filtered off and the filtrate was concentrated *in vacuo*. The residue was chromatographed on silica gel (hexane: acetone: chloroform=6:1:trace). The first fraction was extracted with acetone. Evaporation of the solvent gave a yellow oil. Recrystallization of the crude material from hexane gave pure **10** as yellow crystals, mp 114—116 °C in 51% yield. The pure **10** was identified by direct comparison with the spectral data of an authentic sample obtained by reaction of 1,2-ethanedithiol with **5**. The second fraction was extracted with acetone. Evaporation of the solvent gave a yellow oil. The crude material was recrystallized from hexane to give **13** as yellow crystals, mp 79—81 °C, in 2.9% yield. ^{1}H-NMR (in $CDCl_3$): δ 4.10 (t, J=1.9 Hz, Hα, 4H), 4.03 (t, J=6.5 Hz, 4H, -OCH_2), 3.87 (t, J=1.9 Hz, Hβ, 4H), 2.78—3.00 (m, 20H). MS (70 eV): m/e 576 (M^+). IR (KBr): 3100, 2930, 1485, 1250, 1015, and 490 cm^{-1}. Found: C, 46.12; H, 5.70%. Calcd for $C_{22}H_{32}O_2S_6Fe$: C, 45.83; H, 5.56%.

Reaction of 5 with 1,3-Propanedithiol. 1,3-Propanedithiol (1.0 ml, 9.6 mmol) was added to 250 ml of absolute ethanol containing sodium hydroxide (0.277 g, 6.9 mmol) under nitrogen, and the mixture was stirred at room temperature. After 10 min, a solution of **5** (0.711 g, 2.07 mmol) in 100 ml of absolute ethanol was added all at once, and the mixture then stirred for 14 h at reflux temperature. The usual work-up gave a yellow oil, which was chromatographed on alumina using dichloromethane as eluent. The fraction gave yellow crystals. Recrystallization of the crude product from hexane gave pure **14**, mp 149—150 °C, in 64% yield. ^{1}H-NMR (in $CDCl_3$): δ 4.19 (t, J=2.0 Hz, Hα, 4H), 3.91 (t, J=2.0 Hz, Hβ, 4H), 4.10 (t, J=6.5 Hz, -OCH_2, 4H), 2.70—3.03 (m, -SCH_2, 8H), 2.08 (q, J=6.3 Hz, CH_2, 2H). MS (70 eV): m/e 378 (M^+). IR (KBr): 3080, 2910, 1485, 1245, 1075, and 610 cm^{-1}. Found: C, 53.69; H, 5.70%. Calcd for $C_{17}H_{22}O_2S_2Fe$: C, 53.97; H, 5.82%. The second fraction gave crude **15** as a yellow oil. Recrystallization of the crude material from hexane gave pure **15**, mp 84—86 °C, in 8.6% yield. ^{1}H-NMR (in $CDCl_3$): δ 4.07 (t, J=1.9 Hz, Hα, 4H), 4.00 (t, J=6.4 Hz, -OCH_2 4H), 3.83 (t, J=1.9 Hz, Hβ, 4H), 2.66—2.98 (m, 12H), 2.05 (q, J=6.2 Hz, CH_2, 4H). MS (70 eV): m/e 484 (M^+). IR (KBr): 3100, 2910, 1485, 1245, 1075, and 490 cm^{-1}.

Found: C, 49.77; H, 5.73%. Calcd for $C_{20}H_{28}O_2S_4Fe$: C, 49.58; H, 5.82%.

Extraction Ability. Extraction ability of the ferrocenophanes and benzo-15-crown-5 with metal picrate was examined by the method described in a previous paper.[3]

References

1) R. E. Izatt and J. J. Christensen, "Synthetic Multidentate Macrocyclic Componds," Academic Press, New York (1978).

2) J. F. Biernat and T. Wilczewski, *Tetrahedron*, **36**, 2521 (1980); G. Oepen and F. Vogtle, *Liebigs Ann. Chem.*, **1979**, 1094; A. P. Bell and C. D. Hall, *J. Chem. Soc., Chem. Commun.*, **1980**, 163; P. J. Hammond, A. P. Bell, and C. D. Hall, *J. Chem. Soc., Perkin Trans. 1*, **1983**, 707.

3) S. Akabori, Y. Habata, Y. Sakamoto, M. Sato, and S. Ebine, *Bull. Chem. Soc. Jpn.*, **56**, 537 (1983).

4) M. Sato, M. Kubo, S. Ebine, and S. Akabori, *Tetrahedron Lett.*, **23**, 185 (1982).

5) M. Sato, H. Watanabe, S. Ebine, and S. Akabori, *Chem. Lett.*, **1982**, 1753.

6) S. Akabori, H. Fukuda, Y. Habata, M. Sato, and S. Ebine, *Chem. Lett.*, **1982**, 1393.

7) S. Akabori, Y. Habata, M. Sato, and S. Ebine, *Bull. Chem. Soc. Jpn.*, **56**, 1459 (1983).

8) D. St. C. Black and I. A. McLean, *Tetrahedron Lett.*, **1969**, 3961.

9) W. Rosen and D. H. Busch, *J. Am. Chem. Soc.*, **91**, 4694 (1970).

10) C. J. Pedersen, *J. Org. Chem.*, **36**, 254 (1971).

11) L. A. Ochrymowycz, C. -P. Mak, and J. D. Michna, *J. Org. Chem.*, **39**, 2079 (1974).

12) M. Russo, L. Mortillaro, L. Credari, and C. de Checchi, *Polym. Lett.*, **3**, 455 (1965).

13) The purity of 1,2-ethanedithiol was carefully checked by gas chromatography and mass spectrometry (99.5%). It does not contain any bis(2-mercaptoethyl) sulfide.

14) In the reaction of 1,1′-bis(hydroxymethyl)ferrocene with α-(2-haloethyl)-ω-halopoly(oxyethylene), the vinyl derivatives corresponding to **17** and **18** were isolated. Ref. 6.

15) C. J. Pedersen, *Fed. Proc.*, **27**, 1305 (1968).

16) T. -L. Ho, "Hard and Soft Acids and Bases Principles in Organic Chemistry," Academic Press, New York and London (1977), p. 163.

17) H. F. Frendorff, *J. Am. Chem. Soc.*, **93**, 600 (1971).

18) T. E. Jones, D. B. Rorabacher, and L. A. Ochrymowycz, *J. Am. Chem. Soc.*, **97**, 7486 (1975).