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Synthesis of Lariat Ferrocenocrown Ethers and Their Alkali Metal Complexes

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Synopsis. Lariat ferrocenocrown ethers were synthesized by the reaction of disodium salt of 1,1′-dihydroxyferrocene with *N*-substituted bis(2-chloroethyl)amines and/or by the reaction of bis(2-chloroethoxy)ferrocene with disodium salts of *N*-substituted bis(2-hydroxyethyl)amines. Crystalline 1:1 complexes of *N*-(2-methoxyethyl)-4-aza-1,7-dioxa-[7]ferrocenophane with LiClO$_4$ and NaClO$_4$ were also isolated.

Recently, the syntheses of highly functionalized crown ethers have been described,1) and in this connection several research groups2) reported the syntheses and physicochemical properties of ferrocenocrown ethers. We have previously reported on both syntheses and extractability for metal cations of polythia-,3) polyoxa-,4) and oxathia[*n*]ferrocenophanes.5) It was found that these compounds showed high extractability for Tl$^+$ and Ag$^+$ and low extractability for alkali and alkaline earth metal cations. However, little is known concerning oxaaza[*n*]ferrocenophanes and lariat ferrocenocrown ethers. We now wish to report on the syntheses of lariat ferrocenocrown ethers and their metal complexes.

The reaction of potassium salt of **1** with **2** gave mononuclear ferrocenocrown ether **4** and its dimer **6** in 20 and 2% yields, respectively, while the reaction of **1** and **3** gave only **5** in the range from 9 to 20% yields. The reaction of **7** with **8** in the presence of NaH and 18-crown-6 as a phase-transfer catalyst6) gave only **11** in 5% yield, while the reaction of **7** with **9** gave the cyclized products **10** and **12** in 4 and 10% yield, respectively.

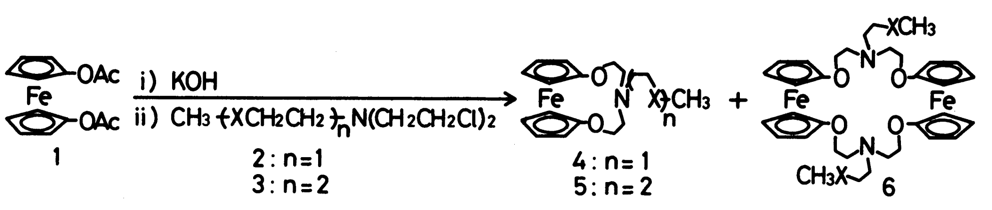
The extractability of **4** and **5** for alkali metal picrates was measured by the method described in the previous paper.4a) All of the lariat ferrocenocrown ethers showed little extractability. However, it was found that the selectivity for alkali metal cations of **4a** increased more than that of other ferrocenocrown ethers. The extractability of **4a** toward alkali metal cations was in the following order: K$^+$ (3%)>Rb$^+$=Cs$^+$(2%)>Na$^+$(0.6%)>Li$^+$(0.8). Also, the extractability of the crown ethers depends on the length and kind of the side arm. Compounds **5a** and **5b**, which contained an alkyl group as a side arm, showed a lower extractability compared with **4a**, which is explained in terms of the steric hindrance of a too lengthy side arm.

In contrast with the low extractability, the complex of alkali metal perchlorate with **4a**, and **4b** was isolated quantitatively. These complexes showed a higher melting point than the corresponding ligand and were confirmed by elemental analyses to be a 1:1 complex. Compound **4a** also gave a 1:1 complex with sodium

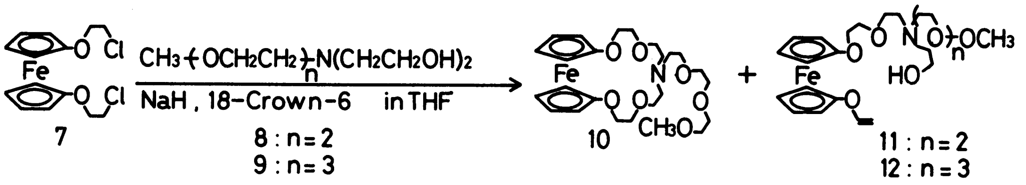
TABLE 1. MELTING POINT, MASS AND NMR SPECTRAL DATA OF LARIAT FERROCENOCROWN ETHERS AND THEIR METAL COMPLEXES

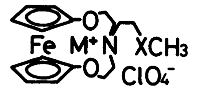
Comp	Mp θ_m/°C	Mass$^{a)}$ (M$^+$)	^{1}H-NMR spectra/(δ values, in acetonitrile-d_3)$^{b)}$
4a	46.0—46.5	345	4.17(t, J=1.8Hz, 4H), 3.78(t, J=1.8Hz, 4H), 4.00(t, J=4.6Hz, 4H), 3.45(t, J=5.4Hz, 2H), 3.29(s, 3H), 2.91(t, J=4.6Hz, 4H), 2.79(t, J=5.4Hz, 2H)
4b	37.0—37.5	343	4.15(t, J=1.8Hz, 4H), 3.77(t, J=1.8Hz, 4H), 3.99(t, J=4.6Hz, 4H), 2.83(t, J=4.6Hz, 4H), 2.56(t, J=5.9Hz, 2H), 1.38(s, 4H), 1.02—0.70(m, 3H)
5a	12.5—13.5	389	4.16(t, J=1.8Hz, 4H), 3.77(t, J=1.8Hz, 4H), 3.99(t, J=4.6Hz, 4H), 3.60—3.40(m, 6H), 3.30(s, 3H), 2.92(t, J=4.6Hz, 4H), 2.80(t, J=6.2Hz, 2H)
5b	43.0—43.5	385	4.15(t, J=1.8Hz, 4H), 3.77(t, J=1.8Hz, 4H), 3.99(t, J=4.6Hz, 4H), 2.82(t, J=4.6Hz, 4H), 2.54(t, J=7.1Hz, 2H), 1.30(s, 10H), 1.02—0.70(m, 3H)
6a$^{c)}$	67.0—67.5	690	4.05(t, J=1.8Hz, 8H), 3.83(t, J=1.8Hz, 8H), 3.98(t, J=6.0Hz, 8H), 2.98(t, J=6.0Hz, 8H), 3.48(t, J=6.6Hz, 4H), 2.83(t, J=6.6Hz, 4H), 3.32(s, 6H)
6b$^{c)}$	oil	686	4.00(t, J=1.8Hz, 8H), 3.74(t, J=1.8Hz, 8H), 3.89(t, J=6.0Hz, 8H), 2.88(t, J=6.0Hz, 8H), 2.62(t, J=6.6Hz, 4H), 1.85—1.14(m, 8H), 1.14—0.80(m, 6H)
10$^{c)}$	oil	521	4.00(t, J=1.8Hz, 4H), 3.79(t, J=1.8Hz, 4H), 3.87(t, J=6.0Hz, 4H), 3.52(s, 8H), 3.30(s, 3H), 2.78(t, J=6.0Hz, 4H), 2.69(t, J=6.0Hz, 2H), 3.73—3.45(m, 10H)
11$^{c)}$	oil	477	4.15(t, J=1.8Hz, 4H), 3.88(t, J=1.8Hz, 4H), 3.85(t, J=6.0Hz, 4H), 3.35(s, 3H), 2.80(t, J=6.0Hz, 6H), 2.70(s, 1H), 3.71—3.40(m, 10H), 6.54(dd, J_{ab}=6.6Hz, J_{ac}=13.2Hz, 1H), 4.59(dd, J_{ac}=13.2Hz, J_{bc}=1.8Hz, 2H), 4.26(dd, J_{ab}=6.6Hz, J_{bc}=1.8Hz, 2H)
12$^{c)}$	oil	521	4.18(t, J=1.8Hz, 4H), 3.91(t, J=1.8Hz, 4H), 3.87(t, J=6.0Hz, 4H), 3.39(s, 3H), 2.88(t, J=6.0Hz, 6H), 3.70(s, 1H), 3.85—3.46(m, 14H), 6.67(dd, J_{ab}=6.6Hz, J_{ac}=13.2Hz, 1H), 4.57(dd, J_{ac}=13.2Hz, J_{bc}=1.8Hz, 2H), 4.28(dd, J_{ab}=6.6Hz, J_{bc}=1.8Hz, 2H)
13a	150—152		4.20(t, J=1.8Hz, 4H), 3.79(t, J=1.8Hz, 4H), 4.00(t, J=4.6Hz, 4H), 3.47(t, J=5.4Hz, 2H), 3.32(s, 3H), 2.91(t, J=4.6Hz, 4H), 2.79(t, J=6.0Hz, 2H)
13b	Dec 190		4.23(t, J=1.8Hz, 4H), 3.73(t, J=1.8Hz, 4H), 3.98(t, J=4.6Hz, 4H), 3.47(t, J=5.4Hz, 2H), 3.33(s, 3H), 2.86(t, J=4.6Hz, 4H), 2.75(t, J=6.0Hz, 2H)
14a	Dec 170		4.23(t, J=1.8Hz, 4H), 3.83(t, J=1.8Hz, 4H), 4.12(t, J=4.6Hz, 4H), 3.20(t, J=4.6Hz, 4H), 2.91(t, J=5.9Hz, 2H), 1.46(s, 4H), 1.02—1.80(m, 3H)

a) The mass spectra were taken on a Hitachi M-80 mass spectrometer(70eV). b) NMR spectra were recorded with tetramethylsilane as internal standard on a JEOL-FX-90Q spectrometer. c) Measured in CDCl$_3$.



2~6 a:X=O, b:X=CH2





13a : X=O, M=Li
13b : X=O, M=Na
14a : X=CH2, M=Li

perchlorate, while **4b** gave no crystalline complex. As shown in the ^{1}H-NMR spectral data in Table 1, there was only a little difference in the chemical shift between the ligand and the corresponding complex. The signals of the α- and β-protons of the ferrocene ring and the methylene protons in the complexes shifted down field as compared with those in the free ligand. A similar trend was observed on the addition of alkali metal perchlorate to a solution of ligand in acetonitrile-d_3. The tendency for this down-field shift observed here was also similar to that shown in the ^{1}H-NMR data of the polyoxa[n]ferrocenophanes and these alkali metal thiocyanate complexes.[4b)]

Experimental

Reaction of 1 with 2a. **1** (2.24 mmol) was added to potassium hydroxide (12.3 mmol) in water (10 cm^3) under nitrogen, and the mixture was stirred under reflux. After 1 h, a solution of **2a** (2.69 mmol) in 60% ethanol (70 cm^3) was added at one time and the mixture was then stirred for 5 h at reflux temperature. After the usual work-up, the reaction mixture was chromatographed on silica-gel TLC (hexane–acetone). The first band gave red oil which was crystallized from hexane to give **4a** in 26% yield. Found: C, 58.90; H, 6.91; N, 4.25%. Calcd for $C_{17}H_{23}O_3NFe$: C, 59.15; H, 6.72; N, 4.06%. The second band gave **6a** as red crystals (from hexane) in 2% yield. Found: C, 58.91; H, 6.99; N, 3.60%. Calcd for $C_{34}H_{46}O_6N_2Fe_2$: C, 59.15; H, 6.72; N, 3.47%.

Similarly, reaction of **1** (6.08 mmol) with **2b** (7.24 mmol) gave **4b** and **6b** in 20 and 3% yields, respectively. **4b** Found: C, 63.25; H, 7.30; N, 4.23%. Calcd for $C_{18}H_{26}O_2NFe$: C, 62.99; H, 7.34; N, 4.07%. **6b**, Found: C, 62.81; H, 7.63; N, 4.15%. Calcd for $C_{36}H_{50}O_4N_2Fe_2$: C, 62.99; H, 7.34; N, 4.08%.

Similarly, reaction of **1** (5.23 mmol) with **3a** (6.5 mmol) gave **5a** in 20% yield. Found: C, 58.60; H, 7.12; N, 3.85%. Calcd for $C_{19}H_{27}O_4NFe$: C, 58.61; H, 7.00; N, 3.60%.

Similarly, reaction of **1** (5.0 mmol) with **3b** (5.3 mmol) gave **5b** in 14% yield. Found: C, 65.51; H, 8.34; N, 3.69%. Calcd for $C_{21}H_{31}O_2NFe$: C, 65.44; H, 8.12; H, 3.64%.

Reaction of 7 with 9. A solution of **9** (3.46 mmol) in the presence of sodium hydride (16.2 mmol) and 18-crown-6 (3.7 mmol) in THF (150 cm^3) was stirred under reflux for 10 h and then a solution of **7** (3.19 mmol) in THF (50 cm^3) was added to the mixture all at one time. After 48 h, the mixture was chromatographed on silica-gel TLC (hexane:acetone=1:1). The first band gave **10** as red oil in 4% yield. Found: C, 57.51; H, 7.72; N, 2.85%. Calcd for $C_{25}H_{39}NO_7Fe$: C, 57.57; H, 7.55; N, 2.69%. The second band gave **12** as red oil in 10% yield. Found: C, 57.82; H, 7.41; N, 2.75%. Calcd for $C_{25}H_{39}NO_7Fe$: C, 57.57; H, 7.55; N, 2.69%.

Similarly, reaction of **7** (2.91 mmol) with **8** (3.29 mmol) gave **11** as red oil in 5% yield. Found C, 58.10; H, 7.65; N, 3.18%. Calcd for $C_{23}H_{35}NO_6Fe$: C, 57.86; H, 7.40; N, 2.93%.

General Procedure for the Alkali Metal Perchlorate Complex. A solution of **4a** or **4b** (0.1 mmol) in acetonitrile (2 cm^3) was added to an acetonitrile solution (2 cm^3) containing alkali metal perchlorate (0.1 mmol). The mixture was heated for a few minutes, and allowed to stand in an ice bath. After the precipitates had been completed, the complex was filtered and then washed with a small portion of acetonitrile. **13a**: Found: C, 45.22; H, 5.16; N, 3.11%. Calcd for $C_{17}H_{23}NO_7FeLiCl$: C, 45.21; H, 5.14; N, 3.10%. **13b**. Found: C, 43.60; H, 4.99; N, 3.05%. Calcd for $C_{17}H_{23}NO_7FeNaCl$: C, 43.65; H, 4.97; N, 3.00%. **14a**. Found: C, 48.03; H, 5.67; N, 3.13%. Calcd for $C_{18}H_{25}NO_6FeLiCl$: C, 48.07; H, 5.62; N, 3.12%.

References

1) R. E. Izatt and J. J. Christensen, "Synthetic Multidentate Macrocyclic Compound," Academic Press, New York (1977).

2) G. Oepen and F. Vogtle, *Liebigs Ann. Chem.*, **1979**, 1094. A. P. Bell and D. Hall, *J. Chem. Soc., Chem. Commun.*, **1980**, 163; B. Czech and A. Ratajczak, *Polish J. Chem.*, **54**, 767 (1980).

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

4) a) S. Akabori, Y. Habata, Y. Sakamoto, M. Sato, and S. Ebine, *Bull. Chem. Soc. Jpn.*, **56**, 537 (1983); b) S. Akabori, Y. Habata, and M. Sato, *Bull. Chem. Soc. Jpn.*, **57**, 68 (1984).

5) S. Akabori, S. Shibahara, Y. Habata, and M. Sato, *Bull. Chem. Soc. Jpn.*,**57**, 63 (1984); M. Sato, M. Kubo, S. Ebine, and S. Akabori, *Bull. Chem. Soc. Jpn.*, **57**, 421 (1984).

6) S. Akabori and H. Tuji, *Bull. Chem. Soc. Jpn.*, **51**, 1197 (1978).