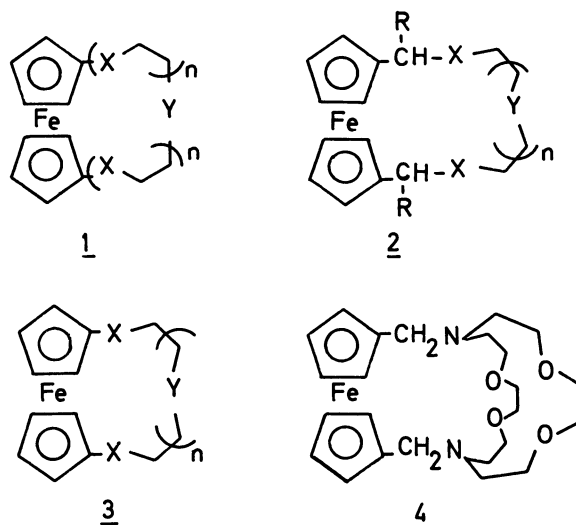


SYNTHESIS AND COMPLEXING PROPERTIES OF NOVEL FERROCENE CROWN ETHERS

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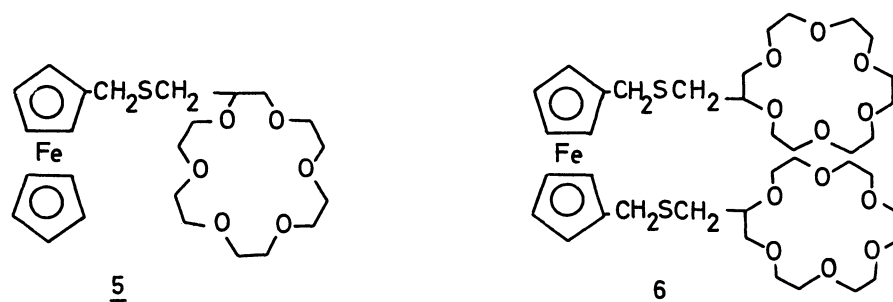
Two novel ferrocene crown compounds in which the ferrocene nucleus bears one and two 18-crown-6 units are synthesized and their alkali metal cation complexation is examined in solvent extraction. The ferrocene biscrown exhibits selectivity for K^+ and Rb^+ in competitive extraction.

Crown compounds with a ferrocene unit incorporated into the macrocyclic ring have recently received considerable attention. Polyoxaferrocenophanes 1 ($X = Y = O$)^{1,2)} and 2 ($X = Y = O$)³⁾ polythiaferrocenophanes 1 ($X = Y = S$)⁴⁾ polyoxathiaferrocenophanes 1 ($X = O, Y = S$)⁵⁾ 2 ($X = S, Y = O$)⁶⁻⁸⁾ and 3 ($X = S, Y = O$)⁹⁾ as well as the ferrocene cryptand 4^{6,10,11)} have been synthe-

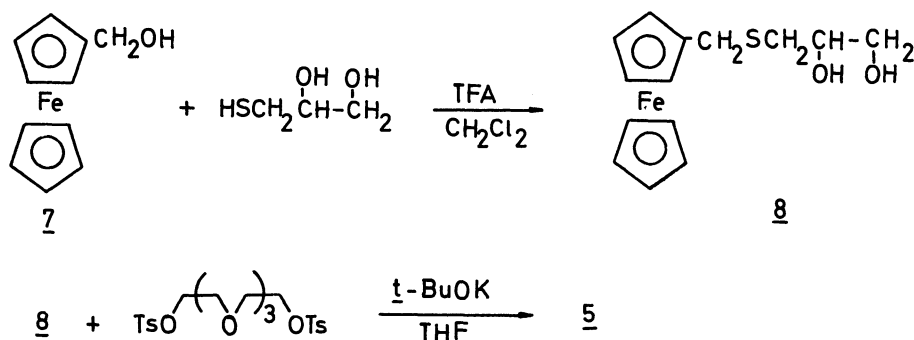


sized. Most of these multidentate ligands exhibit rather weak binding of alkali metal cations, but better complexation of silver and thallium ions.^{1-6,9-11)}

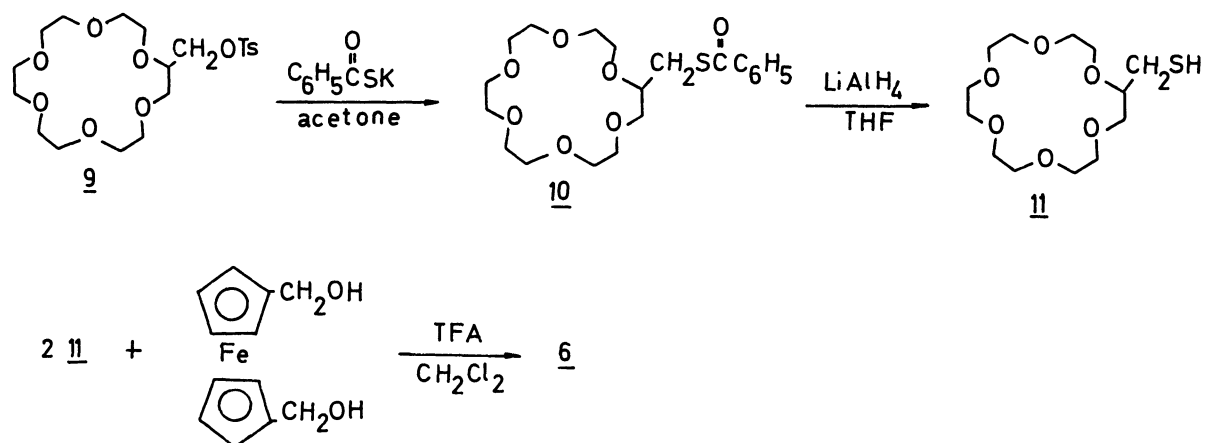
In this communication we wish to report the preparation of a new type of ferrocene functionalized crown 5 and the corresponding biscrown 6 and their complexing behavior towards alkali metal cations.



Reaction of hydroxymethylferrocene, 7, with commercially-available 3-mercapto-1,2-propanediol and trifluoroacetic acid gave, after column chromatography (alumina, EtOAc-EtOH, 5:1), (S-ferrocenylmethyl)glycerol 8¹²⁾ in 82% yield as brown-yellow crystals with mp 44-46 °C. Cyclization of 8 with the ditosylate of pentaethylene glycol and potassium *t*-butoxide afforded the ferrocene crown 5¹³⁾ in 20% yield as a light brown, viscous oil after column chromatography (neutral alumina, EtOAc).



The first step of the synthetic route to the ferrocene biscrown 6 involved refluxing the tosylate of hydroxymethyl-18-crown-6, 9,¹⁴⁾ with potassium thiobenzoate in acetone to produce the crown thiobenzoate 10¹⁵⁾ as a colorless oil in 91% yield. Reduction of 10 with lithium aluminum hydride afforded crude mercaptomethyl-18-crown-6, 11, which was placed under vacuum (0.01 Torr, 70 °C, 10 h) to remove contaminating benzyl alcohol and then used in the next step without further purification. Reaction of 1,1'-di(hydroxymethyl)ferrocene, 12, with trifluoroacetic acid and two moles of 11 gave, after chromatography (alumina, EtOAc), the ferrocene biscrown 6¹⁶⁾ in 88% yield as a brown, viscous oil.



The structures of both new ferrocene crown compounds were verified by elemental analysis^{13,16)} and by their ^1H NMR and IR spectra. The ^1H NMR spectrum of 5 consists of a multiplet overlapping a singlet at δ 3.4–3.8 for all protons (27H) except the ferrocene protons and a singlet at δ 4.11 for the nine ferrocene ring protons. The IR spectrum of 5 shows CH_2S vibrations at 1467 and 1454 cm^{-1} and an ether linkage absorption at 1122 cm^{-1} . The ^1H NMR spectrum of 6 exhibits a multiplet at δ 2.46–2.70 for the four methylene protons located between sulfur and the crown ring, a multiplet overlapping a singlet (δ 3.46–3.83, 50H) for all other protons except those of the ferrocene rings, and a multiplet centered at δ 4.40 for the ferrocene protons. In the IR spectrum of 6, the ether linkage absorption at 1116 cm^{-1} is the most characteristic band.

Since biscrown compounds may exhibit more selective alkali metal cation complexation than their monocyclic analogs,¹⁷⁾ it was of interest to compare the cation complexing properties of the new ferrocene crown compounds 5 and 6. After 0.25 M aqueous solutions KSCN were shaken with equal volumes of 0.050 M chloroform solutions of the ferrocene crown compounds, the chloroform phases were separated and shaken with 5% HCl. Cation concentrations in the resulting acidic aqueous phases were determined by ion chromatography. The metals loading of the organic phases were 44% and 128% for 5 and 6, respectively. The high metals loading for 6 reveals that some molecules of 6 complex with two potassium cations. This suggests that 6 adopts conformations in which the two crown ether units act independently rather than in concert to form sandwich complexes. In agreement, when an aqueous solution which was 0.25 M in each LiSCN, NaSCN, KSCN, RbSCN and CsSCN was extracted with an equal volume of 0.050 M 6 in chloroform followed by stripping and analysis, a 140% metals loading was found with a cation selectivity of K^+ (72%) Rb^+ (27%) \gg Na^+ (1%) and Li^+ and Cs^+ being undetectable. This selectivity order is inconsistent with an anticipated favoring of Cs^+ complexation if 6 were to form a sandwich complex.

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- 12) Data for **8**. IR (CHCl_3 , cm^{-1}): 3430 (OH). ^1H NMR (CDCl_3 , δ): 2.2-3.0 (4H, m, $\text{CH}_2\text{S} + \text{OH}$), 3.35-3.85 (5H, m+s, $\text{CpCH}_2\text{S} + \text{CH}_2\text{O} + \text{CHO}$), 4.14 (9H, s, Cp). Found: C, 54.85%; H, 5.99%. Calcd for $\text{C}_{14}\text{H}_{18}\text{FeO}_2\text{S}$: C, 54.92%; H, 5.92%.
- 13) Found: C, 56.41%; H, 7.35%. Calcd for **5** ($\text{C}_{24}\text{H}_{36}\text{FeO}_6\text{S}$): C, 56.69%; H, 7.14%.
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- 15) Data for **10**. IR (neat, cm^{-1}): 1662 (C = O), 1116 (C - O). ^1H NMR (CDCl_3 , δ): 3.27 (2H, d, CH_2S), 3.5-4.1 (23H, m, CH_2O), 7.25-8.20 (5H, m, Ph). Found: C, 57.96%; H, 7.14%. Calcd for $\text{C}_{20}\text{H}_{30}\text{O}_7\text{S}$: C, 57.95%; H, 7.29%.
- 16) Found: C, 54.76%; H, 7.40%. Calcd for **6** ($\text{C}_{38}\text{H}_{62}\text{FeO}_{12}\text{S}_2$): C, 54.93%; H, 7.52%.
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