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 $\underline{1} (X = Y = 0)^{1,2}$ and $\underline{2} (X = Y = 0)^{3}$ polythiaferrocenophanes $\underline{1} (X = Y = S)^{4}$ polyoxathiaferrocenophanes $\underline{1} (X = 0, Y = S)^{5} \underline{2} (X = S, Y = 0)^{6-8}$ and $\underline{3} (X = S, Y = 0)^{9}$ as well as the ferrocene cryptand $\underline{4}^{6,10,11}$ 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, $\underline{7}$, with commercially-available 3-mercapto-1,2-propanediol and trifluoroacetic acid gave, after column chromatography (alumina, EtOAc-EtOH, 5:1), (S-ferrocenylmethyl)glycerol $\underline{8}^{12}$ in 82% yield as brown-yellow crystals with mp 44-46 °C. Cyclization of $\underline{8}$ with the ditosylate of pentaethylene glycol and potassium <u>t</u>-butoxide afforded the ferrocene crown $\underline{5}^{13}$ 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 <u>6</u> involved refluxing the tosylate of hydroxymethyl-18-crown-6, $\underline{9}$,¹⁴) with potassium thiobenzoate in acetone to produce the crown thiobenzoate $\underline{10}^{15}$ as a colorless oil in 91% yield. Reduction of <u>10</u> with lithium aluminum hydride afforded crude mercaptomethyl-18-crown-6, <u>11</u>, 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, <u>12</u>, with trifluoro-acetic acid and two moles of <u>11</u> gave, after chromatography (alumina, EtOAc), the ferrocene biscrown <u>6</u>¹⁶ in 88% yield as a brown, viscous oil.

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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 <u>5</u> 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 <u>5</u> shows CH₂S vibrations at 1467 and 1454 cm⁻¹ and an ether linkage absorption at 1122 cm⁻¹. The ¹H NMR spectrum of <u>6</u> 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 <u>5</u> and <u>6</u>. 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% HC1. 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 <u>5</u> and <u>6</u>, respectively. The high metals loading for <u>6</u> reveals that some molecules of <u>6</u> complex with two potassium cations. This suggests that <u>6</u> 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 <u>6</u> in chloroform followed by stripping and analysis, a 140% metals loading was found with a cation selectivity of K⁺ (72%) Rb⁺ (27%) >> Na⁺ (1%) and Li⁺ and Cs⁺ being undetectable. This selectivity order if inconsistent with an anticipated favoring of Cs⁺ complexation if <u>6</u> were to form a sandwich complex.

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- 12) Data for <u>8</u>. IR (CHCl₃, cm⁻¹): 3430 (OH). ¹H NMR (CDCl₃, δ): 2.2-3.0 (4H, m, CH₂S + OH),
 3.35-3.85 (5H, m+s, Cp<u>CH₂S</u> + CH₂O + CHO), 4.14 (9H, s, Cp). Found: C, 54.85%; H, 5.99%.
 Calcd for C₁₄H₁₈FeO₂S: C, 54.92%; H, 5.92%.
- 13) Found: C, 56.41%; H, 7.35%. Calcd for <u>5</u> (C₂₄H₃₆FeO₆S): C, 56.69%; H, 7.14%.
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- 15) Data for <u>10</u>. IR (neat, cm⁻¹): 1662 (C = 0), 1116 (C 0). ¹H NMR (CDCl₃, δ): 3.27 (2H, d, CH₂S), 3.5-4.1 (23H, m, CH₂O), 7.25-8.20 (5H, m, Ph). Found: C, 57.96%; H, 7.14%. Calcd for C₂₀H₃₀O₇S: C, 57.95%; H, 7.29%.
- 16) Found: C, 54.76%; H, 7.40%. Calcd for <u>6</u> (C₃₈H₆₂FeO₁₂S₂): C, 54.93%; H, 7.52%.
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