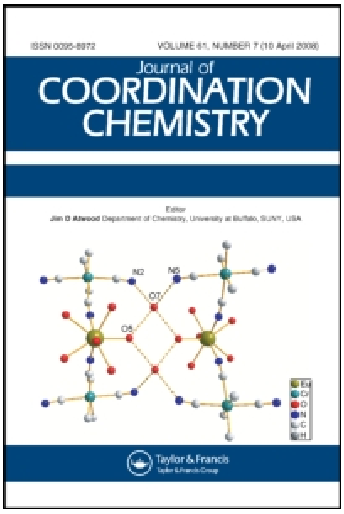

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Synthesis, Metal Ion Complexation Properties, and Electrochemical Behavior of Ferrocenyl Thioacetal Crown Compounds

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SYNTHESIS, METAL ION COMPLEXATION PROPERTIES, AND ELECTROCHEMICAL BEHAVIOR OF FERROCENYL THIOACETAL CROWN COMPOUNDS

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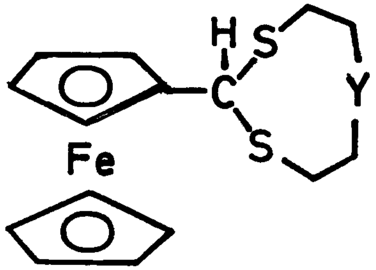
Abstract Condensation of ferrocenecarboxyaldehyde with dithiols under Lewis acid catalysis produces ferrocenyl thioacetal crown compounds in good to excellent yields. Complexation behavior of several ferrocenyl thioacetal crown compounds toward alkali metal cations, Ag(I), Tl(I), Cu(II), Pb(II) and Zn(II) is assessed by picrate extractions from aqueous solutions into chloroform. Electrochemical behavior of several ferrocenyl thioacetal crown compounds in the absence and presence of sodium ions is investigated by cyclic voltammetry.

Keywords: Ferrocenecarboxyaldehyde, dithiols

INTRODUCTION

The design and synthesis of macrocyclic compounds which contain the ferrocene moiety as an integral part of the macrocyclic skeleton[1-9] or as a pendant unit[10-13] have recently received considerable attention in the chemical literature. We now report the preparation of novel ferrocenyl thioacetal crown compounds 1-7 and, for 1-3, 6 and 7, their complexation behavior toward several mono- and divalent cation species and their electrochemical properties.

	Y
1	-O-
2	$-OCH_2CH_2O-$
3	$-O(CH_2CH_2O)_2-$
4	$-O(CH_2CH_2O)_3-$
5	$-O(CH_2CH_2O)_4-$



6 -S-
7 $-OCH_2CH_2SCH_2CH_2O-$

EXPERIMENTAL

Ferrocenecarboxaldehyde, 2-mercaptoethyl ether, 2-mercaptoethyl sulfide, and hydroquinone were obtained from Aldrich. Dithiols $HS(CH_2CH_2O)_nCH_2CH_2SH$ with n = 2-5 and $(HSCH_2CH_2OCH_2CH_2)_2S$ were synthesized by the literature procedures.[14,15] Metal picrates were prepared by reactions of metal carbonates with picric acid in hot water followed by cooling to promote crystallization.

Synthesis of Ferrocenyl Thioacetal Crown Compounds-General Procedure

In a capped 250 ml polypropylene bottle, 1.00 g (4.60 mmol) of ferrocenecarboxaldehyde, 100-140 ml of C_6H_6-Et_2O (1:1), 0.10 g of hydroquinone, and 5.00 mmol of dithiol were stirred at room temperature for 30 minutes. Using a syringe pump, 0.65 g (4.60 mmol) of $BF_3 \cdot Et_2O$ dissolved in 9 ml of C_6H_6 was added during a 3-hour period via a syringe needle through a small hole in the cap. After the addition was completed, the cap was sealed and the reaction solution was stirred at room temperature for 5-10 days with periodic monitoring by TLC (alumina, C_6H_6-EtOAc). The product solution was washed with H_2O and the solvent was removed in vacuo. The resulting viscous oil was purified by column chromatography on alumina with C_6H_6 or C_6H_6-EtOAc as eluent to give the product.

2-Ferrocenyl-1,3-dithia-8-crown-3 (1)

Yellow crystals, mp 104-105 °C (recrystallized from EtOH), in 84% yield. IR (KBr) 1248 (C-S), 1111 (C-O) cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.4-3.1 (m, 4H), 3.4-4.3 (m, 13H), 5.40 (s, 1H). MS, m/e 334 (M^+). Anal. Calcd. for $C_{15}H_{13}FeOS_2$: C, 53.90; H, 5.43. Found: C, 53.82; H, 5.47.

2-Ferrocenyl-1,3-dithia-11-crown-4 (2)

Yellow crystals, mp 105 °C (recrystallized from EtOH), in 72% yield. IR (KBr) 1244 (C-S), 1113 (C-O) cm^1. ^{1}H NMR ($CDCl_3$) δ 2.4-3.0 (m, 4H), 3.55-4.3 (m, 17H), 5.25 (s, 1H). MS, m/e 378 (M^+). Anal. Calcd. for $C_{17}H_{22}FeO_2S_2$: C, 53.97; H, 5.86. Found: C, 54.14; H, 5.80.

2-Ferrocenyl-1,3-dithia-14-crown-5 (3)

Yellow crystals, mp 72-73 °C (recrystallized from EtOH), in 92% yield. IR (KBr) 1251 (C-S), 1112 (C-O) cm^1. ^{1}H NMR ($CDCl_3$) δ 2.75-3.1 (m, 4H), 3.65-3.85 (m, 12H), 4.2-4.35 (m, 9H), 5.35 (s, 1H). MS, m/e 422 (M^+). Anal. Calcd. for $C_{19}H_{26}FeO_3S_2$: C, 54.03; H, 6.20. Found: C, 53.90; H, 6.35.

2-Ferrocenyl-1,3-dithia-17-crown-6 (4)

Dark brown oil in 62% yield. IR (film) 1248 (C-S), 1114 (C-O) cm^1. ^{1}H NMR ($CDCl_3$) δ 2.6-3.15 (m, 4H), 3.5-3.9 (m, 16H), 4.05-4.3 (m, 9H), 5.20 (s, 1H). MS, m/e 466 (M^+). Anal. Calcd. for $C_{21}H_{30}FeO_4S_2$: C, 54.07; H, 6.44. Found: C, 53.97; H, 6.66.

2-Ferrocenyl-1,3-dithia-20-crown-7 (5)

Dark brown oil in 64% yield. IR (film) 1249 (C-S), 1113 (C-O) cm^1. ^{1}H NMR ($CDCl_3$) δ 2.55-3.1 (m, 4H), 3.45-4.0 (m, 20H), 4.05-4.4 (m, 9H), 5.05 (s, 1H). MS, m/e 510 (M^+). Anal. Calcd. for $C_{23}H_{34}FeO_5S_2$: C, 54.11; H, 6.67. Found: C, 54.11; H, 7.05.

2-Ferrocenyl-1,3,6-trithia-8-crown-3 (6)

Yellow crystals, mp 152-154 °C (recrystallized from EtOAc), in 31% yield. IR (KBr) 1300 (C-S) cm^1. ^{1}H NMR ($CDCl_3$) δ 2.90 (s, 8H), 4.15-4.4 (m, 9H), 5.00 (s, 1H). MS, m/e 350 (M^+). Anal. Calcd. for $C_{15}H_{18}FeS_3$: C, 51.42; H, 5.14. Found: C, 51.09; H, 5.25.

2-Ferrocenyl-1,3,9-trithia-14-crown-5 (7)

Yellow crystals, mp 92-93 °C (recrystallized from EtOH), in 78% yield. IR (KBr) 1288 (C-S), 1111 (C-O) cm^1. ^{1}H NMR ($CDCl_3$) δ 2.7-3.0 (m, 8H), 3.55-4.0 (m, 8H), 4.05-4.4 (m, 9H), 5.30 (s, 1H). MS, m/e 438 (M^+). Anal. Calcd. for $C_{19}H_{26}FeO_2S_3$: C, 52.05; H, 5.94. Found: C, 52.03; H, 5.81.

Picrate Extraction into Deuteriochloroform

Ferrocenyl thioacetal crown solutions (5.0 mM) were prepared in EtOH-free deuteriochloroform. Extractions were conducted by adding 0.50 ml of a 5.0 mM crown compound solution in deuteriochloroform to 0.50 ml of a 5.0 mM metal picrate solution in a centrifuge tube and agitating the mixture with a vortex mixer for 1 minute. Five identical samples were run concurrently. The mixtures were centrifuged for 10 minutes to assure complete layer separation. Precisely measured aliquots were removed from both layers (only from the aqueous layer if the organic layer was cloudy) and diluted in acetonitrile. Visible spectra of these solutions were measured in the region of 300-500 nm.

Cyclic Voltammetry

Cyclic voltammograms were generated with a Bioanalytical Systems CV-1B apparatus. Platinum button working and auxiliary electrodes (Bioanalytical Systems) were used in conjunction with an aqueous saturated calomel reference mini-electrode. Reported measurements were performed with a freshly cleaned[17] working electrode. The aqueous SCE reference electrode in 0.1 M $NaNO_3$ was separated from the working electrode compartment (1.0 mM ferrocene compound and 0.1 M supporting electrolyte of Bu_4NClO_4 in acetonitrile or dichloromethane). The three-compartment cell with sintered glass spacers was thermostated at 25.0 ± 0.1 °C in a water bath.

The reference electrode potential was calibrated[18] against (hydroxyethyl)ferrocene (E° = +402 mV vs. NHE)[19] just prior to measurements on a ferrocenyl thioacetal crown ether in the same medium. Reported reduction potentials were calculated as the average of the cathodic and anodic peak potentials (50 mV/s sweep rate) and are the mean values of four independent determinations.

RESULTS AND DISCUSSION

Synthesis

Ferrocenyl thioacetal crown compounds 1-5 and 7 were prepared by boron trifluoride-catalyzed condensations of ferrocenecarboxaldehyde with dithiols in yields of 62-87%. Presumably, the much lower 31% yield of 6 results from formation of a highly strained ring. Use of a glass reaction vessel or omission of hydroquinone gave reduced yields of the ferrocenyl thioacetal crown compounds with apparent formation of polymeric materials.

Complexation behavior of 1-3, 6 and 7 was assessed by determining the ability of the ferrocenyl thioacetal crown compounds to extract metal picrates from water into deuteriochloroform.[16] For extractions of sodium, potassium, rubidium, cesium and silver picrates, the percentage of extraction was based only upon the reduced absorption of the aqueous phase after extraction due to the formation of insoluble complexes in the organic phase. Such precipitation was especially pronounced for silver picrate extractions. Results are recorded in Table I.

TABLE I Percentage of Metal Picrate Extracted from the Aqueous Phase into Deuteriochloroform.

	Li(I)	Na(I)	K(I)	Rb(I)	Cs(I)	Ag(I)	Tl(I)	Cu(II)	Pb(II)	Zn(II)
1	9	13	12	16	23	51	14	6	7	6
2	8	30	36	20	35	61	15	10	11	12
3	6	23	17	18	34	58	16	14	18	10
6	7	20	21	29	24	73	>1	11	13	3
7						62	11	20	22	11

For each of the ferrocenyl thioacetal crown compounds examined, Ag(I) was the best extracted metal ion. Among the remaining mono- and divalent metal ion species, there was rather low differentiation. However, it is interesting to compare the data for Tl(I) extraction by closely-related ligands 1 and 6. Replacement of the single ring oxygen atom in the former with sulfur almost totally inhibits the extraction of Tl(I).

Cyclic voltammograms of 1-3, 6 and 7 in acetonitrile solution (0.10 M in Bu_4NClO_4), with initial anodic sweep, were as expected for a reversible, one-electron oxidation of the ferrocenyl thioacetal crown compounds to the corresponding ferrocenium cations. Reduction potentials in the absence and presence of sodium tetraphenylborate are recorded in Table II.

TABLE II Reduction Potentials in Acetonitrile.

Compound	E^0 (mV) vs. NHE with 0.1 M sodium tetraphenylborate absent	present
1	+445	+447
2	+431	+435
3	+406	+416
6	+453	+457
7	+408	+408

In the absence of sodium tetraphenylborate, the reduction potential is noted to decrease with increasing crown ring size, 8-crown-3 (1 and 6) > 11-crown-4 (2) > 14-crown-5 (3 and 7). Within the estimated experimental error of ±5 mV, the presence of sodium ion does not appreciably influence the reduction potential in acetonitrile. This latter result is consistent with the rather low complexing ability of the ferrocenyl thioacetal crown ethers for sodium cations found in the picrate extraction experiments.

Reduction potentials for ferrocenyl thioacetal crown compounds 1 (+441 mV vs. NHE), 2 (+412 mV) and 3 (+376 mV) were evaluated from cyclic voltammograms of dichloromethane solutions (0.10 M in Bu_4NClO_4) and exhibit the same ring size ordering found in acetonitrile. However, the range of reduction potentials spanned by the series of 1-3 is larger in dichloromethane (65 mV) than in acetonitrile (39 mV). More significantly, the negative shift in E° value in going from acetonitrile to dichloromethane is not uniform as would be expected for a simple medium effect, but increases appreciably as the crown ring size is enlarged. Thus, the cathodic shifts for 1, 2 and 3 are -4, -19 and -30 mV, respectively. This dependence of the effect of solvent variation upon the crown ring size suggests that acetonitrile interacts with the crown ring and stabilizes the Fe(II) oxidation state for the pendant ferrocenyl unit. Due to such interactions with acetonitrile, the ring size effect for variation of the reduction potentials is better indicated by the results obtained in dichloromethane, for which specific solvation of the crown ring should not be an important consideration.

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