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Structure and Electrochemical Behavior of 2,8-Dithia-5-oxa[9](1,1′)ferrocenophane and 2,11-Dithia-5,8-dioxa[12](1,1′)ferrocenophane

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Structures of the title compounds have been determined by single-crystal X-ray crystallography. The crystals of 2,8-dithia-5-oxa[9](1,1′)ferrocenophane (I) are triclinic with $a = 7.719$ (3) Å, $b = 9.856$ (3) Å, $c = 10.514$ (4) Å, $\alpha = 90.45$ (3)°, $\beta = 104.69$ (3)°, $\gamma = 98.75$ (3)°, space group $P\bar{1}$, and $d(\text{calcd}, Z = 2) = 1.51$ g cm^{-3}. The crystals of 2,11-dithia-5,8-dioxa[12](1,1′)ferrocenophane (II) are monoclinic with $a = 18.478$ (8) Å, $b = 10.288$ (5) Å, $c = 19.179$ (7) Å, $\beta = 98.29$ (4)°, space group $I2/a$, and $d(\text{calcd}, Z = 8) = 1.44$ g cm^{-3}. Both structures were solved by the Patterson technique and refined by least-squares to final agreement factors of $R_F = 0.028$ ($R_w = 0.033$) for I and of $R_F = 0.046$ ($R_w = 0.054$) in the case of II. The two cyclopentadienyl rings of the ferrocenyl moieties are nearly parallel, the dihedral angles between the least-squares planes defined by the two rings being 2.4° and 3.4° for I and II, respectively. In each case, the ferrocenyl moiety has an almost eclipsed conformation; the twist angles are 7.8° and 6.7° for I and II, respectively. The bridging chains exhibit the gauche and anti conformations that are found in crown ether compounds. Reduction potentials of the ferrocenium cations derived from I and II in acetonitrile are comparable with that of ferrocene itself. This demonstrates that also in solution the bridging chains do not significantly distort the preferred, parallel orientation of the cyclopentadienyl rings.

Introduction

A number of ferrocenophane compounds with single trimethylene[1-4] or triheteratomic bridges[5-8] have been reported. Of primary interest has been the fluxional behavior of the bridge and the possible distortion of the cyclopentadienyl rings from the preferred, parallel orientation. Crownlike ferrocenophanes have also been studied to probe for possible communication between a complexed metal ion and the iron atom.[9-18] However, only one crownlike ferrocenophane[19] and one metal ion complex[20] have been structurally characterized. We now report determination of the crystal and molecular structures of 2,8-dithia-5-oxa[9](1,1′)ferrocenophane (I) and 2,11-dithia-5,8-dioxa[12](1,1′)ferrocenophane (II) and the electrochemical behavior of these two compounds in acetonitrile in the presence and absence of sodium tetraphenylborate.

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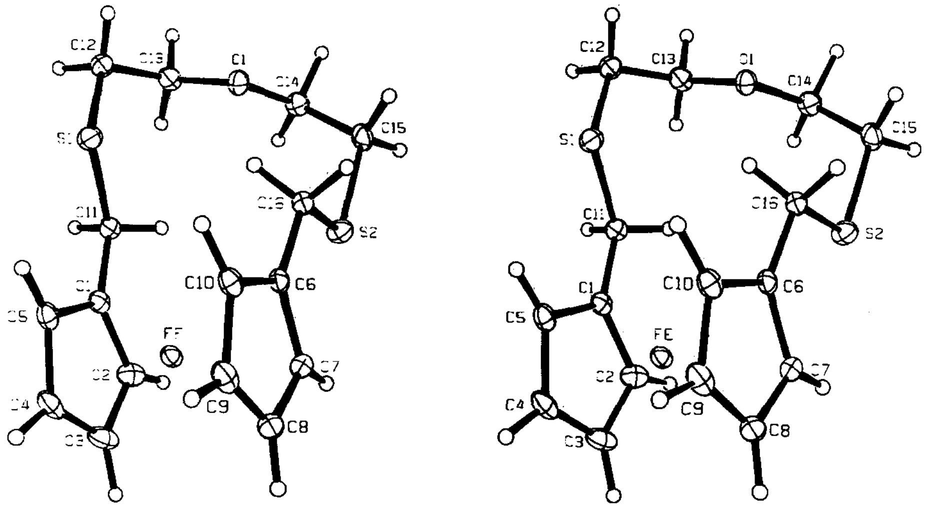

Figure 1. Stereoscopic view of I with the numbering system identified. Hydrogen numbers are the same as the carbons to which they are bonded.

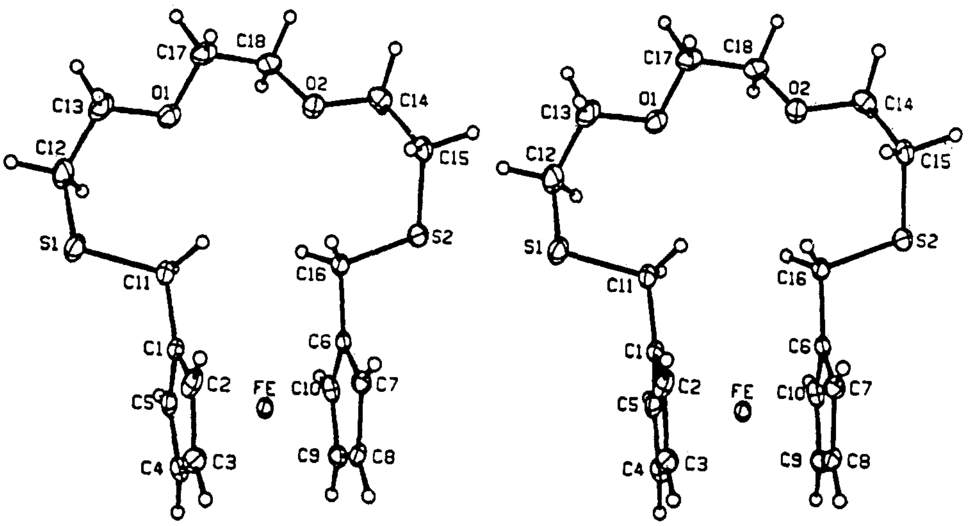

Figure 2. Stereoscopic view of II with the numbering system identified. Hydrogen numbers are the same as the carbons to which they are bonded.

Experimental Section

Synthesis of Ferrocenophanes I and II. Ferrocenophane II was prepared by the reported method.[15] Although a synthesis of ferrocenophane I has been reported previously,[11] the following procedure increased the yield from 14% to 31%. During 2 h, 0.48 g (1.95 mmol) of 1,1′-bis(hydroxymethyl)ferrocene dissolved in 60 mL of dichloromethane and 0.31 g (2.24 mmol) of 2-mercaptoethyl ether dissolved in 50 mL of dichloromethane were simultaneously added by two dropping funnels into 200 mL of vigorously stirred and refluxing dichloromethane which contained 7 drops of trifluoroacetic acid. After 48 h, the reaction mixture was washed with 5% ammonium hydroxide and then with water until the washings were neutral. After the solution was dried over magnesium sulfate, the solvent was removed in vacuo and the residue was chromatographed on basic, deactivated alumina with benzene as eluent to give as the first colored band 0.21 g (31%) of orange crystals with a melting point of 76–78 °C (lit.[11] mp 78–80 °C). MS: *m/z* 348 (M^+). IR (KBr): 1246 (CS), 1116 (CO) cm^{-1}. ^1H NMR ($CDCl_3$): 2.65–2.85 (t, 4 H), 3.65–3.85 (t, 8 H), 4.05–4.20 (m, 8 H).

Crystals of both I and II were prepared by diffusion of 95% ethanol into diethyl ether solutions of the ferrocenophane.

Crystal Data, Structure Solutions, and Refinement. Data collection for both crystals was performed on an Enraf-Nonius CAD-4 computer-controlled diffractometer. Accurate cell constants were obtained by centering 25 strong, high-angle reflections. Compound II was found to crystallize in space group $C2/c$ [a = 24.639 (9) Å, b = 10.288 (5) Å, c = 19.179 (8) Å, β = 132.09 (4)°]. Due to the obtuseness of the β angle, the structure was refined in the nonconventional space group $I2/a$. A summary of the crystallographically important parameters for data collection and processing is given in Table I. Intensities were measured with a scan rate depending on the net counts obtained in a rapid prescan of each reflection. Two standard reflections were monitored periodically during the course of the data collection as a check of crystal stability and electronic reliability, and these did not vary significantly. In reducing the data, Lorentz and polarization corrections were applied as well as an empirical absorption correction based on azimuthal psi scans of several reflections having chi near 90 degrees.[21] Data processing and calculations were made by using Molecular Structure Corporation's TEXRAY 230 modifications of the SDP-PLUS series of programs. Both structures were solved by the Patterson technique that revealed the positions of the Fe atoms. All the remaining non-hydrogen atoms were found from successive difference Fourier maps. Hydrogens were added at ideally calculated positions and in the case of I were refined keeping their isotropic temperature factors constant. Theoretically calculated positions of the hydrogens were included in the last cycle of least squares for II but were not refined. No unusually high correlations were noted between any of the variables in the last cycle of the full-matrix least-squares refinement. Final atomic coordinates and equivalent temperature factors for both compounds are presented in Table II, parts A and B. Anisotropic thermal parameters have been deposited (Table 1, parts A and B). The stereodrawings (Figures

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Table I. Summary of Data Collection and Processing Parameters

	I	II
cryst color and shape	orange parallelipiped	orange prism
cryst dimens (mm)	0.32 × 0.1 × 0.1	0.2 × 0.1 × 0.1
space group	$P\bar{1}$	$I2/a$
a (Å)	7.719 (3)	18.478 (7)
b (Å)	9.856 (3)	10.288 (5)
c (Å)	10.514 (4)	19.179 (8)
α (deg)	90.45 (3)	
β (deg)	104.69 (3)	98.29 (4)
γ (deg)	98.75 (3)	
V (Å^3)	763.8 (11)	3607.9 (2)
Z	2	8
mol formula	$FeS_2OC_{16}H_{20}$	$FeS_2O_2C_{18}H_{24}$
mol wt	348.3	392.4
D(calcd) (g cm^{-3})	1.51	1.44
radiatn (Å)	Mo K α (λ = 0.71069)	same
absorptn coeff (cm^{-1})	12.4	10.6
data collectn range	$4° \leq 2\theta \leq 55°$	$4° \leq 2\theta \leq 44°$
scan technique	$\theta/2\theta$	same
scan width	$\Delta\theta = (0.9 \pm 0.35 \tan \theta)°$	same
max scan time (s)	180	same
scan speed range (deg min^{-1})	0.7–5.0	same
total (unique) data collected	3556	2269
data with $I > 3\sigma(I)$	3190	1838
no. of parameters refined	241	208
$R_F = \sum\|\|F_o\| - \|F_c\|\|\sum\|F_o\|$	0.028	0.046
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2\|\sum w\|F_o\|^2]^{1/2}$	0.033	0.054
weighting scheme	$w = \sigma(F_o)^{-2}$	same
largest residual peak (e/Å^3)	0.2	0.3
largest shift/estimated std dev, final cycle	0.21	0.08

1–4) were obtained through use of Johnson's ORTEP program.[22]

Electrochemical Studies. Cyclic voltammograms were generated with a Bioanalytical Systems CV-1B apparatus. Platinum button working and auxiliary electrodes were used in conjunction with an aqueous saturated calomel reference minielectrode. Reported measurements were obtained with a freshly cleaned[23] working electrode. The aqueous SCE reference electrode in 0.10 M sodium nitrate was separated from the working electrode compartment (1.0 mM ferrocene substrate and 0.10 M tetrabutylammonium perchlorate in acetonitrile) by a central compartment which contained 0.10 M tetrabutylammonium perchlorate in acetonitrile. This three-compartment cell with sintered glass spacers was thermostated at 25.0 ± 0.1 °C.

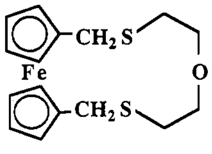
The reference electrode potential was calibrated[24] against (hydroxyethyl)ferrocene ($E°$ = +402 mV vs SHE)[25] immediately before measurements on I and II in the same medium. Reduction potentials were calculated as the average of cathodic and anodic peak potentials (sweep rate = 50 mV/s) and are mean values from four independent determinations. The estimated uncertainty in $E°$ values is ±5 mV.

Results and Discussion

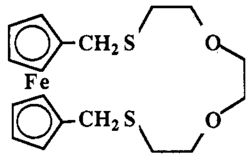
X-ray Crystallographic Study of Ferrocenophanes I and II. Both compounds exist in the crystalline state as discrete molecules held together by van der Waals forces. The atomic numbering systems employed are given in the stereodrawings of the molecules (Figures 1 and 2). The packing diagrams are shown in Figures 3 and 4. Bond distances and angles are given in Tables III and IV and torsion angles in Table V.

In both cases, the molecules contain two cyclopentadienyl rings η^5-bonded to iron. These rings are linked via a 2,8-dithia-5-oxa[9] chain in the case of I and by a 2,11-dithia-5,8-dioxa[12] chain in the case of II. The two cyclopentadienyl rings exhibit a conformation which is close to eclipsed with mean twist angles[26] of 7.8° and 6.7° for I and II, respectively. An almost exact eclipsed conformation was previously found in the related complex *meso*-1,12-dimethyl-2,11-dithia-5,8-dioxa[12](1,1′)-ferrocenophane (III).[19,27] This eclipsed conformation, which is usually found in substituted ferrocenyl compounds,[1–3,6,8] is in contrast to that observed in ferrocene itself which is staggered.[28] A situation that is intermediate between eclipsed and staggered was observed by Struchkov et al.[4] in [3]-(1,1′)[4](3,2′)ferrocenophan-6-one where one cyclopentadienyl ring is rotated relative to the other by an angle of 27°.

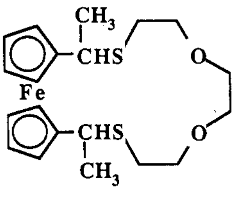
As was found for III, no substantial deviations from ideal geometry were observed for the Cp rings of I or II. Thus, the two cyclopentadienyl rings were found to be nearly parallel, the angle between the least-squares planes defined by the two rings being 2.4° and 3.4° for I and II, respectively (an angle of 2.3° was reported for III). The almost eclipsed conformation of the Cp rings and their virtual parallelism seem to indicate that the bridging chains are sufficiently free of strain that no significant distortion of the ferrocenyl moiety is required. This behavior is in contrast to that observed in cases of strained compounds where constraint is imposed either by the presence of a short chain (two atoms) and/or short multiple chains. In these cases, strain is accommodated by ring tilting and tilt angles as large as about 23° have been observed.[1] The two Cp rings are virtually planar, the largest deviation of any carbon from the best mean plane is 0.005 and 0.009 Å for I and II, respectively. (Details of least-squares planes have been deposited.) The iron to ring carbon distances range from 2.039 (1) to 2.068 (1) Å (mean 2.050 Å) and from 2.015 (5) to 2.052 (4) Å (mean 2.040 Å). Interesting, the distance



I



II



III

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[26] The twist angle was calculated by averaging the five dihedral angles between planes defined by the two ring centroids and one carbon atom of the first Cp ring and the two ring centroids and the corresponding carbon of the second ring.

[27] Compound III differs from II only by having a methyl group and a hydrogen instead of two hydrogens attached to each carbon which is directly bonded to the Cp rings.

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Table II. Atomic Coordinates, Equivalent Temperature Factors of the Non-Hydrogen Atoms, and Isotropic Temperature Factors of the Hydrogens for Compounds I and II

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
				A. Compound I					
Fe	0.25287 (3)	0.17731 (2)	0.39012 (2)	2.198 (5)	H2	0.387 (3)	0.279 (2)	0.187 (2)	5.0
S1	−0.21052 (6)	0.09289 (5)	0.11948 (5)	2.94 (1)	H3	0.581 (3)	0.140 (2)	0.352 (2)	5.0
S2	0.04982 (7)	0.52938 (5)	0.27545 (5)	3.27 (1)	H4	0.373 (3)	−0.074 (2)	0.405 (2)	5.0
O1	−0.3054 (2)	0.3835 (1)	0.0700 (1)	2.91 (3)	H5	0.039 (3)	−0.053 (2)	0.275 (2)	5.0
C1	0.1592 (2)	0.1251 (2)	0.1916 (2)	2.47 (3)	H7	0.362 (3)	0.453 (2)	0.442 (2)	5.0
C2	0.3419 (3)	0.1947 (2)	0.2228 (2)	3.25 (4)	H8	0.509 (3)	0.291 (2)	0.603 (2)	5.0
C3	0.4505 (3)	0.1172 (2)	0.3153 (2)	3.80 (4)	H9	0.261 (3)	0.091 (2)	0.633 (2)	5.0
C4	0.3374 (3)	0.0012 (2)	0.3427 (2)	3.55 (4)	H10	−0.046 (3)	0.134 (2)	0.490 (2)	5.0
C5	0.1569 (3)	0.0052 (2)	0.2661 (2)	2.91 (4)	H11A	0.008 (3)	0.141 (2)	−0.002 (2)	5.0
C6	0.1048 (2)	0.3179 (2)	0.4402 (2)	2.33 (3)	H11B	0.018 (3)	0.267 (2)	0.097 (2)	5.0
C7	0.2946 (3)	0.3698 (2)	0.4789 (2)	3.10 (4)	H12A	−0.484 (3)	0.137 (2)	0.009 (2)	5.0
C8	0.3818 (3)	0.2778 (2)	0.5670 (2)	3.50 (4)	H12B	−0.372 (3)	0.104 (2)	−0.101 (2)	5.0
C9	0.2487 (3)	0.1689 (2)	0.5830 (2)	3.26 (4)	H13A	−0.434 (3)	0.326 (2)	−0.114 (2)	5.0
C10	0.0771 (3)	0.1932 (2)	0.5045 (2)	2.76 (4)	H13B	−0.220 (3)	0.317 (2)	−0.078 (2)	5.0
C11	0.0048 (2)	0.1681 (2)	0.0917 (2)	2.60 (4)	H14A	−0.362 (3)	0.582 (2)	0.012 (2)	5.0
C12	−0.3697 (3)	0.1526 (2)	−0.0185 (2)	3.21 (4)	H14B	−0.156 (3)	0.531 (2)	0.003 (2)	5.0
C13	−0.3287 (3)	0.3016 (2)	−0.0460 (2)	3.13 (4)	H15A	−0.248 (3)	0.586 (2)	0.249 (2)	5.0
C14	−0.2429 (3)	0.5242 (2)	0.0563 (2)	3.10 (4)	H15B	−0.115 (3)	0.687 (2)	0.182 (2)	5.0
C15	−0.1558 (3)	0.5916 (2)	0.1911 (2)	3.30 (4)	H16A	−0.115 (3)	0.416 (2)	0.413 (2)	5.0
C16	−0.0420 (2)	0.3857 (2)	0.3570 (2)	2.44 (3)	H16B	−0.129 (3)	0.318 (2)	0.295 (2)	5.0
				B. Compound II					
Fe	0.11077 (5)	0.12383 (8)	0.87118 (4)	2.29 (2)	H2	0.221	0.218	0.806	5
S1	0.1178 (1)	0.2075 (2)	0.6307 (1)	4.45 (5)	H3	0.176	0.353	0.902	5
S2	0.1359 (1)	−0.3310 (2)	0.8500 (1)	3.96 (4)	H4	0.038	0.350	0.882	5
O1	0.1101 (3)	−0.1084 (5)	0.5852 (2)	4.3 (1)	H5	−0.003	0.211	0.777	5
O2	0.1586 (3)	−0.3176 (4)	0.6824 (2)	3.7 (1)	H7	0.230	−0.019	0.922	5
C1	0.1086 (4)	0.1818 (6)	0.7685 (3)	3.0 (1)	H8	0.171	0.117	1.008	5
C2	0.1716 (4)	0.2320 (7)	0.8118 (4)	3.8 (2)	H9	0.033	0.091	0.979	5
C3	0.1462 (5)	0.3082 (7)	0.8654 (4)	4.9 (2)	H10	0.009	−0.066	0.878	5
C4	0.0688 (5)	0.3065 (7)	0.8546 (4)	4.5 (2)	H11A	0.148	0.029	0.712	5
C5	0.0463 (4)	0.2290 (7)	0.7956 (4)	3.6 (2)	H11B	0.055	0.051	0.695	5
C6	0.1237 (4)	−0.0737 (6)	0.8775 (3)	2.6 (1)	H12A	0.026	0.075	0.567	5
C7	0.1792 (4)	−0.0112 (6)	0.9233 (3)	3.0 (1)	H12B	0.068	0.169	0.511	5
C8	0.1463 (4)	0.0643 (6)	0.9711 (3)	3.4 (2)	H13A	0.176	0.019	0.545	5
C9	0.0687 (4)	0.0501 (6)	0.9557 (4)	3.4 (2)	H13B	0.104	−0.035	0.487	5
C10	0.0557 (4)	−0.0346 (6)	0.8989 (4)	3.3 (2)	H14A	0.110	−0.474	0.720	5
C11	0.1069 (5)	0.1008 (7)	0.7045 (4)	4.1 (2)	H14B	0.196	−0.502	0.699	5
C12	0.0787 (5)	0.1112 (8)	0.5558 (4)	5.0 (2)	H15A	0.240	−0.344	0.793	5
C13	0.1210 (5)	−0.0055 (5)	0.5389 (4)	5.3 (2)	H15B	0.214	−0.494	0.819	5
C14	0.1628 (4)	−0.4352 (7)	0.7214 (4)	4.0 (2)	H16A	0.186	−0.142	0.802	5
C15	0.1958 (4)	−0.4061 (6)	0.7953 (4)	3.6 (2)	H16B	0.093	−0.151	0.777	5
C16	0.1354 (4)	−0.1634 (6)	0.8190 (3)	3.4 (2)	H17A	0.124	−0.247	0.513	5
C17	0.1432 (4)	−0.2252 (8)	0.5665 (4)	4.4 (2)	H17B	0.200	−0.213	0.574	5
C18	0.1240 (4)	−0.3337 (7)	0.6116 (4)	3.9 (2)	H18A	0.142	−0.422	0.592	5
					H18B	0.067	−0.336	0.611	5

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

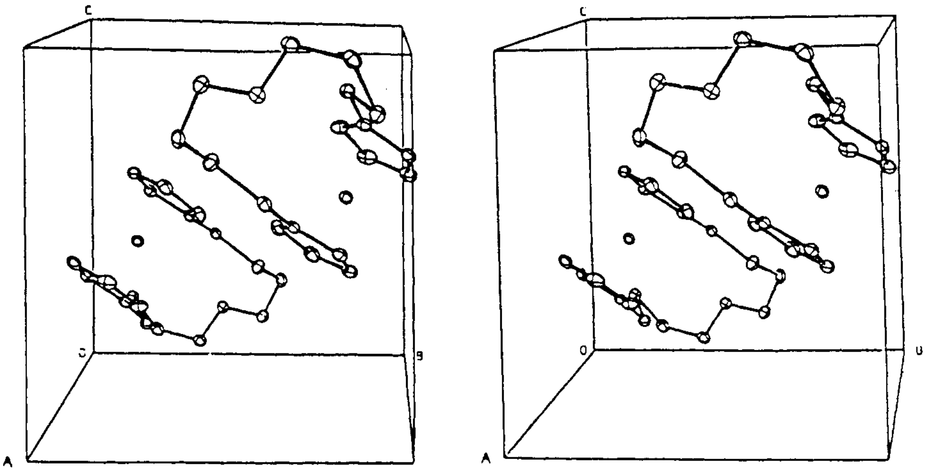

Figure 3. Stereoscopic view of the molecular packing for I. Hydrogen atoms are omitted for clarity.

between the Fe atom and carbons C1 and C6 (the carbons directly bonded to the linking chain) are slightly, but significantly, longer than the other Fe–C(Cp) bonds. This effect slightly disturbs the parallelism of the Cp rings

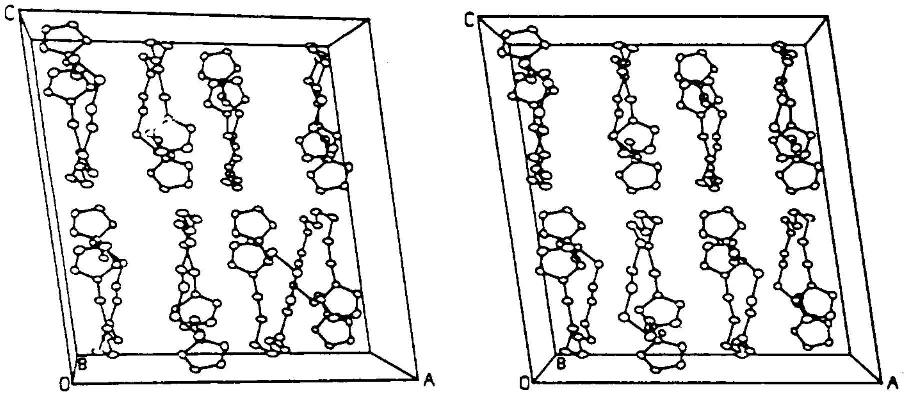

Figure 4. Stereoscopic view of the molecular packing for II. Hydrogen atoms are omitted for clarity.

Table III. Bond Lengths (Å) with Estimated Standard Deviations in Parentheses.

	I	II
(a) Within the Fe–$(C_5H_5)_2$ moiety		
Fe–C1	2.061 (1)	2.052 (4)
Fe–C2	2.045 (1)	2.041 (5)
Fe–C3	2.043 (1)	2.015 (5)
Fe–C4	2.045 (1)	2.041 (5)
Fe–C5	2.054 (1)	2.048 (4)
Fe–C6	2.068 (1)	2.048 (4)
Fe–C7	2.052 (1)	2.040 (4)
Fe–C8	2.040 (1)	2.028 (4)
Fe–C9	2.039 (1)	2.042 (5)
Fe–C10	2.050 (1)	2.048 (5)
(b) Within the C_5H_5 Rings		
C1–C2	1.427 (1)	1.425 (7)
C2–C3	1.424 (1)	1.425 (8)
C3–C4	1.408 (2)	1.417 (8)
C4–C5	1.428 (1)	1.397 (7)
C5–C1	1.424 (1)	1.417 (7)
C6–C7	1.428 (1)	1.406 (6)
C7–C8	1.420 (1)	1.405 (7)
C8–C9	1.411 (1)	1.429 (9)
C9–C10	1.428 (1)	1.399 (7)
C10–C6	1.421 (1)	1.429 (7)
(c) Within the Bridging Chain		
C1–C11	1.493 (1)	1.480 (7)
C11–S1	1.809 (1)	1.825 (5)
S1–C12	1.814 (1)	1.808 (5)
C12–C13	1.500 (1)	1.494 (9)
C13–O1	1.414 (1)	1.415 (7)
O1–C14	1.417 (1)	
O1–C17		1.418 (7)
C17–C18		1.487 (8)
C18–O2		1.424 (5)
O2–C14		1.420 (6)
C14–C15	1.506 (1)	1.491 (7)
C15–S2	1.809 (1)	1.805 (6)
S2–C16	1.807 (1)	1.824 (5)
C16–C6	1.495 (1)	1.493 (7)

leading to the observed dihedral angles of 2.4° and 3.4° and is probably due to steric hindrance between the groups directly attached to the Cp rings. The distances of the iron atom from the planes of the two rings are 1.655, 1.655, 1.649, and 1.645 Å. These distances compare well with the values of 1.655 and 1.649 Å reported for III and the value of 1.66 Å observed in ferrocene[28] and bis(ferrocenyl).[29]

The carbon–carbon bond distances in the Cp rings range from 1.408 (2) to 1.428 (1) Å (average 1.422 Å) and from 1.397 (7) to 1.429 (7) Å (average 1.415 Å). A value of 1.418 Å was found for III, and a mean bond length of 1.40 Å has been reported for ferrocene and bis(ferrocenyl). The bond

Table IV. Bond Angles (deg) with Estimated Standard Deviations in Parentheses

	I	II
C2–C1–C5	107.27 (8)	107.5 (4)
C1–C2–C3	108.15 (9)	107.1 (5)
C2–C3–C4	108.34 (9)	108.5 (5)
C3–C4–C5	107.94 (9)	107.6 (5)
C4–C5–C1	108.29 (9)	109.2 (5)
C7–C6–C10	107.32 (8)	106.9 (4)
C6–C7–C8	108.21 (9)	108.3 (4)
C7–C8–C9	108.30 (9)	108.9 (4)
C8–C9–C10	107.88 (8)	106.3 (4)
C9–C10–C6	108.29 (8)	109.5 (4)
C2–C1–C11	124.99 (8)	127.2 (5)
C5–C1–C11	127.61 (8)	125.1 (5)
C1–C11–S1	111.11 (6)	108.3 (3)
C11–S1–C12	101.63 (5)	102.2 (3)
S1–C12–C13	115.83 (6)	116.8 (4)
C12–C13–O1	109.70 (8)	109.8 (5)
C13–O1–C14	112.86 (7)	
C13–O1–C17		111.7 (5)
O1–C17–C18		109.9 (5)
C17–C18–O2		110.8 (4)
C18–O2–C14		112.7 (4)
O1–C14–C15	108.79 (8)	
O2–C14–C15		108.3 (4)
C14–C15–S2	113.82 (6)	115.9 (4)
C15–S2–C16	100.72 (4)	101.0 (2)
S2–C16–C6	111.51 (6)	109.5 (3)
C16–C6–C1	127.24 (8)	125.5 (5)
C16–C6–C10	125.25 (8)	127.7 (4)

Table V. Torsion Angles (deg) within the Bridging Chain[a]

angle	I	II	III[b]
C1–C11–S1–C12	−176.7	−157.8	−161.7
C11–S1–C12–C13	−45.4	−70.6	156.4
S1–C12–C13–O1	−53.1	78.7	61.8
C12–C13–O1–C14	172.2		
C13–O1–C14–C15	−158.6		
O1–C14–C15–S2	66.2		
C12–C13–O1–C17		174.0	178.7
C13–O1–C17–C18		−174.2	171.7
O1–C17–C18–O2		−69.4	−77.7
C17–C18–O2–C14		−160.1	86.8
C18–O2–C14–C15		−176.8	−176.4
O2–C14–C15–S2		77.3	179.2
C14–C15–S2–C16	−88.4	−77.8	−86.9
C15–S2–C16–C6	−177.7	−150.5	154.3

[a] The estimated standard deviations of the torsion angles for compounds I and II are ~0.1–0.3°. [b] The numbering system is that employed for compounds I and II.

angles of the Cp rings are normal, ranging from 107.27 (8)° to 108.34 (9)° and from 106.3 (4)° to 109.5 (4)°.

The lengths of the C(bridge)–C(Cp) type bonds of compound I [1.493 (1) and 1.495 (1) Å] are close to the standard value for $C(sp^2)$–$C(sp^3)$ bond [1.506 (1) Å].[30] As expected,

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[29] MacDonald, A. C.; Trotter, J. *Acta Crystallogr.* **1964**, *17*, 872.

slightly larger values [1.500 (1) and 1.506 (1) Å] are observed for the $C(sp^3)$–$C(sp^3)$ type bonds of the bridging chain. These differences are not statistically significant in the case of compound II due to the higher estimated standard deviations of the bond lengths.

The C–S distances of 1.809 (1), 1.814 (1), 1.809 (1), 1.807 (1) Å and 1.825 (5), 1.808 (5), 1.805 (6), 1.824 (5) Å are all close to the value of 1.81 Å found in dimethyl and diethyl sulfide.[30] The range of C–O distances observed [1.414 (1), 1.417 (1) Å and 1.415 (7), 1.418 (7), 1.424 (5), 1.420 (6) Å] are within the range found in the tricyclic crown ether $C_{56}H_{68}O_{10}$ [1.374 (8)–1.456 (8) Å].[31]

The values of the torsion angles shown in Table V can be used to define the C1–C6 bridging chain conformation. In crown ether compounds, the preferred conformations about the C–C and C–O bonds are gauche (g) and anti (a), respectively.[31,32] As can easily be seen from the data in Table V, this conformational preference is observed in I and II even though some deviations were reported for III. This deviation from the minimum conformation energy of III was related to the presence of the ferrocenyl moiety.[19] Both conformations, g and a, were found for the C–S bond.

An interesting feature of the structure for II is that the molecule is nearly symmetric with respect to a pseudo twofold axis which passes through the iron atom and bisects the C17–C18 bond. The proximity of carbons C11 and C16 (the chain carbons directly attached to the Cp rings) leads to steric hindrance between the hydrogens that is minimized when they assume an offset, effectively staggered conformation. This situation is different from that found in I where steric hindrance is avoided by twisting the two half chains. In the case of III, potential steric hindrance between the two methyl groups bonded to the carbons directly attached to the Cp rings is relieved by mutual rotation of the Cp rings. Consequently, the two carbons that carry the methyl groups no longer face each other (as they do in I and II).

Electrochemical Studies. Cyclic voltammograms of I and II in acetonitrile solution (0.10 M in tetrabutylammonium perchlorate), with initial anodic sweep, were as expected for a reversible, one-electron oxidation of the ferrocenophanes to the corresponding ferricenium cations. Electrochemical reversibility was established[33] by peak-to-peak separations of 60–70 mV (50 mV/s sweep rate, 59 mV theoretical), i_{pa}/i_{pc} ratios of 1.0 ± 0.1, the linearity of i_{pa} vs (sweep rate)$^{1/2}$ plots, and the invariance of $(E_{pa} + E_{pc})/2$ values over a fivefold range in sweep rate. No new electroactive species were detected in the second and subsequent sweeps of steady-state voltammograms.

Reduction potentials (vs SHE) of the ferricenium cations derived from I and II are +405 and +419 mV, respectively, demonstrating that the ferrocene with cyclopentadienyl groups linked by a 2,8-dithia-5-oxanonyl chain is a slightly stronger reductant than the analogue with a 2,11-dithia-5,8-dioxadodecyl bridging unit. Potentials for I (+400 mV) and II (+416 mV) measured in the presence of 0.10 M sodium tetraphenylborate (added to acetonitrile solutions which also contained 0.10 M tetrabutylammonium perchlorate) showed that sodium cations had little influence on the thermodynamic oxidizability of both ferrocenes, although a very small cathodic shift in the cyclic voltammograms was noted. All reversibility criteria were satisfied in electrochemical measurements on solutions of I and II containing 0.10 M sodium tetraphenylborate. Since the complexation affinity of the ferrocenophanes toward sodium cation has not yet been determined, the absence of a strong perturbation in $E°$ values does not necessarily imply that the Fe(II,III) redox equilibrium is totally unaffected by complexed sodium cations.

The reduction potentials of ferrocenophanes I and II are comparable to that of the ferrocene parent (+422 mV),[25] as might be expected when the bridging polyether chains do not impose a significant distortion on the preferred, parallel orientation of the cyclopentadienyl rings. Thus, in this circumstance the doubly degenerate (e_g) ferrocene HOMO, consisting of the fully occupied iron $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals, remain essentially nonbonding.[34] Interestingly, the simple alkyl substituents of 1,1′-dimethylferrocene ($E°$ = +341 mV)[25] induce a far greater shift in the ferricenium/ferrocene reduction potential than do either of the structurally more complex ferrocenyl crown ether bridging groups that are also bonded in a 1,1′ fashion through carbon atoms to the cyclopentadienyl rings.

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Registry No. I, 76375-07-0; II, 80973-97-3; 1,1′-bis(hydroxymethyl)ferrocene, 1291-48-1; 2-mercaptoethyl ether, 2150-02-9.

Supplementary Material Available: Tables of anisotropic temperature factors and least-squares planes (4 pages); listings of observed and calculated structure factor amplitudes for I and II (26 pages). Ordering information is given on any current masthead page.

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