Unusually High Oxidation Half-Wave Potentials of Di- and Trichalcogena[3]ferrocenophanes. The Effect of Chalcogen Atoms in the Bridge

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(Received October 6, 1989)

1,2,3-Trithia[3]ferrocenophane (**1a**) and related compounds show a well-defined reversible one-electron oxidation wave (Fe(III)/Fe(II)) in cyclic voltammetry. The [3]ferrocenophanes with S and/or Se atoms in the bridge show unusually high oxidation half-wave potentials which have not been observed either in [3]ferrocenophane or in 1,1′-bis(methylchalcogeno)ferrocenes. The effect of chalcogen atoms at the 1,3-positions in the bridge on the positive shift of half-wave potentials is larger than that at the 2-position. Two kinds of electron-attracting effects of chalcogen atoms at the 1,3-positions in the bridge are proposed: an inductive electron-attracting effect ("through-bond" effect) and the interaction between the d-orbitals of Fe and chalcogen ("through-space" interaction). The role of the sulfur atom at the 2-position in the bridge is to stabilize the electron attracted by the sulfur atoms at the 1,3-positions by conjugation of three sulfur atoms.

Since the discovery of the fluxionality of the 1,2,3-trithia[3]ferrocenophane by Davison and Smart,[1] several reports on the activation energies and on the mechanism of bridge reversal of chalcogen-atom-bridged [3]ferrocenophanes using variable temperature NMR technique have appeared.[2] An X-ray crystallographic study of 1,2,3-trithia[3]ferrocenophane was also reported.[3] The Mössbauer spectra of 1,2,3-trithia[3]ferrocenophane (**1a**) were also reported by Good et al.[4] They estimated the delocalization of d-electrons of iron through the three-sulfur bridge, based on the isomer shift (ΔE_Q) value, which is about one half of those of other ferrocenophanes. The electrochemistry of ferrocenophanes has been studied by Kasahara et al.,[5a] Sato et al.,[5b] and Toma et al.[5c] Kasahara et al. have reported that the values of oxidation half-wave potentials ($E_{1/2}$) of [*n*]ferrocenophanes decrease with the decrease in the number (*n*) of methylene groups. On the other hand, the electrochemical behavior of 1,2,3-trichalcogena[3]ferrocenophanes has not yet been studied despite the interesting behavior of the three-sulfur bridge of **1a** found in the Mössbauer spectra.[4] We have preliminarily reported the unusually high oxidation potentials of trithia and triselena[3]ferrocenophanes.[6] We wish to report here full details of the electrochemical results of [3]ferrocenophanes which have chalcogen atoms in their bridge and to discuss the stability of chalcogen-atom-bridged [3]ferrocenophanes against electrochemical oxidation, based on photoelectron spectroscopy.

Experimental

Materials. The ferrocenophanes (**1a**—**1e** and **2a**—**2e**) used in this study were prepared according to the methods given in the literature,[1,7—11] and were identified by the measurements of ^{1}H NMR, ^{13}C NMR, and mass spectra.

Tetraethylammonium perchlorate (TEAP) used as a supporting electrolyte was of special polarographic grade; it was purchased from Nakarai Chemicals, Co., Ltd. Silver perchlorate of guaranteed reagent grade, purchased from Wako Pure Chemical Industries, Ltd., was recrystallized from water and was vacuum-dried in the dark at room temperature for 2 days, then at 50 °C for 3 days. The purification of acetonitrile was carried out by Walter and Ramaley's method.[12]

Measurements. Cyclic voltammograms and normal pulse voltammograms were recorded with a Huso polarograph Model 312 equipped with a Riken Denshi X-Y recorder Model F-42DG and a Huso potential scanning unit Model 321. All the measurements were carried out at 25 °C under argon atmosphere by a three electrode system consisting of a test electrode (stationary platinum disk: 2 mm in diameter), a coiled platinum wire counter electrode, and Ag| 0.1 mol dm^{-3} $AgClO_4$ in acetonitrile as a reference electrode.

The ^{1}H and ^{13}C NMR spectra of the ferrocene derivatives used in this study were recorded on a JEOL GX-270 FT-NMR spectrometer with tetramethylsilane (TMS) as an internal standard in CD_2Cl_2. The assignments of ^{13}C NMR spectra were based on the assignments of ^{1}H NMR spectra by Abel et al.[2] and of ^{13}C-^{1}H COSY NMR spectra measured in this study. The ^{77}Se NMR spectra were measured on the same instrument using diphenyl diselenide as an internal standard (464.1 ppm from dimethyl selenide in $CDCl_3$) in $CDCl_3$.

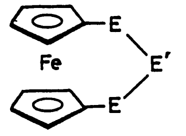
The photoelectron spectra were measured using the instrument described elsewhere.[13]

The electronic absorption spectra in methanol solutions of the ferrocene derivatives used in this study were recorded on a Hitachi 228 spectrophotometer.

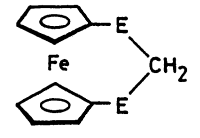
Results and Discussion

The compounds which we studied are listed below.

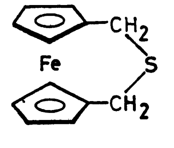
1. Electrochemistry. 1,2,3-Trithia[3]ferrocenophane (**1a**) exhibits a one-electron reversible oxidation ascribable to Fe(III)/Fe(II) of the ferrocene moiety (Fig. 1). The oxidation reversible half-wave potentials ($E^r_{1/2}$) of the trichalcogena[3]ferrocenophanes and the related ferrocene derivatives are listed in Table 1.



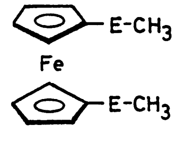
1a: E=E'=S
2a: E=E'=Se
1d: E=S, E'=Se
2d: E=Se, E'=S



1b: E=S
2b: E=Se



1c



1e: E=S
2e: E=Se

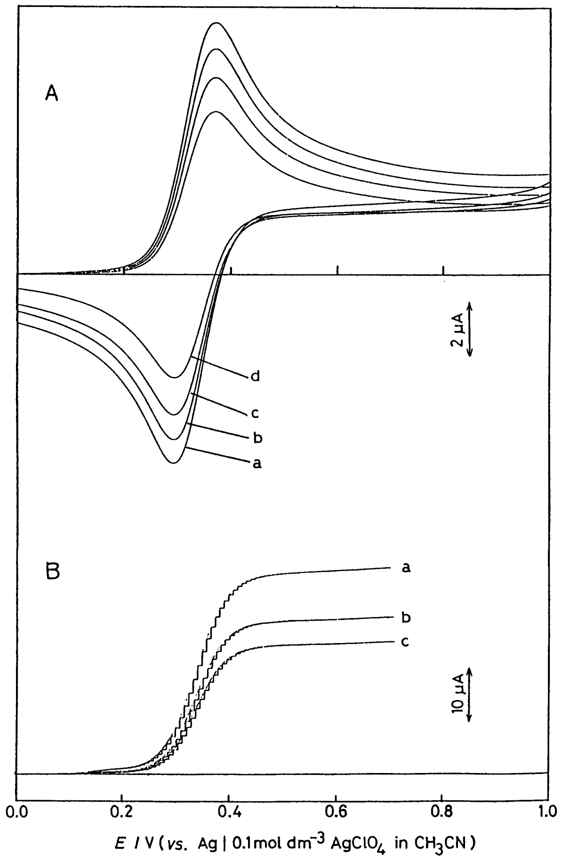


Fig. 1. (A): Cyclic voltammograms of **1a** (scan rate/mV s^{-1}: (a) 100, (b) 80, (c) 60, (d) 40) in 0.1 mol dm^{-3} TEAP-acetonitrile solutions. (B): corresponding normal pulse voltammograms (sampling time/ms: (a) 30, (b) 50, (c) 70).

The $E^{\mathrm{r}}_{1/2}$ value of **1a** is 335 mV (vs. Ag|0.1 mol dm^{-3} $AgClO_4$ in CH_3CN). This value is 310 mV more positive than that of ferrocene. A similar positive shift of the $E^{\mathrm{r}}_{1/2}$ value is also observed for 1,2,3-triselena[3]ferrocenophane (**2a**) in which two cyclopentadienyl rings are bridged by three selenium atoms, 1,3-dithia[3]ferrocenophane (**1b**), and 1,3-diselena[3]ferroceno-phane(**2b**) in which two chalcogen atoms are at the 1,3-positions in the bridge. In contrast to the above results, the $E^{\mathrm{r}}_{1/2}$ values of non-bridged chalcogen compounds such as 1,1'-bis(methylthio)ferrocene (**1e**) and 1,1'-bis(methylseleno)ferrocene (**2e**), are more negative than those of chalcogen-bridged ferrocenes. The $E^{\mathrm{r}}_{1/2}$ value of **1e** is 25 mV more negative than that of ferrocene. These results suggest that a characteristic property of high $E^{\mathrm{r}}_{1/2}$ values of trichalcogena[3]ferrocenophanes is due to the bridging of two cyclopentadienyl rings in ferrocene by at least two chalcogen atoms at 1- and 3-positions.

In order to evaluate the factors which control the magnitude of the positive shift of the $E^{\mathrm{r}}_{1/2}$ values, the following two effects were taken into consideration: (1) the effect of bridging by chalcogen atoms and (2) the effect of the number and position of the chalcogen

Table 1. Half-Wave Potentials and Chemical Shifts of the Compounds **1**, **2**, and Ferrocene

	Ferrocene	1a	1b	1c	1d	1e	2a	2b	2d	2e
$E^{\mathrm{r}}_{1/2}$/mV 1)	25	335	245	62	293	0	238	206	277	49
^1H NMR 2)										
δ-H_2	4.14	4.52	4.34	4.18	4.51	4.26	4.49	4.34	5.33	4.28
δ-H_5	4.14	3.83	4.34	4.18	3.80	4.26	3.88	4.34	3.88	4.28
δ-H_3	4.14	4.38	4.10	4.07	4.32	4.20	4.37	4.12	4.41	4.18
δ-H_4	4.14	4.45	4.10	4.07	4.43	4.20	4.38	4.12	4.51	4.18
other	—	—	4.17 3)	3.00 3)	—	2.29 4)	—	4.18 3)	—	2.12 4)
^{13}C NMR 2)										
δ-C_1	68.28	90.76	82.86	88.46	93.13	85.80	88.79	78.90	87.71	128.44
δ-C_2	68.28	79.41	73.76	70.31	79.12	72.34	78.49	74.91	78.81	74.70
δ-C_5	68.28	68.71	73.76	70.31	69.43	72.34	69.90	74.91	69.95	74.70
δ-C_3	68.28	69.88	71.10	68.84	69.61	70.19	71.10	70.85	70.92	70.71
δ-C_4	68.28	72.22	71.10	68.84	71.68	70.19	71.46	70.85	71.55	70.71
other	—	—	53.17 3)	28.55 3)	—	19.86 4)	—	34.39 3)	—	9.40 4)

1) vs. Ag | 0.1 mol dm^{-3} $AgClO_4$ in CH_3CN. 2) In ppm from internal TMS. Measured at room temperature in CD_2Cl_2. 3) Methylene group. 4) Methyl group.

atoms on the oxidation potential of the bridged ferrocene.

(1) [3]Ferrocenophanes, in which two cyclopentadienyl rings are bridged by three methylene chains, exhibit no unusual electrochemical properties: its $E_{1/2}$ value has been reported to be 363 mV (vs. SCE),[5a] which corresponds to −41 mV vs. Ag|0.1 mol dm^{-3} $AgClO_4$ in CH_3CN. Based on the $E_{1/2}^{r}$ value of [3]ferrocenophane[5a] and the reported quarter-wave potential value of 1,1′-diethylferrocene[14] (194 mV vs. SCE in CH_3CN corresponds to −88 mV vs. Ag|0.1 mol dm^{-3} $AgClO_4$ in CH_3CN), the shift of the $E_{1/2}$ value from non-bridged 1,1′-diethylferrocene to methylene bridged [3]ferrocenophane is positive but the magnitude of the shift is only 47 mV. Compared to these values, the positive shifts of the $E_{1/2}^{r}$ value from **1e** to **1b** (245 mV) and that from **2e** to **2b** (157 mV) are unusually large. These results show that the effect of bridging of chalcogen atoms on the $E_{1/2}^{r}$ value is five (in -S-CH_2-S-) to three (in -Se-CH_2-Se-) times larger than that of methylene.

(2) The effect of one sulfur atom at the 1- or 3-position in the bridge on the positive shift of the $E_{1/2}^{r}$ value can be estimated from the difference of the $E_{1/2}^{r}$ values ($\Delta E_{1/2}^{r\alpha}$) between **1b** (-S-CH_2-S-) and [3]ferrocenophane ($\Delta E_{1/2}^{r\alpha}$=286 mV). The effect of one sulfur atom at the 1- or 3-position is thus ($\Delta E_{1/2}^{r\alpha}$)/2=143 mV. Similarly, the effect of the sulfur atom at the 2-position in the bridge on the positive shift of $E_{1/2}^{r}$ ($\Delta E_{1/2}^{r\beta}$) between **1c** (-CH_2-S-CH_2-) and [3]ferrocenophane ($\Delta E_{1/2}^{r\beta}$=103 mV). A schematic diagram of the $E_{1/2}^{r}$ values of these compounds is shown in Fig. 2. In order to examine whether these $\Delta E_{1/2}^{r\alpha}$ and $\Delta E_{1/2}^{r\beta}$ values have additivity or not, these values were applied to **1a** (-S-S-S-): the sum of $\Delta E_{1/2}^{r}$ value of **1a**, 389 mV, is 54 mV higher than the observed value, 335 mV. This suggests some additional factors which include the interaction between the two types of sulfur atoms, the sulfur atoms at the 1- and 3-position and that at the 2-position. Similar effects are observed in the case where chalcogen atoms are replaced by selenium atoms. These results show that the electron-attracting effect of one sulfur atom at the 1- or 3-position on the positive shift of the $E_{1/2}^{r}$ is larger than that of the sulfur atom at the 2- position of the bridge in the chalcogen-atom-bridged [3]ferrocenophanes.

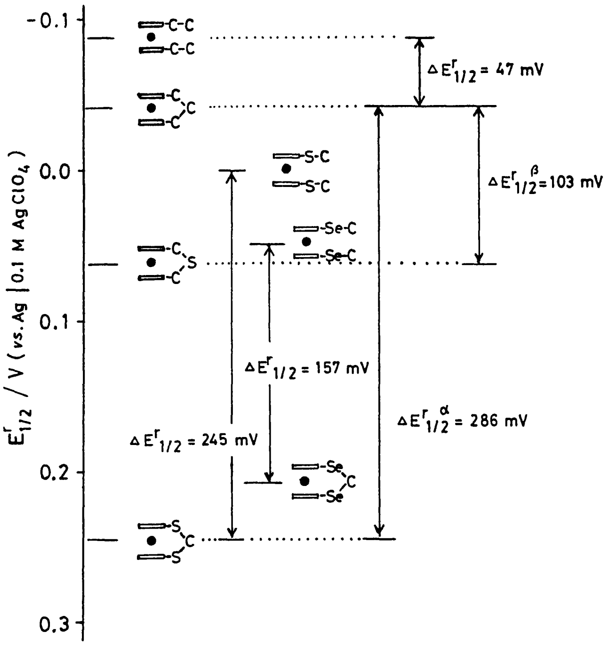


Fig. 2. Diagram of the effects of chalcogen atoms in the bridge and the effects of bridging on $E_{1/2}^{r}$ values.

2. **^{77}Se and ^{13}C NMR.** The first measurement of the ^{77}Se NMR spectra of five compounds which have selenium atoms in their bridge: **2a**, **2b**, **2d**, **1d**, and **2e** have been made. The results are shown in Table 2.

The ^{77}Se NMR spectrum of **2a** consists of two signals ascribed to the selenium atoms at the 1- and 3-

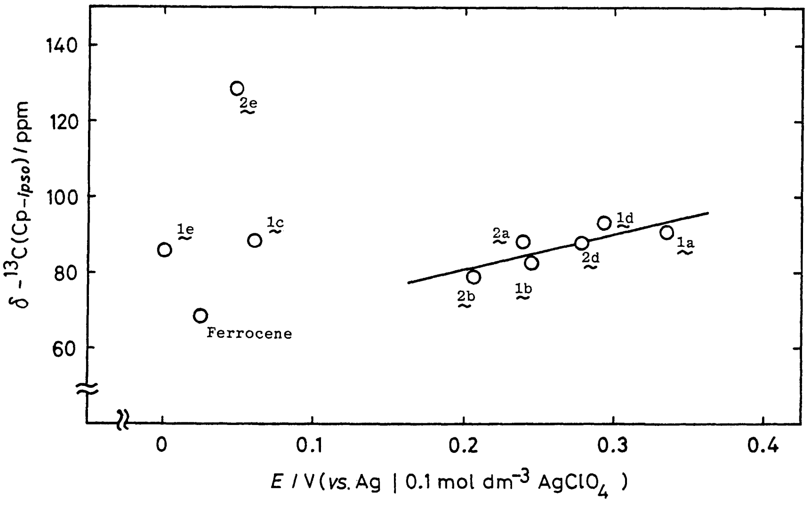


Fig. 3. Plots of $E_{1/2}^{r}$ values vs. chemical shifts of ipso carbon in (C_5H_4) rings.

Table 2. ^{77}Se NMR Chemical Shifts of **1d** and **2**[a)]

	2a	**2b**	**2d**	**1d**	**2e**
δ-Se$_{1,3}$	307.6	182.4	387.6	—	102.6
δ-Se$_2$	919.7	—	—	1101.1	—

a) In ppm from internal diphenyl diselenide, measured at room temperature in CDCl$_3$ at 51.6 MHz.

position and a signal ascribed to the selenium atom at the 2-position in the bridge. The signal which appears at 307.6 ppm corresponds to the former, and the other signal at 919.7 ppm corresponds to the latter. These assignments are based on the result that **2d** has a signal in higher field than **1d**. There is an interesting tendency that the compound with a higher oxidation potential gives the signal in a lower field. But no satisfactory explanation for the relationship between the oxidation half-wave potential and the chemical shifts of ^{77}Se NMR can be made yet.

A linear relationship between the oxidation half-wave potentials and the chemical shifts of ipso-carbon in ^{13}C NMR was obtained for all bridged ferrocenes except **1c** (Fig. 3). This linear relationship suggests that the chalcogen atoms, which are located in the bridge, attract electrons from the ferrocene moiety through the bonds.

3. Photoelectron Spectroscopy. In order to obtain more direct evidence for the electron-attracting effect of the three-sulfur-atom-bridge in **1a**, we compared the photoelectron spectra of **1a** with those of **1e** and ferrocene. The ionization potential (IP) values of **1a**, **1e**, and ferrocene are given in Table 3. In all the compounds, the lowest-lying bands in the spectra can be assigned to the electron emission from the MO's mainly localized at Fe 3d orbitals in character.[15] The first vertical ionization potential (IP) of **1a** is 7.30 eV, which is much higher than those of **1e** (6.83 eV) and ferrocene (6.86 eV). These results indicate that the positive charge on the Fe atom in **1a** is increased relative to that in **1e** and ferrocene, if the relaxation effects of these compounds in the final ionic state are similar. The band at IP=8.75 eV observed in the spectrum of ferrocene is attributed to the degenerate MO consisting mainly of the π-orbitals of the cyclopentadienyl rings. This band is split into two bands in **1a** and **1e**, owing to the lowering of the symmetry of these compounds. The higher-lying π-bands of **1a** is observed at IP=9.87 eV but that of **1e** is seen at IP=8.88 eV. These data can be interpreted by the electron density of the cyclopentadienyl rings; the density of **1a** is less than that of **1e** or ferrocene. Detailed discussions of the photoelectron and Penning ionization electron spectra will be given elsewhere.[15]

Table 3. Vertical Ionization Potentials[a)] of **1a**, **1e**, and Ferrocene

	1a	**1e**	Ferrocene
Fe-3d	7.30	6.83	6.86
	7.55	7.17	7.23
n$_s$	8.52	ca. 7.9	—
	9.35	8.33	—
Cp-π	9.87	8.88	8.75

a) In eV.

4. Electronic Absorption Spectra and Related Phenomena. With respect to the electronic absorption spectra (Fig. 4), the chalcogen-containing [3]ferrocenophanes can be classified into two groups, A and B, according to the absorption patterns in their spectra. The compounds of group A, with a bridge constructed by three chalcogen atoms, show an intense absorption band at a region of 330—370 nm which is not observed in the group B compounds which have no bridge or have a bridge constructed by chalcogen atoms and carbon atoms($-$E-CH$_2$-E- or -CH$_2$-E-CH$_2$-, E: chalcogen atom). This new band originates from the MO correlated to the conjugated chalcogen atoms in the bridge. A similar classification of the compounds can be made based on the signal patterns in ^{1}H NMR spectra. Group A compounds show four nonequivalent signals ascribable to the cyclopentadienyl ring protons in ^{1}H NMR.[2] This shows that the ring inversion with bridge reversal[1,2] of group A compounds is slow at room temperature on the NMR time scale. The high activation energies reported for the bridge reversal in the chalcogen-bridged [3]ferrocenophanes ($>$50 kJ mol^{-1})[2] suggest that 1,2,3-trichalcogena[3]ferrocenophanes have rigid bonds in their bridge at room temperature.

This result is in accord with the presence of partial double bonding in the three-sulfur bridge of **1a** proposed by Good et al.[4]

5. General Discussion. The results described in the preceeding sections show that the unusually high

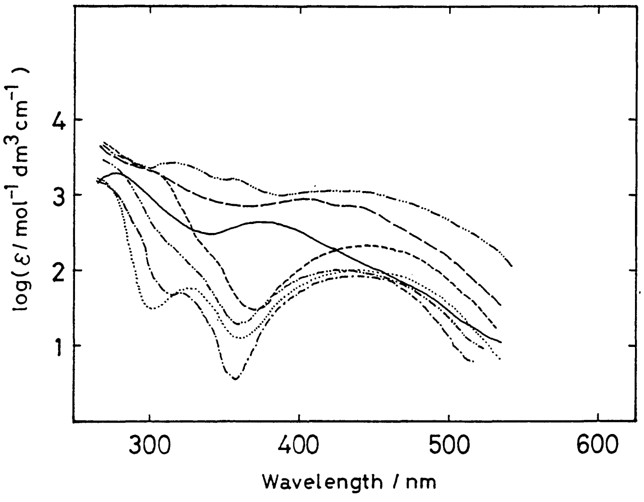


Fig. 4. Electronic absorption spectra of **1a** (——), **1b** (— - - —), **1c** (— - —), **1d** (— —), **1e** (----), **2a** (— --- —), and ferrocene (------) in methanol solutions.

oxidation half-wave potentials of the chalcogen-bridged [3]ferrocenophanes are ascribed to the stabilization of the electrons in HOMO localized at the iron atom. The stabilization comes from the electron attraction by the chalcogen atoms in the bridge. The roles of the chalcogen atoms at the 1- and 3-positions are more important than that at 2-position. The explanation is the electron-attracting effect of chalcogen atoms at the 1- and 3-positions in the bridge: The chalcogen atom attached to a conjugated system donates electrons by mesomeric effect but attracts electrons by inductive effect. The opposite electronic effect of chalcogen atoms between bridged and non-bridged ferrocenes can be explained by the degree of overlap of p-orbitals of chalcogen atoms and π-orbitals of cyclopentadienyl rings: in the bridged compounds, the p-orbitals of the chalcogen atoms at 1,3-positions have poor overlap with π-orbitals of the cyclopentadienyl rings due to the twisting of C–S or C–Se bonds by bridging. Consequently, the inductive effect of the sulfur atom is dominant over its mesomeric effect, and this results in the higher oxidation half-wave potentials of **1a**, **1b**, and **1d**. But in a non-bridged compound such as **1e**, the electron-donating mesomeric effect is dominant over the electron-attracting inductive effect, since the overlap of the p-orbitals of sulfur atoms with the π-orbitals of the cyclopentadienyl rings is possible.

Another explanation might be possible for the electron-attracting effect of chalcogen-atom-bridge in di- and trichalcogena[3]ferrocenophanes: that is "through-space" interaction between the occupied d-orbital (HOMO, $d_{x^2-y^2}$) of the iron atom of the ferrocene moiety and the unoccupied d-orbital (d_{xz}) chalcogen atoms at the 1,3-position in the bridge. A similar interaction of the occupied d-orbital of iron with the unoccupied p-orbital of α-carbonium ion is reported for the stabilization of 1-ferrocenylalkyl cation.[16] However, we do not have any evidence that this type of interaction is operating in the di- and trichalcogena[3]ferrocenophanes.

As described in section 4, the sulfur atom at the 2-position plays an important role in stabilizing the electrons on the sulfur atoms at the 1- and 3-position: the electrons on the 1- and 3-position can be delocalized on three sulfur atoms if the overlap of p-orbitals of the three sulfur atoms is possible. The characteristic absorption band of **1a** and the high value of energy barrier for the bridge reversal of **1a**[2] strongly suggest the presence of partial double bonding in the -S-S-S- bridge. This implies that the delocalization of electrons is present in the three-sulfur-atom bridge, which brings about the unusually high stability of **1a** against the removal of an electron from iron. A similar effect of adjacent three chalcogen atoms was found in other trichalcogen-atom-bridged [3]ferrocenophanes based on the results of electrochemical and spectroscopic data.

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