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The synthesis and properties of ferroceno[1′,2′;1″,2″]bis(1,3-dithiol-2-thione and -2-one) derivatives

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Abstract

The *t*-butyl and bis(*t*-butyl) derivatives of hexathia[3.3]ferrocenophane were prepared from the corresponding trithia[3]ferroceno-phanes. The former was a mixture of chair–chair and chair–boat isomers, and the latter existed only chair–boat isomer. The hexa-thia[3.3]ferrocenophanes were led to the tetrathiols with LiAlH$_4$, which allowed to react with 1,1′-thiocarbonyldiimidazol to give the corresponding ferroceno[1′,2′;1″,2″]bis(1,3-dithiol-2-thione) derivatives. Mono *t*-butyl and unsubstituted analogs were prepared in a similar manner. The X-ray structural determination showed that these derivatives adopted the conformation in which the 1,3-dithiol-2-thi-one rings were heaped on top of each other. In the crystal of ferroceno[1′,2′;1″,2″]bis(1,3-dithiol-2-thione), the molecules packed so as to put the axis of molecule in order and to overlap one another above and below. The desulfurizative coupling of the ferroc-eno[1′,2′;1″,2″]bis(1,3-dithiol-2-thione) derivatives was unsuccessful.

1. Introduction

Much recent interest has been focused in the creation of the substances bringing out a novel functionality. One aspect of such investigations is related to the charge-transfer complexes between electron-sufficient and electron-deficient compounds. Since the finding of tetrathiafulvalene (TTF) in 1973 [1], the property of the cation-radicals and charge-transfer complexes has been investigated extensively in the view of organic metals and superconductors [2] and other functionalities [3]. The electron-rich compounds such as TTF is still searching at present. The TTF derivatives substituted by one of electron-rich organometallics, ferrocene, were prepared [4,5]. Although no ferrocene-condensed TTF derivatives have been reported, a strikingly similar tetratioethylene derivatives was prepared [6]. From the interest as the starting material for substituted THF, enormous substituted 1,3-dithiol-2-

thione derivatives have been prepared [7,8]. So, we here report the preparation and some reactions of ferroceno-1′,2′;1″,2″-bis(1,3-dithiol-2-thione) derivatives, being the starting material for the complexes with a hidden potential to be led to ferrocene-condensed TTF derivatives, cyclic or ladder oligomers bridged by a tetrathioethylene group. One or two *t*-butyl substituents were introduced in order to increase the solubility of products and to acquire the suitable conformation for the constitution of cyclic or ladder oligomers.

2. Results and discussion

2.1. Synthesis and structural assignment

6,12-Bis(*t*-butyl)-1,2,3-trithia[3]ferrocenophane (**1**) [9] was converted with LiAlH$_4$ to the corresponding dithiol, which was lithiated with *n*-BuLi/TMEDA and followed by the reaction with sulfur to give the ferrocenophane with two S$_3$-bridges (**3**) as red-brown crystals in moderate yield (Scheme 1). In the ^{1}H NMR spectrum of **3**, only two sets of doublets for the η-C$_5$H$_2$-ring protons was observed, along

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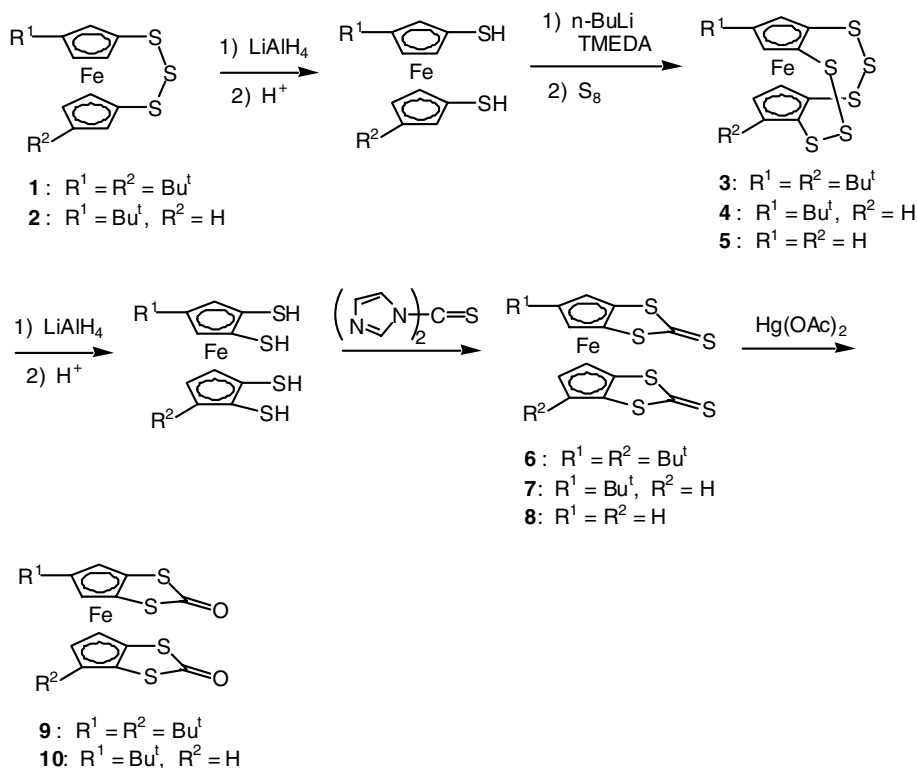
Scheme 1.

with two singlets for the two *t*-butyl protons at δ 1.24 and 1.26, implying the existence of only one product. The coupling constant for one set of doublets ($J = 2.9$ Hz) at δ 4.02 and 4.62 is larger than that for the other set of doublets ($J = 1.8$ Hz) at δ 3.86 and 4.73. The signals with large coupling constant are assigned to the ring protons neighboring each other. So, in ferrocenophane **3**, it is suggested that one η-C_5H_2-ring is substituted unexpectedly in the 1, 2, and 3-positions, while the other η-C_5H_2-ring in the 1, 2, and 4-positions. This is probably because the di-lithiation by *n*-BuLi/TMEDA complex is directed to the 5,5'-position of the ferrocene ring owing to the arrangement of bulky two *t*-butyl groups in the 3,4'-positions. Moreover, the conformation of the two S_3-bridges is suggested to be chair–boat because of the steric repulsion due to the neighboring *t*-butyl group. The structure of **3** was definitely established by single-crystal X-ray diffraction. The crystallographic data are collected in Table 1 and the selected bond distances and bond angles are summarized in Table 2. The ORTEP view of **3** is shown in Fig. 1. From Fig. 1, it is clear that the molecule is the 1,2,3:1',2',4'-isomer. The structural parameters of **3** are very similar to those of FcS₃ [10], Fc(S₃)₂ [11], or (*t*-Bu)₂FcS₃ [9]. The molecule consists of two nearly parallel Cp rings with a *t*-butyl group that are linked by two S_3-bridges. The tilt angle is 5.13(3)°, implying that there is scanty strain imposed by the two S_3-bridges on the Cp rings. The S_3-bridge next to the *t*-butyl group is folded far apart from the *t*-butyl group, so that the conformation of the two S_3-bridges becomes chair–boat.

6-*t*-Butyl-1,2,3-trithia[3]ferrocenophane (**2**) [9] was converted with LiAlH₄ to the corresponding dithiol and then the lithiation with *n*-BuLi/TMEDA and the subsequent reaction with sulfur gave the ferrocenophane with two S_3-bridges (**4**) as yellow crystals in moderate yield. The ^{1}H NMR spectrum of **4** showed that this compound was a mixture (3:1) of two isomers, chair–chair and chair–boat, being contrary to the case of **3** existing as only one isomer. The chair–chair form showed a singlet at δ 4.05 for the η-C_5H_2-ring protons and a doublet at δ 4.17 ($J = 2.7$ Hz) and a triplet at δ 4.68 ($J = 2.7$ Hz) for the η-C_5H_3-ring protons, because it has a plane of symmetry in the molecule. In the chair–boat form, the molecule has no symmetrical factor and then two doublets at δ 3.99 and 4.61 ($J = 1.8$ Hz) for the protons of the η-C_5H_2-ring with *t*-butyl group and three signals at δ 4.12 (dd, $J = 2.7$ and 1.5 Hz), 4.60 (t, $J = 2.7$ Hz), and 4.72 (dd, $J = 2.7$ and 1.5 Hz) for the η-C_5H_3-ring protons were observed. From the ^{1}H NMR data, **4** is assigned as 6-*t*-butyl-1,2,3,9,10,11-hexathia[3.3]ferrocenophane.

Complex **3** was reduced with LiAlH₄ to afford the corresponding tetrathiol, which was subsequently treated with 1,1'-thiocarbonyldiimidazol in THF to give red-violet crystals (**6**) in 43% yield. The ^{1}H NMR spectrum of **6** exhibited two sets of doublet for the η-C_5H_2-ring protons, indicating that **6** was a single product. The coupling constant for one set of doublets ($J = 2.9$ Hz) at δ 4.35 and 4.61 was larger than that for the other set of doublets ($J = 1.5$ Hz) at δ 4.41 and 4.53, suggesting that the former doublet stems from the neighboring ring-protons. In the ^{13}C NMR

Table 1
Crystallographic data for compounds **3**, **6**, **7**, and **8**

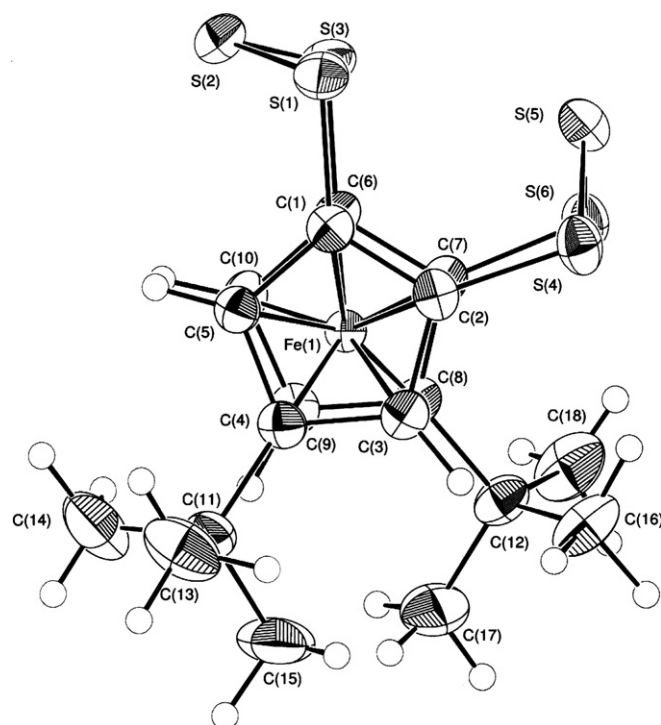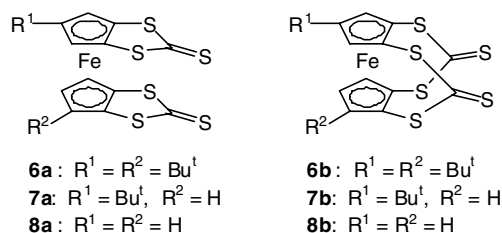|	3	6	7	8
Molecular formula	$C_{18}H_{22}S_6Fe$	$C_{20}H_{22}S_6Fe$	$C_{16}H_{14}S_6Fe$	$C_{12}H_6S_6Fe$
Molecular weight	486.605	510.627	454.519	398.411
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P-1$	$P21/n$	$P21/c$	$C2/c$
a (Å)	7.5150(3)	9.9040(3)	10.7920(5)	18.9680(8)
b (Å)	10.7500(5)	17.3320(6)	7.5920(4)	9.2810(4)
c (Å)	14.0380(7)	13.1370(5)	23.0820(11)	16.0700(8)
α (°)	76.722(3)	90	90	90
β (°)	84.879(4)	104.4090(10)	97.511(3)	105.233(2)
γ (°)	69.544(2)	90	90	90
V (Å^3)	1034.11(8)	2184.11(3)	1874.9(2)	2729.6(2)
Z	2	4	4	8
D_{calc} (Mg m^{-3})	1.563	1.553	1.610	1.939
Crystal dimension (mm)	$0.20 \times 0.15 \times 0.08$	$0.18 \times 0.06 \times 0.02$	$0.20 \times 0.12 \times 0.02$	$0.12 \times 0.10 \times 0.02$
Radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
Reflection (hkl) limits	$-9 \leqslant h \leqslant 9$, $-13 \leqslant k \leqslant 13$, $0 \leqslant l \leqslant 17$	$-10 \leqslant h \leqslant 9$, $0 \leqslant k \leqslant 22$, $0 \leqslant l \leqslant 16$	$-13 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 9$, $0 \leqslant l \leqslant 29$	$-24 \leqslant h \leqslant 23$, $0 \leqslant k \leqslant 11$, $0 \leqslant l \leqslant 20$
Total reflections measured	3773	4286	3937	3158
Unique reflections	3773	4286	2327	2063
Linear absorption coefficient (mm^{-1})	1.34	1.27	1.47	2.00
Least square parameters	226	271	208	172
R	0.036	0.031	0.039	0.031
Rw	0.097	0.070	0.140	0.077
S	0.999	1.275	1.954	2.642
Maximum peak in final Fourier map (e Å^{-3})	0.25	0.28	0.47	0.54
Minimum peak in final Fourier map (e Å^{-3})	-0.59	-0.39	-0.55	-0.51

$R = (\sum ||F_o| - |F_c||)/\sum |F_o|$. $Rw = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. $S = [\sum w(|F_o| - |F_c|)^2/N_{obs} - N_{para}]^{1/2}$.

spectrum of **6**, two thiocarbonyl carbon signals appeared at δ 218.96 and 219.23. It was reported that the reaction of 1,1′-ferrocenedithiol with 1,1′-thiocarbonyldiimidazol led to the heteroannularly bridged ferrocenophane [6]. Therefore, from the NMR spectral data, two possible structures are proposed; one is homoannularly bridged by two trithiocarbonate groups (**6a**) and the other is heteroannularly bridged (**6b**), as shown in Scheme 2. However, from the NMR spectral data we cannot decide whether either structure of **6a** or **6b** is correct, although the former is plau-

Table 2
Selected bond distances and bond angles for compound **3**

Bond distances (Å)

C(1)–S(1)	1.752(3)	C(2)–S(4)	1.754(3)
C(6)–S(3)	1.752(3)	C(7)–S(6)	1.759(3)
S(1)–S(2)	2.0547(13)	S(2)–S(3)	2.0528(13)
S(4)–S(5)	2.0519(13)	S(5)–S(6)	2.0595(14)
C(4)–C(11)	1.516(5)	C(8)–C(12)	1.529(5)
Fe(1)–C(Cp)	2.065(av.)	C(Cp)–C(Cp)	1.434(av.)

Bond angles (°)

C(1)–S(1)–S(2)	101.93(12)	S(1)–S(2)–S(3)	104.68(5)
C(6)–S(3)–S(2)	101.88(12)	C(2)–S(4)–S(5)	102.70(11)
S(4)–S(5)–S(6)	105.17(6)	C(7)–S(6)–S(5)	103.67(12)
C(2)–C(1)–S(1)	125.6(2)	C(1)–C(2)–S(4)	128.9(2)
C(7)–C(6)–S(3)	124.5(2)	C(6)–C(7)–S(6)	126.6(2)

Fig. 1. ORTEP view for complex **3**.

6a : R¹ = R² = Buᵗ
7a: R¹ = Buᵗ, R² = H
8a : R¹ = R² = H

6b : R¹ = R² = Buᵗ
7b: R¹ = Buᵗ, R² = H
8b : R¹ = R² = H

Scheme 2.

sible on the basis of the color of the product suggesting the extension of conjugation.

By a similar procedure used in the preparation of **6**, red-violet crystals (**7**) was obtained in 81% yield from **4**. In the ^{1}H NMR spectrum (C_6D_6) of **7**, the signal for the η-C_5H_2-ring protons were observed at δ 3.33 as a singlet (2H), those for the η-C_5H_3-ring protons appeared at δ 3.51 as a doublet (2H, $J = 2.5$ Hz) and δ 3.68 as a triplet (1H, $J = 2.5$ Hz), implying that **7** has a plane of symmetry in the molecule. In the coincidence with this, the ^{13}C NMR spectrum of **7** showed only six signals for the Cp-ring carbons. The structures homoannularly (**7a**) and heteroannularly bridged by two trithiocarbonate linkers (**7b**), consisting with these spectral data, are postulated (Scheme 2). In the ^{13}C NMR spectrum, the two carbon signals for the thiocarbonyl group were observed at δ 219.97 and 220.97. If complex **7** adopts structure **7b**, only one signal for the thiocarbonyl carbon should be observed due to the presence of a plane of symmetry in the molecule. The result of the ^{13}C NMR spectrum confirms structure **7a** as a correct structure for **7**.

In a similar manner, from 1,2,3,9,10,11-hexathia[3.3]ferrocenophane (**5**) [9] brown crystals (**8**) were obtained, which was scarcely soluble in almost organic solvent. The ^{1}H NMR spectrum of **8** in $CDCl_3$ showed one doublet at δ 4.57 ($J = 2.4$ Hz) and one triplet at δ 4.49 ($J = 2.4$ Hz) for the η-C_5H_3-ring protons, and the ^{13}C NMR spectrum of **8** showed only one thiocarbonyl carbon signal at 235.20 ppm. These NMR data support both structures of 1,3,9,11-dithia[3,3](4,16)(8,12)ferrocenophane-2,10-dithione (**8a**) and ferroceno[1′,2′;1″,2″]bis(1,3-dithiol-2-thione) (**8b**).

2.2. Solid-state structure

A single-crystal X-ray diffraction of **6** and **7** was carried out. The crystallographic data are collected in Table 1 and the selected bond distances and bond angles are summarized in Table 3 for **6** and Table 4 for **7**. The ORTEP view of **6** shown in Fig. 2 indicates that the correct structure of **6** is 3,4′-bis(*t*-butyl)ferroceno[1′,2′;1″,2″]bis(1,3-dithiol-2-thione) (**6a**), in which the trithiocarbonato group is bonded homoannularly to ferrocene and the 1,3-dithiol-2-thione ring system fused with ferrocene is constructed. The molecule has two nearly parallel Cp rings fused to a 1,3-dithiol-2-thione ring [tilt angle = 3.48(3)°]. It is the most important feature that the two 1,3-dithiol-2-thione
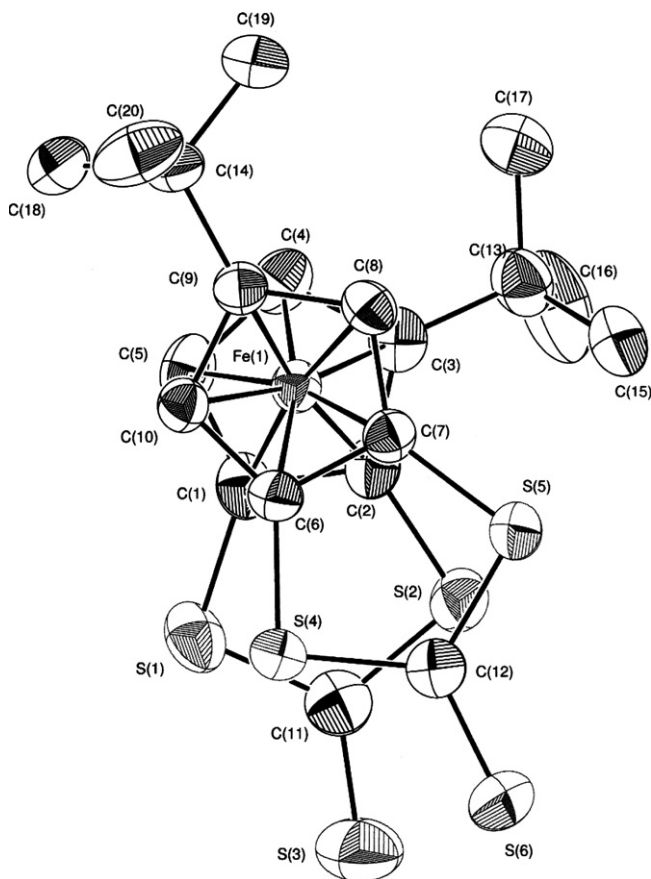
Table 3
Selected bond distances and bond angles for compound **6**

Bond distances (Å)

C(1)–S(1)	1.743(4)	C(2)–S(2)	1.746(4)
C(6)–S(4)	1.740(3)	C(7)–S(5)	1.747(3)
C(11)–S(1)	1.740(4)	C(11)–S(2)	1.745(3)
C(12)–S(4)	1.753(3)	C(12)–S(5)	1.744(4)
C(11)–S(3)	1.629(4)	C(12)–S(6)	1.627(4)
Fe(1)–C(Cp)	2.063(av.)	C(Cp)–C(Cp)	1.427(av.)

Bond angles (°)

C(1)–S(1)–C(11)	97.0(2)	C(2)–S(2)–C(11)	97.1(2)
C(6)–S(4)–C(12)	96.5(2)	C(7)–S(5)–C(12)	96.7(2)
S(1)–C(11)–S(2)	114.9(2)	S(4)–C(12)–S(5)	115.0(2)
C(2)–C(1)–S(1)	115.8(3)	C(1)–C(2)–S(2)	115.3(3)
C(7)–C(6)–S(4)	116.3(2)	C(6)–C(7)–S(5)	115.5(2)

Table 4
Selected bond distances and bond angles for compound **7**

Bond distances (Å)

C(1)–S(1)	1.732(6)	C(2)–S(2)	1.741(6)
C(6)–S(4)	1.741(6)	C(7)–S(5)	1.743(7)
C(11)–S(1)	1.741(6)	C(11)–S(2)	1.741(6)
C(12)–S(4)	1.751(6)	C(12)–S(5)	1.740(7)
C(11)–S(3)	1.625(6)	C(12)–S(6)	1.618(7)
Fe(1)–C(Cp)	2.055(av.)	C(Cp)–C(Cp)	1.426(av.)

Bond angles (°)

C(1)–S(1)–C(11)	96.7(3)	C(2)–S(2)–C(11)	96.6(3)
C(6)–S(4)–C(12)	96.9(3)	C(7)–S(5)–C(12)	96.9(3)
S(1)–C(11)–S(2)	115.0(4)	S(4)–C(12)–S(5)	114.6(4)
C(2)–C(1)–S(1)	115.9(4)	C(1)–C(2)–S(2)	115.8(4)
C(7)–C(6)–S(4)	115.6(5)	C(6)–C(7)–S(5)	115.9(5)

rings in **6** adopt the arrangement in which both 1,3-dithiol-2-thione rings lie approximately on top of each other although they slip by ca. 20° from the complete superimposition and then two Cp rings are intermediate between the eclipsed and staggered forms. As a result, the nearest intramolecular S–S distance is 3.5785(10) Å [S(1)–S(4)], being shorter than the sum of the van der Waals radii of a sulfur atom (1.85 Å). The S(2)–S(5) distance [3.7855(9) Å] is also near to the sum of the van der Waals radii of a sulfur atom. This suggests the existence of a certain intramolecular interaction between the S atoms. A similar conformation of the molecule and a short S–S intramolecular distance were reported in 1,1′-bis[5,6-dihydro-1,3-dithiolo[4,5-b][1,4]dithiin-2-ylidene]methyl]ferrocene [12]. Therefore, the conformation observed for complex **6** is considered to be caused rather by a significant attractive interaction operating between the two 1,3-dithiol-2-thione rings than by the avoidance of the large steric repulsion due to the *tert*-butyl groups. This speculation is also supported by the solid-state structure of complex **7**. The ORTEP view of **7** is shown in Fig. 3, which confirms that **7** is 3-*t*-butylferroceno[1′,2′;1″,2″]bis(1,3-dithiol-2-thione). Also in structure **7**, the two 1,3-dithiol-2-thione rings are positioned on top of each other and slip by about 18° out of the complete overlapping. The nearest intramolecular S–S distance is 3.536(3) Å [S(2)–S(5)], and the S(1)–S(4)
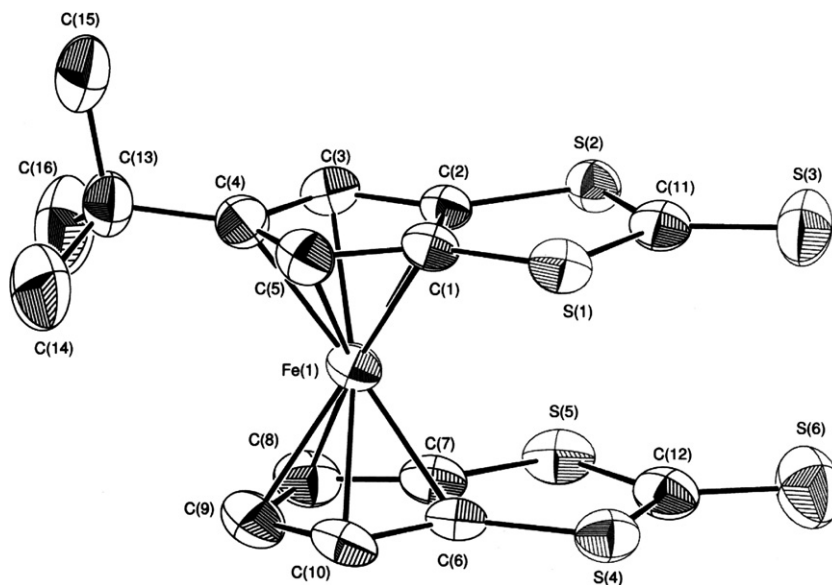
Fig. 2. ORTEP view for complex **6**.

Table 5
Selected bond distances and bond angles for compound **8**

Bond distances (Å)			
C(1)–S(1)	1.737(4)	C(2)–S(2)	1.733(4)
C(6)–S(4)	1.738(4)	C(7)–S(5)	1.731(4)
C(11)–S(1)	1.737(4)	C(11)–S(2)	1.731(5)
C(12)–S(4)	1.739(4)	C(12)–S(5)	1.731(5)
C(11)–S(3)	1.628(5)	C(12)–S(6)	1.626(5)
Fe(1)–C(Cp)	2.049(av.)	C(Cp)–C(Cp)	1.422(av.)

Bond angles (°)			
C(1)–S(1)–C(11)	96.3(2)	C(2)–S(2)–C(11)	96.6(2)
C(6)–S(4)–C(12)	96.6(2)	C(7)–S(5)–C(12)	97.1(2)
S(1)–C(11)–S(2)	115.4(2)	S(4)–C(12)–S(5)	115.1(2)
C(2)–C(1)–S(1)	115.7(3)	C(1)–C(2)–S(2)	115.8(3)
C(7)–C(6)–S(4)	115.6(3)	C(6)–C(7)–S(5)	115.5(3)

only a little in the direction which 1,3-dithiol-2-thione rings go away from each other and the tilt angle [2.54(3)°] is merely smaller than that in **6** [3.48(3)°]. This may contribute to the increase of the S–S distances in **6** and also supports a more attractive interaction in **7** than in **6**. The large extent of the slipping of the Cp ring in **6** compared with **7** seems to be due to the steric repulsion of two bulky *tert*-Bu groups. These results stimulate us to investigate the solid-structure of the unsubstituted ferroceno[1′,2′; 1″,2″]bis(1,3-dithiol-2- thione) (**8**).

The recrystallization of **8** from hot chlorobenzene gave dark-green crystals as a single crystal, the X-ray diffraction of which was then undertaken. The crystallographic data were collected in Table 1 and the bond distances and bond angles are summarized in Table 5. The ORTEP view is shown Fig. 4. From Fig. 4, the structure of **8** was confirmed to be ferroceno[1′,2′;1″,2″]bis(1,3-dithiol-2-thione). The structural parameters of **8** are very similar to that of **6** or **7**. However, the two 1,3-dithiol-2-thione rings take the conformation in which both rings

distance [3.546(3) Å] is also short. These intramolecular S–S distances in **7** are shorter than the corresponding distances in **6**. This suggests that a larger attractive interaction operates between the S atoms in **7** than in **6**. The two Cp-rings fused to a 1,3-dithiol-2-thione ring in **7** are inclined
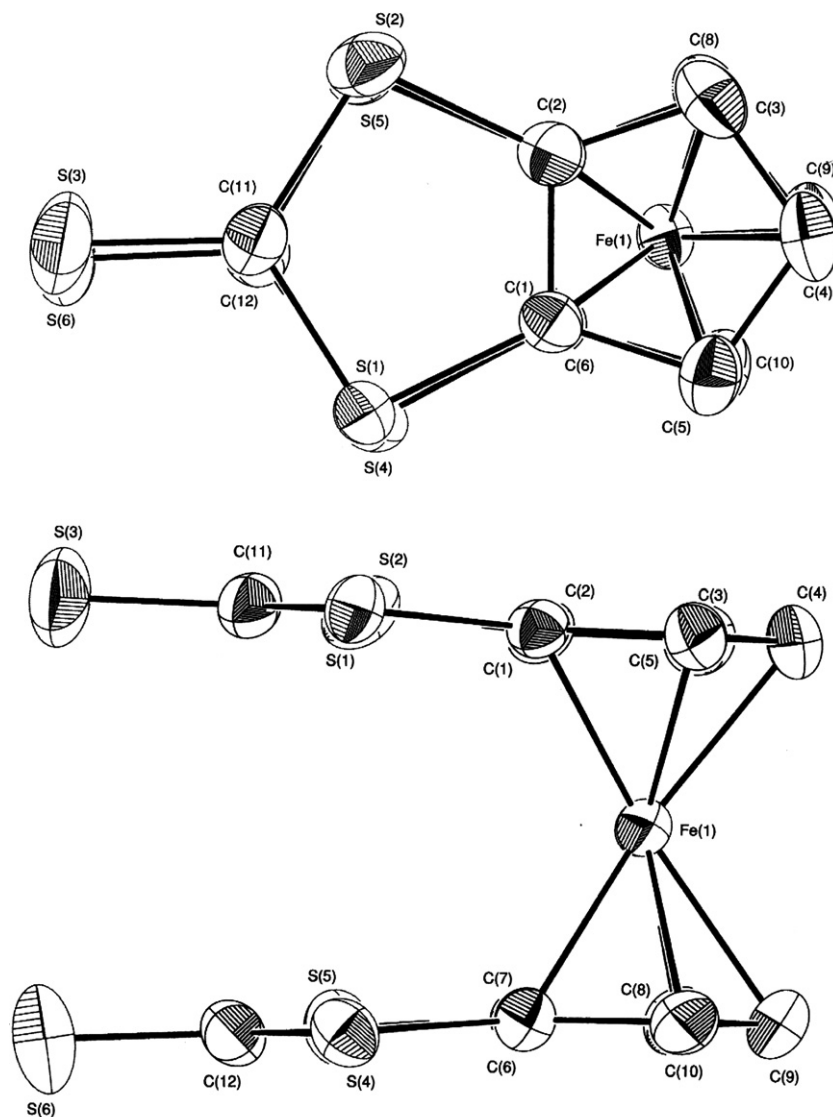

Fig. 3. ORTEP view for complex **7**.

Fig. 4. ORTEP view for complex **8**. Plane view (upper) and side view (bottom).

lie on top of each other with more remarkable superimposition of two 1,3-dithiol-2-thione rings than that in **6** and **7**. The two 1,3-dithiol-2-thione rings slip only by <2.5° out of the position of superimposition, as seen in Fig. 4 (upper). The intramolecular S–S distances [S(1)–S(4) 3.567(2) and S(2)–S(5) 3.6317(15) Å] are somewhat longer than those in **7**, though the slipping angle of 1,3-dithiol-2-thione rings in **8** is smaller than that in **7**. This seems to be attributed to the van der Waals repulsion, since the tilt angle [1.97(3)°] of the Cp-rings in **8** is comparable with that of in **6** [2.54(3)°] but the 1,3-dithiol-2-thione rings are bent backward apart from the Ru atom toward the Cp rings [2.93(3)° and 4.20(3)°], as seen in Fig. 4 (bottom). These findings suggest that a strong intramolecular S–S interaction is importantly responsible for the adoption of the superimposed conformation of the 1,3-dithiol-2-thione rings also in **8**.

The crystal packing of **8** is very interesting. As seen in Fig. 5, the 1,3-dithiol-2-thione rings fused by the Cp ring of **8** are parallel to the *b*-axis and are heaped on top of that of another molecule one another along a diagonal line between *a* and *c* axes and the molecules form discrete columns, as seen in Fig. 5. Moreover, the 1,3-dithiol-2-thione rings of neighboring two molecules are confronted each other and the molecules are slipped up and down only by half of the distance between the Cp rings of ferrocene. Therefore, the intermolecular S–S interaction is worthy of our notice. Seven S–S intermolecular distances within the sum (3.70 A) of the van der Waals radii are recognized in **8** and the distances are spread in the range of 3.2235(15)–3.685(15) Å. The shortest distance is reduced by as much as 0.48 Å from the sum of the van der Waals radii, which suggests the presence of a strong S–S intermolecular interaction.
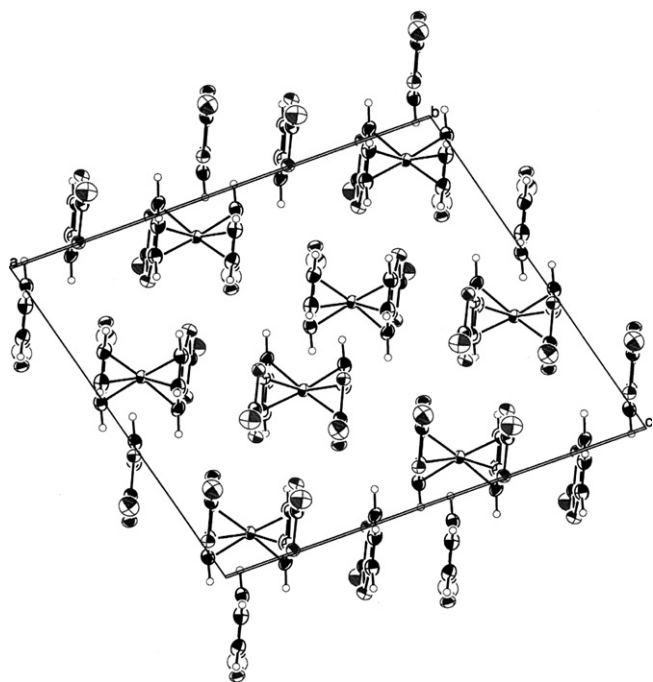
Fig. 5. Crystal packing of molecules **8**.

2.3. Spectral features

Metallocene-fused 1,3-dithiol-2-thione is a novel ring system and the effect of the fused metallocene in the system arouses our interest. The electronic spectral data and the chemical shift of the thiocarbonyl carbon in the ^{13}C NMR spectrum are summarized in Table 6. A strong absorption bands were observed near 355 nm in the electronic spectra of **6**–**8**, along with the shoulder near 375 nm. No large substituent effect due to a *t*-butyl group was recognized. Since ferrocene has no strong absorption band in this region, these absorption bands seem to be related to the 1,3-dithiol-2-thione chromophore. It was reported that 1,3-dithiol-2-thione and benzo-1,3-dithiol-2-thione showed the main absorption band at 367 (log ε 4.19) and 363 (4.34) nm [13]. It is worthy to note that the fusion of benzene or ferrocene ring to 1,3-dithiol-2-thione ring brings about some blue shift of that absorption. The thiocarbonyl carbon signals for **6**–**8** appeared near 220 ppm, whether a *t*-Bu substituent is present or not. It was reported that the corresponding carbon signals for 1,3-dithiol-2-thione and benzo-1,3-

dithiol-2-thione appeared at 213.2 [14] and 211.8 ppm [15], respectively. Some high-field shift of the thiocarbonyl carbon ($\Delta = 7$–22 ppm) is caused by the fusion of ferrocene to the 1,3-dithiol-2-thione ring. This may be probably due to the increase of polarization in the thiocarbonyl group as a result of the fusion of an electron-releasing ferrocene. In the accordance with this, the carbon signal at the 2-position in 2-methylthio-1,3-dithiolium cation was reported to appear at 166.4 ppm [14]. On the other hand, the chemical shift of the carbonyl carbon signals for **9** and **10** in the ^{13}C NMR spectrum is similar to that for 1,3-dithiol-2-one (194.1 ppm) [14]. Less polarization of a carbonyl group compared with a thiocarbonyl group seems to be responsible for the similarity of both carbonyl chemical shifts.

2.4. Electrochemical study

The cyclic voltammograms of 1.3-dithiol-2-thione derivatives **6**–**8** were measured in a solution of 0.1 M *n*-Bu$_4$N-ClO$_4$ in CH$_2$Cl$_2$ with use of a glassy carbon electrode and a sweep rate of 0.1 V s^{-1}. The reversible redox wave of the ferrocene moiety and irreversible oxidation waves were observed. The reversible redox potentials were obtained from the cyclic voltammogram in which the scan was turned back at 0.65 V. The redox potentials and the oxidation potentials are summarized in Table 7. The clear redox potentials of the ferrocene moiety of **6**–**8** remained nearly constant notwithstanding the substitution mode of a *t*-Bu group. On the other hand, the oxidation wave of the 1,3-dithiol part was unclear and the potential likely dependent on the substitution pattern of the ferrocene moiety.

In the repetitive scan of **8** in the range between −0.35 and 1.55 V, an interesting change of waves was observed, as seen in Fig. 6. The first forward scan yielded the oxidation wave of the ferrocene part at 0.37 V and the backward scan gave a reduction wave at 0.43 V. At the second forward scan, the oxidation wave of the ferrocene part at 0.37 V observed in the first scan diminished and a new oxidation wave was observed at 0.55 V. The reduction wave at 0.42 V remained intact but an additional wave appeared at 0.28 V. Such change was not observed when the backward scan began at 0.65 V. These observations suggest that a certain oxidation reaction takes place at high potential to yield a new species. The anodic shift of the oxidation potential in the ferrocene site suggests the generation of positive charge

Table 6
Electronic and ^{13}C NMR spectral data for compounds **6**, **7**, and **8**

Complex	Absorption maxima (log ε)[a]				Thiocarbonyl carbon (δ)[b]
6	293(3.88)	352(4.43)	374sh(4.18)	469(3.1)	218.96, 219.23
7	291.5(3.96)	358(4.38)	376sh(4.21)	471.5(3.0)	219.97, 220.97
8	300(3.9)	355(4.4)	382sh(4.0)	479(2.9)	235.20

[a] In CH$_2$Cl$_2$.
[b] In CDCl$_3$.

Table 7
Redox and oxidation potential of complexes **6**–**8** (V vs. FcH/FcH$^+$)

Complex	$E_{1/2}$	$E_{pa}(1)$	$E_{pa}(2)$
6	0.29	–	1.4 (sh)
7	0.28	1.1 (sh)	1.3 (sh)
8	0.31	0.8 (sh)	1.11

sh, shoulder. $E_{1/2}$ was obtained from the CV chart in which the scan was turn back at 0.65 V.
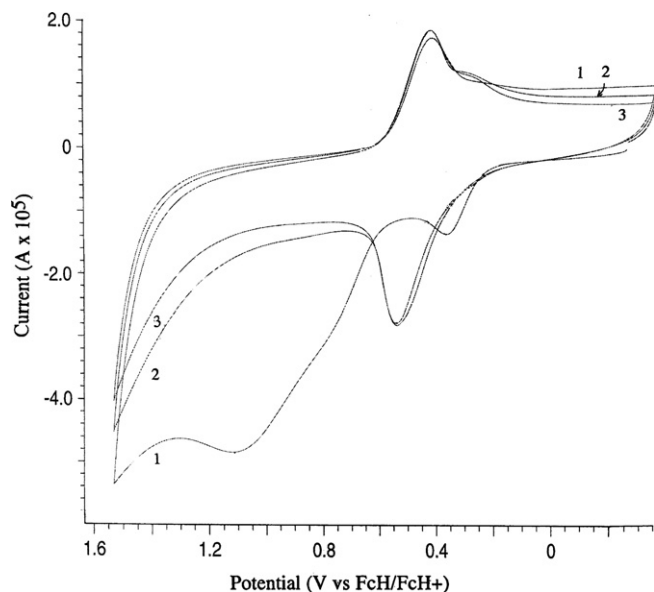
Fig. 6. Cyclic voltammogram of the repetitive scan for **8** in 0.1 M (*n*-Bu)$_4$NClO$_4$ solution in CH$_2$Cl$_2$. The numbers in the chart are the scan number.

adjacent to the ferrocene site. Probably, the loss of an electron from a thiocarbonyl group causes a coupling of the S atoms to result in a dimeric product, because it was reported that the oxidation of thiourea gave a dimeric cation connecting with a S–S bond [16] and a 1,3-dithiolium cation was a stable 6π-electron aromatic system [17]. In the multi-scan of **8**, the oxidation wave at 0.54 V and the reduction waves at 0.42 V reduced their magnitude quickly in the repetitive scan over three scans. This implies that the oxidation species is unstable.

2.5. Reactions

Complexes **6** and **7** were reacted with Hg(OAc)$_2$ in CH$_2$Cl$_2$/AcOH to give the corresponding 1,3-dithiol-2-one derivatives **9** and **10** in good yields, respectively. The conversion from **6** to **9** was, for example, confirmed by the appearance of the carbonyl frequency at 1695 and 1632 cm^{-1} in the IR spectrum and the carbonyl carbon signal at 194.57 and 194.94 ppm in the ^{13}C NMR spectrum.

Ferroceno[1′,2′;1″,2″]bis(1,3-dithiol-2-thione) derivatives, **6** and **7**, were refluxed in P(OEt)$_3$ or with PPh$_3$ in xylene but the starting material was recovered. The desulfurization of **6** and **7** with Co$_2$(CO)$_8$ was also unsuccessful. These findings are consistent with the fact that electron-sufficient 1,3-dithiol-2-thiones did not proceed well, while electron-deficient derivatives produced the corresponding coupling product in high yield [18]. In fact, it was reported that the reaction of ferrocene-substituted 1,3-dithiol-2-thione with P(OR)$_3$ or PPh$_3$ did not give the coupling product [4]. On addition, the deoxygenative coupling reaction of the 1,3-dithiol-2-one derivatives, **9** and **10**, with P(OR)$_3$ or PPh$_3$ was also not successful, although the treatment of

the ruthenocenyl-substituted 1,3-dithiol-2-one with P(OEt)$_3$ afforded the corresponding TTF derivative [19].

3. Experimental

All reactions were carried out under an atmosphere of N$_2$ or Ar. NMR spectra were recorded on Bruker AC300P or DRX400 spectrometer. IR (ATR) spectra were recorded on Perkin–Elmer System 2000 spectrometer. Solvents were purified by distillation from the drying agent prior to use as follows: CH$_2$Cl$_2$ (CaCl$_2$); ClCH$_2$CH$_2$Cl (CaCl$_2$); THF (Na-benzophenone); ether (LiAlH$_4$). 6,12-di(*t*-butyl)-1,2,3-trithia[3](4,9)ferrocenophane (**1**) [9], 6-(*t*-butyl)-1,2,3-trithia[3](4,9)ferrocenophane (**2**) [9], and 1,2,3,9,10,11-hexathia[3.3]ferrocenophane (**5**) [11] were prepared according to the literatures. Other reagents were used as received from commercial suppliers.

Cyclic voltammetric measurements was carried out with ALS 600 Electrochemical Analyzer in 1 M (*n*-Bu)$_4$NClO$_4$ solution in CH$_2$Cl$_2$ at 20 °C. A three-electrode cell containing of a glassy carbon disk working electrode (diameter 0.3 cm), Pt-coil counter electrode and an Ag/AgCl reference electrode was employed. The potentials were referensed vs. that of FcH/FcH$^+$ which was obtained by the preceding measurement of ferrocene at the same conditions. All solution were degassed with high-purity N$_2$ prior to making the electrochemical measurements.

3.1. 1,1′-Bis(t-butyl)ferrocene

This was prepared according to the method described about *t*-butylferrocene [20]. To a suspension of Mg turnings (4.52 g, 186 mmol) in anhydrous Et$_2$O (100 ml) was added iodine (6.09 g, 24 mmol) little by little under N$_2$ and the mixture was stirred for 30 min. A solution of iodomethane (10 ml, 161 mmol) in anhydrous Et$_2$O (20 ml) was added for a period of 1 h to the mixture. While Et$_2$O was removed on warming, toluene (100 ml) was added at the same time. After the addition had been completed, 1,1′-diacetylferrocene (2.7 g, 10 mmol) in warm toluene (10 ml) was added to the mixture. The mixture was refluxed for 18 h. After cooling to room temperature, the mixture was poured into ice water. The insoluble material was dissolved by adding 4 M H$_2$SO$_4$. The organic layer was separated, washed with H$_2$O, and dried over MgSO$_4$. After evaporation, the residue was chromatographed on SiO$_2$ to give the title compound as red-orange oil (2.7 g, 90%). The ^{1}H NMR spectrum was in complete agreement with that of the literature [9].

3.2. 3,4′-Di(t-butyl)ferrocene-1,1′-dithiol

Common procedure. To a suspension of LiAlH$_4$ (65 mg, 1.7 mmol) in anhydrous Et$_2$O (55 ml) was added **1** (0.30 g, 0.76 mmol). The mixture was refluxed for 2 h. After cooling to room temperature, the mixture was extracted with N$_2$-saturated 1 N KOH aqueous solution (30 ml). The aqueous solution was washed with N$_2$-saturated Et$_2$O and then

was acidified to pH 3 with 2 N HCl aqueous solution under bubbling of N_2. The solution was extracted with N_2-saturated Et_2O (20 ml). The extract was dried over $MgSO_4$ and then evaporated in vacuo to give yellow oily product (0.27 g). This product was very sensitive to air and therefore immediately used in the next reaction. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.23 (s, 18H, Me), 2.90 (s, 2H, SH), 3.96 (d, 4H, $J = 1.8$ Hz, η-C$_5$H$_3$), and 4.28 (t, 2H, $J = 1.8$ Hz, η-C$_5$H$_3$).

3.3. 4-(t-Butyl)ferrocene-1,1'-dithiol

This was similarly prepared from **2**. Yellow oil (80%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.21 (s, 9H, Me), 2.88 (s, 1H, SH), 2.89 (s, 1H, SH), 4.03 (t, 1H, η-C$_5$H$_4$), 4.12 (m, 2H, η-C$_5$H$_4$), 4.21 (m, 2H, η-C$_5$H$_4$), and 4.26 (m, 2H, η-C$_5$H$_4$).

3.4. 5,15-Di(t-butyl)-1,2,3,9,10,11-hexa[3.3](4,13)(8,12)-ferrocenophane (3)

Common procedure. *n*-BuLi (1.6 M in hexane) (26 ml, 42 mmol) and TMEDA (6.3 ml, 42 mmol) was added to a solution of 3,4'-Di(*t*-butyl)ferrocene-1,1'-dithiol (2.5 g, 6.9 mmol) in anhydrous hexane (80 ml). The solution was stirred for 2 days at room temperature under Ar. To the solution was added sulfur powder (2.8 g, 87 mmol) and then the mixture was refluxed for 4 h. After cooling to room temperature, the mixture was poured into water (100 ml). The mixture was extracted with hexane (150 ml). The extract was dried over $MgSO_4$ and then evaporated in vacuo. The residue was chromatographed on SiO$_2$ to give orange crystals, which were recrystallized from hexane. Yield: 1.0 g (31%). M.p. 170–173 °C. Anal. Calc. for C$_{18}$H$_{22}$S$_6$Fe: C, 44.43; H, 4.56. Found: C, 44.56; H, 4.45%. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.24 (s, 9H, Me), 1.26 (s, 9H, Me), 3.86 (d, $J = 1.8$ Hz, 1H, η-C$_5$H$_2$), 4.02 (d, $J = 2.9$ Hz, 1H, η-C$_5$H$_2$), 4.62 (d, $J = 2.9$ Hz, 1H, η-C$_5$H$_2$), and 4.73 (t, $J = 1.8$ Hz, 1H, η-C$_5$H$_2$). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 31.67 (Me in *t*-Bu), 32.13 (C in *t*-Bu), 32.83 (Me in *t*-Bu), 67.43 (η-Cp), 67.94 (η-Cp), 71.64 (η-Cp), 77.91 (η-Cp), 90.00 (η-Cp), 91.00 (η-Cp), 95.50 (η-Cp), 97.22 (η-Cp), 106.34 (η-Cp), and 112.14 (η-Cp).

3.5. 6-(t-Butyl)-1,2,3,9,10,11-hexathia[3.3](4,13)(8, 12)-ferrocenophane (4)

Yellow crystals (28%). M.p. 220 °C (dec.). Anal. Calc. for C$_{14}$H$_{15}$S$_6$Fe: C, 39.09; H, 3.28. Found: C, 39.40; H, 3.09%. ^{1}H NMR (CDCl$_3$, 400 MHz): (chair–chair isomer) δ 1.23 (s, 9H, Me), 4.05 (s, 2H, η-C$_5$H$_2$), 4.17 (d, $J = 2.7$ Hz, 2H, η-C$_5$H$_3$), and 4.68 (t, $J = 2.7$ Hz, 1H, η-C$_5$H$_3$). (chair–boat isomer) δ 1.23 (s, 9H, Me), 3.99 (d, 1H, $J = 1.8$ Hz, η-C$_5$H$_2$), 4.12 (dd, 1H, $J = 2.7$ and 1.5 Hz, η-C$_5$H$_3$), 4.60 (t, 1H, $J = 2.7$ Hz, η-C$_5$H$_3$), 4.61 (d, $J = 1.8$ Hz, 1H, η-C$_5$H$_2$), and 4.72 (dd, 1H, η-C$_5$H$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 30.85 (C in *t*-Bu), 31.03 (C in *t*-Bu), 31.13 (Me in *t*-Bu), 31.21 (Me in *t*-Bu), 66.88

(η-Cp), 68.91 (η-Cp), 70.17 (η-Cp), 72.20 (η-Cp), 73.33 (η-Cp), 75.64 (η-Cp), 80.15 (η-Cp), 98.91 (η-Cp), 99.63 (η-Cp), 100.01 (η-Cp), 100.91 (η-Cp), 101.39 (η-Cp), 105.89 (η-Cp), 108.32 (η-Cp), and 128.33 (η-Cp).

3.6. 3,4'-Di(t-butyl)ferrocene-1,1',2,2'-tetrathiol

Common procedure. This complex was prepared from **3** using the procedure similar to that for 3,4'-di(*t*-butyl)ferrocene-1,1'-dithiol and then immediately used in the next reaction because it was very sensitive to air. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.17 (s, 9H, Me), 1.33 (s, 9H, Me), 2.84 (s, 1H, SH), 3.13 (s, 1H, SH), 3.22 (s, 2H, SH), 4.14 (d, 1H, $J = 1.6$ Hz, η-C$_5$H$_2$), 4.18 (d, 1H, $J = 2.6$ Hz, η-C$_5$H$_2$), 4.30 (d, 1H, $J = 1.6$ Hz, η-C$_5$H$_2$), and 4.41 (d, 1H, $J = 2.6$ Hz, η-C$_5$H$_2$).

3.7. 4-(t-Butyl)ferrocene-1,1',2,2'-tetrathiol

This was similarly prepared from **4**. Yellow solid (98%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.20 (s, 9H, Me), 3.04 (s, 4H, SH), 4.18 (s, 2H, η-C$_5$H$_2$), 4.20 (t, 1H, η-C$_5$H$_3$), and 4.26 (d, 1H, $J = 2.6$ Hz, η-C$_5$H$_3$).

3.8. 3,4'-Di(t-butyl)-ferroceno[1',2'; 1'',2'']bis(1,3-dithiol-2-thione) (6)

Common procedure. 1,1'-Thiocarbonyldiimidazol (0.70 g, 3.9 mmol) was added to a solution of 3,4'-Di(*t*-butyl)ferrocene-1,1',2,2'-tetrathiol (0.60 g, 1.4 mmol) in anhydrous THF (45 ml) under Ar. After being stirred for 5 min, the solution was filtered. The filtrate was evaporated in vacuo and the residue was chromatographed on SiO$_2$ to give the title compound which was recrystallized from CH_2Cl_2/hexane. Dark red-violet crystals (0.31 g, 43%). M.p. 221–226 °C. IR (ATR): 1070 and 1058 cm^{-1} (ν C=S). Anal. Calc. for C$_{20}$H$_{14}$S$_6$Fe: C, 47.04; H, 4.34. Found: C, 47.44; H, 4.44%. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.24 (s, 9H, Me), 1.28 (s, 9H, Me), 4.35 (d, 1H, $J = 2.9$ Hz, η-C$_5$H$_2$), 4.41 (d, 1H, $J = 1.5$ Hz, η-C$_5$H$_2$), 4.53 (d, 1H, $J = 1.5$ Hz, η-C$_5$H$_2$), and 4.61 (d, 1H, $J = 2.9$ Hz, η-C$_5$H$_2$). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 30.87 (Me in *t*-Bu), 31.47 (C in *t*-Bu), 58.80 (η-Cp), 60.36 (η-Cp), 60.77 (η-Cp), 69.21 (η-Cp), 95.89 (η-Cp), 96.07 (η-Cp), 97.08 (η-Cp), 97.61 (η-Cp), 99.67 (η-Cp), 105.29 (η-Cp), 218.96 (C=S), and 219.23 (C=S).

3.9. 4-(t-Butyl)-ferroceno[1',2';1'',2'']bis(1,3-dithiol-2-thione) (7)

Dark red-violet crystals (32%). M.p. 167 °C. IR (ATR): 1072 cm^{-1} (ν C=S). Anal. Calc. for C$_{16}$H$_{14}$S$_6$Fe: C, 42.28; H, 3.11. Found: C, 41.91; H, 2.82%. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 0.85 (s, 9H, Me), 3.33 (s, 2H, η-C$_5$H$_2$), 3.51 (d, 2H, $J = 2.5$ Hz, η-C$_5$H$_3$), and 3.68 (t, 1H, η-C$_5$H$_3$). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 31.10 (C in *t*-Bu), 31.44 (Me in *t*-Bu), 59.43 (η-C$_5$H$_4$), 62.83 (η-C$_5$H$_4$), 72.36

(η-C_5H_4), 98.19 (η-C_5H_4), 98.79 (η-C_5H_4), 105.98 (η-C_5H_4), 219.97 (C=S), and 220.97 (C=S).

3.10. Ferroceno[1',2';1'',2'']bis(1,3-dithiol-2-thione) (*8*)

Dark-greenish crystals (34%). M.p. 230 °C (dec.). IR (KBr): 1069 cm^{-1}. Anal. Calc. for $C_{12}H_6S_6Fe$: C, 36.18; H, 1.52. Found: C, 36.57; H, 1.52%. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.49 (t, $J = 2.4$ Hz, 1H, η-C_5H_3), and 4.57 (d, 2H, $J = 2.4$ Hz, η-C_5H_3). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 62.69 (η-C_5H_3), 71.51 (η-C_5H_3), 98.58 (η-C_5H_3), 235.20 (C=S).

3.11. 3,4'-Di(t-butyl)-ferroceno[1',2';1'',2'']bis(1,3-dithiol-2-one) (*9*)

Common procedure. To a solution of **6** (25 mg, 0.049 mmol) in CH$_2$Cl$_2$ (6 ml) was added mercury(II) acetate (100 mg, 0.31 mmol) in acetic acid (5 ml) and the mixture was stirred for 17 h at room temperature. After filtration, the filtrate was washed with H$_2$O several times and then dried over MgSO$_4$. Evaporating in vacuo, the residue was chromatographed on SiO$_2$ to give the tile compound. The recrystallization from diethyl ether gave orange crystals (19 mg, 81%). M.p. 122–123 °C. Anal. Calc. $C_{20}H_{22}O_2S_4Fe$ for: C, 50.20; H, 4.63. Found: C, 50.39; H, 4.50%. IR (ATR): 1695 and 1632 cm^{-1} (v CO). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.25 (s, 9H, Me), 1.26 (s, 9H, Me), 4.26 (d, 1H, $J = 2.6$ Hz, η-C_5H_2), 4.37 (d, 1H, $J = 1.5$ Hz, η-C_5H_2), 4.49 (d, 1H, $J = 1.5$ Hz, η-C_5H_2), and 4.58 (d, 1H, $J = 2.6$ Hz, η-C_5H_2). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 30.80 (Me in *t*-Bu), 31.53 (C in *t*-Bu), 59.64 (η-Cp), 60.78 (η-Cp), 61.51 (η-Cp), 66.73 (η-Cp), 86.54 (η-Cp), 87.60 (η-Cp), 88.25 (η-Cp), 90.15 (η-Cp), 96.22 (η-Cp), 102.19 (η-Cp), 194.57 (C=O), and 194.94 (C=O).

3.12. 4-t-Butyl-ferroceno[1',2';1'',2'']bis(1,3-dithiol-2-one) (*10*)

Orange crystals (47%). M.p. 113 °C. Anal. Calc. $C_{16}H_{14}O_2S_4Fe$ for: C, 45.50; H, 3.34. Found: C, 45.38; H, 3.21%. IR (ATR): 1694 cm^{-1} (v CO). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.25 (s, 9H, Me), 1.26 (s, 9H, Me), 4.26 (d, 1H, $J = 2.6$ Hz, η-C_5H_2), 4.37 (d, 1H, $J = 1.5$ Hz, η-C_5H_2), 4.49 (d, 1H, $J = 1.5$ Hz, η-C_5H_2), and 4.58 (d, 1H, $J = 2.6$ Hz, η-C_5H_2). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 30.80 (Me in *t*-Bu), 31.53 (C in *t*-Bu), 59.64 (η-Cp), 60.78 (η-Cp), 61.51 (η-Cp), 66.73 (η-Cp), 86.54 (η-Cp), 87.60 (η-Cp), 88.25 (η-Cp), 90.15 (η-Cp), 96.22 (η-Cp), 102.19 (η-Cp), 194.57 (C=O), and 194.94 (C=O).

3.13. Structure determination

The crystallographic data are listed in Table 1 for **3**, **6**, **7** and **8**. Data collection of their crystal data was performed at room temperature on Mac Science DIP3000 image pro-

cessor with graphite monochromated Mo Kα radiation and an 18-kW rotating anode generator. The structures were solved with the SIR97 method in MAXUS (software-package for structure determination) and refined finally by full-matrix least-squares procedure. Absorption correction was carried out by the Sortav method and anisotropic refinement for non-hydrogen atom was carried out. The hydrogen atoms, located from difference Fourier maps or calculation, were isotropically refined.

4. Supplementary material

CCDC 628269, 628270, 628271 and 628272 contain the supplementary crystallographic data for **3**, **6**, **7** and **8**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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