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Preparation and properties of dinuclear bis[dicarbonyl(cyclopentadienyl)]diiron(II) complexes with S–S coupled, dimerized sulfur-rich dithiolate ligands

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Abstract

Dinuclear bis[dicarbonyl(cyclopentadienyl)]diiron(II) complexes with the bridging, S–S coupled, dimerized sulfur-rich dithiolate ligands, $[Fe(C_5H_5)(CO)_2(C_3S_5–C_3S_5)Fe(C_5H_5)(CO)_2]$ (**1**) and $[Fe(C_5H_5)(CO)_2(C_8H_4S_8–C_8H_4S_8)Fe(C_5H_5)(CO)_2]$ (**2**), were prepared by reactions of $[Fe(C_5H_5)(CO)_2I]$ with $Na_2[C_3S_5]$ or $Na_2[C_8H_4S_8]$ [$C_3S_5^{2-}$ = 4,5-disulfanyl-1,3-dithiole-2-thionate(2-) and $C_8H_4S_8^{2-}$ = 2-{(4,5-ethylenedithio)-1,3-dithiole-2-ylidene}-1,3-dithiole-4,5-dithionate(2-)] in ethanol, followed by oxidation in the air. The dinuclear structures of these complexes were established by the X-ray crystallography for **1** and by molecular weight and the electrospray mass spectra of **2**. Complex **2** exhibited the $(C_8H_4S_8)_2$ ligand-centered oxidation at a low potential, and reacted with iodine to afford the oxidized species $[Fe(C_5H_5)(CO)_2(C_8H_4S_8\text{-}C_8H_4S_8)Fe(C_5H_5)(CO)_2]I_x$ ($x = 6.0$ and 10.5), of which the oxidized $I_{10.5}$-species containing I_3^- and I_5^- ions exhibited electrical conductivity of 1.7×10^{-4} S cm^{-1} measured for a compacted pellet at room temperature. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Iron(II) complexes; Dithiolate complexes; Cyclopentadienyl complexes; Oxidation; X-ray crystal structure

1. Introduction

Metal complexes with sulfur-rich dithiolate ligands attract much attention, since their oxidized species often behave as good electrical conductors [1–12]. Particularly, C_3S_5–metal complexes [$C_3S_5^{2-}$=4,5-disulfanyl-1,3-dithiole-2-thionate(2-)] have been extensively studied, of which some $[M(C_3S_5)_2]^{n-}$ [$n < 1$: M = Ni(II) and Pd(II)] complexes are known as superconductors [1–4]. Various metal complexes with the $C_8H_4S_8^{2-}$ [2-{(4,5-ethylenedithio)-1,3-dithiole-2-ylidene}-1,3-dithiole-4,5-dithionate(2-)] ligand and related sulfur-rich dithiolate ligands as further extended π-electron delocalized systems are also expected to become excellent electrical conductors, because more effective electron-conduction pathways among the complexes can be formed through more S···S interactions in the solid state [5–13]. Oxidized, planar $[M(C_8H_4S_8)_2]^{n-}$ [$n < 1$; M = Ni(II), Pt(II) and Au(III)] complexes [7–9] and non-planar $[M(O)(C_8H_4S_8)_2]^{n-}$ [$n < 1$; M = V(IV) and Mo(IV)] complexes [14] exhibited high electrical conductivities. $C_8H_4S_8$–cyclopentadienylmetal complexes were also oxidized to afford good electrical conductors with the $C_8H_4S_8$ ligand-centered oxidation, as observed for $[Co(C_5H_5)(C_8H_4S_8)]^+$ [15] and $[M(C_5H_5)(C_8H_4S_8)_2]^{n-}$ [$n < 1$; M = Ti(IV), Zr(IV) and Hf(IV)] complexes [16–18].

In the course of our studies on $C_8H_4S_8$–cyclopentadienylmetal complexes, we have found novel dinuclear bis[dicarbonyl(cyclopentadienyl)]diiron(II) complexes with bridging S–S coupled, dimerized C_3S_5 and $C_8H_4S_8$ ligands. This paper reports preparations of these complexes, their oxidation properties and electrical conduc-

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tivities of the oxidized species, together with the X-ray crystal structure of [Fe(C_5H_5)(CO)$_2$(C_3S_5–C_3S_5)Fe(C_5H_5)(CO)$_2$].

2. Experimental

2.1. Materials

4,5-Bis(cyanoethylthio)-1,3-dithiole-2-thione, $C_3S_5(CH_2CH_2CN)_2$ [19], and 4,5-bis(cyanoethylthio)-1,3-dithiole-[(4,5-ethylenedithio)-1,3-dithiole-2-ylidene], $C_8H_4S_8(CH_2CH_2CN)_2$ [9,20,21], were prepared according to the literature methods. Ferrocenium tetrafluoroborate was prepared by the literature method [22]. Dicarbonyl(cyclopentadienyl)iodoiron(II) was commercially available. All the following reactions were performed under an argon atmosphere.

2.2. Preparation of Fe(C_5H_5)(CO)$_2$(C_3S_5–C_3S_5)Fe(C_5H_5)(CO)$_2$] (**1**)

$C_3S_5(CH_2CH_2CN)_2$ (280 mg, 0.90 mmol) was added with stirring to an EtOH (30 cm^3) solution containing Na metal (70 mg, 3.0 mmol) under ultrasonic waves. To the resulting red brown solution of $Na_2[C_3S_5]$ was added with stirring an EtOH (20 cm^3) solution of [Fe(C_5H_5)(CO)$_2$I] (300 mg, 1.0 mmol). After the violet solution was stirred for 1 h at room temperature (r.t.), CH_2Cl_2 (400 cm^3) was added to the solution, which was filtered through silica gel in the air. The filtrate was concentrated under reduced pressure to afford dark brown solids of **1**, which were collected by filtration, washed with diethyl ether, and dried in vacuo (60% yield). Anal. Calc. for $C_{20}H_{10}Fe_2O_4S_{10}$: C, 32.17; H, 1.35. Found: C, 31.87; H, 1.54%. IR (KBr disk), ν(C=O): 1974, 2025 cm^{-1}. ^{1}H-NMR (d_6-DMSO): δ 5.44 (s, C_5H_5).

2.3. Preparation of [Fe(C_5H_5)(CO)$_2$($C_8H_4S_8$–$C_8H_4S_8$)Fe(C_5H_5)(CO)$_2$] (**2**)

An EtOH (20 cm^3) solution of [Fe(C_5H_5)(CO)$_2$I] (300 mg, 1.0 mmol) was added with stirring to an EtOH (30 cm^3) solution of $Na_2[C_8H_4S_8]$ obtained by the reaction of $C_8H_4S_8$–$(CH_2CH_2CN)_2$ (490 mg, 1.0 mmol) with Na metal (70 mg, 3.0 mmol) as described for **1**. Immediately the solution turned dark blue and it was stirred for 1 h at r.t.. To the solution was added CH_2Cl_2 (400 cm^3) and the solution was filtered through silica gel in the air. By a procedure similar to that described for **1**, from the filtrate was obtained dark brown solids of **2** (67% yield). Anal. Calc. for $C_{30}H_{18}Fe_2O_4S_{16}$: C, 33.76; H, 1.70. Found: C, 33.56; H, 2.02%. IR (KBr disk), ν(C=O): 1974, 2025 cm^{-1}. ^{1}H-NMR (d_6-DMSO): δ 3.38 (4H, s, CH_2), δ 5.30 (5H, s, C_5H_5).

2.4. Preparations of [Fe(C_5H_5)(CO)$_2$($C_8H_4S_8$–$C_8H_4S_8$)-Fe(C_5H_5)(CO)$_2$]$I_{5.7}$ (**3**) and [Fe(C_5H_5)(CO)$_2$-($C_8H_4S_8$–$C_8H_4S_8$)Fe(C_5H_5)(CO)$_2$]$I_{10.5}$ (**4**)

To a $CHCl_3$ (50 cm^3) solution of **2** (110 mg, 0.10 mmol) was added with stirring a $CHCl_3$ (20 cm^3) solution of iodine (70 mg, 0.28 mmol) to afford immediately black microcrystals of **3**. They were collected by centrifugation, washed with $CHCl_3$, and dried in vacuo (85% yield). Anal. Calc. for $C_{30}H_{18}Fe_2I_{5.7}O_4S_{16}$: C, 19.71; H, 0.99. Found: C, 19.68; H, 1.12%. IR (KBr disk), ν(C=O): 2000, 2042 cm^{-1}. Similarly, a reaction of a $CHCl_3$ (50 cm^3) solution of **2** (55 mg, 0.050 mmol) with a $CHCl_3$ (20 cm^3) solution of iodine (130 mg, 0,50 mmol) yielded black microcrystals of **4** (70% yield). Anal. Calc. for $C_{30}H_{18}Fe_2I_{10.5}O_4S_{16}$: C, 15.02; H, 0.76. Found: C, 15.05; H, 0.97%. IR (KBr disk), ν(C=O): 2007, 2045 cm^{-1}.

2.5. Physical measurements

Electronic absorption, IR, ESR [23], and powder reflectance spectra [24] were recorded as described previously. Raman spectra were measured using a JASCO NR-1800 laser-Raman spectrophotometer. ^{1}H-NMR spectra were recorded at 270 MHz using a JEOL EX-270 spectrometer, the chemical shifts being measured relative to tetramethylsilane as an internal standard. Cyclic voltammograms of the complexes in $CHCl_3$ or in benzonitrile were measured using [NBu^n_4][ClO_4] as an electrolyte and electrical resistivities of the complexes were measured at r.t. for compacted pellets by the conventional two-probe method [24]. X-ray photoelectron spectra were obtained by irradiating the complexes with Mg–K_α X-rays (300 W) at 25 °C using an ULVAC-PHI ESCA 5700 photoelectron spectrometer, and were calibrated with the carbon $1s_{1/2}$ photoelectron peak (285 eV). Electrospray ionization (ESI) mass spectra were obtained as described previously [25]. Molecular weight of complex **2** was determined in CH_2Cl_2 at 25 °C using a Knauer vapor pressure osmometer.

2.6. Crystal structure determination of complex **1**

Diffraction data were collected for a single crystal of approximate dimensions $0.3 \times 0.2 \times 0.2$ mm on a Rigaku AFC-5R four-circle diffractometer with a graphite-monochromated Mo–K_α ($\lambda = 0.71069$ Å) radiation. Crystallographic data are summarized in Table 1. The unit-cell parameters were determined from 25 independent reflections with 2θ over the range of 25.3–26.0°. Three standard reflections were monitored after every 150 reflections. No significant decays in their intensities were observed throughout the data collection. The reflection data were corrected for Lorentz and polarization effects as well as for absorption by the North-Phillips method [26] (transmission factors, 0.784–0.997).

The structure was solved by the direct method (SIR92) [27] and refined on F by the full-matrix least-square techniques. All the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were fixed at geometrically calculated positions with temperature factors of 1.2 times those of the bonded carbon atoms. Calculations were performed with the TEXSAN structure analysis package [28] on an SGI-O2 workstation at the Graduate School of Science, Osaka University. Atomic scattering factors were taken from the usual sources [29]. Fig. 2 was drawn with a local version of ORTEP II [30].

Table 1
Crystallographic and experimental data for $Fe(C_5H_5)(CO)_2$-$(C_3S_5$–$C_3S_5)Fe(C_5H_5)(CO)_2]$ **1**

Molecular formula	$C_{20}H_{10}Fe_2O_4S_{10}$
Molecular weight	746.63
Crystal system	Monoclinic
Space group	$C2/c$ (no. 15)
a (Å)	21.092(2)
b (Å)	11.859(2)
c (Å)	12.286(2)
β (°)	118.188(9)
V (Å^3)	2708.8(6)
Z	4
D_{calc} (g cm^{-3})	1.831
F(000)	1496.00
μ (Mo–K$_\alpha$) (mm^{-1})	1.87
T (°C)	23
Measured 2θ range	6.0–60.0
No. of reflections collected	3959
No. of reflections with $[I > 3\sigma(I)]$	2090
R [a]	0.034
R_w [b]	0.040
R_{int}	0.019

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.
[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$; $w^{-1} = \sigma^2(F_o) + 0.0003F_o^2$.

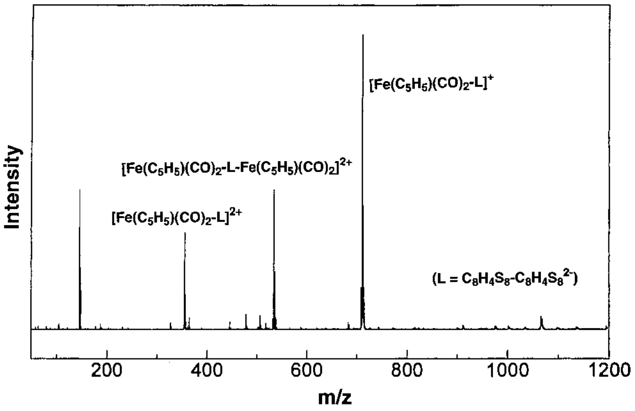

Fig. 1. Positive-ion ESI mass spectrum of complex **2** in acetonitrile.

3. Results and discussion

3.1. Formation of the dinuclear diiron(II) complexes 1 and 2

$[Fe(C_5H_5)(CO)_2I]$ reacts with Na_2L ($L = C_3S_5^{2-}$ or $C_8H_4S_8^{2-}$) probably to afford the $[Fe(C_5H_5)(CO)_2L]^-$ species in the first stage. However, these formally Fe(II) complexes with the four-electron affording dithiolate ligands are unstable because of a 20-electron system around the Fe(II) ion. Thus, they are easily oxidized in the dithiolate ligand moieties under the air, followed by the S–S coupling of the ligand moieties to yield the dinuclear diiron(II) complexes **1** and **2** with the stable 18-electron system around the Fe(II) ion. The dinuclear structure has been revealed for **1** by the X-ray crystal structure analysis, as described below. Molecular weight determination of **2** in dichloromethane (Measured: 1050; Calculated for the dinuclear complex $C_{30}H_{18}Fe_2O_4S_{16}$: 1067) has confirmed the dinuclear configuration. Furthermore, an ESI mass spectrum of **2** measured in acetonitrile indicates the fragmentations of $[Fe(C_5H_5)(CO)_2(C_8H_4S_8)]^+$, $[Fe(C_5H_5)(CO)_2(C_8H_4S_8)_2$-$Fe(C_5H_5)(CO)_2]^{2+}$ and $[Fe(C_5H_5)(CO)_2(C_8H_4S_8)]^{2+}$ (Fig. 1). The neutral complex **2** is oxidized by electrolysis at the electrospray inlet, since it has rather low oxidation potentials, as described below. Dinuclear complexes containing the $Fe(C_5H_5)(CO)_2$ groups bridged by a dithiolate ligand were also reported for $[\{Fe(C_5H_5)(CO)_2\}_2\{S_2C_2(CN)_2\}]$ [31] and $[Fe(C_5H_5)$-$(CO)_2$–SC_6H_4S–$Fe(C_5H_5)(CO)_2]$ [32].

3.2. Crystal structure of complex 1

A perspective view of complex **1** is illustrated in Fig. 2, together with the atom-labelling scheme. Selected bond distances and angles are summarized in Table 2. There are no significant intermolecular atom–atom contacts in the crystal phase. Two $Fe(C_5H_5)(CO)_2$ groups are bound through an Fe–S coordination, two C_3S_5 moieties being coupled through the S–S bond to form the bridging dithiolate(2-) ligand. The molecule has a C_2 axis at the midpoint of the S(1)–S*(1) bond, around which the atoms are related to those with asterisks.

The coordination of the iron atom forms a pseudo-octahedral arrangement of the ligand around the metal, so-called a ‘three-legged piano stool’ configuration [33], as observed for other compounds having the $Fe(C_5H_5)(CO)_2$ group [34–36]. The Fe–S distance [2.296(1) Å] is somewhat shorter than tetra- and penta-coordinate Fe(II)–thiolate complexes; $[Fe(SPh)_4]^{2-}$ [2.338(6)–2.353(6) Å] [37], $[Fe(S$-o-t-$BuCONHC_6$-$H_4)_4]^{2-}$ [2.322(6)–2.336(6) Å] [38] and $[Fe(TPA)$-$(SC_6H_2$–Me_3-2,4,6)] [TPA = tris(2-pyridylmethyl)amine] [2.345(1) Å] [39]. It is longer than those of di- and

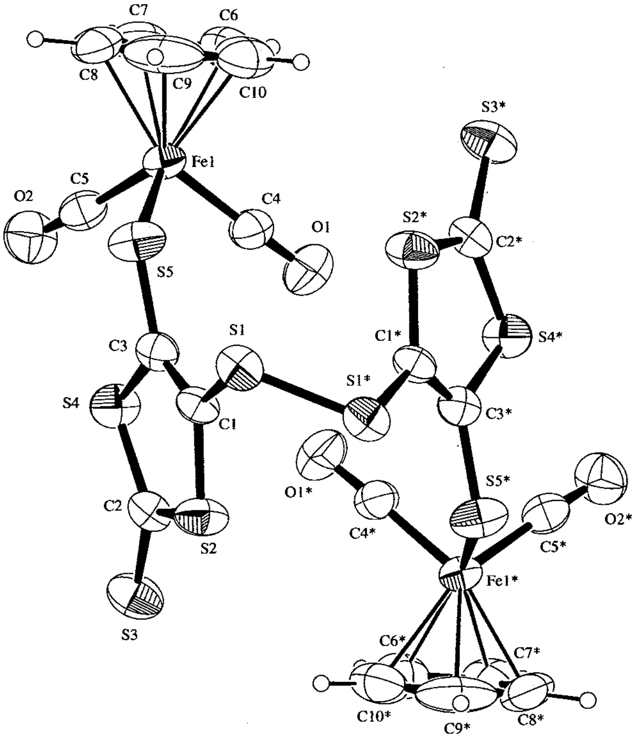

Fig. 2. Molecular geometry of complex **1** together with the atom-labelling scheme.

Table 2
Selected bond distances (Å) and angles (°) for $Fe(C_5H_5)(CO)_2(C_3S_5{-}C_3S_5)Fe(C_5H_5)(CO)_2]$ **1** with standard deviations

Bond distances			
Fe–S(5)	2.296(1)	Fe–C(4)	1.769(4)
Fe–C(5)	1.766(4)	Fe–C(6)	2.077(4)
Fe–C(7)	2.072(4)	Fe–C(8)	2.068(4)
Fe–C(9)	2.093(4)	Fe–C(10)	2.100(4)
S(1)–S(1′)	2.078(2)	S(1)–C(1)	1.746(4)
S(2)–C(1)	1.743(4)	S(2)–C(2)	1.723(4)
S(3)–C(2)	1.645(4)	S(4)–C(2)	1.725(4)
S(4)–C(3)	1.748(4)	S(5)–C(3)	1.732(4)
O(1)–C(4)	1.132(5)	O(2)–C(5)	1.143(4)
Bond angles			
S(5)–Fe–C(4)	95.0(1)	S(5)–Fe–C(5)	97.1(1)
C(4)–Fe–C(5)	94.6(2)	S*(1)–S(1)–C(1)	101.2(1)
C(1)–S(2)–C(2)	97.6(2)	C(2)–S(4)–C(3)	98.9(2)
Fe–S(5)–C(3)	111.5(1)	S(1)–C(1)–S(2)	119.9(2)
S(1)–C(1)–C(3)	122.8(3)	S(2)–C(1)–C(3)	117.7
S(2)–C(2)–S(3)	123.6(2)	S(2)–C(2)–S(4)	112.2(2)
S(3)–C(2)–S(4)	124.2(2)	S(4)–C(3)–S(5)	120.9(2)
S(4)–C(3)–C(1)	113.9(3)	S(5)–C(3)–C(1)	124.9(3)
Fe–C(4)–O(1)	177.0(4)	Fe–C(5)–O(2)	175.2(3)

tri-coordinate Fe(II)-thiolate complexes; $[Fe\{S(C_6H_3{-}Mes_2{-}2,6)\}_2]$ [2.277(2), 2.275(2) Å] [40], and $[Fe(SC_6H_2{-}t{-}Bu_3{-}2,4,6)_3]^-$ [2.259(4)–2.334(4) Å] [41] and $[Fe(SC_6H_2{-}t{-}Bu_3{-}2,4,6)_2\{C_5H_4N{-}C(SiMe_3)_2{-}2\}]$ [2.259(4), 2.261(3) Å] [42]. The distance is longer than that of the $Fe(C_5H_5)(CO)$-thiolate compound, $[Fe(C_5H_5)(CO)\{SC(NEt_2)(SCNCOPh)\}]$ [2.235(2) Å] [43]. The C–C and C–S bond distances of the C_3S_5 moiety are close to those for C_6S_{12} [44], $C_6S_{10}(CS_2)_{0.5}$ [45], C_6S_{10} [46] and other C_3S_5–metal complexes reported previously [47–49]. The S–S distance [2.078(2) Å] is close to those of C_6S_{12} (2.061 Å, average) [44], $C_6S_{10}(CS_2)_{0.5}$ [2.0757(9) Å] [45] and C_6S_{10} [2.082(1) Å] [46], and shorter than those of $[C_6S_{10}]^{2-}$ [2.135(4) Å] and $[C_{12}S_{16}]^{2-}$ salts [2.157(12) Å] [50]. S(1)–S(5) and C(1)–C(3) atoms are almost coplanar (± 0.026 Å) and the dihedral angle between the two C_3S_5 least-square planes is 59.7(3)°. The torsion angle of the C(1)–S(1)–S*(1)–C*(1) moiety is 64.5(2)°, which is larger than that (52.1°) of the $[C_6S_{10}]^{2-}$ salt [50].

3.3. Electrochemical property of complexes **1** and **2**

Cyclic voltammograms of **1** in chloroform and **2** in benzonitrile are illustrated in Fig. 3. The oxidation peak at the first potential (+0.16 V vs. Ag/Ag^+) observed for **1** is likely to correspond to the first Fe(II) to Fe(III) oxidation process of this dinuclear complex, since the Fe(II) to Fe(III) oxidation for other Fe(II)–thiolate complexes occurs at low potentials: $[Fe(SPh)_4]^{2-}$ (−0.53 V vs. SCE) [37,51] and $[Fe(S{-}RCONHC_6H_4)_4]^{2-}$ salts (R = o-CF_3, o-Me, t-Bu, p-Me) (−0.13– −0.57 V vs. SCE) [37]. Furthermore, this oxidation potential of **1** is similar to the first oxidation potentials of $[Fe(C_5H_5)(CO)_2\{SC(S)OEt\}L]$ (L = PBu_3, PPh_3) (+0.12– +0.30 V vs. $[Fe(C_5H_5)_2]/[Fe(C_5H_5)_2]^+$) [52]. Thus, the second oxidation potential observed at +0.39 V (vs. Ag/Ag^+) for **1** is likely to be ascribed to the $(C_3S_5)_2$ ligand-centered oxidation. This $(C_3S_5)_2$ ligand-centered oxidation occurs at a higher

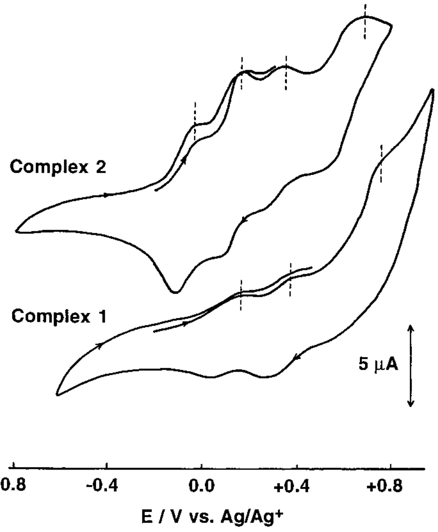

Fig. 3. Cyclic voltammograms of **1** in chloroform and **2** in benzonitrile (1.0×10^{-3} mol dm^{-3}) at room temperature; 0.1 mol dm^{-3} $[NBu_4][ClO_4]$. Sweep rate: 500 mV s^{-1}.

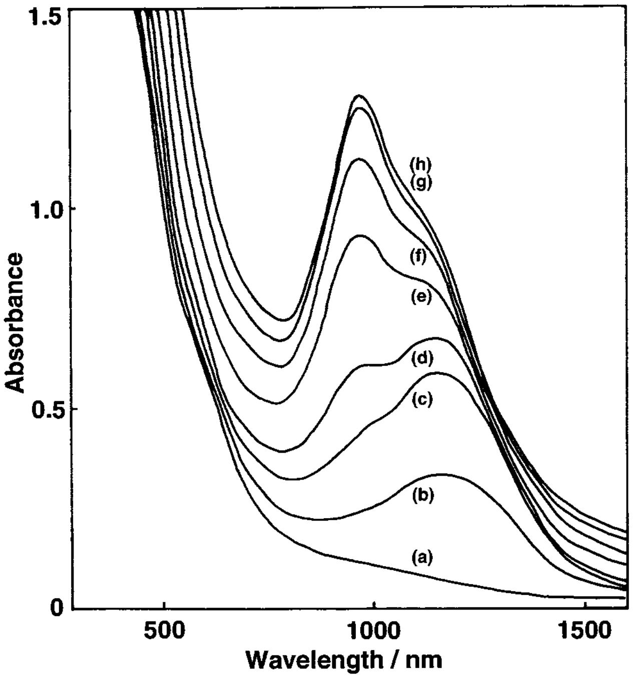

Fig. 4. Electronic absorption spectra of **2** (2.0×10^{-4} mol dm^{-3}) in chloroform in the presence of iodine: (a) 0; (b) 0.5×10^{-4}; (c) 1.0×10^{-4}; (d) 1.5×10^{-4}; (e) 2.0×10^{-4}; (f) 3.0×10^{-4}; (g) 4.0×10^{-4}; (h) 6.0×10^{-4}; (i) 8.0×10^{-4} mol dm^{-3}.

potential than the C_3S_5 ligand-centered oxidations for neutral C_3S_5–metal complexes: $[Co(C_5H_5)(C_3S_5)]$, +0.338 V [15,53] and $[Pd(C_5H_4NCH{=}NBu)(C_3S_5)]$, +0.32 V (vs. Ag/Ag$^+$) [54].

Complex **2** has lower oxidation potentials (−0.07, +0.17, +0.33 and +0.66 V vs. Ag/Ag$^+$) compared with those of complex **1**. The first one-electron oxidation process at −0.07 V is ascribed to the oxidation of the $(C_8H_4S_8)_2$ ligand center, since neutral metal complexes with the $C_8H_4S_8^{2-}$ ligand exhibit often low oxidation potentials corresponding to the $C_8H_4S_8$ ligand-centered oxidation: $[Pt(SEt_2)_2(C_8H_4S_8)]$, +0.07 V [9], $[Ru(bpy)_2(C_8H_4S_8)]$, +0.01 V [23], $[Pd(C_5H_4NCH{=}NBu)(C_8H_4S_8)]$, −0.075 V and $[Pd(bpy)(C_8H_4S_8)]$, −0.10 V (vs. Ag/Ag$^+$) [54]. This is consistent with the appearance of ESR signal at $g = 2.008$ observed for a solution of this complex in the presence of a small amount of iodine as an oxidant, as described below. The succeeding two-electron oxidation peak at +0.17 V is reasonably ascribed to the Fe(II) to Fe(III) oxidations as observed for **1**. Furthermore, the third one-electron oxidation peak at +0.33 V (vs. Ag/Ag$^+$) can be ascribed to the second oxidation of the $(C_8H_4S_8)_2$ ligand moiety. This occurs at a rather low potential compared with the second $C_8H_4S_8$ ligand-centered oxidation of neutral $C_8H_4S_8$–metal complexes: $[Pt(SEt_2)_2(C_8H_4S_8)]$, +0.45 V [9] and $[Ru(bpy)_2(C_8H_4S_8)]$, +0.49 V (vs. Ag/Ag$^+$) [23]. This is due to the preferred charge delocalization in the extended $(C_8H_4S_8)_2$ ligand. Both the complexes exhibit further oxidation peaks at higher potentials.

*3.4. Oxidation of complexes **1** and **2** and electrical conductivities of the oxidized species **3** and **4***

The oxidation of complex **1** proceeds by the reaction with bromine to afford solids of oxidized species, although no solids have been obtained by the reaction with iodine because of somewhat high oxidation potentials of **1**. The obtained solids, however, have shown no IR absorption bands due to CO and C_5H_5 groups around the Fe(II) center, but a band has appeared at 1059 cm^{-1}, which is ascribed to $(C_3S_5)_2$ [46]. Thus, the oxidation of **1** seems to cleave easily the Fe–S bond, leading to the coupling of the C_3S_5 moieties.

On the other hand, complex **2** is readily oxidized by iodine to form the stable product **3**. It contains the I_3^- and I_5^- ions as the counter anion, which has been confirmed by the stretching bands of these anions observed at 111 and 168 cm^{-1} with similar intensities in the Raman spectrum [54,55]. Fig. 4 shows the electronic absorption spectra of **2** in chloroform in the presence of various amounts of iodine. Addition of iodine has afforded at first an appreciable band at 1200 nm, the intensity of which has increased until the addition of iodine in the half molar amount of **2**. This band is due to the charge transfer (CT) transition between the Fe(II) center and the oxidized $(C_8H_4S_8)_2$ ligand, as often observed for oxidized, sulfur-rich dithiolate–metal complexes: $[Co(C_5H_5)(C_8H_4S_8)](I_3)$ [15], $[Ru(bpy)_2(C_8H_4S_8)]^0$ [23], $[Pt(bpy)(C_8H_4S_8)](I_3)_{0.9}$ [56], and $[Pt(C_6S_8R_2)_2]^0$ ($R = C_{10}H_{21}$, $C_{14}H_{29}$, and $C_{18}H_{37}$) [57]. Further addition of iodine beyond the half-molar amount of **2** has given an intense band at 950 nm. This is ascribed to the CT transition between the Fe(III) center and the oxidized $(C_8H_4S_8)_2$ ligand.

The reaction of **2** with an excess amount of iodine has afforded black solids of the oxidized species **4** having both I_3^- and I_5^- ions as the counter anion. Thus, **4** is considered to be oxidized somewhat beyond two electrons, containing the oxidized $(C_8H_4S_8)_2$ ligand and the Fe(III) state. In accordance with this finding, **4** has shown an almost isotropic ESR signal at $g = 2.008$ with the peak-to-peak linewidth of 2.8 mT (in the powder state at room temperature). This indicates the $(C_8H_4S_8)_2$ ligand-centered oxidation, as observed for the oxidized $C_8H_4S_8$–metal complexes with the $C_8H_4S_8$ ligand-centered oxidation [9,15,17,23]. Solids **3** obtained by the reaction with a slight excess of iodine has also exhibited an ESR signal at $g = 2.008$. A dichloromethane solution of **2** with < 0.5 molar equivalent of iodine has also afforded an ESR signal at $g = 2.006$. Thus, these findings are consistent with the low oxidation potential corresponding to the $(C_8H_4S_8)_2$ ligand-centered oxidation deduced from the cyclic voltammogram.

Although an XPS band of **2** has appeared at 708.5 eV as the binding energy of Fe $2p_{3/2}$ electrons, the oxidized species **4** has shown an XPS band at 709.9 eV and a shoulder band at 708.6 eV. The energy of the former band is ascribed to that of Fe(III) species having the C_5H_5 group [58,59]. These findings indicate that **4** contains both the Fe(III) and Fe(II) centers.

Complexes **1** and **2** are essentially insulators with the electrical conductivities of $< 10^{-8}$ S cm^{-1} measured for compacted pellets at room temperature. The oxidized complex **3**, less than two-electron oxidized species with the oxidized $(C_8H_4S_8)_2$ moiety and with the Fe(II) and Fe(III) states, shows electrical conductivity of 8.7×10^{-6} S cm^{-1}, while the further oxidized species **4** behaves as a rather better electrical conductor with the conductivity of 1.7×10^{-4} S cm^{-1}. An appreciably higher conductivity of **4** comes from a formation of effective electron-conduction pathway through non-bonded S···S contacts among the oxidized $(C_8H_4S_8)_2$ moieties even in the bulky geometry of the complex. Such an effective S···S contact is similar to those of bulky $C_8H_4S_8$–metal complexes with rather high electrical conductivities [15,18,23,56].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC no. 155637 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R.A. Clark, A.E. Underhill, Coord. Chem. Rev. 110 (1991) 115.
[2] G. Matsubayashi, Reviews on Heteroatom Chemistry, vol. 4, Myu, Tokyo, 1991, p. 171.
[3] R.-M. Olk, B. Olk, W. Dietzsch, R. Kirmse, W. Hoyer, Coord. Chem. Rev. 117 (1992) 99.
[4] A.E. Pullen, R.-M. Olk, Coord. Chem. Rev. 188 (1999) 211.
[5] N.L. Narvor, N. Robertson, T. Weyland, J.D. Kilburn, A.E. Underhill, M. Webster, N. Svenstrup, J. Becher, J. Chem. Soc. Chem. Commun. (1996) 1363.
[6] N.L. Narvor, N. Robertson, E. Wallace, J.D. Kilburn, A.E. Underhill, P.N. Bartlett, M. Webster, J. Chem. Soc. Dalton Trans. (1996) 823.
[7] M. Nakano, A. Kuroda, T. Maikawa, G. Matsubayashi, Mol. Cryst. Liq. Cryst. 284 (1996) 301.
[8] M. Nakano, A. Kuroda, G. Matsubayashi, Inorg. Chim. Acta 254 (1997) 189.
[9] M. Nakano, A. Kuroda, H. Tamura, R. Arakawa, G. Matsubayashi, Inorg. Chim. Acta 279 (1998) 165.
[10] M. Kumasaki, H. Tanaka, A. Kobayashi, J. Mater. Chem. 8 (1998) 295.
[11] K. Ueda, M. Goto, M. Iwamatsu, T. Sugimoto, S. Endo, N. Toyota, K. Yamamoto, H. Fujita, J. Mater. Chem. 8 (1998) 2195.
[12] A. Kobayashi, H. Tanaka, M. Kumasaki, H. Torii, B. Narymbetov, T. Adachi, J. Am. Chem. Soc. 121 (1999) 10763.
[13] H. Tanaka, Y. Okano, H. Kobayashi, W. Suzuki, A. Kobayashi, Science 291 (2001) 285.
[14] G. Matsubayashi, M. Nakano, K. Saito, T. Yonamine, R. Arakawa, J. Organomet. Chem. 611 (2000) 364.
[15] H. Mori, M. Nakano, H. Tamura, G. Matsubayashi, J. Organomet. Chem. 574 (1999) 77.
[16] G. Matsubayashi, M. Nakano, K. Saito, H. Tamura, Mol. Cryst. Liq. Cryst. 343 (2000) 29.
[17] K. Saito, M. Nakano, H. Tamura, G. Matsubayashi, Inorg. Chem. 39 (2000) 4815.
[18] K. Saito, M. Nakano, H. Tamura, G. Matsubayashi, J. Organomet. Chem. 625 (2001) 7.
[19] L. Valade, J.-P. Legros, M. Bousseau, P. Cassoux, M. Garbauskas, M. Interrante, J. Chem. Soc. Dalton Trans. (1985) 783.
[20] N. Svenstrup, K.M. Rasmussen, T.K. Kansen, J. Becher, Synthesis (1994) 809.
[21] L. Binet, J.M. Fabre, C. Montginoul, K.B. Simonsen, J. Becher, J. Chem. Soc. Perkin Trans. 1 (1996) 783.
[22] K. Akiba, G. Matsubayashi, T. Tanaka, Inorg. Chim. Acta 165 (1989) 245.
[23] K. Natsuaki, M. Nakano, G. Matsubayashi, Inorg. Chim. Acta 299 (2000) 112.
[24] A. Nakahama, M. Nakano, G. Matsubayashi, Inorg. Chim. Acta 284 (1999) 55.
[25] G. Matsubayashi, T. Maikawa, H. Tamura, M. Nakano, R. Arakawa, J. Chem. Soc. Dalton Trans. (1996) 1539.
[26] A.C.T. North, D.C. Philips, F.C. Mathews, Acta Crystallogr. 24A (1968) 351.
[27] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Cryst. 27 (1994) 435.
[28] TEXSAN: Crystal Structure Analysis Package, Molecular Structure Corp. The Woodlands, TX, 1992.
[29] International Tables for X-ray Crystallography, vol. 4, Kynoch Press, Birmingham, UK, 1974.
[30] C.K. Johnson, ORTEP-II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
[31] J. Locke, J.A. McCleverty, Inorg. Chem. 5 (1966) 1157.
[32] D. Sellmann, E. Unger, Z. Naturforsch. 33b (1978) 1438.
[33] B.K. Blackburn, S.G. Davis, K.H. Sutton, M. Whittaker, Chem. Soc. Rev. 17 (1988) 147.
[34] S.J. Archer, G.A. Harvey, J.R. Moss, A.M. Crouch, Inorg. Chim. Acta 201 (1992) 43.
[35] J. Zakrzewski, A. Tosik, M. Bukowska-Strzyzewska, J. Organomet. Chem. 495 (1995) 83.
[36] A. Tosik, M. Bukowska-Strzyzewska, B. Rudolf, J. Zakrzewski, J. Organomet. Chem. 531 (1997) 41.

[37] D. Coucouvanis, D. Swenson, N.C. Baenziger, D.G. Holah, A. Kostikas, A. Simopoulos, V. Petrouleas, J. Am. Chem. Soc. 98 (1976) 5721.
[38] T. Okamura, S. Takamizawa, N. Ueyama, A. Nakamura, Inorg. Chem. 37 (1998) 18.
[39] Y. Zang, L. Que Jr., Inorg. Chem. 34 (1995) 1030.
[40] J.J. Ellison, K. Ruhlandt-Senge, P.P. Power, Angew. Chem. Int. Ed. Engl. 33 (1994) 1178.
[41] F.M. MacDonnell, K. Ruhlandt-Senge, J. Ellison, R.H. Holm, P.P. Power, Inorg. Chem. 34 (1995) 1815.
[42] H.K. Lee, B.-S. Luo, T.C.W. Mak, W.-P. Leung, J. Organomet. Chem. 489 (1995) C71.
[43] E. Roman, D. Catheline, D. Astruc, P. Batail, L. Ouahab, F. Varret, J. Chem. Soc. Chem. Commun. (1982) 129.
[44] X. Yang, T.B. Rauchfuss, S.R. Wilson, J. Am Chem. Soc. 111 (1989) 3465.
[45] X. Yang, T.B. Rauchfuss, S. Wilson, J. Chem. Soc. Chem. Commun. (1990) 34.
[46] T. Akasaka, H. Tamura, M. Nakano, G. Matsubayashi, submitted.
[47] S. Tanaka, G. Matsubayashi, J. Chem. Soc. Dalton Trans. (1992) 2837.
[48] G. Matsubayashi, K. Douki, H. Tamura, M. Nakano, W. Mori, Inorg. Chem. 32 (1993) 5990.
[49] F. Matsuda, H. Tamura, G. Matsubayashi, Inorg. Chim. Acta 295 (1999) 243.
[50] J.G. Breitzer, A.L. Simirnov, L.F. Szczepura, S.R. Wilson, T.B. Rauchfuss, Inorg. Chem. 40 (2001) 1421.
[51] K.S. Hagen, J.G. Reynolds, R.H. Holm, J. Am. Chem. Soc. 103 (1981) 4054.
[52] M. Moran, I. Cuadrado, J.R. Masaguer, J. Losada, J. Organomet. Chem. 335 (1987) 255.
[53] H. Ushijima, S. Sudoh, M. Kajitani, K. Shimizu, T. Akiyama, A. Sugimori, Inorg. Chim. Acta 175 (1990) 11.
[54] M. Cowie, A. Gleizes, G.W. Grynkewich, D.W. Kalina, M.S. McClure, R.P. Scaringe, R.C. Teitelbaum, S.L. Ruby, J.A. Ibers, C.R. Kannewurf, T.J. Marks, J. Am. Chem. Soc. 101 (1979) 2921.
[55] B.N. Diel, T. Inabe, J.W. Lyding, K.F. Schoch Jr., C.R. Kannewurf, T.J. Marks, J. Am. Chem. Soc. 105 (1983) 1551.
[56] K. Kubo, M. Nakano, H. Tamura, G. Matsubayashi, Inorg. Chim. Acta 311 (2000) 6.
[57] T. Nakazono, M. Nakano, H. Tamura, G. Matsubayashi, J. Mater. Chem. 9 (1999) 2413.
[58] D.O. Cowan, J. Park, M. Barber, J. Livage, Chem. Commun. (1971) 1444.
[59] S. Okuno, G. Matsubayashi, Chem. Lett. (1993) 799.