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# $\eta^5$-$C_5H_5$- and $\eta^5$-$C_5Me_5$-metal complexes (M = Zr(IV) and Hf(IV)) with the sulfur-rich dithiolate $C_8H_4S_8$ ligand and high electrical conductivities of their oxidized species

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## Abstract

$Zr(\eta^5\text{-}C_5H_5)_2(C_8H_4S_8)$, $[NMe_4][Zr(\eta^5\text{-}C_5H_5)(C_8H_4S_8)_2]$, $[NMe_4][Zr(\eta^5\text{-}C_5Me_5)(C_8H_4S_8)_2]$, and $[NMe_4][Hf(\eta^5\text{-}C_5Me_5)(C_8H_4S_8)_2]$ ($C_8H_4S_8^{2-}$ = 2-{(4,5-ethylenedithio)-1,3-dithiole-2-ylidene}-1,3-dithiole-4,5-dithiolate(2-)) were prepared by reactions of $Zr(\eta^5\text{-}C_5H_5)_2Cl_2$, $Zr(\eta^5\text{-}C_5H_5)Cl_3$, $Zr(\eta^5\text{-}C_5Me_5)Cl_3$ or $Hf(\eta^5\text{-}C_5Me_5)Cl_3$ with $[NMe_4]_2(C_8H_4S_8)$ in tetrahydrofuran. They were oxidized by iodine or TCNQ (7,7,8,8-tetracyano-*p*-quinodimethane) in dichloromethane or in acetone to afford 1.0-, 1.3- or 1.8-electron oxidized complexes, $[Zr(\eta^5\text{-}C_5H_5)_2(C_8H_4S_8)]^+$, $[Zr(\eta^5\text{-}C_5H_5)(C_8H_4S_8)_2]^0$, $[M(\eta^5\text{-}C_5Me_5)(C_8H_4S_8)_2]^{0.3+}$ and $[M(\eta^5\text{-}C_5Me_5)(C_8H_4S_8)_2]^{0.8+}$ (M = Zr(IV) and Hf(IV)) species having the $I_3^-$ ion or the $TCNQ^{\bullet-}$ radical anion as a counter ion, with the $C_8H_4S_8$ ligand-centered oxidation. They exhibited electrical conductivities of $1.6 \times 10^{-1}$–$7.6 \times 10^{-4}$ S $cm^{-1}$ measured for compacted pellets at room temperature. Particularly, $[Zr(\eta^5\text{-}C_5H_5)_2(C_8H_4S_8)]^+$ and $[M(\eta^5\text{-}C_5Me_5)(C_8H_4S_8)_2]^{0.3+}$ (M = Zr(IV) and Hf(IV)) complexes as well as $[Ti(L)(C_8H_4S_8)_2]^{0.3+}$ (L = $\eta^5$-$C_5H_5$ and $\eta^5$-$C_5Me_5$) species showed high electrical conductivities (0.010–0.16 S $cm^{-1}$). © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Titanium complexes; Zirconium complexes; Hafnium complexes; Dithiolate complexes; Pentamethylcyclopentadienyl complexes; Electrical conductivity

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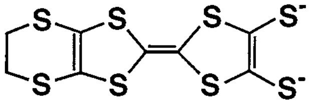
## 1. Introduction

Metal complexes with sulfur-rich dithiolate ligands attract much attention to high electrical conductivities of their partially oxidized species, of which $C_3S_5$-metal complexes ($C_3S_5^{2-}$ = 4,5-disulfanyl-1,3-dithiole-2-thionate(2-)) have been studied extensively [1–6]. Molecular interactions through non-bonded S···S contacts among the $C_3S_5$ ligands form effective electron-conduction pathways in the solid state. However, some $C_3S_5$-metal complexes are unstable on the oxidation and decompose quickly [7–9]. On the other hand, metal complexes with the more sulfur-rich dithiolate $C_8H_4S_8^{2-}$ (2-{(4,5-ethylenedithio)-1,3-dithiole-2-ylidene}-1,3-dithiole-4,5-dithiolate(2-); **A**) ligand are stable on the oxidation of this ligand moiety. Oxidized metal complexes with this ligand [7–10,13–15] and $(RS)_2C_6S_6^{2-}$ (2-{4,5-bis(alkylthio)-1,3-dithiole-2-ylidene}-1,3-dithiole-4,5-dithiolate(2-); R = Me and Et) ligands [16–19] as an extended π-electron-delocalized system were also reported to become good electrical conductors. They form more effective molecular interactions through more S···S contacts in the solid state [7–10,13–19].



**A**

Metal complexes containing both organic groups and the sulfur-rich dithiolate ligands may form molecular inorganic-organic composites having layered structures consisting of self-assembled metal-dithiolate moieties via S···S contacts and separated organic groups. On this standpoint we have studied on some cyclopentadienyl– and pentamethylcyclopentadienyl–metal complexes with the $C_8H_4S_8$ ligand and their stable oxidized species

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Table 1
Reduction and oxidation peak potentials (V vs. $Ag/Ag^+$) and $\Delta E$ ($=E_{cp}-E_{ap}$, mV) in parentheses determined from cyclic voltammograms and absorption maxima ($\lambda$/nm) and molar absorption coefficients ($\varepsilon$/mol$^{-1}$ dm$^3$ cm$^{-1}$) of the $C_8H_4S_8$–metal complexes in solution

| Complex | Solvent | Peak potential | | |
|---|---|---|---|---|
| | | Reduction | Oxidation | |
| $Ti(\eta^5-C_5H_5)_2(C_8H_4S_8)$ [a] | $CH_2Cl_2$ | −1.40 (220) | +0.29 (210) | +0.73 (370) |
| $Ti(\eta^5-C_5Me_5)_2(C_8H_4S_8)$ [a] | $CH_2Cl_2$ | −1.63 (280) | +0.19 (260) | +0.69 (340) |
| $Zr(\eta^5-C_5H_5)_2(C_8H_4S_8)$ (**1**) | $CH_2Cl_2$ | | +0.11 | +0.76 (460) |
| $[NMe_4][Ti(\eta^5-C_5H_5)(C_8H_4S_8)_2]$ [a] | acetone | −1.36 (80) | −0.39 (170) | |
| $[NMe_4][Ti(\eta^5-C_5Me_5)(C_8H_4S_8)_2]$ [a] | acetone | −1.73 (320) | −0.20 (330) | +0.23 (330) |
| $[NMe_4][Zr(\eta^5-C_5H_5)(C_8H_4S_8)_2]$ (**2**) | $CH_2Cl_2$ | | −0.29 (160) | +0.64 (110) |
| $[NMe_4][Zr(\eta^5-C_5Me_5)(C_8H_4S_8)_2]$ (**3**) | $CH_2Cl_2$ | | −0.25 (200) | +0.19 (360) |
| $[NMe_4][Hf(\eta^5-C_5Me_5)(C_8H_4S_8)_2]$ (**4**) | $CH_2Cl_2$ | | −0.26 (180) | +0.09 (190) |
| $\lambda$ ($\varepsilon$) | | | | |
| 316 (21 000) | 456 (2800) | 736 (6500) | | |
| 332 (21 000) | 448 (2700) | 594 (1400) | 826 (4600) | |
| 332 (29 000) | 460 (5200) | | | |
| 328 (43 000) | | 612 (7300) | 816 (6200) | |
| 300 (22 000) | | 600 (4700) | 760 (3500) | |
| 326 (58 000) | 456 (10 500) | | | |
| 318 (41 000) | 440 (7100) | | | |
| 314 (39 000) | 418 (12 000) | 658 (3600) | | |

[a] Ref. [8].

[7,8,20], where some Co(III) and Ti(IV) complexes exhibited high electrical conductivities.

This paper reports the preparation and spectroscopic and electrochemical properties of $[NMe_4][M(L)(C_8H_4S_8)_2]$ (M = Zr(IV) and Hf(IV); L = $\eta^5-C_5H_5$ and $\eta^5-C_5Me_5$) and $Zr(\eta^5-C_5H_5)_2(C_8H_4S_8)$. Electrical conductivities of their oxidized species, together with those of the oxidized, corresponding Ti(IV)-species [8], are discussed based on their electronic states and molecular interactions among the complex moieties in the solid state.

## 2. Experimental

### 2.1. Starting materials

4,5-Bis(cyanoethylthio)-1,3-dithiole-2-[(4,5-ethylenedithio)-1,3-dithiole-2-ylidene], $C_8H_4S_8(CH_2CH_2CN)_2$ was prepared according to the method reported previously [11–13]. TCNQ, $Zr(\eta^5-C_5H_5)_2Cl_2$, $Zr(\eta^5-C_5H_5)Cl_3$, $Zr(\eta^5-C_5Me_5)Cl_3$, and $Hf(\eta^5-C_5Me_5)Cl_3$ were commercially available.

### 2.2. Preparation of $Zr(\eta^5-C_5H_5)_2(C_8H_4S_8)$ (1)

All the following reactions were carried out under Ar atmosphere. To a THF (30 cm$^3$) solution of $C_8H_4S_8(CH_2CH_2CN)_2$ (120 mg, 0.25 mmol) was added with vigorous stirring a MeOH 25% solution (190 mg) of $NMe_4OH$ (0.52 mmol) immediately to afford red–brown solids of $[NMe_4]_2(C_8H_4S_8)$. They were collected by filtration and washed with THF. After they were dissolved in EtOH (30 cm$^3$), the solution was added to a THF (20 cm$^3$) solution of $Zr(\eta^5-C_5H_5)_2Cl_2$ (75 mg, 0.26 mmol) and the solution was stirred for 1 h. The resulting red–brown solids of **1** were collected by filtration, washed with MeOH and diethyl ether, and dried in vacuo (70% yield). Anal. Calc. for $C_{18}H_{14}S_8Zr$: C, 37.40; H, 2.44. Found: C, 37.36; H, 2.44%. IR (KBr, $\nu$, cm$^{-1}$): 2902, 1433, 1391, 1288, 1014, 811, 771. $^1$H-NMR ($CD_2Cl_2$, $\delta$, ppm): 6.17 (s, 5H), 5.93 (s, 5H), 3.33–3.30 (m, 4H).

### 2.3. Preparation of $[NMe_4][Zr(\eta^5-C_5H_5)(C_8H_4S_8)_2]$ (2), $[NMe_4][Zr(\eta^5-C_5Me_5)(C_8H_4S_8)_2]$ (3) and $[NMe_4][Hf(\eta^5-C_5Me_5)(C_8H_4S_8)_2]$ (4)

Red–brown solids of $[NMe_4]_2(C_8H_4S_8)$ prepared by the reaction of a THF solution of $C_8H_4S_8$-$(CH_2CH_2CN)_2$ (420 mg, 0.91 mmol) with a MeOH solution of $NMe_4OH$ (2.0 mmol) as described for the preparation of **1** were suspended in THF (50 cm$^3$). To the suspension was added $Zr(\eta^5-C_5H_5)Cl_3$ (140 mg, 0.52 mmol) and the solution was stirred for 3 h to afford a dark brown precipitate. After it was dissolved in acetone (1500 cm$^3$), the solution was filtered and the filtrate was condensed to a half volume under reduced pressure to yield brown solids of **2**. They were filtered, quickly washed with MeOH to remove $NMe_4Cl$ and with diethyl ether, and dried in vacuo (82% yield). Anal. Calc. for $C_{25}H_{25}NS_{16}Zr$: C, 31.82; H, 2.67; N, 1.48. Found: C, 31.53; H, 2.96; N, 1.37%. IR (KBr, ν, cm$^{-1}$): 2901, 1479, 1405, 1284, 1171, 1016, 946, 888, 802, 769. $^{1}$C (acetone-$d_6$, δ, ppm): 6.08 (s, 5H), 3.46 (s, 12H), 3.40–3.37 (m, 8H).

Similarly, the reactions of $[NMe_4]_2(C_8H_4S_8)$ with $Zr(\eta^5\text{-}C_5Me_5)Cl_3$ and with $Hf(\eta^5\text{-}C_5Me_5)Cl_3$ in THF gave complexes **3** and **4**, respectively. Complex **3** (45% yield). Anal. Calc. for $C_{30}H_{35}NS_{16}Zr$: C, 35.54; H, 3.48; N, 1.38. Found: C, 35.40; H, 3.28; N, 1.24%. IR (KBr, ν, cm$^{-1}$): 2907, 1477, 1421, 1375, 1323, 1285, 1194, 1070, 1036, 946, 887, 770. $^{1}$H-NMR (DMSO-$d_6$, δ, ppm): 3.39–3.36 (m, 8H), 3.07 (s, 12H), 1.82 (s, 15H). Complex **4** (52% yield). Anal. Calc. for $C_{30}H_{35}HfNS_{16}$: C, 32.73; H, 3.20; N, 1.27. Found: C, 32.66; H, 3.13; N, 1.46%. IR (KBr, ν, cm$^{-1}$): 2907, 1477, 1421, 1375, 1323, 1285, 1194, 1070, 1036, 946, 887, 770. $^{1}$H-NMR (DMSO-$d_6$, δ, ppm): 3.39–3.36 (m, 8H), 3.08 (s, 12H), 1.88 (s, 15H).

### *2.4. Preparation of $[Zr(\eta^5\text{-}C_5H_5)_2(C_8H_4S_8)](I_3)$ (**5**)*

A $CH_2Cl_2$ (100 cm$^3$) solution of **1** (58 mg, 0.10 mmol) was added with stirring to a $CH_2Cl_2$ (5 cm$^3$) solution of iodine (130 mg, 0.51 mmol) to afford immediately black microcrystals of **5**. They were collected by filtration, washed with $CH_2Cl_2$, and dried in vacuo (84% yield). Anal. Calc. for $C_{18}H_{14}I_3S_8Zr$: C, 22.55; H, 1.47. Found: C, 22.86; H, 1.57%. IR (KBr, ν, cm$^{-1}$): 2902, 1379, 1333, 1281, 1009, 881, 804, 770.

### *2.5. Preparation of $[Zr(\eta^5\text{-}C_5H_5)(C_8H_4S_8)_2]$ (**6**)*

To an acetone (200 cm$^3$) solution of **2** (91 mg, 0.097 mmol) was added with stirring a $CH_2Cl_2$ (20 cm$^3$) solution of iodine (130 mg, 0.51 mmol) to afford immediately black solids of **6**. They were collected by filtration, washed with acetone and with a large amount of MeOH to remove $NMe_4I$, and dried in vacuo (76% yield). Anal. Calc. for $C_{21}H_{13}S_{16}Zr$: C, 29.01; H, 1.51. Found: C, 29.31; H, 1.61%. IR (KBr, ν, cm$^{-1}$): 2902, 1462, 1408, 1318, 1284, 1168, 1120, 1012, 810, 779.

The reaction of an acetone solution of **2** with a THF solution containing an excess amount of TCNQ also afforded **6** (86% yield). Anal. Calc. for $C_{21}H_{13}S_{16}Zr$: C, 29.01; H, 1.51. Found: C, 29.29; H, 1.59%.

### *2.6. Preparation of $[Zr(\eta^5\text{-}C_5Me_5)(C_8H_4S_8)_2](I_{2.4})$ (**7**)*

To a $CH_2Cl_2$ (100 cm$^3$) solution of **3** (130 mg, 0.13 mmol) was added with stirring a $CH_2Cl_2$ (20 cm$^3$) solution of iodine (140 mg, 0.55 mmol) to afford immediately black solids of **7**. They were collected by centrifugation, washed with acetone and with a large amount of MeOH, and dried in vacuo (35% yield). Anal. Calc. for $C_{26}H_{23}I_{2.4}S_{16}Zr$: C, 25.10; H, 1.86. Found: C, 24.80; H, 1.71%. IR (KBr, ν, cm$^{-1}$): 2906, 1431, 1363, 1319, 1283, 1221, 1168, 1120, 1035, 944, 886, 827, 769.

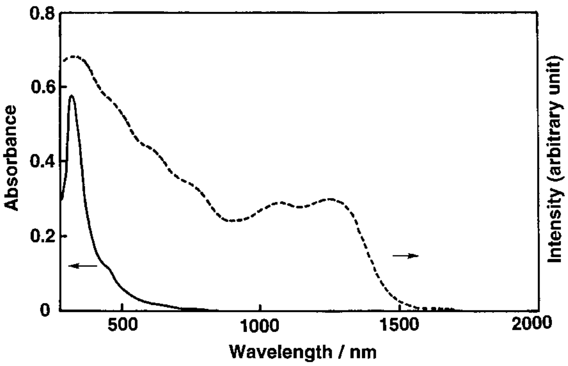

Fig. 1. Electronic absorption spectrum of **2** (1.0 × 10$^{-5}$ mol dm$^{-3}$) in acetone (—) and the powder reflectance spectrum (---).

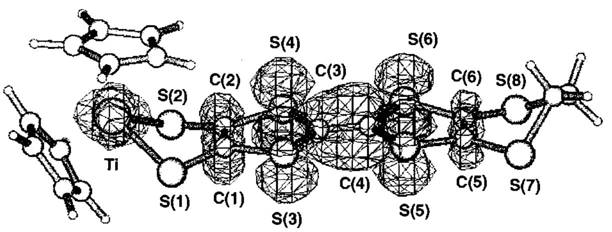

Fig. 2. Spin-density isosurface (0.001 e A$^{-3}$) of the $[Ti(\eta^5\text{-}C_5H_5)_2(C_8H_4S_8)]^+$ radical cation species evaluated by a DFT calculation of level UB3PW91-/LANL2DZ.

### *2.7. Preparation of $[Zr(\eta^5\text{-}C_5Me_5)(C_8H_4S_8)_2](TCNQ)_{0.3}$ (**8**)*

To a $CH_2Cl_2$ (100 cm$^3$) solution containing **3** (130 mg, 0.13 mmol) was added with stirring a THF (20 cm$^3$) solution of TCNQ (140 mg, 0.68 mmol) to yield black solids of **8**. After stirring for 20 min, the resulting solids were collected by filtration, washed with THF and MeOH, and dried in vacuo (60% yield). Anal. Calc. for $C_{29.6}H_{24.2}N_{1.2}S_{16}Zr$: C, 35.52; H, 2.44; N, 1.68. Found: C, 35.27; H, 2.50; N, 1.46%. IR (KBr, ν, cm$^{-1}$): 2910, 2177, 1569, 1460, 1375, 1320, 1283, 1193, 1170, 1121, 1036, 928, 886, 828, 770.

### *2.8. Preparation of $[Hf(\eta^5\text{-}C_5Me_5)(C_8H_4S_8)_2](I_{2.5})$ (**9**) and $[Hf(\eta^5\text{-}C_5Me_5)(C_8H_4S_8)_2](TCNQ)_{0.3}$ (**10**)*

As described for the preparations of **7** and **8**, the reaction of a $CH_2Cl_2$ solution of **4** with a $CH_2Cl_2$ solution containing an excess amount of iodine and the reaction of a $CH_2Cl_2$ solution of **4** with a THF solution of an excess amount of TCNQ afforded **9** and **10**, respectively. Complex **9** (56% yield). Anal. Calc. for $HfI_{2.5}S_{16}C_{26}H_{23}$: C, 23.23; H, 1.72. Found: C, 23.27; H, 1.76%. IR (KBr, $\nu$, cm$^{-1}$): 2908, 1422, 1404, 1366, 1324, 1284, 1227, 1169, 1121, 1010, 885, 770. Complex **10** (76% yield). Anal. Calc. for $C_{29.6}H_{24.2}HfN_{1.2}S_{16}$: C, 32.67; H, 2.24; N, 1.54. Found: C, 32.76; H, 2.25; N, 1.52%. IR (KBr, $\nu$, cm$^{-1}$): 2909, 2177, 1548, 1476, 1408, 1323, 1284, 1234, 1170, 1083, 1010, 918, 886, 771.

### *2.9. Physical measurements*

IR, ESR [21], electronic absorption and powder reflectance spectra [15] were measured as described previously. Raman spectra were measured using a Nipponbunko NR-1800 laser-Raman spectrophotometer at the Graduate School of Science, Osaka University. Cyclic voltammograms of complexes **1**–**4** were measured in acetone and $CH_2Cl_2$ using $[NBu^n_4][ClO_4]$ as an electrolyte, and electrical conductivities of the complexes were measured at room temperature (r.t.) for compacted pellets by the conventional two-probe method as described previously [14].

### *2.10. Theoretical calculations of the $[Ti(\eta^5\text{-}C_5H_5)_2(C_8H_4S_8)]^+$ radical cation species*

In order to elucidate the effect of one-electron oxidation on the molecular structure and the atomic spin densities of the oxidized species, quantum chemical calculations were made by using a GAUSSIAN 94 Rev. E.2 program suite [22] on a DEC Alpha station 500/333 computer. Both the $[Ti(\eta^5\text{-}C_5H_5)_2(C_8H_4S_8)]^0$ molecule and the $[Ti(\eta^5\text{-}C_5H_5)_2(C_8H_4S_8)]^+$ radical cation were geometrically optimized by a hybrid density functional method (B3PW91) [23,24] using an ECP basis set LANL2DZ. Mulliken spin densities for the radical cation species were also evaluated.

## 3. Results and discussion

### *3.1. Electrochemical and spectroscopic properties of complexes **1**–**4***

Cyclic voltammograms of complexes **1**–**4** measured in acetone or dichloromethane have shown quasi-reversible ($\Delta E = E_{cp} - E_{ap} = 80$–$330$ mV) redox waves. Table 1 summarizes reduction and oxidation peak potentials of the complexes, together with those of corresponding Ti(IV)–$C_8H_4S_8$ complexes. The Ti(IV)–$C_8H_4S_8$ complexes are reduced at $-1.36$ to $-1.73$ V (vs. Ag/Ag$^+$), which are ascribed to the Ti(IV) to Ti(III) process [8], while the Zr(IV)- and Hf(IV)–$C_8H_4S_8$ complexes exhibit no reduction waves in this region. The anionic $[M(L)(C_8H_4S_8)_2]^-$ (M = Ti(IV) and Zr(IV); L = $\eta^5$-$C_5H_5$ and $\eta^5$-$C_5Me_5$) complexes are oxidized appreciably low potentials: first oxidation potentials, $-0.39$ to $-0.20$ V (vs. Ag/Ag$^+$). These findings are similar to the cases of $[Pt(C_8H_4S_8)_2]^{2-}$ ($-0.47$ V vs. SCE) [11] and $[M(O)(C_8H_4S_8)_2]^{2-}$ (M = V(IV) and Mo(IV)) complexes ($-0.21$ and $-0.18$ V vs. SCE) [25].

The $C_8H_4S_8$–metal complexes show electronic absorption bands in solution ($10^{-5}$ mol dm$^{-3}$) ascribed to the $\pi$–$\pi^*$ transitions of the $C_8H_4S_8$ ligand at 314–330 and 410–456 nm, as observed for $Na_2(C_8H_4S_8)$, $[Au(C_8H_4S_8)_2]^-$ [10], $[Pt(C_8H_4S_8)_2]^{2-}$ [13] and $[M(O)(C_8H_4S_8)_2]^{2-}$ (M = V(IV) and Mo(IV)) complexes [25]. The Ti(IV) complexes exhibit a ligand-to-metal $\pi$–d charge transfer (MLCT) bands at 594–826 nm, as observed for $Co(\eta^5\text{-}C_5H_5)(C_8H_4S_8)$, $Co(\eta^5\text{-}C_5Me_5)(C_8H_4S_8)$ [7] and $Ru(bpy)_2(C_8H_4S_8)$ (bpy = 2,2′-bipyridine) [15]. Although the Hf(IV) complex **4** also shows the MLCT band at 658 nm, the Zr(IV) complexes **1**–**3** show no appreciable bands in this longer wavelength region. The absorption spectral data of the

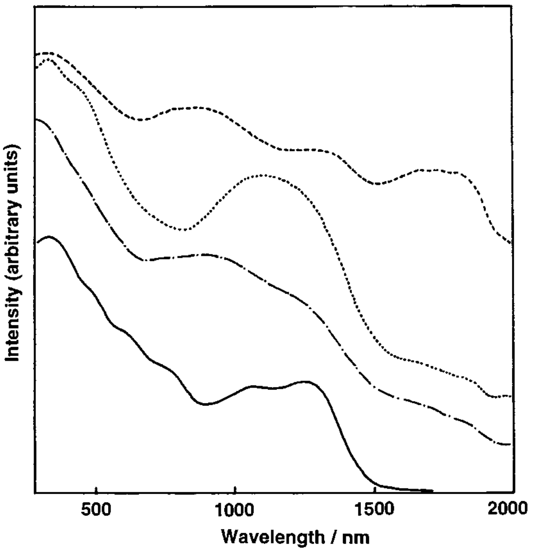

Fig. 3. Powder reflectance spectra of **2** (—) and **3** (···) as well as those of their oxidized species **6** (–·–·–) and **8** (---). Base lines are arbitrarily slidden.

Table 2
Electrical conductivities ($\sigma$)[a] of the oxidized complexes

| Complex | $\sigma_{RT}$/S cm$^{-1}$ |
|---|---|
| $[Zr(\eta^5\text{-}C_5H_5)_2(C_8H_4S_8)](I_3)$ (**5**) | 0.11 |
| $[Zr(\eta^5\text{-}C_5H_5)(C_8H_4S_8)_2]$ (**6**) | $1.0\times10^{-4}$ |
| $[Zr(\eta^5\text{-}C_5Me_5)(C_8H_4S_8)_2](I_3)_{0.8}$ (**7**) | $4.9\times10^{-4}$ |
| $[Zr(\eta^5\text{-}C_5Me_5)(C_8H_4S_8)_2](TCNQ)_{0.3}$ (**8**) | $4.0\times10^{-2}$ |
| $[Hf(\eta^5\text{-}C_5Me_5)(C_8H_4S_8)_2](I_3)_{0.83}$ (**9**) | $1.9\times10^{-4}$ |
| $[Hf(\eta^5\text{-}C_5Me_5)(C_8H_4S_8)_2](TCNQ)_{0.3}$ (**10**) | $1.0\times10^{-2}$ |
| $[Ti(\eta^5\text{-}C_5H_5)(C_8H_4S_8)_2](I_3)_{0.3}$[b] | 0.16 |
| $[Ti(\eta^5\text{-}C_5H_5)(C_8H_4S_8)_2](TCNQ)_{0.3}$[b] | 0.12 |
| $[Ti(\eta^5\text{-}C_5Me_5)(C_8H_4S_8)_2](I_3)_{0.8}$[b] | $7.6\times10^{-4}$ |
| $[Ti(\eta^5\text{-}C_5Me_5)(C_8H_4S_8)_2](TCNQ)_{0.3}$[b] | $5.5\times10^{-2}$ |

[a] Measured for compacted pellets at room temperature.

[b] Ref. [8].

complexes are also summarized in Table 1. Fig. 1 shows the electronic absorption spectrum of complex **2** in acetone and the powder reflectance spectrum. In the solid state bands occur at the region of 1000–1500 nm, which are not observed in solution. This is also similar to the powder reflectance bands of the other complexes. These findings suggest some interactions among the $C_8H_4S_8$–metal complex moieties through some S···S non-bonded contacts in the solid state. The similar bands at longer wavelengths were also observed for the spectra of other $C_8H_4S_8$–metal complexes in the solid state [8,20,25].

### *3.2. Oxidation of complexes **1–4***

Complex **1**, as well as the corresponding Ti($\eta^5$-$C_5H_5$)$_2$- and Ti($\eta^5$-$C_5Me_5$)$_2$-complexes, has a low oxidation potential. Thus, these complexes can be oxidized by iodine. Complexes **2–4** exhibit appreciably lower oxidation potentials to be oxidized by iodine and even by TCNQ. The Raman spectrum of complex **5** has shown a band at 111 $cm^{-1}$ assigned to the symmetric stretching of the $I_3^-$ ion [26,27]. The iodine-oxidized species **7** and **9** are likely to have the $I_3^-$ ion as a counter anion, as observed for $[Ti(\eta^5\text{-}C_5H_5)(C_8H_4S_8)_2](I_3)_{0.3}$, and $[Ti(\eta^5\text{-}C_5Me_5)(C_8H_4S_8)_2](I_3)_{0.8}$ [8]. The TCNQ-oxidized complexes **8** and **10** contain the $TCNQ^{\bullet -}$ radical anion as a counter ion in the $(TCNQ)_2^{2-}$ dimeric form, since they have shown the IR bands assigned to the CN stretching mode at 2150 and 2175 $cm^{-1}$ as observed for K[TCNQ] (2183 $cm^{-1}$) [28]. Thus, complexes **5** and **6** are one-electron oxidized species, while **7** and **9** are 1.8-electron oxidized complexes and **8** and **10** are in the 1.3-electron oxidized state.

These oxidized complexes have exhibited an almost isotropic ESR signal at $g = 2.004$–$2.009$ (peak-to-peak linewidth, 1.0–2.0 mT), except for complex **5** showing a somewhat broad signal at $g = 2.006$ (the linewidth, 11 mT). The unpaired electrons of these oxidized species lead to the electrical conductivities, as described below. The signal intensity of complex **6** is extremely weak, which may be due to a dimeric interation between the oxidized moieties in the solid state. These signals are assigned to the radical species of the oxidized $C_8H_4S_8$ ligand moiety, as observed for the radicals of oxidized $C_3S_5$– [21,29,30] and $C_8H_4S_8$–metal complexes [7,13,25].

The $C_8H_4S_8$ ligand-centered oxidation is confirmed by the calculated spin densities of the $[Ti(\eta^5\text{-}C_5H_5)_2(C_8H_4S_8)]^+$ radical cation species. Geometries of $[Ti(\eta^5\text{-}C_5H_5)_2(C_8H_4S_8)]^0$ and $[Ti(\eta^5\text{-}C_5H_5)_2(C_8H_4S_8)]^+$ species have been optimized by a hybrid density functional method. The optimized structure of the former species can be compared with the X-ray molecular structure of $[Ti(\eta^5\text{-}C_5Me_5)_2(C_8H_4S_8)]^0$ [8], where small differences in bond distances and angles between them stem on the release of the ring distortion by omission of methyl groups for the former species. The effect of one-electron oxidation appears mainly in the coordination mode of the $C_8H_4S_8$ ligand to the titanium atom. The ligating sulfur atoms of the dithiolate ligand move away from the central metal upon oxidation, accompanying with a slight buckle of $TiS_2$–$S_2C_2$ dihedral angle. The calculated spin-density isosurface of the paramagnetic oxidized species is shown in Fig. 2. Mulliken spin densities for this complex evaluated by a DFT calculation show the presence of about 85% spins on the $C_8H_4S_8$ ligand: Ti, 0.156; S(1), −0.003; S(2), 0.003; S(3) 0.153; S(4), 0.149; S(5), 0.119; S(6), 0.129; S(7), 0.014; S(8), 0.007; C(1), 0.057; C(2), 0.053; C(3), 0.032; C(4), 0.109; C(5), 0.020; C(6), 0.028.

Fig. 3 shows the powder reflectance spectra of complexes **2** and **3** together with those of their oxidized species **6** and **8**. Both complexes **2** and **3** show bands at long wavelengths (1100–1300 nm), although the solution spectra of them exhibit no bands in this region. These findings indicate molecular interactions among the complex moieties in the solid state, which are caused by S···S non-bonded contacts. The oxidized species **8** shows a band at a shorter wavelength (900 nm), as observed for other oxidized sulfur-rich dithiolato metal complexes [10,13,31], together with a band around 1300 nm. It shows also a further band around 1800 nm. This new band at the longer wavelength seems to be due to further extended molecular interactions among the oxidized $C_8H_4S_8$ ligand moieties through S···S contacts. The oxidized complexes **5**, **7**, **9** and **10** as well as the oxidized corresponding Ti(IV) complexes also have shown bands at 1500–1800 nm. These molecular interactions in the solid state construct effective electron-conduction pathways of unpaired electrons of the oxidized moieties, as described below. Although the oxidized species **6** shows also bands at 1300 nm and at a shorter wavelength, appreciable bands are not observed at the longer wavelength region. This finding suggests that further molecular interactions in the oxidized state are less effective owing to the dimer formation of this species in the solid state. It is consistent with a rather low electrical conductivity of this species as described below.

### *3.3. Electrical conductivities of the oxidized species of complexes*

Complexes **1–4** are essentially insulators (electrical conductivities of the compacted pellets, $< 10^{-8}$ S $cm^{-1}$ at room temperature). The oxidized species, however, exhibit high electrical conductivities ($1.9 \times 10^{-4} - 1.1 \times 10^{-1}$ S $cm^{-1}$), which are listed in Table 2. For the oxidized $[M(L)(C_8H_4S_8)_2]^{n+}$ ($L = \eta^5$-$C_5H_5$ and $\eta^5$-$C_5Me_5$; M = Ti(IV), Zr(IV) and Hf(IV); $n = 0$–

0.8) complexes the electrical conductivities of the 1.3-electron oxidized species ($n = 0.3$) are appreciably high compared with the other oxidized complexes ($n = 0$ and 0.8). This partially ($n = 0.3$) oxidized state of the complex moiety seems to be more suitable for the electron conduction through the packed complex moieties in the solid state. Particularly $[Ti(\eta^5\text{-}C_5H_5)(C_8H_4S_8)_2]^{0.3+}$ complexes having a less bulky $\eta^5\text{-}C_5H_5$ group exhibit high conductivities (0.12 and 0.16 S $cm^{-1}$). The non-planar geometry around the metal ion is similar to those of penta-coordinate $[M(O)(C_8H_4S_8)_2]$ [M = V(IV) and Mo(IV)] complexes, which also exhibit high conductivities [25]. The electron-conduction pathways are likely to be constructed by the non-bonded S···S contacts between the oxidized $C_8H_4S_8$ ligand moieties. Furthermore, it is noteworthy that complex **5** shows a high electrical conductivity (0.11 S $cm^{-1}$), as observed for $[Co(\eta^5\text{-}C_5H_5)(C_8H_4S_8)]^+$ species [7]. On the other hand, complex **6**, a formally one-electron oxidized species, exhibits a rather low conductivity. This may be due to a dimer formation of the oxidized complex moiety, which is deduced from the extremely weak intensity of the ESR signal and no appearance of electronic reflectance bands through further molecular interactions at longer wavelengths, as described above.

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