

# Preparation and Properties of Cyclopentadienyl- and Pentamethylcyclopentadienyl–Titanium(IV) Complexes with the C<sub>8</sub>H<sub>4</sub>S<sub>8</sub> Ligand, Electrical Conductivities of Their Oxidized Species, and X-ray Crystal Structure of Ti(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)

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Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>) (**1**), Ti(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>) (**2**), [NMe<sub>4</sub>][Ti(C<sub>5</sub>H<sub>5</sub>)(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)<sub>2</sub>] (**3**), and [NMe<sub>4</sub>][Ti(C<sub>5</sub>Me<sub>5</sub>)(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)<sub>2</sub>] (**4**) [C<sub>8</sub>H<sub>4</sub>S<sub>8</sub><sup>2-</sup> = 2-(4,5-ethylenedithio)-1,3-dithiole-2-ylidene]-1,3-dithiole-4,5-dithiolate(2-)] were prepared by reaction of Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub>, Ti(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub>, Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>3</sub>, or Ti(C<sub>5</sub>Me<sub>5</sub>)Cl<sub>3</sub> with Li<sub>2</sub>C<sub>8</sub>H<sub>4</sub>S<sub>8</sub> or [NMe<sub>4</sub>]<sub>2</sub>[C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>] in THF. They were oxidized by iodine, the ferrocenium cation, or TCNQ (7,7,8,8-tetracyano-*p*-quinodimethane) in CH<sub>2</sub>Cl<sub>2</sub> or in acetone to afford one-electron-oxidized and over-one-electron-oxidized species, [Ti(C<sub>5</sub>H<sub>5</sub>)(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)<sub>2</sub>]<sup>•+</sup>, I<sub>3</sub><sup>-</sup>, [Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)][PF<sub>6</sub>]<sup>-</sup>, [Ti(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)<sub>2</sub>]<sup>•+</sup>, I<sub>3</sub><sup>-</sup>, [Ti(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)][PF<sub>6</sub>]<sup>-</sup>, [Ti(C<sub>5</sub>H<sub>5</sub>)(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)<sub>2</sub>]<sup>•+</sup>I<sub>0.9</sub><sup>-</sup>, [Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)<sub>2</sub>][TCNQ]<sub>0.3</sub>, [Ti(C<sub>5</sub>Me<sub>5</sub>)(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)<sub>2</sub>]<sup>•+</sup>I<sub>2.4</sub><sup>-</sup>, and [Ti(C<sub>5</sub>Me<sub>5</sub>)(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)<sub>2</sub>][TCNQ]<sub>0.3</sub>, with the C<sub>8</sub>H<sub>4</sub>S<sub>8</sub> ligand-centered oxidation. They exhibited electrical conductivities of 1.6 × 10<sup>-1</sup> to 7.6 × 10<sup>-4</sup> S cm<sup>-1</sup> measured for compacted pellets at room temperature. The crystal structure of **2** was clarified to consist of isolated dimerized units of the molecules through some sulfur–sulfur nonbonded contacts: monoclinic, *P*2<sub>1</sub>/*c*, *a* = 9.534(2) Å, *b* = 18.227(2) Å, *c* = 17.775(2) Å, β = 94.39(1)°, *Z* = 4.

## Introduction

Oxidized planar [M(C<sub>3</sub>S<sub>5</sub>)<sub>2</sub>]<sup>n-</sup>-type anion complexes [M = Ni(II), Pd(II), Pt(II), and Au(III); *n* < 1; C<sub>3</sub>S<sub>5</sub><sup>2-</sup> = 4,5-disulfanyl-1,3-dithiole-2-thionate(2-)] are well-known to become good electrical conductors,<sup>1–4</sup> and some Ni(II) and Pd(II) complexes behave as superconductors.<sup>4–6</sup> Molecular interactions through many nonbonded S–S contacts among the C<sub>3</sub>S<sub>5</sub> ligands construct effective electron-conduction pathways in the solid state. Metal complexes with the C<sub>8</sub>H<sub>4</sub>S<sub>8</sub><sup>2-</sup> [2-(4,5-ethylenedithio)-1,3-dithiole-2-ylidene]-1,3-dithiole-4,5-dithiolate(2-)]<sup>7–9</sup> and (RS)<sub>2</sub>C<sub>6</sub>S<sub>6</sub><sup>2-</sup> [2-(4,5-bis(alkylthio)-1,3-dithiole-2-ylidene)-1,3-dithiole-4,5-dithiolate(2-); R = Me and Et] ligands<sup>10–13</sup> as a

further π-electron-delocalized system were also reported to exhibit high electrical conductivities. Metal complexes containing both organic groups and the C<sub>3</sub>S<sub>5</sub><sup>2-</sup> or C<sub>8</sub>H<sub>4</sub>S<sub>8</sub><sup>2-</sup> ligand are expected to form molecular inorganic–organic composites having columnar and/or layered structures constructed with nonbonded S–S interactions among the sulfur-rich dithiolate ligands separated by organic groups, leading to unique electrical conductors. Several C<sub>3</sub>S<sub>5</sub>–metal complexes containing cyclopentadienyl and pentamethylcyclopentadienyl groups have been studied.<sup>14–23</sup> However, there has been no evaluation on an electrical conductor. Oxidized C<sub>5</sub>H<sub>5</sub>– and C<sub>5</sub>Me<sub>5</sub>–metal complexes with the further π-electron-extended C<sub>8</sub>H<sub>4</sub>S<sub>8</sub> ligand are expected to form effective molecular packings through many S–S contacts in the solid state and to become good electrical conductors, although they have nonplanar geometries. Previously

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we found a high electrical conductivity of the oxidized species  $[\text{Co}(\text{C}_5\text{H}_5)(\text{C}_8\text{H}_4\text{S}_8)]\cdot\text{I}_3$  despite its bulky geometry.<sup>24</sup>

In this work, some  $\text{C}_5\text{H}_5^-$  and  $\text{C}_5\text{Me}_5^-$ -titanium(IV) complexes with the  $\text{C}_8\text{H}_4\text{S}_8$  ligand have been prepared and their electrochemistry and spectroscopies have been studied. One-electron- and over-one-electron-oxidized species of these complexes have exhibited electrical conductivities of  $1.6 \times 10^{-1}$  to  $7.6 \times 10^{-4} \text{ S cm}^{-1}$  for the compacted pellets at room temperature. The crystal structure of  $\text{Ti}(\text{C}_5\text{Me}_5)_2(\text{C}_8\text{H}_4\text{S}_8)$  has been clarified by the X-ray structural analysis.

## Experimental Section

**Starting Compounds.** 4,5-Bis(cyanoethylthio)-1,3-dithiole-2-[(4,5-ethylenedithio)-1,3-dithiole-2-ylidene],  $\text{C}_8\text{H}_4\text{S}_8(\text{CH}_2\text{CH}_2\text{CN})_2$ ,<sup>9</sup> and  $[\text{Fe}(\text{C}_5\text{H}_5)_2][\text{PF}_6]^{25}$  were prepared according to the literature.  $\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2$ ,  $\text{Ti}(\text{C}_5\text{Me}_5)_2\text{Cl}_2$ ,  $\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_3$ , and  $\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_3$  are commercially available.

**$\text{Ti}(\text{C}_5\text{H}_5)_2(\text{C}_8\text{H}_4\text{S}_8)$  (1).** All of the following reactions were performed under an argon atmosphere. To a THF (30 mL) solution of  $\text{C}_8\text{H}_4\text{S}_8(\text{CH}_2\text{CH}_2\text{CN})_2$  (180 mg, 0.39 mmol) was added with vigorous stirring an  $\text{Et}_2\text{O}$  (0.7 mL) solution of methyllithium (concentration  $1.14 \text{ mol L}^{-1}$ ) for 10 min to afford a dark red solution of  $\text{Li}_2\text{C}_8\text{H}_4\text{S}_8$ , which was stirred for 30 min. To the solution was added a THF (5 mL) solution of  $\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2$  (110 mg, 0.45 mmol), and the solution was stirred for 12 h at room temperature. To the black green suspended solution was added  $\text{CH}_2\text{Cl}_2$  (1000 mL), and the solution was filtered through silica gel. Concentration of the green brown filtrate was followed by addition of hexane to afford a dark brown precipitate of **1**, which was washed with  $\text{CHCl}_3$ , acetone, and  $\text{Et}_2\text{O}$  and dried in vacuo (170 mg, 0.31 mmol, 79%). Anal. Calcd for  $\text{C}_{18}\text{H}_{18}\text{S}_8\text{Ti}$ : C, 40.43; H, 2.64; S, 47.97. Found: C, 40.60; H, 2.85; S, 47.69. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3110, 1437, 1365, 1288, 1017, 900, 820, 770.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 6.04 (s, H5), 5.72 (s, H5), 3.30 (s, H2), 3.29 (s, H2).

**$\text{Ti}(\text{C}_5\text{Me}_5)_2(\text{C}_8\text{H}_4\text{S}_8)$  (2).** To a THF (30 mL) solution of  $\text{C}_8\text{H}_4\text{S}_8(\text{CH}_2\text{CH}_2\text{CN})_2$  (120 mg, 0.25 mmol) was added with vigorous stirring an MeOH (0.76 mL) solution containing  $\text{NMe}_4\text{OH}$  (0.19 mg, 0.51 mmol) to afford immediately red brown solids of  $[\text{NMe}_4]_2[\text{C}_8\text{H}_4\text{S}_8]$ . They were collected by filtration and washed with THF. They were suspended in THF (50 mL) and followed by addition of a THF (10 mL) solution of  $\text{Ti}(\text{C}_5\text{Me}_5)_2\text{Cl}_2$  (100 mg, 0.26 mmol). The suspended solution was stirred for 72 h in the dark. To the solution of the reaction mixtures was added  $\text{Et}_2\text{O}$  (200 mL), and the resulting solution was filtered through silica gel. To the filtrate was added hexane (100 mL), and the solution was allowed to stand in a refrigerator overnight to give black microcrystals of **2**. They were washed with  $\text{Et}_2\text{O}$  and dried in vacuo (81 mg, 0.12 mmol, 49%). Anal. Calcd for  $\text{C}_{28}\text{H}_{34}\text{S}_8\text{Ti}$ : C, 49.83; H, 5.08. Found: C, 50.02; H, 5.13. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 2902, 1441, 1410, 1375, 1286, 1165, 1018, 900, 770.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 3.27 (s, H4), 1.90 (s, H30).

**$[\text{NMe}_4][\text{Ti}(\text{C}_5\text{H}_5)(\text{C}_8\text{H}_4\text{S}_8)_2]$  (3).** Red brown solids of  $[\text{NMe}_4]_2[\text{C}_8\text{H}_4\text{S}_8]$  obtained by the reaction of  $\text{C}_8\text{H}_4\text{S}_8(\text{CH}_2\text{CH}_2\text{CN})_2$  (470 mg, 1.0 mmol) with  $\text{NMe}_4\text{OH}$  (2.2 mmol) as described for the preparation of **2** were suspended in THF (50 mL). To the suspended solution was added  $\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_3$  (130 mg, 0.58 mmol), and the solution was stirred for 3 h to yield a dark green precipitate. To the reaction solution containing the precipitate was added acetone (1500 mL) further to remove  $\text{NMe}_4\text{Cl}$ , and the solution was filtered. The dark green filtrate was condensed to 100 mL under reduced pressure to afford a dark green precipitate. It was filtered, further washed with MeOH to remove  $\text{NMe}_4\text{Cl}$  and with  $\text{Et}_2\text{O}$ , and dried in vacuo (350 mg, 0.39 mmol, 79%). Anal. Calcd for  $\text{C}_{25}\text{H}_{25}\text{NS}_{16}\text{Ti}$ : C, 33.35; H, 2.80; N, 1.56. Found: C, 33.36; H, 3.01; N, 1.56. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 1476, 1407, 1324, 1284, 1015, 945, 900, 808, 768.  $^1\text{H NMR}$  (acetone- $d_6$ ,  $\delta$ , ppm): 6.05 (s, H5), 3.46 (s, H12), 3.39 (s, H8).

**$[\text{NMe}_4][\text{Ti}(\text{C}_5\text{Me}_5)(\text{C}_8\text{H}_4\text{S}_8)_2]$  (4).** To a THF (50 mL) solution suspended with the solids of  $[\text{NMe}_4]_2[\text{C}_8\text{H}_4\text{S}_8]$  prepared by the reaction of  $\text{C}_8\text{H}_4\text{S}_8(\text{CH}_2\text{CH}_2\text{CN})_2$  (93 mg, 0.20 mmol) with  $\text{NMe}_4\text{OH}$  (0.42 mmol) as described for **2** was added with stirring a THF (10 mL) solution of  $\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_3$  (34 mg, 0.12 mmol), and the solution was stirred for 3 h to give black solids. From the solution was isolated **4** as dark green solids by procedures similar to those described for **3** (48 mg, 0.050 mmol, 50%). Anal. Calcd for  $\text{C}_{30}\text{H}_{35}\text{NS}_{16}\text{Ti}$ : C, 37.13; H, 3.64; N, 1.44. Found: C, 37.16; H, 3.41; N, 1.56. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 2901, 1476, 1372, 1324, 1285, 1170, 1022, 944, 898, 768.  $^1\text{H NMR}$  ( $\text{DMSO}-d_6$ ,  $\delta$ , ppm): 3.37 (s, H8), 3.09 (s, H12), 1.96 (s, H15).

**$[\text{Ti}(\text{C}_5\text{H}_5)_2(\text{C}_8\text{H}_4\text{S}_8)]\cdot\text{I}_3$  (5).** To a  $\text{CH}_2\text{Cl}_2$  (100 mL) solution of iodine (100 mg, 0.41 mmol) was added with stirring a  $\text{CH}_2\text{Cl}_2$  (5 mL) solution of **1** (78 mg, 0.15 mmol) to afford immediately black microcrystals of **5**. They were collected by filtration, washed with  $\text{CH}_2\text{Cl}_2$ , and dried in vacuo (110 mg, 0.12 mmol, 80%). Anal. Calcd for  $\text{C}_{18}\text{H}_{14}\text{I}_3\text{S}_8\text{Ti}$ : C, 23.62; H, 1.54. Found: C, 23.66; H, 1.54. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 1432, 1363, 1311, 1215, 1012, 908, 825.

**$[\text{Ti}(\text{C}_5\text{H}_5)_2(\text{C}_8\text{H}_4\text{S}_8)][\text{PF}_6]$  (6).** To a  $\text{CH}_2\text{Cl}_2$  (100 mL) solution of  $[\text{Fe}(\text{C}_5\text{H}_5)_2][\text{PF}_6]$  (320 mg, 0.97 mmol) was added with stirring a  $\text{CH}_2\text{Cl}_2$  (5 mL) solution of **1** (100 mg, 0.19 mmol) to afford immediately black microcrystals of **6**. They were collected by filtration, washed with  $\text{CH}_2\text{Cl}_2$ , and dried in vacuo (98 mg, 0.14 mmol, 73%). Anal. Calcd for  $\text{C}_{18}\text{H}_{14}\text{F}_6\text{PS}_8\text{Ti}$ : C, 31.18; H, 2.08. Found: C, 31.15; H, 2.32. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 1435, 1371, 1317, 833, 557.

**$[\text{Ti}(\text{C}_5\text{Me}_5)_2(\text{C}_8\text{H}_4\text{S}_8)]\cdot\text{I}_3$  (7).** To a  $\text{CH}_2\text{Cl}_2$  (100 mL) solution of  $\text{I}_2$  (130 mg, 0.50 mmol) were added with stirring powdered solids of **2** (68 mg, 0.10 mmol), and the suspended solution was stirred for 1 h. Black solids of **7** were collected by filtration, washed with a large amount of  $\text{CH}_2\text{Cl}_2$ , and dried in vacuo (40 mg, 0.038 mmol, 38%). Anal. Calcd for  $\text{C}_{28}\text{H}_{34}\text{I}_3\text{S}_8\text{Ti}$ : C, 31.86; H, 3.25. Found: C, 31.88; H, 3.20. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 2902, 1376, 1337, 1286, 1231, 1014, 958.

**$[\text{Ti}(\text{C}_5\text{Me}_5)_2(\text{C}_8\text{H}_4\text{S}_8)][\text{PF}_6]$  (8).** To a  $\text{CH}_2\text{Cl}_2$  (50 mL) solution of  $[\text{Fe}(\text{C}_5\text{H}_5)_2][\text{PF}_6]$  (86 mg, 0.26 mmol) were added with stirring powdered solids of **2** (39 mg, 0.058 mmol). The suspended solution was stirred for 1 h to afford black solids of **8**. They were collected by filtration, washed with  $\text{CH}_2\text{Cl}_2$ , and dried in vacuo (59 mg, 0.074 mmol, 73%). Anal. Calcd for  $\text{C}_{26}\text{H}_{34}\text{F}_6\text{PS}_8\text{Ti}$ : C, 41.02; H, 4.18. Found: C, 41.08; H, 4.20. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 2902, 1456, 1404, 1118, 958, 837, 768, 554.

**$[\text{Ti}(\text{C}_5\text{H}_5)(\text{C}_8\text{H}_4\text{S}_8)_2]\cdot\text{I}_{0.9}$  (9).** To an acetone (100 mL) solution of **3** (86 mg, 0.096 mmol) was added with stirring a  $\text{CH}_2\text{Cl}_2$  (20 mL) solution of  $\text{I}_2$  (160 mg, 0.62 mmol) to afford immediately black solids of **9**. They were collected by filtration, washed with acetone and with MeOH to remove  $\text{NMe}_4\text{I}$ , and dried in vacuo (62 mg, 0.066 mmol, 70%). Anal. Calcd for  $\text{C}_{21}\text{H}_{13}\text{I}_{0.9}\text{S}_{16}\text{Ti}$ : C, 26.82; H, 1.39. Found: C, 27.24; H, 1.57. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 1365, 1316, 1281, 1202, 823.

**$[\text{Ti}(\text{C}_5\text{H}_5)(\text{C}_8\text{H}_4\text{S}_8)_2][\text{TCNQ}]_{0.3}$  (10).** To an acetone (100 mL) solution of **3** (90 mg, 0.10 mmol) was added with stirring a THF (20 mL) solution of TCNQ (100 mg, 0.51 mmol) to afford immediately black microcrystals of **10**. They were collected by filtration, washed with THF, and dried in vacuo (72 mg, 0.082 mmol, 82%). Anal. Calcd for  $\text{C}_{24.6}\text{H}_{14.2}\text{N}_{1.2}\text{S}_{16}\text{Ti}$ : C, 33.29; H, 1.61; N, 1.89. Found: C, 33.21; H, 1.70; N, 1.57. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 2175, 2149, 1430, 1374, 1320, 1286, 1207, 816.

**$[\text{Ti}(\text{C}_5\text{Me}_5)(\text{C}_8\text{H}_4\text{S}_8)_2]\cdot\text{I}_{2.4}$  (11).** A  $\text{CH}_2\text{Cl}_2$  (20 mL) solution of  $\text{I}_2$  (130 mg, 0.52 mmol) was added with stirring to a  $\text{CH}_2\text{Cl}_2$  (100 mL) solution of **4** (100 mg, 0.11 mmol) to afford immediately black microcrystals of **11**. They were collected by filtration, washed with  $\text{CH}_2\text{Cl}_2$ , and further with MeOH to remove  $\text{NMe}_4\text{I}$ , and dried in vacuo (70 mg, 0.059 mmol, 55%). Anal. Calcd for  $\text{C}_{26}\text{H}_{23}\text{I}_{2.4}\text{S}_{16}\text{Ti}$ : C, 26.00; H, 1.93. Found: C, 26.03; H, 1.83. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 2902, 1441, 1372, 1322, 1285, 1200, 1169, 1017, 962, 774.

**$[\text{Ti}(\text{C}_5\text{Me}_5)(\text{C}_8\text{H}_4\text{S}_8)_2][\text{TCNQ}]_{0.3}$  (12).** To a  $\text{CH}_2\text{Cl}_2$  (50 mL) solution of **4** (52 mg, 0.054 mmol) was added with stirring a THF (10 mL) solution of TCNQ (60 mg, 0.29 mmol) to afford immediately black microcrystals of **12**. They were collected by filtration, washed with THF and MeOH, and dried in vacuo (39 mg, 0.041 mmol, 75%). Anal. Calcd for  $\text{C}_{29.6}\text{H}_{24.2}\text{N}_{1.2}\text{S}_{16}\text{Ti}$ : C, 37.12; H, 2.55; N, 1.76. Found: C, 37.55; H, 2.60; N, 1.88. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 2902, 2175, 2150, 1567, 1430, 1376, 1321, 1284, 1204, 1170, 1020, 942, 828, 774.

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**Table 1.** Crystallographic Data for **2**

chem formula	C <sub>28</sub> H <sub>34</sub> S <sub>8</sub> Ti	fw	647.96
<i>a</i>	9.534(2) Å	space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)
<i>b</i>	18.227(2) Å	<i>T</i>	23 °C
<i>c</i>	17.775(2) Å	<i>λ</i>	0.71069 Å
<i>β</i>	94.39(1)°	<i>ρ</i> <sub>calcd</sub>	1.456 g cm <sup>-3</sup>
<i>V</i>	3079.7(6) Å <sup>3</sup>	<i>μ</i>	8.4 cm <sup>-1</sup>
<i>Z</i>	4	<i>R</i> <sup>a</sup>	0.036
		<i>R</i> <sub>w</sub> <sup>a</sup>	0.040

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}; w^{-1} = \sigma^2(F_o) + 0.0001 F_o^2.$$

**Physical Measurements.** Electronic absorption, IR, ESR,<sup>26</sup> and powder reflectance spectra<sup>27</sup> were recorded as described previously. <sup>1</sup>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. Line shape analyses of temperature-dependent <sup>1</sup>H NMR spectra were performed by computer simulation based on the literature equation for the fluxional system.<sup>28,29</sup> Raman spectra were measured for compacted pellets using JASCO R-800 and Nipponbunko NR-1800 laser-Raman spectrophotometers at the Graduate School of Science, Osaka University. Cyclic voltammograms of the complexes were measured using [NBu<sub>4</sub>][ClO<sub>4</sub>] or [NBu<sub>4</sub>][PF<sub>6</sub>] as an electrolyte, as described previously.<sup>30</sup> Electrical resistivities of the complexes were measured for compacted pellets by the conventional two-probe method at room temperature.<sup>31</sup>

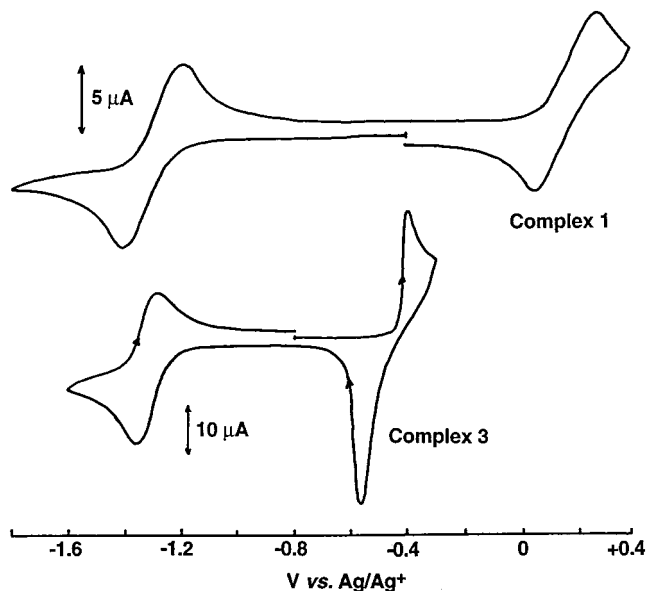
**X-ray Data Collection and Structure Determination of 2.** Diffraction data were collected on a Rigaku AFC-7R four-circle diffractometer with graphite-monochromated Mo Kα (*λ* = 0.71069 Å) radiation at the Graduate School of Science, Osaka University. Crystallographic data are summarized in Table 1.

The unit-cell parameters were determined from 25 independent reflections with 2θ over the range of 26.1–26.9°. 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, but not for absorption (transmission factors, 0.935–0.998).

The structure was solved by the direct method (SHELXS-86)<sup>32</sup> and refined on *F* by the full-matrix least-squares technique. All of 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<sup>33</sup> on an SGI O<sub>2</sub> workstation at the Graduate School of Science, Osaka University. Atomic scattering factors were taken from the usual sources.<sup>34</sup> Figures 2 and 3 were drawn with a local version of ORTEP II.<sup>35</sup>

## Results and Discussion

**Electrochemistry of Complexes 1–4.** Figure 1 shows cyclic voltammograms of **1** in CH<sub>2</sub>Cl<sub>2</sub> and **3** in acetone. Complex **1** is reduced at –1.40 V (vs Ag/Ag<sup>+</sup>). This is ascribed to the Ti(IV) to Ti(III) process, since it is well-known that the reversible one-



**Figure 1.** Cyclic voltammograms of complexes **1** ( $1.0 \times 10^{-3}$  mol L<sup>-1</sup>, in CH<sub>2</sub>Cl<sub>2</sub>) and **3** ( $2.0 \times 10^{-3}$  mol L<sup>-1</sup>, in acetone) at room temperature. Supporting electrolyte: 0.1 mol L<sup>-1</sup> [NBu<sub>4</sub>][ClO<sub>4</sub>]. Sweep rate: 0.1 V s<sup>-1</sup>.

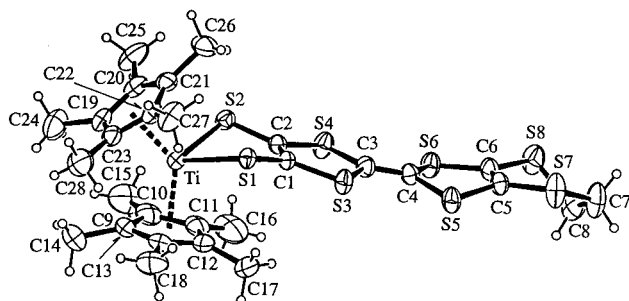
electron-reduction process takes place on the metal for Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>X<sub>2</sub> (X = Cl, Br)<sup>36</sup> and Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>-dithiolenes complexes.<sup>37,38</sup> The oxidation peak at +0.29 V is ascribed to the C<sub>8</sub>H<sub>4</sub>S<sub>8</sub> ligand-centered oxidation, as low oxidation potentials observed for other C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>-metal complexes.<sup>8,9,24,30</sup> This oxidation peak potential is appreciably lower than that (0.50 V vs Ag/Ag<sup>+</sup>) of Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(C<sub>3</sub>S<sub>5</sub>).<sup>16,17</sup> Complex **2** is reduced at –1.63 V corresponding to the Ti(IV) to Ti(III) process and exhibits a peak potential at +0.19 V for the C<sub>8</sub>H<sub>4</sub>S<sub>8</sub> ligand oxidation measured in CH<sub>2</sub>Cl<sub>2</sub>. However, they occur at somewhat low potentials compared with **1** because of the presence of more electron-releasing C<sub>5</sub>Me<sub>5</sub> groups. Complex **3** having two electron-releasing C<sub>8</sub>H<sub>4</sub>S<sub>8</sub> ligands exhibits redox waves at an appreciably low potential (–0.39 V) for the C<sub>8</sub>H<sub>4</sub>S<sub>8</sub> ligand oxidation in acetone, although the Ti(IV)/Ti(III) reduction occurs at a potential (–1.36 V) similar to that of **1**. Their potentials are also low compared with those of Ti(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(C<sub>3</sub>S<sub>5</sub>) (–0.99 and +0.30 V vs Ag/Ag<sup>+</sup>).<sup>19</sup> The C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>-metal complexes are likely to be oxidized at low potentials compared with C<sub>3</sub>S<sub>5</sub>-metal complexes.<sup>8,9,24,30,39</sup> Complex **4** having the electron-releasing C<sub>5</sub>Me<sub>5</sub> group exhibits a rather high oxidation potential (–0.29 V in acetone) for the C<sub>8</sub>H<sub>4</sub>S<sub>8</sub> ligand compared with that of **3**.

**Crystal Structure of Complex 2 and Molecular Geometries of Complexes 1–4.** Figure 2 shows the molecular geometry of **2** together with the atom-numbering scheme. Selected bond distances and angles are summarized in Table 2. Two π-bonded C<sub>5</sub>Me<sub>5</sub> rings and two sulfur atoms construct a pseudotetrahedral coordination sphere of the titanium(IV) ion. Methyl groups deviate considerably out of each cyclopentadienyl plane; the largest out-of-plane deviation [0.492(8) Å] is observed for the C(14) atom, C(24) and C(28) atoms being deviated from the plane [0.350(8) and 0.316(7) Å, respectively] because of

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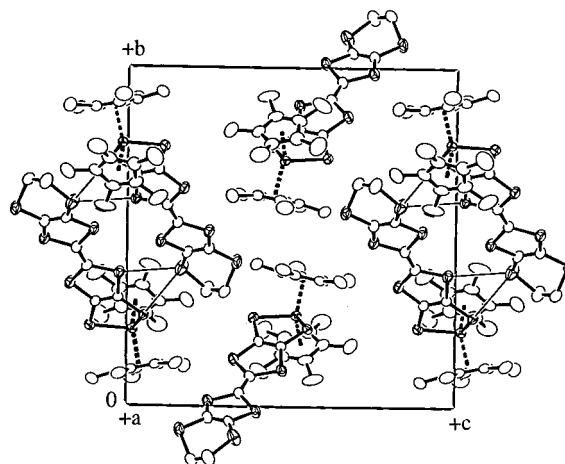
**Figure 2.** Molecular geometry of **2** together with the atomic numbering scheme. Thermal ellipsoids are shown at the 50% probability level.

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for **2**

Ti–S(1)	2.455(1)	Ti–S(2)	2.459(1)	Ti–C(9)	2.432(3)
Ti–C(10)	2.390(4)	Ti–C(11)	2.460(4)	Ti–C(12)	2.458(4)
Ti–C(13)	2.398(4)	Ti–C(19)	2.439(3)	Ti–C(20)	2.415(4)
Ti–C(21)	2.435(4)	Ti–C(22)	2.416(3)	Ti–C(23)	2.445(4)
S(1)–C(1)	1.727(3)	S(2)–C(2)	1.726(3)	S(3)–C(1)	1.761(3)
S(3)–C(3)	1.759(3)	S(4)–C(2)	1.760(3)	S(4)–C(3)	1.743(4)
S(5)–C(4)	1.756(3)	S(5)–C(5)	1.760(3)	S(6)–C(4)	1.758(3)
S(6)–C(6)	1.747(3)	S(7)–C(5)	1.736(4)	S(7)–C(7)	1.799(5)
S(8)–C(6)	1.744(3)	S(8)–C(8)	1.805(4)	C(1)–C(4)	1.356(4)
C(3)–C(4)	1.343(4)	C(5)–C(6)	1.330(5)	C(7)–C(8)	1.487(6)
S(1)–Ti–S(2)	83.40(3)	Ti–S(1)–C(1)	97.4(1)		
Ti–S(2)–C(2)	96.8(1)	C(1)–S(3)–C(3)	95.5(2)		
C(2)–S(4)–C(3)	95.9(2)	C(4)–S(5)–C(5)	93.6(2)		
C(4)–S(6)–C(6)	93.8(2)	C(5)–S(7)–C(7)	104.3(2)		
C(6)–S(8)–C(8)	97.8(2)	S(1)–C(1)–C(2)	122.8(3)		
S(3)–C(1)–C(2)	116.8(2)	S(2)–C(2)–C(1)	124.5(3)		
S(4)–C(2)–C(1)	116.9(3)	S(3)–C(3)–S(4)	114.6(2)		
S(5)–C(4)–S(6)	113.9(2)	S(5)–C(5)–C(6)	116.9(3)		
S(7)–C(5)–C(6)	128.2(3)	S(6)–C(6)–C(5)	117.9(3)		
S(8)–C(6)–C(5)	123.1(3)	S(7)–C(7)–C(8)	116.9(3)		
S(8)–C(8)–C(7)	113.5(3)				

repulsion between the cyclopentadienyl rings. C(16) and C(17) atoms in the vicinity of the dithiolene ligand also deviate from the plane [0.306(9) and 0.273(9) Å, respectively], while the deviations of the other methyl carbon atoms are 0.08–0.16 Å from the plane. Two C<sub>5</sub>Me<sub>5</sub> rings make a dihedral angle of 44.2(2)°. These findings resemble those of Ti(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(C<sub>3</sub>S<sub>5</sub>).<sup>19</sup> Ti–S distances [2.455(1), 2.459(1) Å] are close to those of Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(C<sub>3</sub>S<sub>5</sub>) [2.431(2) Å]<sup>17</sup> and Ti(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(C<sub>3</sub>S<sub>5</sub>) [2.25(9), 2.46(8) Å].<sup>19</sup> The complex exhibits a characteristic folding of the TiS<sub>2</sub>C<sub>2</sub> plane along the S(1)–S(2) axis by a value of 35.9°, which is close to that of Ti(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(C<sub>3</sub>S<sub>5</sub>) [38.0(9), 38.3(9)°].<sup>19</sup> They are considerably small compared with those of Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>–(dithiolene) complexes; Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(C<sub>3</sub>S<sub>5</sub>) [47.4(3)°], Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>–(C<sub>4</sub>H<sub>4</sub>S<sub>4</sub>) [49.2(1), 51.2(1)°],<sup>17</sup> and Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(S<sub>2</sub>C<sub>2</sub>(CN)<sub>2</sub>) [43°].<sup>40</sup> This is ascribed to an increased electron density on the metal center caused by the more electron-releasing C<sub>5</sub>Me<sub>5</sub> ligand.<sup>19,41</sup> S(3), S(4), S(5), S(6), C(3), and C(4) atoms are nearly coplanar (±0.03 Å), the other sulfur atoms deviating to the same side of the best plane by 0.17–0.92 Å. The planes formed by atoms S(1), S(2), S(3), S(4), C(1), and C(2) and by S(5), S(6), C(5), and C(6) make angles of 3.6° and 17.1°, respectively, with the central plane of the tetrathiafulvalene skeleton. This tub conformation is similar to those of C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>(CH<sub>2</sub>CH<sub>2</sub>CN)<sub>2</sub><sup>9</sup> and tetrakis(methylthio)tetrathiafulvalene.<sup>42</sup>

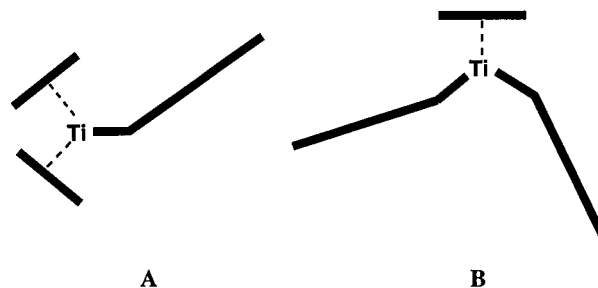
The packing diagram of the complex molecule is shown in Figure 3. Two molecules related to each other with a center of



**Figure 3.** Packing diagram of **2**. Fine lines represent S–S nonbonded contacts less than 3.7 Å.

symmetry have some S–S nonbonded contacts within the sum of van der Waals radii (3.7 Å) forming a dimerized unit: S(1)–S(7') (–x, 1 – y, –z) [3.649(2) Å] and S(3)–S(7'') [3.419(1) Å]. Similar S–S contacts were observed for sulfur-rich compounds with molecular skeletons close to that of **2**: C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>(CH<sub>2</sub>CH<sub>2</sub>CN)<sub>2</sub>,<sup>9</sup> C<sub>6</sub>S<sub>4</sub>(SMe)<sub>4</sub>,<sup>42</sup> C<sub>10</sub>S<sub>8</sub>(SMe)<sub>4</sub>,<sup>43</sup> and Hg(C<sub>6</sub>S<sub>8</sub>Et<sub>2</sub>)<sub>2</sub>.<sup>10</sup> There are no significant contacts between the dimers for the present complex.

Complex **1** shows two C<sub>5</sub>H<sub>5</sub> signals at 5.72 and 6.04 δ in the <sup>1</sup>H NMR spectrum measured at 25 °C in DMSO-*d*<sub>6</sub>. This is due to the nonequivalence of the C<sub>5</sub>H<sub>5</sub> rings in conformation A, as confirmed by the above-mentioned molecular structure of complex **2**. The signals coalesce at 50 °C, resulting in a single



peak at elevated temperatures owing to rapid exchange around the folding S–S axis of the dithiolate ligand. The energy barrier for the inversion process between the folded conformations is estimated to be 12.4 kcal mol<sup>–1</sup> on the basis of the varying C<sub>5</sub>H<sub>5</sub> signals. Similar behavior was observed for several Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(dithiolate) complexes.<sup>14,17,19</sup> Complex **2** also showed two C<sub>5</sub>Me<sub>5</sub> signals (1.74 and 1.85 δ) at –80 °C in CD<sub>2</sub>Cl<sub>2</sub>, the coalescence temperature of these signals being –51 °C with the energy barrier of 6.5 kcal mol<sup>–1</sup>.

For complexes **3** and **4** having two dithiolate ligands, conformation B is reasonable, since X-ray molecular structures as the B form were determined for some [Ti(L)(dithiolate)]<sup>–</sup> (L = C<sub>5</sub>H<sub>5</sub> and C<sub>5</sub>Me<sub>5</sub>) complexes.<sup>17,44,45</sup> Although two C<sub>8</sub>H<sub>4</sub>S<sub>8</sub> ligands are expected to be magnetically inequivalent for this conformation, no separated CH<sub>2</sub> signals of the ligands were observed even at –90 °C in CD<sub>2</sub>Cl<sub>2</sub> for **3** and **4**.

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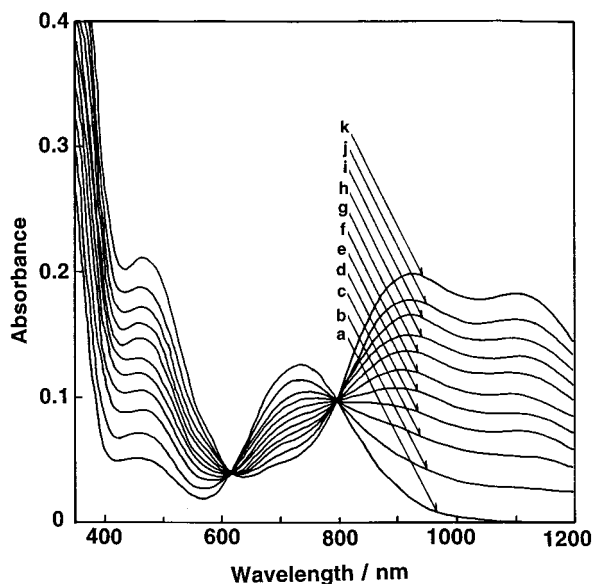
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**Figure 4.** Electronic absorption spectra of **1** ( $2.0 \times 10^{-5}$  mol L<sup>-1</sup>) in CH<sub>2</sub>Cl<sub>2</sub> in the presence of iodine. Concentration of iodine (mol L<sup>-1</sup>): (a) 0; (b)  $6.0 \times 10^{-6}$ ; (c)  $1.2 \times 10^{-5}$ ; (d)  $1.8 \times 10^{-5}$ ; (e)  $2.4 \times 10^{-5}$ ; (f)  $3.0 \times 10^{-5}$ ; (g)  $3.6 \times 10^{-5}$ ; (h)  $4.2 \times 10^{-5}$ ; (i)  $4.8 \times 10^{-5}$ ; (j)  $5.4 \times 10^{-5}$ ; (k)  $6.0 \times 10^{-5}$ .

**Spectroscopic Properties and Electrical Conductivities of the Oxidized Complexes.** As shown in Figure 4, the electronic absorption spectrum of complex **1** exhibits bands ascribed to the  $\pi$ - $\pi^*$  transitions of the C<sub>8</sub>H<sub>4</sub>S<sub>8</sub> ligand at 316 and 456 nm, as observed for Na<sub>2</sub>[C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>], [NBu<sub>4</sub>][Au(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)<sub>2</sub>],<sup>8</sup> and [NBu<sub>4</sub>]<sub>2</sub>[Pt(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)<sub>2</sub>].<sup>9</sup> Furthermore, the complex shows a ligand-to-metal  $\pi$ -d charge transfer (LMCT) band at 736 nm. Complex **2** exhibits a similar absorption spectrum, where  $\pi$ - $\pi^*$  bands occur at 332 and 448 nm and two LMCT bands at 594 and 826 nm in CH<sub>2</sub>Cl<sub>2</sub>. Complexes **3** and **4** also show two LMCT bands in the region of 600–820 nm, together with an intense  $\pi$ - $\pi^*$  band at 330 nm.

Electronic absorption spectra of **1** in CH<sub>2</sub>Cl<sub>2</sub> in the presence of various amounts of iodine as an oxidant are also displayed in Figure 4. By the addition of some amounts of iodine to the solution of **1**, the spectrum of **1** is changed with the generation of isosbestic points, resulting in the spectrum of the one-electron-oxidized [Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)<sup>+</sup> species. The LMCT band is shifted to a longer-wavelength region. On the oxidation of **2–4**, the longer-wavelength shifts of the LMCT bands were also observed.

The oxidized C<sub>8</sub>H<sub>4</sub>S<sub>8</sub> ligand is stable, as deduced from the above spectral change of **1** upon oxidation. This is in contrast to the instability of the oxidized C<sub>3</sub>S<sub>5</sub> ligand bonded with the titanium(IV) ion, as the rapid destruction was observed for the oxidation of Ti(C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>(C<sub>3</sub>S<sub>5</sub>).<sup>17,19</sup> Complexes **1** and **2** were oxidized by some oxidants to afford one-electron-oxidized species **5–8**. Complexes **3** and **4** exhibiting a very low oxidation potential were reacted with iodine to give over-one-electron-oxidized complexes **9** and **11**. They were also oxidized even by TCNQ to give 1.3-electron-oxidized species **10** and **12**.

The Raman spectrum of **5** exhibited a scattering band at 111 cm<sup>-1</sup> which is assigned to the symmetric stretching of the I<sub>3</sub><sup>-</sup> ion.<sup>46,47</sup> This indicates that **5** is a one-electron-oxidized species. In accordance with this, **5** exhibited an intense, sharp isotropic

**Table 3.** Electrical Conductivities ( $\sigma$ )<sup>a</sup>

complex	$\sigma_{RT}$ , S cm <sup>-1</sup>	complex	$\sigma_{RT}$ , S cm <sup>-1</sup>
<b>5</b>	$8.9 \times 10^{-4}$	<b>9</b>	0.16
<b>6</b>	$2.9 \times 10^{-3}$	<b>10</b>	0.12
<b>7</b>	$9.9 \times 10^{-4}$	<b>11</b>	$7.6 \times 10^{-4}$
<b>8</b>	$3.0 \times 10^{-4}$	<b>12</b>	0.055

<sup>a</sup> Measured for compacted pellets at room temperature.

ESR signal at  $g = 2.003$  (peak-to-peak line width, 3.5 mT). This signal is ascribed to the radical species of the C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>-ligand moiety, as observed for the radicals of sulfur-rich compounds: the tetrathiafulvalenium radical cation<sup>48,49</sup> and partially oxidized C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>-metal (Pt(II),<sup>9</sup> Co(III),<sup>24</sup> V(IV) and Mo(IV)<sup>39</sup>) and C<sub>3</sub>S<sub>5</sub>-metal (Co(III),<sup>50</sup> Cu(I),<sup>51</sup> Au(III),<sup>49</sup> Re(IV),<sup>52</sup> Mo(IV) and W(IV)<sup>26</sup>) complexes with the sulfur-rich ligand-centered oxidation. Complexes **6–8** also showed sharp, isotropic ESR signals ( $g = 2.004$ – $2.008$ ; line width = 1.1–2.6 mT). Thus, in these oxidized complexes the C<sub>8</sub>H<sub>4</sub>S<sub>8</sub> ligand-centered oxidation is likely to occur. Complexes **9** and **11** also showed a Raman band at 111 and 110 cm<sup>-1</sup>, respectively, indicating the presence of the I<sub>3</sub><sup>-</sup> ion. Complexes **10** and **12** contain the TCNQ<sup>•-</sup> radical anion as the (TCNQ)<sub>2</sub><sup>2-</sup> dimer, since they showed the IR absorption frequencies of 2175 and 2150 cm<sup>-1</sup> assigned to the  $\nu_{CN}$  mode, as observed for Li[TCNQ] and deduced from a linear relationship for  $\nu_{CN}$  frequency vs fractional charge of TCNQ.<sup>53,54</sup> The absorption at 828 cm<sup>-1</sup> for **10** ascribed to the C–H out-of-plane frequency also indicates the presence of the TCNQ<sup>•-</sup> radical anion.<sup>55,56</sup>

Electrical conductivities of the oxidized complexes measured at room temperature for compacted pellets are listed in Table 3. Complexes **1–4** are essentially insulators, while all of the oxidized species **5–12** behave as semiconductors. Conductivities of complexes **5–8** having two C<sub>5</sub>H<sub>5</sub> or two C<sub>5</sub>Me<sub>5</sub> groups are not high. This seems to come from an inadequate molecular packing in the solid state, which results in ineffective S $\cdots$ S nonbonded interactions among the C<sub>8</sub>H<sub>4</sub>S<sub>8</sub> ligand moieties. On the other hand, **9**, **10**, and **12** exhibit high conductivities, which are due to an effective molecular packing favorable for the formation of electron-conduction pathways, although **11** has a lower conductivity. Considering the molecular geometry of [Ti(L)(dithiolate)<sub>2</sub>]<sup>-</sup> (L = C<sub>5</sub>H<sub>5</sub> and C<sub>5</sub>Me<sub>5</sub>) complexes,<sup>17,44,45</sup> an effective packing diagram of the [Ti(C<sub>5</sub>H<sub>5</sub>)(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)<sub>2</sub>] moieties may be assumed. Previously, the one-electron-oxidized species, [Co(C<sub>5</sub>H<sub>5</sub>)(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)<sup>+</sup> salts, showed a high conductivity (0.16–0.19 S cm<sup>-1</sup> at room temperature),<sup>24</sup> and [V(O)(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)<sub>2</sub>]<sup>m-</sup> and [Mo(O)(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)<sub>2</sub>]<sup>m-</sup> ( $m, n < 1$ ) complexes having a coordination geometry around the metal ion similar to those of **9–12** also exhibit high conductivities (0.29–5.9 S cm<sup>-1</sup> at room temperature).<sup>39</sup> Thus, these findings suggest the usefulness of

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the C<sub>8</sub>H<sub>4</sub>S<sub>8</sub> ligand for the construction of the electron-conduction pathways of various metal complexes.

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**Supporting Information Available:** An X-ray crystallographic file in CIF format for the structure determination of **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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