© 2004 The Chemical Society of Japan

Preparation and Oxidation of Pt(II) Complexes Containing Both *C*-Deprotonated 2-Phenylpyridine (ppy^-) and a Sulfur-Rich Dithiolate Ligand and X-ray Crystal Structure of $[NBu^n{}_4][Pt(ppy)(C_8H_4S_8)]$

Yusuke Suga, Motohiro Nakano, Hatsue Tamura, and Gen-etsu Matsubayashi*

Department of Applied Chemistry, Graduate School of Engineering, Osaka University,
1-16, Machikaneyama, Toyonaka, Osaka 560-0043

Received May 17, 2004; E-mail: matsu@ch.wani.osaka-u.ac.jp

$[NEt_4][Pt(ppy)(C_3S_5)]$ (ppy^- = *C*-deprotonated 2-phenylpyridine(−); $C_3S_5{}^{2-}$ = 4,5-disulfanyl-1,3-dithiole-2-thionate(2−)), $[NEt_4]$-, $[NBu^n{}_4][Pt(ppy)(C_8H_4S_8)]$ ($C_8H_4S_8{}^{2-}$ = 2-{(4,5-ethylenedithio)-1,3-dithiole-2-ylidene}-1,3-dithiole-4,5-dithiolate(2−)) and $[NEt_4][Pt(ppy)(C_{10}\text{–}C_6S_8)]$ ($C_{10}\text{–}C_6S_8{}^{2-}$ = 2-{bis(decylthio)-1,3-dithiole-2-ylidene}-1,3-dithiole-4,5-dithiolate(2−)) were prepared. They showed an intense electronic absorption band due to an intramolecular mixed metal/dithiolate ligand-to-ppy ligand charge transfer transition, which is somewhat sensitive to the solvent. The complexes exhibited first oxidation potentials of −0.27 to +0.02 V (vs Ag/Ag^+) due to the dithiolate ligand-centered oxidation. They were oxidized by TCNQ and iodine to afford [Pt(ppy)(L)] and $[Pt(ppy)(L)](I_{1.0\text{–}4.2})$ (L = $C_3S_5{}^{2-}$, $C_8H_4S_8{}^{2-}$, and $C_{10}\text{–}C_6S_8{}^{2-}$). Electrical conductivities of the oxidized $C_8H_4S_8$- and $C_{10}\text{–}C_6S_8$-species measured for compacted pellets at room temperature were 6.2×10^{-6}–7.8×10^{-3} $S\,cm^{-1}$, while those of the oxidized C_3S_5-species were very low [$(3.8\text{–}6.2) \times 10^{-9}$ $S\,cm^{-1}$]. The X-ray crystal structure of $[NBu^n{}_4][Pt(ppy)(C_8H_4S_8)]$ was clarified.

Metal complexes with sulfur-rich dithiolate ligands, such as $C_3S_5{}^{2-}$ [4,5-disulfanyl-1,3-dithiole-2-thionate(2−)], $C_8H_4S_8{}^{2-}$ [2-{(4,5-ethylenedithio)-1,3-dithiole-2-ylidene}-1,3-dithiole-4,5-dithiolate(2−)] and related anions, are of much interest in their oxidized states due to their electrical and magnetic properties.[1–7] For these physical properties, the molecular packings and nonbonding sulfur–sulfur contacts of the complexes in the solid state are important.

Planar metal complexes with unsymmetrical coordinating ligands may form unique molecular packings in the solid state through the polar property around the metal ion. In addition, in the sulfur-rich dithiolate metal complexes nonbonding sulfur–sulfur contacts also affect greatly the molecular arrangements. Planar metal complexes of the [M(N–N)(S–S)] type (M = Pd^{II} and Pt^{II}) having an electron-donating dithiolate ($S\text{–}S^{2-}$) ligand and a π-electron-accepting diimine (N–N) ligand are polarized around the metal ion between these ligands.[8–14] For planar [M(N–C)(S–S)] ($N\text{–}C^-$ = *C*-deprotonated 2-phenylpyridine(−) (ppy^-)) complexes one may also expect the similar polarized property around the metal ion.[14] Recently, we reported several polarized metal complexes, [M(diimine)(sulfur-rich dithiolate)] (M = Pd^{II} and Pt^{II})[15–17] and $[Au^{III}$(ppy)(sulfur-rich dithiolate)], and their oxidized complexes as electrical conductors.[18,19] In their oxidized species, many sulfur–sulfur contacts form the electron-conduction pathways in the solid state. Furthermore, the association of long alkyl chains in the solid state may also assist unique molecular arrangements.[20–23] We reported some sulfur-rich dithiolato–Pt^{II} complexes having long alkyl chains in the ligands and their oxidized species behaving as electrical conductors.[15,24] Thus, polarized ppy–Pt^{II} complexes with a sulfur-rich dithiolate ligand having long alkyl chains are of interest.

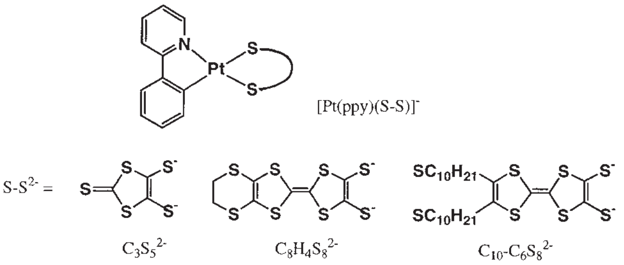

Chart 1.

In this work, Pt^{II}-complexes of the type of [Pt(ppy)(sulfur-rich dithiolate)]$^-$ (sulfur-rich dithiolate = $C_3S_5{}^{2-}$, $C_8H_4S_8{}^{2-}$ and $C_{10}\text{–}C_6S_8{}^{2-}$ (2-{bis(decylthio)-1,3-dithiole-2-ylidene}-1,3-dithiole-4,5-dithiolate(2−))) (Chart 1) and their oxidized species have been prepared. Spectroscopic and electrochemical properties of the complexes and electrical conductivities of their oxidized species, together with the X-ray crystal structure of $[NBu^n{}_4][Pt(ppy)(C_8H_4S_8)]$, are described.

Experimental

Preparation. (*C*-Deprotonated 2-phenylpyridine)chloroplatinum(II), $[\{Pt(ppy)Cl\}_2]$, was prepared according to the literature procedure with little modification.[25] $C_3S_5(CH_2CH_2CN)_2$,[26] $C_8H_4S_8(CH_2CH_2CN)_2$[27–29] and $(C_{10}H_{21})_2C_6S_8(CH_2CH_2COOEt)_2$ $[C_{10}\text{–}C_6S_8(CH_2CH_2COOEt)_2]$,[24] as pro-ligand compounds of $C_3S_5{}^{2-}$, $C_8H_4S_8{}^{2-}$ and $C_{10}\text{–}C_6S_8{}^{2-}$ dithiolate anions, respectively, were also prepared by the literature methods. 7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ) was commercially available.

$[NEt_4][Pt(ppy)(C_3S_5)]$ (1). All the following reactions were

Published on the web October 9, 2004; DOI 10.1246/bcsj.77.1877

performed under an argon atmosphere. Sodium metal (62 mg, 2.7 mmol) and $C_3S_5(CH_2CH_2CN)_2$ (160 mg, 0.52 mmol) were dissolved in ethanol (90 mL). To the solution of $Na_2[C_3S_5]$ was added a dimethyl sulfoxide (1.0 mL) solution of $[\{Pt(ppy)Cl\}_2]$ (200 mg, 0.26 mmol) and NEt_4Br (440 mg, 2.1 mmol) and the solution was stirred for 3 h at room temperature. The resulting red violet solids of **1** were collected by filtration, washed with methanol, and dried in vacuo (15% yield). Calcd for $C_{22}H_{28}N_2PtS_5$: C, 39.10; H, 4.18; N, 4.14%. Found: C, 38.94; H, 4.22; N, 4.19%. ^{1}H NMR ([D$_6$]DMSO) δ 1.15 (t, 12H), 3.18 (q, 8H), 7.01 (m, 2H), 7.23 (m, 1H), 7.53 (d, 1H; $^3J(^1H–^{195}Pt)$, 40 Hz), 7.68 (d, 1H), 7.97 (t, 1H), 7.99 (d, 1H), 8.85 (d, 1H; $^3J(^1H–^{195}Pt)$, 33 Hz).

[NEt$_4$][Pt(ppy)(C$_8$H$_4$S$_8$)] (2). Similarly, red violet solids of **2** were prepared by the reaction of an ethanol (90 mL) solution of $Na_2[C_8H_4S_8]$ obtained by the reaction of sodium metal (62 mg, 2.7 mmol) and $C_8H_4S_8(CH_2CH_2CN)_2$ (250 mg, 0.52 mmol) with a dimethyl sulfoxide (1.0 mL) solution containing $[\{Pt(ppy)Cl\}_2]$ (200 mg, 0.26 mmol) and NEt_4Br (440 mg, 2.1 mmol) (85% yield). Calcd for $C_{27}H_{32}N_2PtS_8$: C, 44.33; H, 5.10; N, 2.95%. Found: C, 43.85; H, 4.88; N, 3.03%. ^{1}H NMR ([D$_6$]DMSO) δ 1.15 (t, 12H), 3.18 (q, 8H), 3.30 (s, 4H), 7.01 (m, 2H), 7.23 (m, 1H), 7.53 (d, 1H; $^3J(^1H–^{195}Pt)$, 40 Hz), 7.68 (d, 1H), 7.98 (d, 1H), 8.01 (d, 1H), 8.85 (d, 1H; $^3J(^1H–^{195}Pt)$, 33 Hz).

[NBu$^n_4$][Pt(ppy)(C$_8$H$_4$S$_8$)] (3). This was prepared by a similar procedure, using NBu_4Br instead of NEt_4Br. Red violet solids of **3** were recrystallized from methanol to afford dark violet plates suitable for X-ray structure analysis.

[NEt$_4$][Pt(ppy)(C$_{10}$–C$_6$S$_8$)] (4). This was also prepared by the reaction of an ethanol solution of $Na_2[C_{10}–C_6S_8]$ obtained by the reaction of sodium metal and $C_{10}–C_6S_8(CH_2CH_2COOEt)_2$ with a dimethyl sulfoxide solution of $[\{Pt(ppy)Cl\}_2]$ and NEt_4Br as violet solids by a similar procedure to that described for **1** (64% yield). Calcd for $C_{45}H_{70}N_2PtS_8$: C, 49.56; H, 6.47; N, 2.57%. Found: C, 49.29; H, 6.47; N, 2.64%. ^{1}H NMR ([D$_6$]DMSO) δ 0.85 (t, 6H), 1.13 (t, 12H), 1.26 (m, 28H), 1.37 (m, 10H), 1.55 (m, 4H), 2.83 (m, 4H), 3.23 (q, 8H), 6.98 (m, 2H), 7.17 (q, 1H), 7.51 (d, 1H; $^3J(^1H–^{195}Pt)$, 40 Hz), 7.64 (d, 1H), 7.94 (t, 1H), 7.96 (s, 1H), 8.83 (d, 1H; $^3J(^1H–^{195}Pt)$, 33 Hz).

[Pt(ppy)(C$_3$S$_5$)] (5). A dichloromethane (20 mL) solution of TCNQ (76 mg, 0.38 mmol) was added with stirring to a dichloromethane (20 mL) solution of **1** (50 mg, 0.074 mmol) to afford immediately black solids of **5**. They were collected by centrifugation, washed with methanol, and dried in vacuo (74% yield). Calcd for $C_{14}H_8NPtS_5$: C, 30.82; H, 1.48; N, 2.57%. Found: C, 30.64; H, 1.55; N, 2.59%.

[Pt(ppy)(C$_8$H$_4$S$_8$)] (6). Similarly, a dichloromethane (25 mL) solution of **2** (100 mg, 0.12 mmol) was reacted with a dichloromethane (30 mL) solution of TCNQ (120 mg, 0.60 mmol) to afford black solids of **6** (71% yield). Calcd for $C_{19}H_{12}NPtS_8$: C, 32.33; H, 1.71; N, 1.98%. Found: C, 32.37; H, 1.83; N, 2.17%.

[Pt(ppy)(C$_{10}$–C$_6$S$_8$)] (7). Black solids of **7** were also prepared by a reaction of **4** (100 mg, 0.090 mmol) with TCNQ (94 mg, 0.46 mmol) in a mixture of dichloromethane (20 mL) and acetonitrile (40 mL) (13% yield). Calcd for $C_{37}H_{50}NPtS_8$: C, 46.27; H, 5.25; N, 1.46%. Found: C, 45.85; H, 4.93; N, 1.87%.

[Pt(ppy)(C$_3$S$_5$)](I$_{1.0}$) (8). A dichloromethane (15 mL) solution of iodine (94 mg, 0.37 mmol) was added with stirring to a dichloromethane (15 mL) solution of **1** (50 mg, 0.073 mmol) to afford immediately black solids of **8**. They were collected by centrifugation, washed with methanol, and dried in vacuo (68% yield). Calcd for $C_{14}H_8I_{1.0}NPtS_5$: C, 24.80; H, 1.19; N, 2.08%. Found: C, 24.87; H, 1.27; N, 2.18%.

[Pt(ppy)(C$_8$H$_4$S$_8$)](I$_{4.2}$) (9). Similarly, a dichloromethane (25 mL) solution of **2** (100 mg, 0.12 mmol) was reacted with a dichloromethane (30 mL) solution of iodine (150 mg, 0.60 mmol) to afford black solids of **9** (80% yield). Calcd for $C_{19}H_{12}I_{4.2}NPtS_8$: C, 18.42; H, 0.98; N, 1.13%. Found: C, 18.16; H, 1.04; N, 1.15%.

[Pt(ppy)(C$_{10}$–C$_6$S$_8$)](I$_{3.2}$) (10). Black solids of **10** were also prepared by a reaction of **4** (100 mg, 0.090 mmol) with iodine (120 mg, 0.47 mmol) in a mixture of dichloromethane (20 mL) and acetonitrile (40 mL) (13% yield). Calcd for $C_{37}H_{50}I_{3.2}NPtS_8$: C, 32.52; H, 3.69; N, 1.03%. Found: C, 32.50; H, 3.66; N, 1.26%.

Physical Measurements. IR, electronic absorption, ESR[30] and powder reflectance spectra[24] were recorded as described previously. ^{1}H NMR spectra were recorded at 500 MHz using a JEOL-GSX 500 spectrometer, the chemical shifts being measured relative to tetramethylsilane as an internal standard.[18] Raman spectra were measured using a Nippon-bunko NR-1800 laser-Raman spectrophotometer. Cyclic voltammograms of the complexes in dichloromethane were measured using $[NBu^n_4][ClO_4]$ as an electrolyte.[15] Electrical resistivities of the oxidized complexes were measured at room temperature for compacted pellets by the conventional two-probe method.[15]

Crystal Structure Determination of [NBu$^n_4$][Pt(ppy)(C$_8$H$_4$S$_8$)] (3). Diffraction data were collected on a Rigaku RAXIS-RAPID imaging plate diffractometer equipped with a Rigaku low temperature device (liquid nitrogen as the coolant) and graphite-monochromated Mo Kα ($\lambda = 0.71069$ Å) radiation at the Graduate School of Engineering, Osaka University. For the data collection up to $2\theta = 60.0°$, two sets of exposures ($\phi = 0.0°$, $\chi = 45.0°$, and $\omega = 130.0°$ to $190.0°$; $\phi = 180.0°$, $\chi = 45.0°$, and $\omega = 0.0°$ to $160.0°$) were measured by scans of 2.0° in ω. Indexing was performed for reflections obtained from three oscillations exposed for 180 s. Final values of the cell parameters were obtained from least-squares refinement of the positions of 53609 observed reflections ($2.5° < 2\theta < 59.8°$). Equivalent reflections were merged by use of the PROCESS-AUTO program package. 11125 Reflections were unique ($R_{int} = 0.050$) out of 38580 ones. They were corrected for absorption using the program ABSCOR[31] (transmission factors: 0.548–0.668) and for Lorenz and polarization effects. Crystallographic data are summarized in Table 1.

The structure was solved by the Patterson method (PATTY)[32] and expanded using Fourier techniques (DIRDIF94)[33] and refined on F^2 by the full-matrix least-squares method (SHELXL97).[34] All

Table 1. Crystallographic Data for [NBu$^n_4$][Pt(ppy)(C$_8$H$_4$S$_8$)] (**3**)

Empirical formula	$C_{35}H_{48}N_2PtS_8$
Molecular weight	948.39
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	9.6826(2)
b/Å	25.1367(4)
c/Å	16.2354(2)
β/°	98.230(1)
V/Å^3	3910.8(1)
Z	4
T/K	223
μ/mm^{-1}	4.043
Reflections collected	38580
Independent reflections	11125
R, wR (all data)	0.064, 0.068

the non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were geometrically calculated and refined with isotropic thermal parameters riding on those of the parent atoms. Atomic scattering factors were taken from the usual sources.[35] Figure 5 was drawn with a local version of ORTEP II.[36]

Crystallographic data (excluding structure factors) have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and deposition number CCDC 233842.

Results and Discussion

Spectroscopic and Electrochemical Properties of Complexes $[NEt_4][Pt(ppy)(C_3S_5)]$ (1), $[NEt_4][Pt(ppy)(C_8H_4S_8)]$ (2), and $[NEt_4][Pt(ppy)(C_{10}–C_6S_8)]$ (4). Electronic absorption spectra of complex **4** in some solvents are shown in Fig. 1. The band observed at around 520 nm is somewhat sensitive to the solvent: 532 nm ($\mathcal{E}$, 6600 $mol^{-1}\,dm^3\,cm^{-1}$) in benzene, 520 nm ($\mathcal{E}$, 7400) in *N*,*N*-dimethylformamide and 512 nm ($\mathcal{E}$, 7400) in dichloromethane. This band is tentatively assigned as the mixed dithiolate ligand/metal-to-ppy ligand charge transfer (CT) transition, as observed for $[Au^{III}(ppy)(dithiolate)]$.[14,18] Such bands are similar to the mixed dithiolate/metal-to-diimine ligand CT transition bands observed for [M(diimine)(dithiolate)] type Pt^{II}- and Au^{III}-complexes, which have a large solvent dependency.[8–14,18] The bands of these neutral complexes polarized around the metal ions exhibit appreciable negative solvatochromic properties, whereas for the present anionic complex the solvatochromism is weak. In Table 2 are summarized the absorption band maxima of **1**, **2**, and **4** in various solvents, together with those of $[Pt(bpy)(C_8H_4S_8)]$ (bpy = 2,2′-bipyridine)[16] for comparison. The solvent-dependencies of the CT bands of **1**, **2**, and **4** are less appreciable compared with that of $[Pt(bpy)(C_8H_4S_8)]$. These findings suggest that the present anionic complexes are weakly polarized between the electron-donating sulfur-rich dithiolate ligand and the π-electron-accepting ppy ligand in the ground state.

Cyclic voltammograms of **2** and **4** measured in dichloromethane are shown in Fig. 2. Two oxidation peaks occur at −0.27 and +0.16 V (vs Ag/Ag^+) for **2**, which correspond to the first and second oxidations of the $C_8H_4S_8$-ligand center, respectively, as observed for other $C_8H_4S_8$–metal complexes.[15,16,30,37,38] The oxidation peak potentials observed at +0.48 and +0.89 V are reasonably ascribed to the oxidations of Pt^{II}-to-Pt^{III} and Pt^{III}-to-Pt^{IV}, respectively. These oxidation peaks are also similar to those of **4**: −0.26, +0.22, +0.47, and +0.76 V (vs Ag/Ag^+). The first oxidation peak potentials due to the oxidation at these dithiolate ligand-centers are low, as observed for other anionic Pt^{II}–$C_8H_4S_8$ and -related dithiolate complexes.[24,27] On the other hand, the first oxidation potential (+0.02 V) of the C_3S_5-complex **1** is somewhat higher than those of **2** and **4**. The present anionic complexes exhibit lower first oxidation potentials than the corresponding Au^{III}-analogs, $[Au(ppy)(C_8H_4S_8)]$ (−0.06 V) and $[Au(ppy)(C_{10}–C_6S_8)]$ (+0.21 V vs

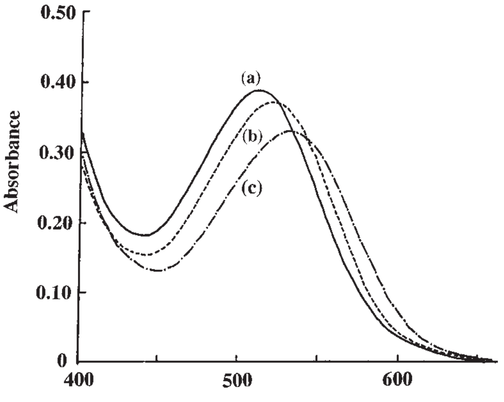

Fig. 1. Electronic absorption spectra of complex **4** (5.0×10^{-5} $mol\,L^{-1}$) in (a) dichloromethane (b) *N*,*N*-dimethylformamide, and (c) benzene.

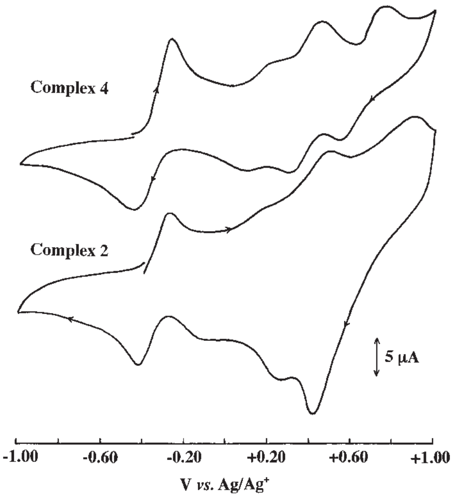

Fig. 2. Cyclic voltammograms of complexes **2** and **4** (1.0×10^{-3} $mol\,L^{-1}$) in dichloromethane; supporting electrolyte, 0.1 $mol\,L^{-1}$ $[NBu^n{}_4][ClO_4]$; sweep rate, 500 $mV\,s^{-1}$.

Table 2. Electronic Absorption Band Maxima (nm) of the Intramolecular CT Bands for Complexes **1**, **2**, and **4** in Various Solvents

Solvent	Dielectric constant[a)]	1	2	4	$[Pt(bpy)(C_8H_4S_8)]$[b)]
Benzene	2.28			532	
Chloroform	4.81	504	514	510	876
Dichloromethane	8.93	506	502	512	760
Acetone	21.01	522	524	528	
Acetonitrile	36.64	510	502	506	
N,*N*-Dimethylformamide	36.71	524	518	520	678
Dimethyl sulfoxide	47.24	522	512		659

a) Ref. 45. b) bpy = 2,2′-bipyridine; Ref. 16.

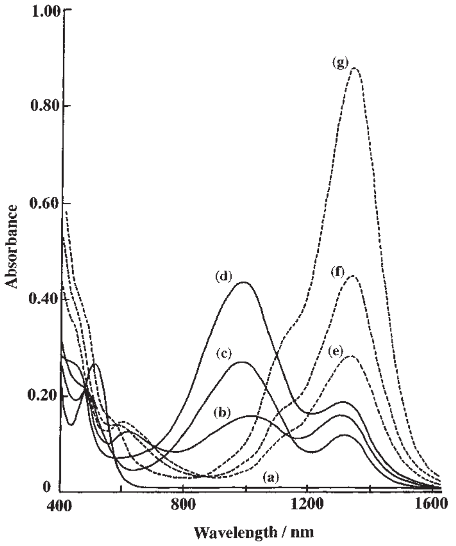

Fig. 3. Electronic absorption spectra of complex **4** (5.0×10^{-5} mol L^{-1}) in dichloromethane in the presence of iodine. Concentration of iodine (mol L^{-1}): (a) 0, (b) 1.0×10^{-4}, (c) 2.0×10^{-4}, (d) 3.0×10^{-4}, (e) 1.0×10^{-3}, (f) 1.2×10^{-3}, (g) 2.2×10^{-3}.

Ag/Ag$^+$).[18] A similar tendency was observed for the anionic and neutral C_3S_5– and $C_8H_4S_8$–Au^I-complexes.[38] Thus, the oxidation of **2** and **4** by a reaction of TCNQ or iodine is able to afford one-electron- and two-electron-oxidized species.

Oxidation of Complexes 1, 2 and 4. Figure 3 shows the electronic absorption spectra of **4** in the presence of various amounts of iodine as an oxidant in dichloromethane. Upon the oxidation of **4** by iodine, new bands appear at 990 and 1310 nm due to the metal-to-$C_8H_4S_8$ ligand CT transition of the one-electron-oxidized species, as observed for the oxidation of other sulfur-rich dithiolate-metal complexes.[5,16,24] The further addition of iodine affords an intense band at 1350 nm with a shoulder at 1100 nm, which is due to the two-electron-oxidized species. The bands for the one-electron-oxidized complex have been confirmed by comparison with the very similar bands at 985 and 1310 nm observed for the spectrum of [Pt(ppy)(C_{10}–C_6S_8)] (**7**) dissolved in nitrobenzene, which has been isolated by the reaction of **4** with TCNQ, as described below. Upon the oxidation of **2** by iodine, new bands have been observed at 985 and 1330 nm for the one-electron-oxidized complex and at 1150 and 1380 nm for the two-electron-oxidized species. On the other hand, the oxidation of **1** by iodine has afforded a broad band at 760 nm, which is due to the one-electron-oxidized species. However, no appreciable band has appeared at longer wavelengths upon further oxidation, which suggests that the proceeding oxidation does not occur essentially on the C_3S_5-ligand center.

One-electron-oxidized complexes [Pt(ppy)(C_3S_5)] (**5**), [Pt(ppy)($C_8H_4S_8$)] (**6**), and [Pt(ppy)(C_{10}–C_6S_8)] (**7**) have been isolated by reactions of **1**, **2**, and **4** with excess amounts of TCNQ as an oxidant. The reactions with excess amounts of iodine have afforded the further-electron-oxidized species [Pt(ppy)(C_3S_5)]($I_{1.0}$) (**8**), [Pt(ppy)($C_8H_4S_8$)]($I_{4.2}$) (**9**), and [Pt(ppy)(C_{10}–C_6S_8)]($I_{3.2}$) (**10**) containing iodide ions. Complex **8** has the iodide ion, while **9** and **10** contain both I_3^- and I_5^- ions, which have been confirmed by the I–I–I and I–I–I–I stretching bands[39,40] at 111, 165 and 110, 167 cm^{-1} for **9** and **10**, respectively, as observed in the Raman spectra. Thus, these findings suggest that they are formally ca. 1.5- and 1.4-electron-oxidized species.

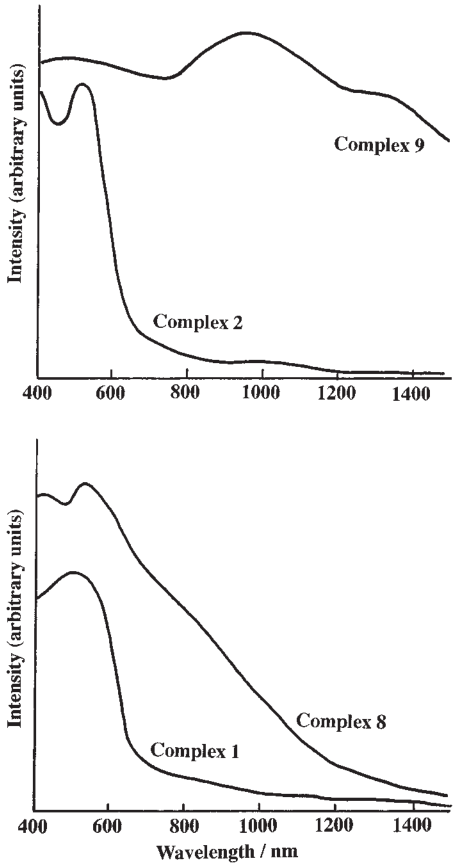

Fig. 4. Powder reflectance spectra of complexes **1** and **2**, and their oxidized species **8** and **9**.

Powder ESR spectra of the oxidized species have exhibited an almost isotropic signal centered at $g = 2.003$–2.008 (peak-to-peak line widths, 0.1–2.4 mT). These findings suggest the sulfur-rich dithiolate ligand-centered oxidation, as observed for other oxidized C_3S_5–,[15,41] $C_8H_4S_8$–,[5,24,37,42] and C_{10}–C_6S_8–metal complexes.[16,24]

Figure 4 shows the powder reflectance spectra of **8** and **9** together with those of the unoxidized species **1** and **2**. Complex **8** shows bands at around 600 and 750 nm which correspond to the bands observed in the solution spectrum. No additional appreciable bands occur at longer wavelengths, suggesting that there is no significant molecular interaction in the solid state. The spectrum of **9** shows broad bands at longer wavelengths, together with the bands at around 900 and 1300 nm due to the one-electron- and two-electron-oxidized species. This finding is likely to be due to intermolecular interactions through nonbonding S–S contacts in the solid state, assisted by the $C_8H_4S_8$ ligand-centered oxidation, as observed for other oxidized sulfur-rich dithiolate–metal complexes.[16,30,43] The powder reflectance spectrum of **10** also exhibited broad bands at longer wavelengths due to the S–S interactions.

Although complexes **1**, **2**, and **4** are essentially insulators, the oxidized species **5**–**10** exhibited electrical conductivities.

The electrical conductivities measured for compacted pellets at room temperature are listed in Table 3. The oxidized C_3S_5-complexes have very low electrical conductivities, while the oxidized $C_8H_4S_8$- and C_{10}–C_6S_8-complexes exhibit higher conductivities. Although there seem to be no significant molecular interactions for **2**–**4** in the solid state, as shown in the crystal structure of **3**, these oxidized species have some molecular interactions, as expected from the reflectance spectra of **9** (Fig. 4) and of **10**, which result in the formation of an electron-conduction pathway through some S–S contacts. The formally 1.5-electron- and 1.4-electron-oxidized complexes **9** and **10** exhibit higher electrical conductivities than the one-electron-oxidized species **6** and **7**, indicating more effective molecular interactions in the positively charged sulfur-rich dithiolate ligand moieties. However, even **9** and **10** have lower conductivities than the oxidized complexes of $[Au(ppy)(C_8H_4S_8)]$ and $[Au(ppy)(C_{10}–C_6S_8)]$ corresponding to **2** and **4**, respectively.[18]

Crystal Structure of $[NBu^n{}_4][Pt(ppy)(C_8H_4S_8)]$ (3). The crystal structure of the $[Pt(ppy)(C_8H_4S_8)]^-$ complex has been clarified for complex **3**. The molecular structure of **3** is shown in Fig. 5, together with the atom labeling scheme. Selected bond lengths and angles are summarized in Table 4. The basic molecular structure of **3** is that of a slightly distorted square plane around the Pt^{II}-center. As far as we know, there are no X-ray structural data of Pt^{II}–ppy complexes. Thus, the data of **3** may be compared with those of the square planar Au^{III}–dithiolate complexes with the ppy^- ligand. The Pt–N [2.043(3) Å] and Pt–C lengths [2.010(3) Å] are close to those of $[Au(ppy)(C_8H_4S_8)]$ (Au–N, 2.063(3) Å and Au–C, 2.041(5) Å),[18] [Au(ppy)(tdt)] (tdt^{2-} = 3,4-toluene-dithiolate(2−); Au–N, 2.079(5) Å and Au–C, 2.035(7) Å)[14] and $[Au(ppy)(S_2CNEt_2)]^+$ complexes (Au–N, 2.058(11) Å and Au–C, 2.036(7) Å).[44] The Pt–S(1) bond [2.2618(10) Å] trans to the Pt–N bond is shorter than the Pt–S(8) bond [2.3536(9) Å] trans to the Pt–C bond through the structural trans influence. This effect was also observed for the above-mentioned [Au(ppy)(dithiolate)] complexes. Pt, S(1), S(2), S(3), S(6), S(7), S(8), C(1), C(2), C(3), C(8), C(9), and N atoms are nearly coplanar (±0.038 Å). This planar geometry around the metal atom in-

Table 3. Electrical Conductivities (σ)[a)] of the Oxidized Complexes

Complex	σ_{RT}/S cm^{-1}
$[Pt(ppy)(C_3S_5)]$ (**5**)	3.8×10^{-9}
$[Pt(ppy)(C_8H_4S_8)]$ (**6**)	6.1×10^{-5}
$[Pt(ppy)(C_{10}–C_6S_8)]$ (**7**)	6.2×10^{-6}
$[Pt(ppy)(C_3S_5)](I_{1.0})$ (**8**)	6.6×10^{-9}
$[Pt(ppy)(C_8H_4S_8)](I_{4.2})$ (**9**)	7.8×10^{-3}
$[Pt(ppy)(C_{10}–C_6S_8)](I_{3.2})$ (**10**)	1.6×10^{-4}

a) Measured for compacted pellets at room temperature.

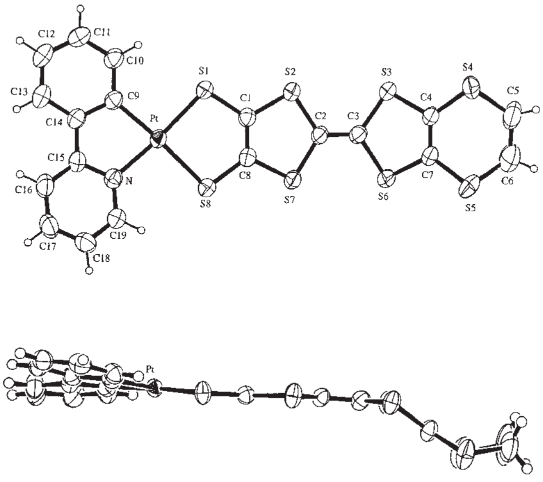

Fig. 5. Molecular geometry of the anion moiety of complex **3** together with the atom-labeling scheme.

Table 4. Selected Bond Lengths (Å) and Angles (°) of $[NBu^n{}_4][Pt(ppy)(C_8H_4S_8)]$ (**3**)

Pt–S(1)	2.2618(10)	Pt–S(8)	2.3536(9)	Pt–N	2.043(3)
Pt–C(9)	2.010(3)	S(1)–C(1)	1.743(3)	S(2)–C(1)	1.770(4)
S(2)–C(2)	1.757(3)	S(3)–C(3)	1.759(4)	S(3)–C(4)	1.740(4)
S(4)–C(5)	1.788(5)	S(5)–C(6)	1.757(6)	S(5)–C(7)	1.727(3)
S(6)–C(3)	1.765(3)	S(6)–C(7)	1.759(4)	S(7)–C(2)	1.756(4)
S(7)–C(8)	1.766(3)	S(8)–C(8)	1.735(4)	C(1)–C(8)	1.336(5)
C(2)–C(3)	1.330(5)	C84)–C(7)	1.331(5)	C(5)–C(6)	1.428(7)

S(1)–Pt–S(8)	90.39(3)	S(1)–Pt–C(9)	93.84(11)
S(8)–Pt–N	95.29(9)	N–Pt–C(9)	80.76(13)
Pt–S(1)–C(1)	102.1(1)	C(1)–S(2)–C(2)	95.6(2)
C(3)–S(3)–C(4)	93.0(2)	C(4)–S(4)–C(5)	102.5(2)
C(6)–S(5)–C(7)	101.5(3)	C(3)–S(6)–C(7)	93.0(2)
C(2)–S(7)–C(8)	96.0(2)	Pt–S(8)–C(8)	99.6(1)
S(1)–C(1)–C(8)	123.3(3)	S(2)–C(1)–C(8)	117.3(3)
S(2)–C(2)–S(7)	114.0(2)	S(2)–C(2)–C(3)	123.4(3)
S(7)–C(2)–C(3)	122.6(3)	S(3)–C(3)–S(6)	111.7(2)
S(3)–C(3)–C(2)	125.5(3)	S(6)–C(3)–C(2)	122.7(3)
S(3)–C(4)–C(7)	116.5(3)	S(4)–C(4)–C(7)	124.8(3)
S(4)–C(5)–C(6)	120.4(4)	S(5)–C(6)–C(5)	123.7(4)
S(5)–C(7)–C(4)	124.9(3)	S(6)–C(7)–C(4)	117.0(3)
S(7)–C(8)–C(1)	116.8(3)	S(8)–C(8)–C(1)	124.4(3)

cluding the $C_8H_4S_8$ ligand is in contrast to the appreciable folding of the metal–S_2C_2(dithiolate) plane along the S(1)–S(8) axis of the $C_8H_4S_8$ ligand observed for [Ti(C_5Me_5)$_2$-($C_8H_4S_8$)]^{37} and [$NBu^n{}_4$][Sn(Ph)($C_8H_4S_8$)$_2$]^{43} (the dihedral angle between the metal–C_2 and the S_2C_2 planes, 35.9° and 41.9°, respectively). Furthermore, for the $C_8H_4S_8$ ligand moiety, S(1), S(2), S(3), S(6), S(7), S(8), C(1), C(2), C(3), and C(8) are coplanar (±0.059 Å), and the plane makes an angle of 31.7° with the plane formed by S(3)–S(6), C(4) and C(7) atoms. This is similar to the cases of [Au(ppy)($C_8H_4S_8$)],[18] [Ti(C_5Me_5)^2($C_8H_4S_8$)][37] and $C_8H_4S_8(CH_2CH_2CN)_2$,[27] where the planes formed by S(1), S(2), S(7), S(8),C(1), and C(8) and by S(3)–S(6), C(4) and C(7) make angles of 17.1–31.0° with the central plane of the tetrathiafulvalene S_4C_2 skeleton [S(2), S(3), S(6), S(7), C(2), and C(3)].

The anion moieties form a dimer unit through the nonbonding S–S contact [S(5)–S(5′), 3.352(3) Å] in the solid state. However, there are no further significant S–S contacts or molecular overlaps among the anionic moieties. This may be due to the anionic character of the present complex, which leads to some repulsion between the molecules, although neutral related complexes, [Au(ppy)($C_8H_4S_8$)][18] and [Pd(*N*-butylpyridine-2-carbaldimine)(C_3S_5)],[16] form one- and two-dimensional molecular interactions through some S–S contacts in the solid state.

We are grateful to Professor S. Suzuki (Graduate School of Science) for measurement of ESR spectra. This research was supported in part by Grants-in-Aid for scientific research (nos. 14044056 and 15550049) from the Ministry of Education, Culture, Sports, Science and Technology.

References

1 P. Cassoux, L. Valade, K. Kobayashi, A. Kobayashi, R. A. Clark, and A. E. Underhill, *Coord. Chem. Rev.*, **110**, 115 (1991).

2 R.-M. Olk, B. Olk, W. Dietzsch, R. Kirmse, and E. Hoyer, *Coord. Chem. Rev.*, **117**, 99 (1992).

3 A. E. Pullen and R.-M. Olk, *Coord. Chem. Rev.*, **188**, 211 (1999).

4 H. Tanaka, Y. Okano, H. Kobayashi, W. Suzuki, and A. Kobayashi, *Science*, **291**, 285 (2001).

5 G. Matsubayashi, M. Nakano, and H. Tamura, *Coord. Chem. Rev.*, **226**, 143 (2002).

6 N. Robertson and L. Cronin, *Coord. Chem. Rev.*, **227**, 93 (2002).

7 E. Fujiwara, A. Kobayashi, H. Fujiwara, and H. Kobayashi, *Inorg. Chem.*, **43**, 1122 (2004).

8 G. Matsubayashi, M. Hirao, and T. Tanaka, *Inorg. Chim. Acta*, **144**, 217 (1988).

9 J. A. Zuleta, M. S. Burberry, and R. Eisenberg, *Coord. Chem. Rev.*, **97**, 47 (1990).

10 J. M. Bevilacqua and R. Eisenberg, *Inorg. Chem.*, **33**, 2913 (1994).

11 S. D. Cummings and R. Eisenberg, *Inorg. Chem.*, **34**, 2007 (1995).

12 S. D. Cummings and R. Eisenberg, *J. Am. Chem. Soc.*, **118**, 1949 (1996).

13 C.-T. Chen, S.-Y. Liao, K.-J. Lin, C.-H. Chen, and T.-Y. J. Lin, *Inorg. Chem.*, **38**, 2734 (1999).

14 M. A. Mansour, R. J. Lachicotte, H. J. Gysling, and R. Eisenberg, *Inorg. Chem.*, **37**, 4625 (1998).

15 A. Nakahama, M. Nakano, and G. Matsubayashi, *Inorg. Chim. Acta*, **284**, 55 (1999).

16 K. Kubo, M. Nakano, H. Tamura, and G. Matsubayashi, *Inorg. Chim. Acta*, **311**, 6 (2000).

17 K. Kubo, M. Nakano, H. Tamura, and G. Matsubayashi, *Inorg. Chim. Acta*, **336**, 120 (2002).

18 K. Kubo, M. Nakano, H. Tamura, G. Matsubayashi, and M. Nakamoto, *J. Organomet. Chem.*, **669**, 141 (2003).

19 K. Kubo, M. Nakano, H. Tamura, and G. Matsubayashi, *Eur. J. Inorg. Chem.*, **22**, 4093 (2003).

20 Y. Yamamoto, K. Miyamura, and Y. Gohshi, *Mol. Cryst. Liq. Cryst. Sci. Technol.*, **285**, 137 (1996).

21 Y. Kunugi, K. R. Mann, L. L. Miller, and C. L. Exstrom, *J. Am. Chem. Soc.*, **120**, 589 (1998).

22 F. Neve, O. Francescangeli, A. Crispini, and J. Charmant, *Chem. Mater.*, **13**, 2032 (2001).

23 D. B. Mitzi, *Chem. Mater.*, **13**, 3283 (2001).

24 T. Nakazono, M. Nakano, H. Tamura, and G. Matsubayashi, *J. Mater. Chem.*, **9**, 2413 (1999).

25 M. M. Mdleleni, J. S. Bridgewater, R. J. Watts, and P. C. Ford, *Inorg. Chem.*, **34**, 2334 (1995).

26 L. Valade, J.-P. Legros, M. Bousseau, P. Cassoux, M. Garbauskas, and L. V. Interrante, *J. Chem. Soc., Dalton Trans.*, **1985**, 783.

27 M. Nakano, A. Kuroda, H. Tamura, R. Arakawa, and G. Matsubayashi, *Inorg. Chim. Acta*, **279**, 165 (1998).

28 N. Svenstrup, K. M. Rasmussen, T. K. Hansen, and J. Becher, *Synthesis*, **1994**, 809.

29 L. Binet, J. M. Fabre, C. Montginoul, K. B. Simonsen, and J. Becher, *J. Chem. Soc., Perkin Trans. 1*, **1996**, 783.

30 K. Natsuaki, M. Nakano, and G. Matsubayashi, *Inorg. Chim. Acta*, **299**, 112 (2000).

31 T. Higashi, "ABSCOR, a Computer Program for Absorption Correction," Rigaku Corporation, Tokyo, Japan (1995).

32 PATTY: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, and J. M. M. Smits, "DIRDIF94 Program System, Technical Report of the Crystallography Laboratory," University of Nijmegen, The Netherlands (1994).

33 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, and J. M. M. Smits, "DIRDIF94 Program System, Technical Report of the Crystallography Laboratory," University of Nijmegen, The Netherlands (1994).

34 G. M. Sheldrick, "SHELXL 97, a Computer Program for the Refinement of Crystal Structures," University of Göttingen, Germany (1997).

35 "International Tables for X-ray Crystallography," Kynoch Press, Birmingham, England (1974), Vol. 4.

36 C. K. Johnson, "ORTEP-II, Report ORNL-5138," Oak Ridge National Laboratory, Oak Ridge, TN (1976).

37 K. Saito, M. Nakano, H. Tamura, and G. Matsubayashi, *Inorg. Chem.*, **39**, 4815 (2000).

38 T. Ryowa, M. Nakano, H. Tamura, and G. Matsubayashi, *Inorg. Chim. Acta*, in press.

39 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, and T. J. Marks, *J. Am. Chem. Soc.*, **101**, 2921 (1979).

40 B. N. Diel, T. Inabe, J. W. Lyding, K. F. Schoch, Jr., C. R. Kannewurf, and T. J. Marks, *J. Am. Chem. Soc.*, **105**, 1551 (1983).

41 G. Matsubayashi, K. Douki, H. Tamura, M. Nakano, and

W. Mori, *Inorg. Chem.*, **32**, 5990 (1993).

42 H. Mori, M. Nakano, H. Tamura, and G. Matsubayashi, *J. Organomet. Chem.*, **574**, 77 (1999).

43 T. Akasaka, M. Nakano, H. Tamura, and G. Matsubayashi, *Bull. Chem. Soc. Jpn.*, **75**, 2621 (2002).

44 R. V. Parish, J. P. Wright, and R. G. Pritchard, *J. Organomet. Chem.*, **596**, 165 (2000).

45 "CRC Handbook of Chemistry and Physics, 83rd ed," ed by D. R. Lide, CRC (2002).