

# Preparation and oxidation of polarized Au(III) complexes having both the *C*-deprotonated-2-phenylpyridine (ppy) and a sulfur-rich dithiolate ligand and X-ray crystal structure of [Au( $\eta^2$ -*C,N*-ppy)-( $\eta^2$ -*S,S*-C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)]·0.5DMF

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## Abstract

[Au(ppy)(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)] [ppy<sup>−</sup> = *C*-deprotonated-2-phenylpyridine(1-), 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-)] and [Au(ppy)(C<sub>10</sub>-C<sub>6</sub>S<sub>8</sub>)] [C<sub>10</sub>-C<sub>6</sub>S<sub>8</sub><sup>2−</sup> = 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/ligand-to-ligand charge transfer transition which is sensitive to a solvent. They exhibit first oxidation potentials of −0.06 to +0.20 V (vs. Ag/Ag<sup>+</sup>) due to the dithiolate ligand-centered oxidation. They were oxidized by iodine or TCNQ (7,7,8,8-tetracyano-*p*-quinodimethane) to afford [Au(ppy)(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)](I<sub>3</sub>) and [Au(ppy)(C<sub>10</sub>-C<sub>6</sub>S<sub>8</sub>)](I<sub>3</sub>) containing the I<sub>3</sub><sup>−</sup> ion, [Au(ppy)(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)](TCNQ)<sub>0.6</sub> and [Au(ppy)(C<sub>10</sub>-C<sub>6</sub>S<sub>8</sub>)](TCNQ)<sub>0.5</sub> containing the TCNQ<sup>•−</sup> radical anion. Their oxidized complexes behave as electrical conductors with electrical conductivities of 2.0 × 10<sup>−2</sup>–4.0 × 10<sup>−2</sup> S cm<sup>−1</sup> measured for compacted pellets at room temperature. The X-ray crystal structure of [Au(ppy)(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)]·0.5DMF revealed a two-dimensional array of the molecules with some sulfur–sulfur non-bonded contacts.

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## 1. Introduction

Many oxidized metal complexes with sulfur-rich dithiolate ligands, such as C<sub>3</sub>S<sub>5</sub><sup>2−</sup> and C<sub>6</sub>S<sub>8</sub>R<sub>2</sub><sup>2−</sup> (R = alkyl groups), are known to become good electrical conductors [1–5]. They construct effective electron-conduction pathways through some sulfur-sulfur non-bonded contacts in the solid state.

Planar metal complexes of the [M(N–N)(S–S)] type [M = Pd(II), Pt(II) and Au(III)] having a diimine (N–N) ligand as a  $\pi$ -electron acceptor and a dithiolate (S–S)

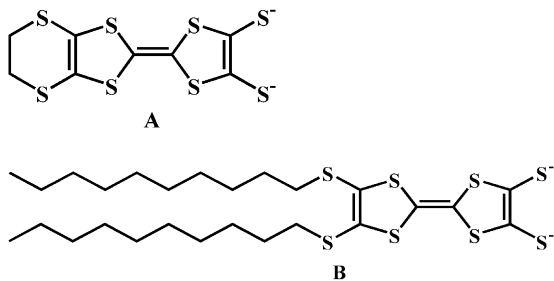
ligand as an electron donor are polarized around the metal ions [6–12]. Metal complexes of this type containing sulfur-rich dithiolate ligands are expected to form unique columnar molecular stackings and/or layered arrangements through electrostatic interactions of the polarized metal-center moieties, metal–metal interactions and many S–S non-bonded contacts in the solid state. Recently, we reported several polarized metal complexes of the [M(diimine) (sulfur-rich dithiolate)] type [M = Pd(II) and Pt(II)] and their oxidized species behaving as electrical conductors [13,14]. Furthermore, some oxidized Pt(II) complexes with C<sub>6</sub>S<sub>8</sub>R<sub>2</sub><sup>2−</sup> (R = long alkyl chains) ligands showed high electrical conductivities owing to the construction of good electron-conduction pathways caused by S–S contacts and

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association of long alkyl chains [15]. Thus, planar metal complexes having a sulfur-rich dithiolate ligand and/or containing long alkyl chains which are polarized around the metal ion are also of interest as new electrical conductors with unique molecular arrangements in the solid state.

In this work, metal complexes of the type of  $[\text{Au}(\eta^2\text{-C},N\text{-ppy})(\text{sulfur-rich dithiolate})]$  ( $\text{ppy}^- = \text{C-deprotonated-2-phenylpyridine}$ ; sulfur-rich dithiolate =  $\text{C}_8\text{H}_4\text{S}_8^{2-}$  (**A**) and  $\text{C}_6\text{S}_8(\text{C}_{10}\text{H}_{21})_2^{2-}$  ( $\text{C}_{10}\text{-C}_6\text{S}_8$ ; **B**)) and their oxidized species have been prepared.



These complexes of the  $[\text{Au}(\text{III})(\text{C}-\text{N})(\text{S}-\text{S})]$  type are expected to be polarized around the metal ion similar to the  $[\text{Au}(\text{III})(\text{diimine})(\text{dithiolate})]^+$  complexes [12]. Spectroscopic and electrochemical properties of the  $[\text{Au}(\eta^2\text{-C},N\text{-ppy})(\text{sulfur-rich dithiolate})]$  complexes and electrical conductivities of their oxidized species are described, together with the crystal structure of  $[\text{Au}(\text{ppy})(\text{C}_8\text{H}_4\text{S}_8)] \cdot 0.5\text{DMF}$ .

## 2. Experimental

### 2.1. Materials

Dichloro(*C*-deprotonated-2-phenylpyridine)gold(III),  $\text{AuCl}_2(\text{ppy})$ , was prepared according to the literature [16]. Pro-ligand compounds, 4,5-bis(cyanoethylthio)-1,3-dithiole-[(4,5-ethylenedithio)-1,3-dithiole-2-ylidene],  $\text{C}_8\text{H}_4\text{S}_8(\text{CH}_2\text{CH}_2\text{CN})_2$ , [17–19] and 4,5-bis(propionylethylenethio)-1,3-dithiol-[[bis(decylthio)-1,3-dithiol-2-ylidene],  $(\text{C}_{10}\text{H}_{21})_2\text{C}_6\text{S}_8(\text{CH}_2\text{CH}_2\text{COOEt})_2$  [ $\text{C}_{10}\text{-C}_6\text{S}_8\text{-}(\text{CH}_2\text{CH}_2\text{COOEt})_2$ ], [15] were prepared according to the literatures.

### 2.2. Preparation of $[\text{Au}(\text{ppy})(\text{C}_8\text{H}_4\text{S}_8)]$ (**1**)

All the following reactions were performed under an argon atmosphere. Sodium metal (26 mg, 1.1 mmol) and  $\text{C}_8\text{H}_4\text{S}_8(\text{CH}_2\text{CH}_2\text{CN})_2$  (230 mg, 0.50 mmol) were dissolved in ethanol (15  $\text{cm}^3$ ). To the solution was added a hot *N,N*-dimethylformamide (DMF) (10  $\text{cm}^3$ ) solution of  $\text{AuCl}_2(\text{ppy})$  (120 mg, 0.30 mmol) and the solution was stirred for 12 h at room temperature (r.t.). The resulting yellow precipitates were collected by filtration, washed with methanol, and dried in vacuo (83% yield). Anal.

Calc. for  $\text{C}_{19}\text{H}_{12}\text{AuNS}_8$ : C, 32.24; H, 1.71; N, 1.98. Found: C, 32.35; H, 1.86; N, 2.22%.  $^1\text{H-NMR}$  (dimethyl sulfoxide- $d_6$ , 50 °C):  $\delta$  (ppm) 3.39 (s, 4H), 7.40 (t, 1H), 7.47 (t, 1H), 7.52 (d, 1H), 7.68 (t, 1H), 8.06 (d, 1H), 8.35 (t, 1H), 8.44 (d, 1H), 8.75 (d, 1H).

The complex was recrystallized from DMF to afford dark green crystals of  $[\text{Au}(\text{ppy})(\text{C}_8\text{H}_4\text{S}_8)] \cdot 0.5\text{DMF}$ , which were suitable for the X-ray crystal structure analysis.

### 2.3. Preparation of $[\text{Au}(\text{ppy})(\text{C}_{10}\text{-C}_6\text{S}_8)]$ (**2**)

Sodium metal (27 mg, 1.2 mmol) and  $\text{C}_{10}\text{-C}_6\text{S}_8(\text{CH}_2\text{CH}_2\text{COOEt})_2$  (400 mg, 0.50 mmol) were dissolved in ethanol (90  $\text{cm}^3$ ). To the solution was added a hot DMF (15  $\text{cm}^3$ ) solution of  $\text{AuCl}_2(\text{ppy})$  (160 mg, 0.38 mmol) and the solution was stirred for 17 h at r.t. The resulting precipitates were collected by filtration, washed with methanol, and dried in vacuo (74% yield). Anal. Calc. for  $\text{C}_{37}\text{H}_{50}\text{AuNS}_8$ : C, 46.18; H, 5.24; N, 1.46. Found: C, 45.80; H, 5.22; N, 1.49%.  $^1\text{H-NMR}$  (chloroform- $d$ , 25 °C):  $\delta$  (ppm) 0.81 (t, 6H), 1.13 (m, 24H), 1.34 (t, 4H), 1.59 (t, 4H), 2.78 (t, 4H), 7.08 (t, 1H), 7.23 (m, 3H), 7.56 (d, 1H), 7.81 (d, 1H), 7.92 (t, 1H), 8.62 (d, 1H).

### 2.4. Preparations of $[\text{Au}(\text{ppy})(\text{C}_8\text{H}_4\text{S}_8)](\text{I}_3)$ (**3**) and $[\text{Au}(\text{ppy})(\text{C}_{10}\text{-C}_6\text{S}_8)](\text{I}_3)$ (**4**)

A dichloromethane (60  $\text{cm}^3$ ) solution of iodine (89 mg, 0.36 mmol) was added with stirring to a DMF (80  $\text{cm}^3$ ) solution of **1** (50 mg, 0.07 mmol). A black solid of **3** obtained immediately was collected by centrifugation, washed with dichloromethane, and dried in vacuo (34% yield). Anal. Calc. for  $\text{C}_{19}\text{H}_{12}\text{AuI}_3\text{NS}_8$ : C, 20.96; H, 1.11; N, 1.29. Found: C, 21.01; H, 1.15; N, 1.39%. Similarly, complex **2** dissolved in dichloromethane was reacted with an excess amount of iodine in acetonitrile to afford a black solid of **4** (15% yield). Anal. Calc. for  $\text{C}_{37}\text{H}_{50}\text{AuI}_3\text{NS}_8$ : C, 33.09; H, 3.75; N, 1.04. Found: C, 33.61; H, 3.78; N, 1.27%. These complexes contain the  $\text{I}_3^-$  ion, as described below.

### 2.5. Preparations of $[\text{Au}(\text{ppy})(\text{C}_8\text{H}_4\text{S}_8)](\text{TCNQ})_{0.6}$ (**5**) and $[\text{Au}(\text{ppy})(\text{C}_{10}\text{-C}_6\text{S}_8)](\text{TCNQ})_{0.5}$ (**6**)

An acetonitrile (100  $\text{cm}^3$ ) solution of TCNQ (7,7,8,8-tetracyano-*p*-quinodimethane) (62 mg, 0.30 mmol) was added with stirring to a DMF (70  $\text{cm}^3$ ) solution of **1** (43 mg, 0.06 mmol). A black solid of **5** obtained immediately was collected by centrifugation, washed with acetonitrile and methanol, and dried in vacuo (20% yield). Anal. Calc. for  $\text{C}_{26.4}\text{H}_{14.4}\text{AuN}_{3.4}\text{S}_8$ : C, 37.89; H, 1.75; N, 5.73. Found: C, 37.95; H, 1.96; N, 6.13%. Similarly, complex **2** dissolved in dichloromethane was reacted with an excess amount of TCNQ in acetonitrile

to afford a black solid of **6** (18% yield). Anal. Calc. for  $C_{43}H_{52}AuN_3S_8$ : C, 48.51; H, 4.93; N, 3.95. Found: C, 48.22; H, 4.92; N, 4.30%. These complexes contain the  $TCNQ^{\bullet-}$  radical anion, as described below.

## 2.6. Physical measurements

Electronic absorption, IR, ESR [20], and powder reflectance spectra [15] were recorded, as described previously. Raman spectra were measured using a Nippon-bunko NR-1800 laser-Raman spectrophotometer at the Graduate School of Science, Osaka University.  $^1H$ -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 in an organic solvent. Cyclic voltammograms of the complexes in dichloromethane were measured using  $[NBu_4][ClO_4]$  as an electrolyte, as described previously [21]. Electrical conductivities of the complexes were measured for compacted pellets at r.t. by the conventional two-probe method [21].

## 2.7. Crystal structure determination of $[Au(ppy)(C_8H_4S_8)] \cdot 0.5DMF$

Intensity data at 233 K 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-K $\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ) at the Graduate School of Science, Osaka University. Crystal data and details of measurements for the complex are summarized in Table 1. For the data collection up to  $2\theta = 60.0^\circ$ , two sets of exposures ( $\varphi = 0.0^\circ$ ,  $\chi = 45.0^\circ$  and  $\omega = 130.0$ – $190.0^\circ$ ;  $\varphi = 180.0^\circ$ ,  $\chi = 45.0^\circ$  and  $\omega = 0.0$ – $162.0^\circ$ ) were measured by scans of  $3^\circ$  in  $\omega$ . The intensity data were processed using the PROCESS-AUTO program package and corrected for Lorentz and polarization effects as well as absorption by Higashi method [22] (transmission factor, 0.279–0.506). Cell constants were obtained by least-squares refinement of 11184 reflections ( $5.4 < 2\theta < 59.9^\circ$ ).

For possible space groups  $P1$  and  $P\bar{1}$  the structure was solved by the direct methods using SIR-92 [23] and refined on  $F^2$  by the full-matrix least-squares technique with SHELXL-97 [24]. The solution for space group  $P1$  resulted in much distorted structures of two independent complexes and an ordered DMF molecule.  $R_1$ ,  $R$ , and  $R_w$  were 0.0325, 0.0385, and 0.0787, respectively, which were nearly equal to  $R$ -factors for the space group  $P\bar{1}$  with half the number of parameters for  $P1$ . Furthermore, the crystal structure was shown to be pseudo-centrosymmetric. Therefore, the space group  $P\bar{1}$  was adopted in spite of a centrosymmetrically disordered DMF molecule with occupancy of 0.5. All the non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms except for those of DMF molecules were geometrically calculated and refined with isotropic thermal parameters riding on those of the parent atoms. Calculations were performed on an SGI-O2 workstation at the Graduate School of Science, Osaka University. Atomic scattering factors were taken from the usual sources [25]. Figs. 1 and 2 were drawn with a local version of ORTEP II [26].

Table 1  
Experimental crystallographic data for  $[Au(ppy)(C_8H_4S_8)] \cdot 0.5DMF$  (**1**)

Formula	$C_{20.5}H_{15.5}AuN_{1.5}O_{0.5}S_8$
$M$	744.30
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>Unit cell dimensions</i>	
$a$ (Å)	7.3342(2)
$b$ (Å)	12.1500(3)
$c$ (Å)	15.3144(6)
$\alpha$ (°)	105.118(2)
$\beta$ (°)	102.667(1)
$\gamma$ (°)	105.865(1)
$V$ (Å <sup>3</sup> )	1203.61(7)
$Z$	2
$D_{calc}$ (g cm <sup>-3</sup> )	2.054
Crystal size (mm <sup>3</sup> )	0.20 × 0.20 × 0.10
$F(000)$	720
$\mu$ (Mo-K $\alpha$ ) (mm <sup>-1</sup> )	6.842
$T$ (°C)	-40
Measured $2\theta$ range (°)	< 60.0
Reflections corrected	13853
Independent reflections	6850
Observed reflections	6238
$R^a$	0.038
$R_w^b$	0.071

$$^a R = \Sigma(F_o^2 - F_c^2) / \Sigma F_o^2$$

$$^b R_w = \Sigma w(F_o^2 - F_c^2)^2; w^{-1} = \sigma^2(F_o^2) + (0.0280P)^2 + 2.5267P, \text{ where } P = (F_o^2 + 2F_c^2)/3.$$

## 3. Results and discussion

### 3.1. Molecular and crystal structure of $[Au(ppy)(C_8H_4S_8)] \cdot 0.5DMF$

The molecular geometry of complex **1** is illustrated in Fig. 1, together with the atom numbering scheme, where the disordered solvated DMF molecule lies on the center of symmetry. Selected bond distances and angles are summarized in Table 2. The Au(III) ion shows the square-planar coordination geometry expected for d<sup>8</sup> metal complexes: the metal ion and four ligand donor atoms are essentially coplanar ( $\pm 0.01 \text{ \AA}$ ). The Au–N [2.063(3) Å] and Au–C distances [2.041(5) Å] are close to those of  $[Au(\eta^2-C,N\text{-ppy})(tdt)]$  ( $tdt^{2-} = 3,4\text{-toluenedithiolate}(2-)$ ) [Au–N, 2.079(5) Å and Au–C, 2.035(7) Å] [12] and  $[Au(\eta^2-C,N\text{-ppy})(S_2CNEt_2)]^+$  complexes [Au–N, 2.058(11) Å and Au–C, 2.036(7) Å] [27]. The Au–

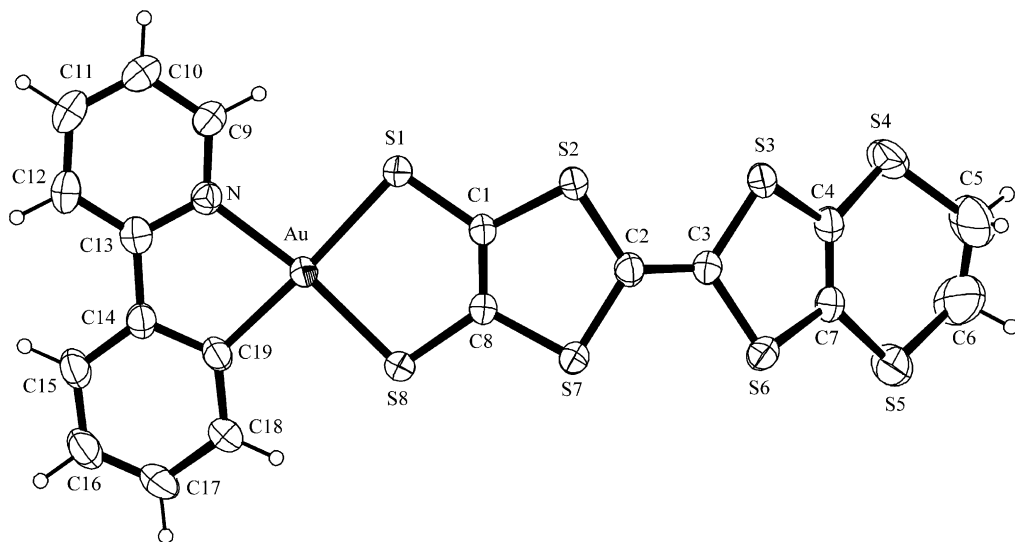


Fig. 1. Molecular geometry of complex 1.

S(1) bond [2.361(1) Å] *trans* to the Au–C bond is longer than the Au–S(8) bond [2.2694 Å] *trans* to the Au–N bond owing to the structural *trans* influence. This was also observed for other gold(III)-complexes of the [Au(C–N)(S–S)] type [12,27–29]. Au, S(1), S(2), S(7),

S(8), C(1) and C(8) atoms including C(19) and N atoms are nearly coplanar ( $\pm 0.03$  Å), which is in contrast to the characteristic folding of the metal–S<sub>2</sub>C<sub>2</sub> plane along the S(1)–S(8) axis of the C<sub>8</sub>H<sub>4</sub>S<sub>8</sub> ligand as observed for [Ti( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)] [30]. S(2), S(3), S(6), S(7), C(2)

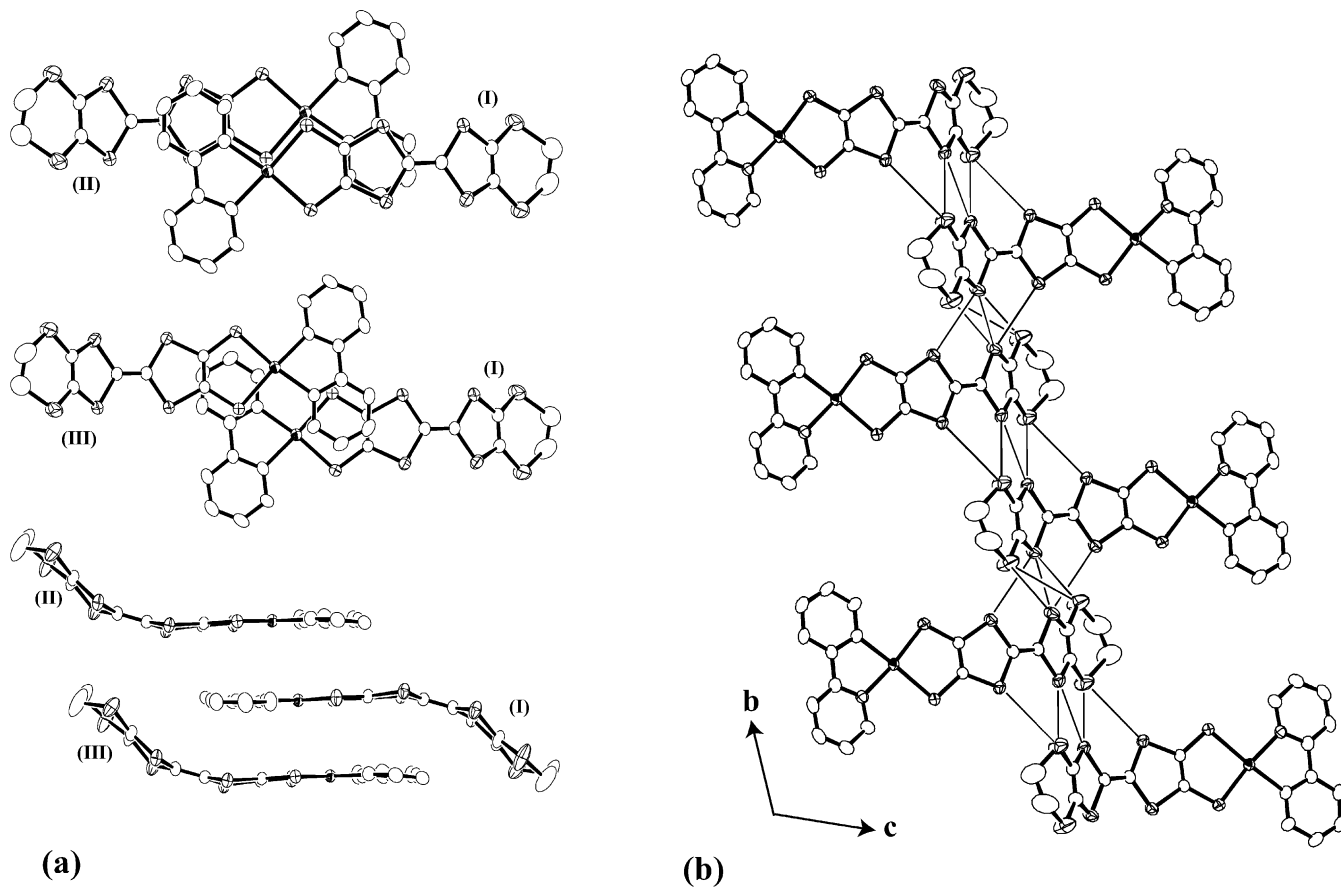


Fig. 2. (a) Molecular stacking of complex 1 along the molecular planes and (b) packing diagram of 1 projected along the *bc* plane. Fine lines show sulfur–sulfur non-bonded contacts ( $< 3.7$  Å).

Table 2  
Selected bond lengths (Å) and bond angles (°) of [Au(ppy)(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)]·0.5DMF

Bond lengths			
Au–S(1)	2.361(1)	Au–S(8)	2.2694(8)
Au–N	2.063(3)	Au–C(19)	2.041(5)
S(1)–C(1)	1.742(3)	S(2)–C(1)	1.758(4)
S(2)–C(2)	1.759(3)	S(3)–C(3)	1.747(5)
S(3)–C(4)	1.768(4)	S(4)–C(4)	1.741(6)
S(4)–C(5)	1.790(6)	S(5)–C(6)	1.732(9)
S(5)–C(7)	1.732(4)	S(6)–C(3)	1.745(4)
S(6)–C(7)	1.770(6)	S(7)–C(2)	1.754(5)
S(7)–C(8)	1.756(3)	S(8)–C(8)	1.744(5)
C(1)–C(8)	1.335(6)	C(2)–C(3)	1.349(6)
C(4)–C(7)	1.338(7)	C(5)–C(6)	1.42(1)
Bond angles			
S(1)–Au–S(8)	91.17(4)	S(1)–Au–N	95.8(1)
S(8)–Au–C(19)	92.34(10)	N–Au–C(19)	80.6(1)
Au–S(1)–C(1)	98.2(2)	Au–S(8)–C(8)	101.1(1)
C(1)–S(2)–C(2)	93.9(2)	C(2)–S(7)–C(8)	93.7(2)
C(3)–S(3)–C(4)	93.0(2)	C(3)–S(6)–C(7)	93.4(2)
C(4)–S(4)–C(5)	99.7(3)	C(6)–S(5)–C(7)	104.0(3)
S(1)–C(1)–C(8)	124.5(3)	S(2)–C(1)–C(8)	117.1(3)
S(2)–C(2)–S(7)	114.2(2)	S(3)–C(4)–S(4)	115.9(3)
S(3)–C(3)–S(6)	113.0(2)	S(3)–C(4)–C(7)	116.8(4)
S(4)–C(4)–C(7)	127.3(3)	S(4)–C(5)–C(6)	118.3(7)
S(5)–C(6)–C(5)	123.2(6)	S(5)–C(7)–C(4)	128.1(4)
S(6)–C(7)–C(4)	116.0(4)	S(7)–C(8)–C(1)	124.4(3)
S(7)–C(8)–S(8)	118.0(2)	S(8)–C(8)–C(1)	124.4(3)

and C(3) atoms are nearly coplanar ( $\pm 0.04$  Å), the other sulfur atoms deviating to the same side of the best plane by 0.96–1.06 Å. The planes formed by Au, S(1), S(2), S(7), S(8), C(1) and C(8) and by S(3), S(4), S(5), S(6), C(4) and C(7) make angles of 20.4 and 31.0°, respectively, with the central plane of the tetrathiafulvalene C<sub>2</sub>S<sub>4</sub> skeleton. This tub form is similar to those of [Ti( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)] [30], C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>(CH<sub>2</sub>CH<sub>2</sub>CN)<sub>2</sub> [31] and (MeS)<sub>4</sub>C<sub>6</sub>S<sub>4</sub> [32].

The molecule is planar around the metal center, as described above. This seems to result in a stacking of the molecules with a zigzag arrangement with the alternate location of the [(NC)Au(SS)] (I) and [(SS)Au(NC)] (II and III) planes (Fig. 2(a)). The stacking manner of the molecules is that the phenyl ring of the ppy ligand in one molecule lies above the C<sub>3</sub>S<sub>2</sub> and AuS<sub>2</sub>C<sub>2</sub> planes of the Au–C<sub>8</sub>H<sub>4</sub>S<sub>8</sub> moiety of the neighboring molecules with the intermolecular distances of 3.386 and 3.520 Å. However, the Au–Au distances of 4.2667(3) and 4.7116(3) Å are too long to indicate any significant molecular interaction through Au–Au contacts between the molecules, as also observed Au–Au distances for [Au( $\eta^2$ -C,N-ppy)(tdt)] (3.81 Å), [Au(<sup>t</sup>Bu<sub>2</sub>-bpy)(tdt)] (3.60 and 3.75 Å) [12] and [Au( $\eta^3$ -C,N,N-dpphen)Cl]<sup>+</sup>

[dpphen<sup>-</sup> = C-deprotonated-2,9-diphenyl-1,10-phenanthroline(1-)] complexes (3.60 Å) [33]. Between the molecules, however, there are several S–S non-bonded contacts of 3.36–3.64 Å, as shown in Fig. 2(b) which is

projected along the *bc* plane. The molecules form a two-dimensional molecular interaction through these S–S non-bonded contacts almost parallel to the *ab* plane.

### 3.2. Spectroscopic and electrochemical properties of 1 and 2

Electronic absorption spectra of 2 in benzene and in DMF are shown in Fig. 3. Intense absorption bands ( $\epsilon$ ,  $> 19000$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>) due to intraligand  $\pi$ – $\pi^*$  transitions of ppy and C<sub>8</sub>H<sub>4</sub>S<sub>8</sub> ligands are observed in the near-ultraviolet spectral region and a weaker low-energy band ( $\epsilon$ , 1800 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>) at 510 nm in benzene. This low-energy band is somewhat sensitive to solvent and the  $\lambda_{\max}$  shifts slightly to a higher energy region in a polar solvent: 490 nm in dichloromethane, 480 nm in benzonitrile and 460 nm in DMF. The band is tentatively assigned as the mixed dithiolate/metal-to-ppy ligand charge transfer (CT) transition, which is similar to the mixed dithiolate/metal-to-diimine ligand CT transitions observed for Pt(II)- and Au(III)-complexes of the [M(diimine)(dithiolate)] type [7,10–13]. This negative solvatochromic transition is also observed for 1 ( $\lambda_{\max}$ , 480 nm in benzonitrile, 460 nm in DMF), which occurs at somewhat lower energies than those of [Au(ppy)(tdt)] ( $\lambda_{\max}$ , 390 nm in DMSO, 410 nm in dichloromethane, and 430 nm in toluene) [12], and at higher energy than those of [Pt(bpy)(C<sub>8</sub>H<sub>4</sub>S<sub>8</sub>)] ( $\lambda_{\max}$ , 670 nm in dichloromethane, 610 nm in DMF) and [Pt(bpy)(C<sub>10</sub>-C<sub>6</sub>S<sub>8</sub>)] ( $\lambda_{\max}$ , 660 nm in dichloromethane, 620 nm in DMF) [13]. These findings suggest that complexes 1 and 2 are also somewhat polarized in the electron-donating sulfur-rich dithiolate ligand and the  $\pi$ -electron accepting ppy ligand in the ground state, as observed for [Pt(diimine)(dithiolate)] [7–10] and [Pt(diimine)(sulfur-rich dithiolate)] complexes [13,14,21].

A cyclic voltammogram of 2 measured in dichloromethane is shown in Fig. 4. Two pseudo-reversible redox waves are observed at  $E_{1/2} = +90$  mV (vs. Ag/Ag<sup>+</sup>,  $\Delta E = E_{pc} - E_{pa} = 250$  mV) and at  $E_{1/2} = +540$  mV (vs. Ag/Ag<sup>+</sup>,  $\Delta E = 150$  mV). These waves correspond to

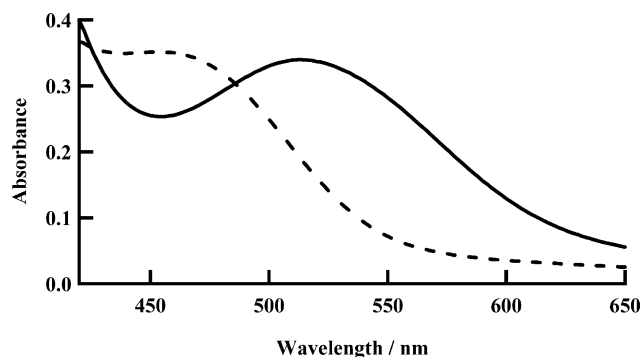


Fig. 3. Electronic absorption spectra of 2 ( $5.0 \times 10^{-4}$  mol dm<sup>-3</sup>) in benzene (—) and in DMF (---).



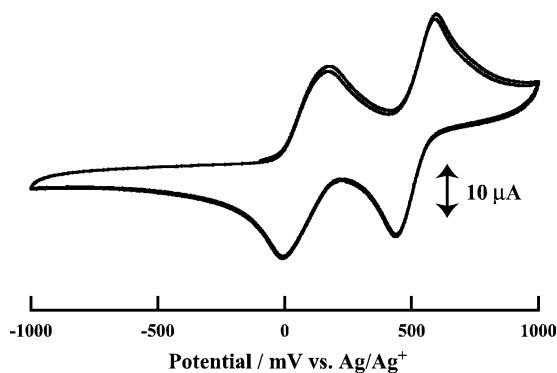


Fig. 4. Cyclic voltammogram of **2** ( $1.0 \times 10^{-3}$  mol dm $^{-3}$ ) in dichloromethane; supporting electrolyte, 0.1 mol dm $^{-3}$  [NBu $_4$ ][ClO $_4$ ]; sweep rate, 500 mV s $^{-1}$ .

the redox processes [Au(ppy)(C $_{10}$ -C $_6$ S $_8$ )] $^{0/+1}$  and [Au(ppy)(C $_{10}$ -C $_6$ S $_8$ )] $^{+1/+2}$ , respectively. The cyclic voltammogram of **1** measured in DMF has also exhibited two oxidation potentials at  $-60$  and  $+430$  mV (vs. Ag/Ag $^+$ ) as irreversible waves. These first oxidation potentials correspond to the dithiolate ligand-centered oxidation, as described below. The first oxidation potentials of **1** and **2** are somewhat higher than those of related polarized [Pt(diimine)(dithiolate)] complexes: [Pt(bpy)(C $_{10}$ -C $_6$ S $_8$ )],  $-110$  mV; [Pt(bpy)(C $_8$ H $_4$ S $_8$ )],  $-180$  mV (vs. Ag/Ag $^+$  in DMF) [13]. These findings and the above-described mixed dithiolate/metal-to-ppy CT energies suggest that energies of the ground states for the present Au(III) complexes are lower than those of the related Pt(II) complexes.

### 3.3. Spectroscopic properties of the oxidized species 3–6 and their electrical conductivities

These metal complexes having low first oxidation potentials can be oxidized by iodine and TCNQ. Fig. 5 shows the spectral change of complex **1** in the presence of various amounts of iodine as an oxidant in benzonitrile. The intramolecular mixed dithiolate/metal-to-ppy

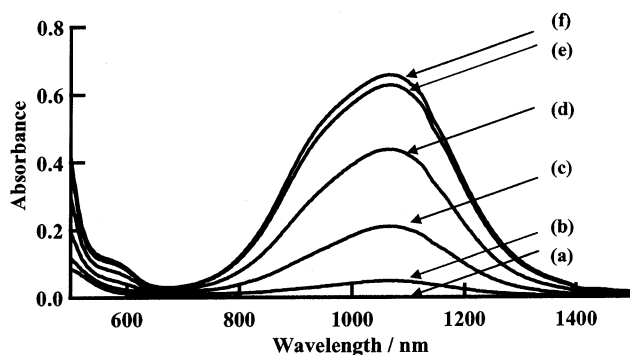


Fig. 5. Electronic absorption spectra of complex **1** ( $5.0 \times 10^{-5}$  mol dm $^{-3}$ ) in benzonitrile in the presence of iodine: (a) 0, (b)  $5.0 \times 10^{-5}$ , (c)  $1.0 \times 10^{-4}$ , (d)  $1.5 \times 10^{-4}$ , (e)  $2.0 \times 10^{-4}$ , (f)  $2.5 \times 10^{-4}$  mol dm $^{-3}$ .

ligand CT band observed at 500 nm is increased slightly in its intensity with increase of amounts of iodine, although the oxidation of [Pt(diimine)(C $_8$ H $_4$ S $_8$ )] complexes causes the higher energy shift of the related mixed dithiolate/metal-to-diimine ligand CT transition [13,21]. Upon the oxidation of **1**, an intense band appears at 1070 nm due to the metal-to-C $_8$ H $_4$ S $_8$  ligand CT transition of the oxidized species. The oxidation of **2** with addition of iodine also causes the band at 1030 nm. Similar bands were observed at low wavelengths for the oxidized species of [Pt(bpy)(C $_8$ H $_4$ S $_8$ )] [13], [Co( $\eta^5$ -C $_5$ H $_5$ )(C $_8$ H $_4$ S $_8$ )] [34], [Ti( $\eta^5$ -C $_5$ H $_5$ ) $_2$ (C $_8$ H $_4$ S $_8$ )], [NMe $_4$ ]-[Ti( $\eta^5$ -C $_5$ H $_5$ )(C $_8$ H $_4$ S $_8$ ) $_2$ ] [30], [Ru(bpy) $_2$ (C $_8$ H $_4$ S $_8$ )] [20] upon the C $_8$ H $_4$ S $_8$  ligand-oxidation.

Reactions of complexes **1** and **2** with excess amounts of iodine have afforded oxidized species **3** and **4**. The presence of the I $_3^-$  ion in **3** and **4** has been confirmed by the I–I–I stretching bands [35,36] observed at 111 and at 110 cm $^{-1}$ , respectively, in the Raman spectra. Complexes **1** and **2** have been also reacted with excess amounts of TCNQ to give oxidized species **5** and **6** containing the TCNQ $^{\bullet-}$  radical anion. The TCNQ $^{\bullet-}$  radical anion moieties are likely present as the (TCNQ) $_2^{\bullet-}$  anion dimer, since both the complexes have shown the IR frequencies of 2178 and 2155 cm $^{-1}$  assigned to the CN stretching bands, as observed for Li(TCNQ) [37]. Thus, the iodine-oxidizing complexes **3** and **4** are essentially one-electron oxidized species, while TCNQ-oxidizing complexes **5** and **6** are partially oxidized ones; they seem to be essentially formally 0.5 electron-oxidized species.

Powder ESR spectra of the oxidized species **3**–**6** have shown almost an isotropic signal centered at  $g = 2.004$ – $2.005$  (the peak-to-peak linewidths, 2.0–3.5 mT). These findings suggest the dithiolate ligand-centered oxidation, as observed for oxidized species of C $_8$ H $_4$ S $_8$ –[13,17,20,30,31,34] and C $_{10}$ -C $_6$ S $_8$ -metal complexes [13,15]. No separated signal due to the TCNQ $^{\bullet-}$  radical anion has been observed for **5** and **6** in both solution and powder spectra of them, since the oxidized complexes and the TCNQ $^{\bullet-}$  radical anion have very similar  $g$  values. One of the  $\nu$ (C=C) stretching IR bands of the C $_8$ H $_4$ S $_8$  and C $_{10}$ -C $_6$ S $_8$  ligands of **1** and **2** occurring at 1437–1461 cm $^{-1}$  are shifted to 1340–1389 cm $^{-1}$  in the oxidized species **3**–**6**. These large low-frequency shifts of 76–103 cm $^{-1}$  are also consistent with the C $_8$ H $_4$ S $_8$  and C $_{10}$ -C $_6$ S $_8$  ligand-centered oxidation, as observed for other C $_8$ H $_4$ S $_8$ - and C $_{10}$ -C $_6$ S $_8$ -metal complexes [13,15].

Fig. 6 shows the powder reflectance spectrum of the oxidized species **3** as well as that of the original species **1**. The intense band at 900 nm observed for **3** is due to the metal-to-dithiolate ligand CT transition, as observed in the spectral change of **1** upon oxidation in solution (Fig. 3). Furthermore, the spectrum of **3** shows broad bands at longer wavelengths, which are likely due to intermolecular interactions through S–S non-bonded con-

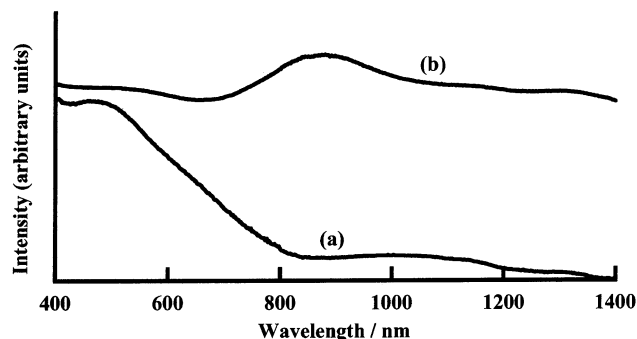


Fig. 6. Powder reflectance spectra of (a) complex **1** and (b) its oxidized species **3**.

tacts in the solid state, assisted by the  $C_8H_4S_8$  ligand-centered oxidation. Similarly, the powder reflectance spectra of **4**, **5** and **6** have shown the broad bands at longer wavelengths due to the S–S interactions. These enhanced S–S contacts in the oxidized species were observed for the crystal structure of the one-electron oxidized  $[Pt(bpy)(C_8H_4S_8)]^+$  complex [14]. These findings reflect the construction of effective electron-conduction pathways resulting in appreciable electrical conductivities of these oxidized species, as described below.

Complexes **1** and **2** are essentially insulators with electrical conductivities of  $< 10^{-9} \text{ S cm}^{-1}$  measured for compacted pellets at room temperature. The oxidized complexes **3–6** behave as electrical conductors with high electrical conductivities, as listed in Table 3. They are appreciably higher than those of previously reported related Pt(II) complexes:  $[Pt(bpy)(C_8H_4S_8 \text{ or } C_{10}-C_6S_8)]^{n+}$  ( $n \leq 1$ ) salts,  $5.6 \times 10^{-5}$ – $6.5 \times 10^{-3} \text{ S cm}^{-1}$  [13]. Furthermore, it is noteworthy that the high electrical conductivities of the  $C_{10}-C_6S_8$  species **4** and **6** are similar to those of the  $[Pt(C_{10}-C_6S_8)_2]^0$  species ( $4.9 \times 10^{-2} \text{ S cm}^{-1}$ ) [15]. These findings suggest that the present oxidized species form much effective molecular packings for the electron-conducting pathways through many S–S contacts in the solid state, as observed for many oxidized  $C_3S_5$ - [1–3] and  $C_8H_4S_8$ -metal complexes [5,14,20,21].

Table 3  
Electrical conductivities ( $\sigma_{r.t.}$ )<sup>a</sup>

Complex	$\sigma_{r.t.} \times 10^2 \text{ (S cm}^{-1}\text{)}$
<b>3</b>	3.8
<b>4</b>	4.0
<b>5</b>	2.0
<b>6</b>	3.4

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

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