X-ray Crystal Structure and Electrical Conductivity of $[Au(ppy)(C_8H_4S_8)]_2[PF_6]$ [$ppy^- = C$-deprotonated 2-phenylpyridine(−); $C_8H_4S_8^{2-}$ = 2-{(4,5-ethylenedithio)-1,3-dithiol-2-ylidene}-1,3-dithiole-4,5-dithionate(2−)]

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Keywords: Gold / S ligands / Oxidation / Sulfur / Electrochemistry

Crystals of $[Au(ppy)(C_8H_4S_8)]_2[PF_6]$ [ppy^- = *C*-deprotonated 2-phenylpyridine(−); $C_8H_4S_8^{2-}$ = 2-{(4,5-ethylenedithio)-1,3-dithiol-2-ylidene}-1,3-dithiole-4,5-dithiolate(2−)] were prepared by current-controlled electrolysis of a benzonitrile solution of $[Au(ppy)(C_8H_4S_8)]$ with $[NEt_4][PF_6]$ as an electrolyte. The X-ray crystal structure analysis revealed the formation of a columnar stacking of two crystallographically independent cations in formally the 0.5-electron-oxidized state. Cation moieties with some S–S non-bonded contacts (< 3.7 Å) along the *a* and *b* axes form a two-dimensional sheet, with the molecular interaction parallel to the *ab* plane. The electrical conductivities measured for a crystal at room temperature were 9.2 and 0.0028 S cm^{-1} along the *a* and *c* axes, respectively. From the activation energy for the electron conduction determined by the conductivities measured for a compacted pellet the complex was estimated to be metallic from room temperature to 110 K. The energy-band calculation for the oxidized species showed two-dimensional electron conduction through the column.

Introduction

Many molecular electron-conducting compounds made from metal complexes containing sulfur-rich dithiolate ligands, such as $C_3S_5^{2-}$ and $C_8H_4S_8^{2-}$, have been extensively studied; their oxidized metal complexes become good electrical conductors and superconductors.[1−6] They construct effective electron-conduction pathways through some sulfur-sulfur non-bonding contacts in the solid state.

Polarized metal complexes containing both a sulfur-rich dithiolate ligand and an N−N or N−C chelating ligand are expected to form unique molecular stackings and/or layered arrangements through electrostatic interaction of the polarized metal-center moieties, metal-metal interactions and some S−S non-bonding contacts in the solid state behaving as an inorganic/organic molecular composite. Recently, we reported the preparation and crystal structures of planar, asymmetric metal complexes of the [M(N−N)(S−S)] type [M = Pd^{II} and Pt^{II}; N−N = diimine ligands and S−S = sulfur-rich dithiolate ligands(2−)][7,8] and of the [Au^{III}(C−N)(S−S)] type [C−N = *C*-deprotonated 2-phenylpyridine(−) (ppy^-); S−S = sulfur-rich dithiolate ligands(2−)];[9] their chemically oxidized species exhibit high electrical conductivities.

This paper reports the crystal structure of the title oxidized species prepared by electrocrystallization of $[Au(ppy)(C_8H_4S_8)]$ in benzonitrile in the presence of $[NEt_4][PF_6]$, together with the electrical conductivities measured for the crystal and energy bands calculated based on the crystal structure.

Results and Discussion

Preparation of the 0.5-Electron-Oxidized Species $[Au(ppy)(C_8H_4S_8)]_2[PF_6]$

The cyclic voltammogram of $[Au(ppy)(C_8H_4S_8)]$ measured in *N*,*N*-dimethylformamide exhibits two oxidation peaks at −60 and +430 mV (versus Ag/Ag^+);[9] the first oxidation occurs on the $C_8H_4S_8$ ligand. The first oxidation potential is slightly higher than that of the diimine/$C_8H_4S_8$-Pt^{II} complex $[Pt(bpy)(C_8H_4S_8)]$ (−180 mV versus Ag/Ag^+).[8] Reactions of $[Au(ppy)(C_8H_4S_8)]$ with iodine and tetracyano-*p*-quinodimethane (TCNQ) also gave the one-electron-oxidized species $[Au(ppy)(C_8H_4S_8)](I_3)$ and the essentially 0.5-electron-oxidized complex $[Au(ppy)(C_8H_4S_8)](TCNQ^{\cdot -})_{0.6}$, respectively.[9] The present 0.5-electron-oxidized species prepared by the electrocrystallization exhibits almost an isotropic ESR signal with g = 2.007 (peak-to-peak linewidth, 5 mT), as observed for other oxidized $C_8H_4S_8$-metal complexes.[7−13] This finding suggests the $C_8H_4S_8$ ligand-centered oxidation, as confirmed from the

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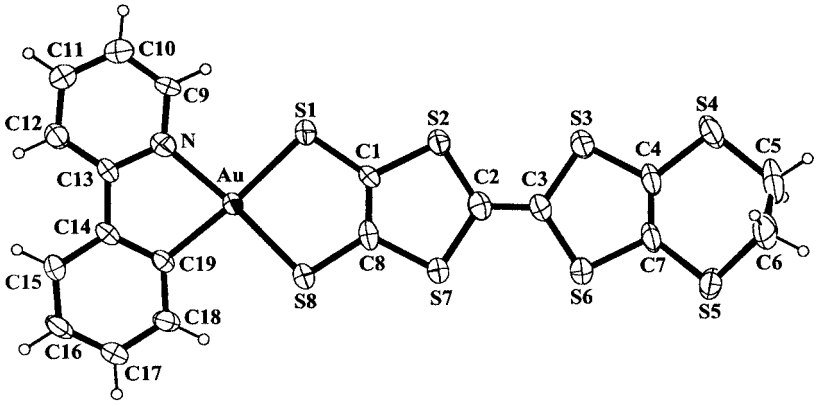

Figure 1. Geometry of one of the cation moieties of $[Au(ppy)(C_8H_4S_8)]_2[PF_6]$ together with the atom-labeling scheme

spin densities calculated for the one-electron-oxidized $C_8H_4S_8$-Ti^{IV} complex.[13]

The powder reflectance spectrum of the present oxidized species exhibits a band at 900 nm due to the metal-to-dithiolate ligand charge-transfer transition[7–9] and broad bands at longer wavelengths. They suggest intermolecular interactions through some S−S non-bonding contacts in the solid state.

Molecular and Crystal Structures of $[Au(ppy)(C_8H_4S_8)]_2[PF_6]$

The crystal structure of the complex consists of two crystallographically independent cations and octahedral anions. The molecular structure of one of the cation moieties of the complex is shown in Figure 1, together with the atom-labeling scheme. The other cation has also almost the same geometry as this. Selected bond lengths and angles are listed in Table 1.

The Au^{III} ion shows a square-planar coordination, as expected for d^8-metal complexes. The Au(1)−N(1) [2.069(6) Å] and Au(1)−C(19) [2.054(7) Å] distances are close to those of the unoxidized species $[Au(ppy)(C_8H_4S_8)]$ [Au−N = 2.063(3) Å and Au−C = 2.041(5) Å].[9] They are also similar to those of [Au(ppy)(tdt)] [tdt^{2-} = 3,4-toluenedithiolate(2−)] [Au−N = 2.079(5) Å and Au−C = 2.035(7) Å][14] and $[Au(ppy)(S_2CNEt_2)]^+$ [Au−N = 2.058(11) Å and Au−C = 2.036(7) Å].[15] The Au(1)−S(1) bond [2.316(2) Å] trans to the Au(1)−C(19) bond is longer than the Au(1)−S(8) bond [2.298(2) Å] trans to Au(1)−N(1) owing to the structural trans influence. This structural trans influence has also been observed for other $[Au^{III}(C-N)(S-S)]$-type complexes.[9,14–17] The $C_8H_4S_8$

Table 1. Selected bond lengths (Å) and angles (°) of $[Au(ppy)(C_8H_4S_8)]_2[PF_6]$

Au(1)−S(1)	2.316(2)	Au(1)−S(8)	2.298(2)	Au(2)−S(9)	2.324(2)
Au(2)−S(16)	2.294(2)	Au(1)−N(1)	2.069(6)	Au(2)−N(2)	2.065(7)
Au(1)−C(19)	2.054(7)	Au(2)−C(38)	2.035(6)	S(1)−C(1)	1.735(7)
S(2)−C(1)	1.753(6)	S(2)−C(2)	1.719(8)	S(3)−C(3)	1.742(8)
S(3)−C(4)	1.744(8)	S(4)−C(4)	1.759(8)	S(4)−C(5)	1.801(11)
S(5)−C(6)	1.790(10)	S(5)−C(7)	1.735(8)	S(6)−C(3)	1.731(8)
S(6)−C(7)	1.746(7)	S(7)−C(2)	1.760(8)	S(7)−C(8)	1.749(7)
S(8)−C(8)	1.731(7)	S(9)−C(20)	1.731(7)	S(10)−C(20)	1.747(7)
S(10)−C(21)	1.739(7)	S(11)−C(22)	1.747(7)	S(11)−C(23)	1.753(6)
S(12)−C(23)	1.756(7)	S(12)−C(24)	1.803(8)	S(13)−C(25)	1.774(9)
S(13)−C(26)	1.741(7)	S(14)−C(22)	1.737(8)	S(14)−C(26)	1.758(7)
S(15)−C(21)	1.746(7)	S(15)−C(27)	1.736(7)	S(16)−C(27)	1.745(7)
C(1)−C(8)	1.344(10)	C(2)−C(3)	1.370(10)	C(4)−C(7)	1.34(1)
C(5)−C(6)	1.49(1)	C(20)−C(27)	1.365(10)	C(21)−C(22)	1.36(1)
C(23)−C(26)	1.325(10)	C(24)−C(25)	1.50(1)		
S(1)−S(4*)[a]	3.579(3)	S(2)−S(4*)[a]	3.636(4)	S(5)−S(10**)[a]	3.339(3)
S(5)−S(9**)[a]	3.441(3)	S(9)−S(12′)[a]	3.665(3)	S(13)−S(16′′)[a]	3.351(3)
S(13)−S(15′′)[a]	3.408(3)				
S(1)−Au(1)−S(8)	91.44(7)	S(1)−Au(1)−N(1)	93.9(2)		
S(8)−Au(1)−C(19)	93.7(3)	N(1)−Au(1)−C(19)	81.1(3)		
S(9)−Au(2)−S(16)	90.93(6)	S(9)−Au(2)−N(2)	95.7(2)		
S(16)−Au(2)−C(38)	93.3(2)	N(2)−Au(2)−C(38)	80.4(2)		
Au(1)−S(1)−C(1)	99.3(3)	Au(1)−S(8)−C(8)	100.3(3)		
S(1)−C(1)−C(8)	124.9(5)	S(8)−C(8)−C(1)	123.8(5)		
Au(2)−S(9)−C(20)	100.5(2)	Au(2)−S(16)−C(27)	101.0(2)		
S(9)−C(20)−C(27)	124.0(5)	S(16)−C(27)−C(20)	123.3(6)		

[a] Symmetry code: * 1 − x, 1 − y, 1 − z; ** 1 − x, −y, 1 − z; ′ −x, −y, 1 − z; ′′ −x, 1 − y, 1 − z.

moiety of $[Au(ppy)(C_8H_4S_8)]_2[PF_6]$ is almost planar, and is similar to that of the one-electron-oxidized complex $[Pt(bpy)(C_8H_4S_8)][BF_4]$.[8] The planar $C_8H_4S_8$ ligand of the oxidized species is in great contrast to the bent geometries of this ligand observed for unoxidized $C_8H_4S_8$-metal complexes such as $[Au(ppy)(C_8H_4S_8)]$[9] and $[Ti(C_5Me_5)_2(C_8H_4S_8)]$.[12] The C(2)−C(3) bond [1.37(1) Å] of the $C_8H_4S_8$ ligands is somewhat longer than the corresponding bond (1.349 Å) in $[Au(ppy)(C_8H_4S_8)]$.[9] This is consistent with the $C_8H_4S_8$ ligand-centered oxidation in the complex, as described above.

The perspective view of the packing diagram of $[Au(ppy)(C_8H_4S_8)]_2[PF_6]$ along the *a* axis is shown in Figure 2. The ppy and $C_8H_4S_8$ ligand moieties of the cations are almost overlapped with themselves in the same molecular orientations along the *a* axis to form a dimer unit with an Au(1)−Au(2) contact of 3.812 Å. This is in a contrast to the unoxidized species $[Au(ppy)(C_8H_4S_8)]$, which has a zigzag arrangement with alternating ppy and $C_8H_4S_8$ ligands because of the polarized orientation around the metal ion.[9] In the present case the cation moieties overlap with one another in the same molecular direction. A similar stacking pattern has also been seen in the cation moieties of $[Pt(bpy)(C_8H_4S_8)][BF_4]$.[8] For these oxidized complexes, some S−S non-bonding contacts (< 3.7 Å) between the oxidized $C_8H_4S_8$ moieties seem to contribute to such molecular arrangements: S(2)−S(14) = 3.682(3); S(6)−S(11) = 3.616(3); S(7)−S(10) = 3.679(2) Å.

As illustrated in Figure 3, the dimer units form a columnar structure along the *a* axis through an S−S non-bonding contact [S(3)−S(15) (1 + *x*, *y*, *z*) = 3.655(3) Å]. Furthermore, there are many S−S non-bonding contacts between the columns (3.339−3.616 Å, in Table 1), resulting in a two-dimensional sheet of molecular interactions parallel to the *ab* plane.

Energy-Band Calculation and Electron Conduction

Figure 4 shows the resultant energy dispersions of several orbitals calculated by the extended Hückel method for the crystal structure of $[Au(ppy)(C_8H_4S_8)]_2[PF_6]$ along the symmetry lines *Γ*-*X*, *X*-*V* and *V*-*C*.[18]

Appreciably significant dispersions are found in the *Γ*-*X* zone, which reflects a large orbital overlapping along the column of the cation moieties parallel to the *a* axis. Fur-

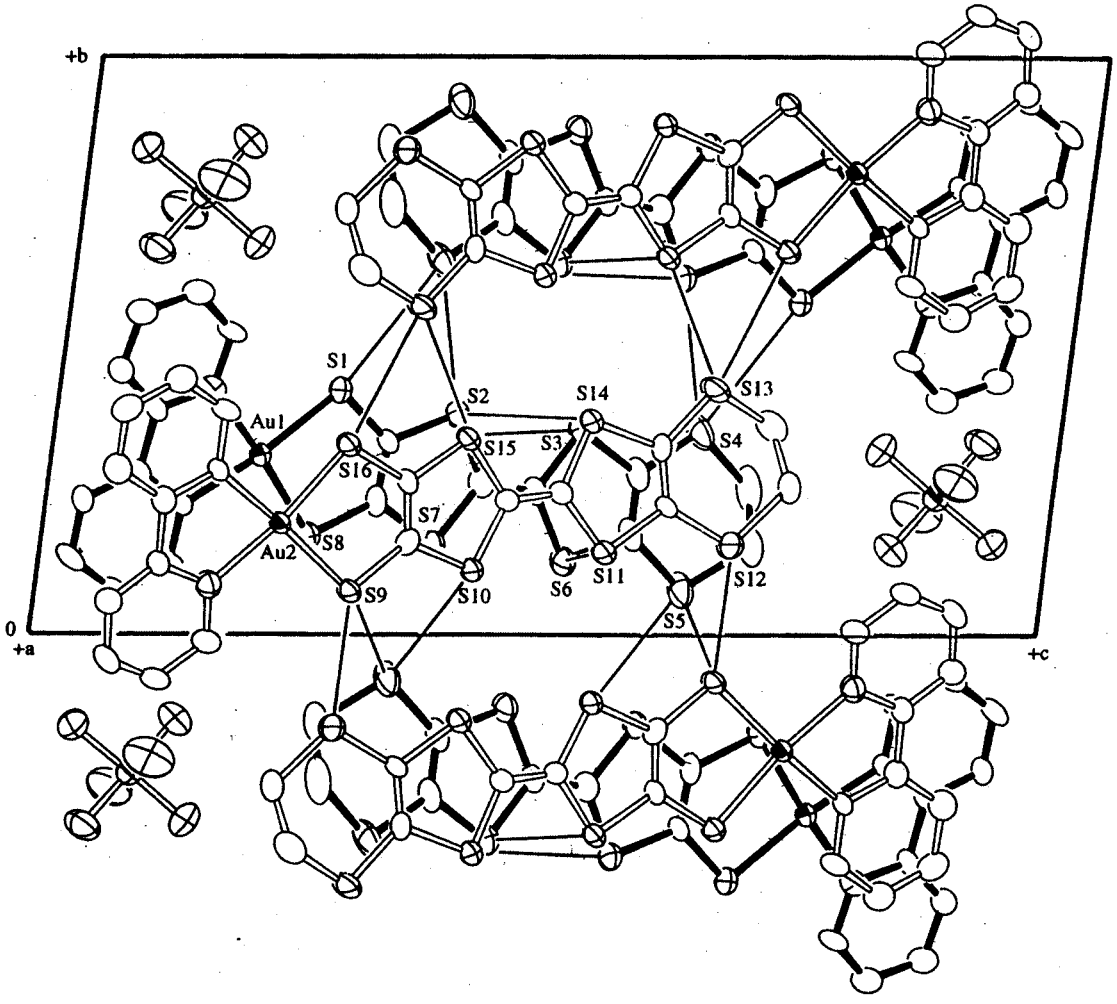

Figure 2. Crystal structure of $[Au(ppy)(C_8H_4S_8)]_2[PF_6]$ projected along the *a* axis; fine lines represent S−S non-bonding contacts of less than 3.7 Å

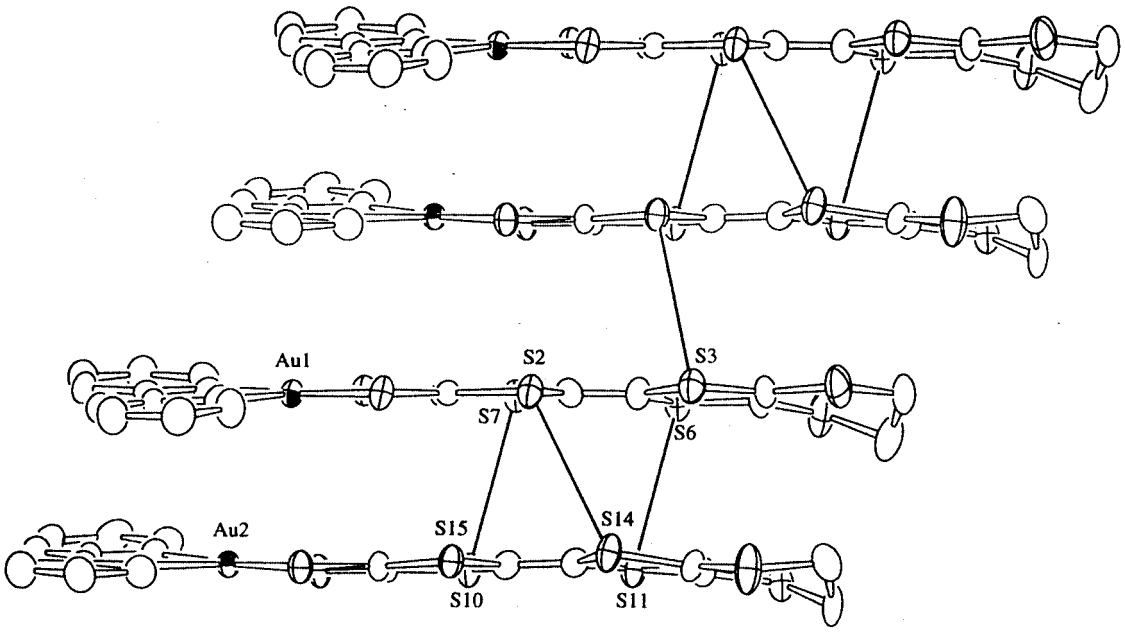

Figure 3. Projection of the overlapping mode of the cation moieties of $[Au(ppy)(C_8H_4S_8)]_2[PF_6]$ along the *a* axis; fine lines represent S−S non-bonding contacts of less than 3.7 Å

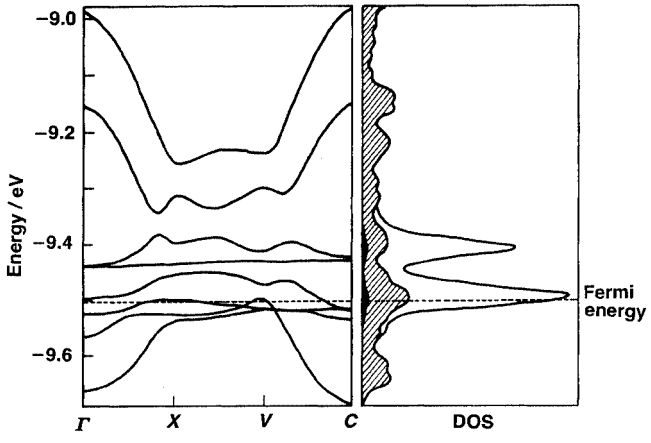

Figure 4. Dispersion of energy bands near the Fermi energy calculated for a crystal of $[Au(ppy)(C_8H_4S_8)]_2[PF_6]$, together with total densities of states (DOS) for gold (dark), ppy (open), and $C_8H_4S_8$ moieties (diagonal lines): *Γ, X, V* and *C* refer to the symmetry points with wave vectors 0, $a^*/2$, $(a^* + b^*)/2$ and $(b^* + c^*)/2$, respectively

thermore, large dispersions of some orbitals are observed in the *V*-*C* zone along the *b* axis, which are attributable to a side-by-side overlap of the $C_8H_4S_8$ moieties in neighboring columns. However, no significant dispersions of orbitals are observed in the *X*-*V* zone along the axis including the *c* component. The ppy ligands and PF_6^- anions are located parallel to the *bc* plane. Thus, no significant dispersions are found between the $C_8H_4S_8$ ligand moieties in the neighboring columns along the *c* axis. The Fermi energy level is located in the sharp ppy band, which is overlapped with $C_8H_4S_8$ bands with large dispersions. This band character, as well as the overlapping among the $C_8H_4S_8$ moieties observed in the crystal structure, suggests a metallic character of the complex along the *a* and *b* axes.

The electrical conductivities of the complex measured for a crystal are 9.2 and 0.0028 S cm^{-1} along almost the *a* and *c* axes, respectively, at room temperature. The activation energy for the electron conduction determined by the electrical conductivities measured for a compacted pellet was 0.0 eV from room temperature to 110 K. Thus, the complex is estimated to be metallic along the *a* axis. This finding, together with extremely low conductivity measured along almost the *c* axis, is consistent with the energy-band dispersions calculated based on the crystal structure of the complex, as described above. The present complex exhibits a much higher electrical conductivity than that (2.0×10^{-2} S cm^{-1} for a compacted pellet) of the essentially 0.5-electron-oxidized species $[Au(ppy)(C_8H_4S_8)](TCNQ^{\cdot -})_{0.6}$,[9] which may be due to a variance of molecular packing of these $[Au(ppy)(C_8H_4S_8)]$ moieties in the crystal.

Experimental Section

Preparation of $[Au(ppy)(C_8H_4S_8)]_2[PF_6]$: A benzonitrile (15 mL) solution of $[Au(ppy)(C_8H_4S_8)]$[9] (3.0 mg, 4.2 μmol) containing $[NEt_4][PF_6]$ (20 mg, 7.2 mmol) as an electrolyte was electrolyzed under current-controlled conditions (0.1 μA) for 10 days in an H-shaped cell equipped with platinum wire electrodes under an argon atmosphere at 30 C. Black needles of the oxidized species that formed on the surface of the anode were collected and dried in vacuo. The chemical formula of the complex was confirmed by the X-ray crystal structure analysis.

Physical Measurements and Energy-Band Calculations: Electronic absorption, powder reflectance and ESR spectra were recorded as described previously.[19,20] Electrical conductivities were measured

for a crystal at room temperature. To determine the activation energy for the electron-conduction the conductivities were measured for a compacted pellet from room temperature to 110 K using an apparatus consisting of a Hioki 3552 LCR Hi-tester and a digital temperature controller (Scientific Instrument Model 9650).[21]

Energy-band calculations based on the extended Hückel method[22,23] for the crystal structure of the cation moieties of $[Au(ppy)(C_8H_4S_8)]_2[PF_6]$ were carried out using standard extended Hückel parameters[23,24] and the conventional weight of 1.75 for the Wolfsberg−Helmholtz relation.[25−27] In the calculations the PF_6^- parts of the crystal were disregarded since they have negligible contributions to the orbitals near the Fermi energy.

Crystal Structure Determination of $[Au(ppy)(C_8H_4S_8)]_2[PF_6]$: A single crystal of the complex of dimensions 0.10 × 0.06 × 0.025 mm obtained electrolytically was used for the crystal structure determination. 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-K_α (λ = 0.71069 Å) radiation at the Graduate School of Engineering, Osaka University. Indexing was performed for reflections obtained from three oscillations exposed for 200 s. Final values of the cell parameters were obtained from least-squares refinement of the positions of 23225 observed reflections. Equivalent reflections were merged by use of the PROCESS-AUTO program package. Of 24467 reflections collected, 12826 were unique (R_{int} = 0.060), which were corrected for absorption using the program ABSCOR[28] (transmission factor: 0.449−0.834) and for Lorenz and polarization effects. Crystallographic data are summarized in Table 2.

Table 2. Experimental crystallographic data for $[Au(ppy)(C_8H_4S_8)]_2[PF_6]$

Formula	$C_{38}H_{24}Au_2F_6N_2PS_{16}$
M	1560.48
Crystal size (mm)	0.10 × 0.06 × 0.025
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	8.2731(2)
b (Å)	12.8828(5)
c (Å)	21.6185(7)
α (°)	83.375(1)
β (°)	87.937(1)
γ (°)	85.809(2)
V (Å^3)	2281.7(1)
Z	2
D_{calc} (g cm^{-3})	2.271
F(000)	1498
μ(Mo-K_α) (mm^{-1})	7.251
T (°C)	−40
Measured 2θ range (°)	6.1−60.0
No. of reflections collected	24467
Independent reflections	12826
Observed reflections	9521
R[a]	0.055
R_w [b]	0.117

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w^2 = \Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2$; $w^{-1} = \sigma^2(F_o^2) + (0.0575P)^2 + 1.8569P$, where $P = (F_o^2 + 2F_c^2)/3$.

The structure was solved by the Patterson method (PATTY)[29] and expanded using Fourier techniques (DIRDIF94)[30] and refined on F^2 by the full-matrix least-squares method (SHELXL-97).[31] Non-hydrogen atoms were refined anisotropically with 1.2-times equivalent temperature factors of the parent atoms. Hydrogen atoms were placed on the positions calculated geometrically. Atomic scattering factors were taken from the usual sources.[32] Figures 1 and 2 were drawn with ORTEP II.[33]

CCDC-208606 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This research was supported in part by grants-in-Aid for scientific research (no. 14044056) from Ministry of Education, Science, Sports and Culture, Japan and by a Strategic Research Base Upbringing Special Coordination Fund for Promoting Science and Technology.

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Received June 16, 2003

