X-ray crystal structure of $[Fe(C_5Me_5)_2][Au(C_3S_5)_2]$ and properties of partially oxidized $[Au(C_3S_5)_2]$ anion complexes

Gen-etsu Matsubayashi* and Akito Yokozawa
Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560 (Japan)

(Received September 24, 1991)

Abstract

$[Fe(C_5Me_5)_2][Au(C_3S_5)_2]$ (**1**) ($C_3S_5^{2-}$ = 4,5-dimercapto-1,3-dithiol-2-thionate) has been prepared by a reaction of $[NBu^n_4][Au(C_3S_5)_2]$ with $[Fe(C_5Me_5)_2][BF_4]$ in *N,N*-dimethylformamide. $[NBu^n_4][Au(C_3S_5)_2]$ has been oxidized electrochemically in the presence of $Fe(C_5Me_5)_2$ and $Fe(C_5H_5)_2$ in acetonitrile to afford $[Fe(C_5Me_5)_2]_{0.33}[Au(C_3S_5)_2]$ (**2**) and $[Fe(C_5H_5)_2]_{0.33}[Au(C_3S_5)_2]$ (**3**). A single-crystal X-ray structure analysis of **1** reveals that dimeric units of the $[Au(C_3S_5)_2]^-$ anion have one-dimensional arrangement through sulfur–sulfur contacts in the crystal phase. The triclinic crystal, space group $P\bar{1}$, has cell dimensions $a = 11.675(5)$, $b = 15.118(6)$, $c = 10.066(4)$ Å, $\alpha = 85.50(4)$, $\beta = 94.63(4)$, $\gamma = 68.87(3)°$ and $Z = 2$. The refinement based on 5804 reflections ($|F_o| > 3\sigma(F)$) converged at $R = 0.042$. The partially oxidized species **2** and **3** exhibit electrical conductivities of 0.093 and 0.12 S cm^{-1}, respectively, measured for compacted pellets at 25 °C and their molecular interactions described based on electronic reflectance and X-ray photoelectron spectra.

Introduction

Planar bis(C_3S_5)gold(III) complexes ($C_3S_5^{2-}$ = 4,5-dimercapto-1,3-dithiol-2-thionate) were reported to be oxidized to afford good electrical conductors [1–3], as well as partially oxidized $[M(C_3S_5)_2]$ complexes (M = Ni(II), Pd(II) and Pt(II)) [4]. In $[NBu^n_4]$-$[Au(C_3S_5)_2]$ the planar $[Au(C_3S_5)_2]^-$ anion moieties are arranged with a one-dimensional molecular interaction through S--S contacts in the crystal phase [1], which is in contrast to less significant molecular interactions observed in the crystals of $[M(C_3S_5)_2]^{2-}$ and $[M(C_3S_5)(C_3Se_5)]^{2-}$ (M = Ni(II) and Pd(II)) anion complexes [5, 6]. It is, therefore, of interest to investigate molecular interactions of $[Au(C_3S_5)_2]^-$ anion complexes in the crystal phase, as well as electrical properties of their oxidized species.

This paper reports the crystal structure of $[Fe(C_5Me_5)_2][Au(C_3S_5)_2]$ having a chain structure of the anion moieties with interanionic molecular interaction through sulfur–sulfur contacts, and spectroscopic and electrical properties of the partially oxidized $[Au(C_3S_5)_2]$ anion complexes having $[Fe(C_5H_5)_2]^+$ and $[Fe(C_5Me_5)_2]^+$ cations.

Experimental

Preparations of the complexes

$[Fe(C_5Me_5)_2][Au(C_3S_5)_2]$ (1)

All the following reactions were performed under a nitrogen atmosphere. An *N,N*-dimethylformamide (dmf) (2 cm^3) solution containing $[NBu^n_4][Au(C_3S_5)_2]$ [1] (12.5 mg, 15 μmol) and $[Fe(C_5Me_5)_2][BF_4]$ [7] (12 mg, 30 μmol) was allowed to stand in a refrigerator for 12 h to afford black microcrystals of complex **1**. They were collected by filtration, washed with dmf and methanol, and dried *in vacuo* (66% yield). *Anal.* Calc. for $C_{26}H_{30}AuFeS_{10}$: C, 34.14; H, 3.28. Found: C, 34.09; H, 3.30%. Needles of complex **1** for the X-ray structure analysis were afforded by a diffusion reaction of $[NMe_4][Au(C_3S_5)_2]$ (50 mg, 750 μmol) with $[Fe(C_5Me_5)_2][BF_4]$ (62 mg, 150 μmol) in acetonitrile (50 cm^3) at 40 °C for 20 days (2% yield).

$[Fe(C_5Me_5)_2]_{0.33}[Au(C_3S_5)_2]$ (2)

An acetonitrile (50 cm^3) solution containing $[NBu^n_4][Au(C_3S_5)_2]$ (20 mg, 24 μmol) and $Fe(C_5Me_5)_2$ (11 mg, 34 μmol) was subjected to a controlled-current (2.0 μA) electrolysis under a nitrogen atmosphere for 30 days at room temperature in an H-type glass cell consisting of platinum wires of 0.5 mm ϕ (for both

---

*Author to whom correspondence should be addressed.

0020-1693/92/$5.00

anode and cathode). Black microcrystals of **2** produced on the anode were collected and dried *in vacuo* (50% yield). *Anal.* Calc. for $C_{12.6}H_{9.9}AuFe_{0.33}S_{10}$: C, 21.70; H, 1.43. Found: C, 21.33; H, 1.38%.

$[Fe(C_5H_5)_2]_{0.33}[Au(C_3S_5)_2]$ *(3)*

A controlled-current (0.5 μA) electrolysis of an acetonitrile (50 cm^3) solution containing $[NBu^n{}_4]$-$[Au(C_3S_5)_2]$ (20 mg, 24 μmol) and $Fe(C_5H_5)_2$ (10 mg, 54 μmol) at room temperature as described above afforded black microcrystals of **3**, which were collected and dried *in vacuo* (35% yield). *Anal.* Calc. for $C_{9.3}H_{3.3}AuFe_{0.33}S_{10}$: C, 17.16; H, 0.51. Found: C, 17.21; H, 0.73%. Complex **3** has another cation–anion ratio compared with $[Fe(C_5H_5)_2]_{0.25}[Au(C_3S_5)_2]$ which was obtained by the electrolysis of the acetonitrile solution of $[NBu^n{}_4][Au(C_3S_5)_2]$ and $[Fe(C_5H_5)_2][PF_6]$ [1].

Physical measurements

Electronic absorption [8], ESR [9] and X-ray photoelectron spectra [10] were recorded as described previously. Powder reflectance spectra were measured using a Shimadzu UV-2200 spectrophotometer equipped with an integrated spherical unit. Electrical conductivities were measured for compacted pellets in the range −30 to 30 °C by the conventional two-probe method [8].

X-ray crystal structure of $[Fe(C_5Me_5)_2][Au(C_3S_5)_2]$ *(1)*

Accurate unit-cell parameters were determined from 25 reflections with 2θ values from 20 to 32°, measured with a Rigaku four-circle diffractometer at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University.

Crystal data. $C_{26}H_{30}AuFeS_{10}$, $M = 915.9$, triclinic, space group $P\bar{1}$, $a = 11.675(5)$, $b = 15.118(6)$, $c = 10.066(4)$ Å, $\alpha = 85.50(4)$, $\beta = 94.63(4)$, $\gamma = 68.87(3)°$, $U = 1632(1)$ Å^3, $Z = 2$, $F(000) = 902.0$, $D_c = 1.864(1)$ g cm^{-3}, and μ(Mo Kα) $= 57.1$ cm^{-1}.

Intensities were collected in the range $3 < 2\theta < 55°$ for a crystal with approximate dimensions $0.10 \times 0.21 \times 0.32$ mm, using graphite-monochromatized Mo Kα ($\lambda = 0.71069$ Å) radiation and the ω–2θ scan technique was used at a 2θ scan rate of 8° min^{-1} and scan width in 2θ of $(1.0 + 0.35\tan\theta)°$. Three check reflections were monitored after every 100 reflections. No significant variation in their intensities was observed throughout the data collection. Lorentz and polarization factors were applied and an absorption correction made [11]. Maximum and minimum transmission coefficients were 1.01 and 1.86, respectively. A total of 7765 unique reflections was measured, of which 5804 with $|F_o| > 3\sigma(F)$ were used for the structure determination.

The structure was solved according to the Patterson and direct (MULTAN) methods [12]. Subsequent Fourier maps showed the positions of all the non-hydrogen atoms, which were refined anisotropically by the block-diagonal least-squares procedure. No attempt was made to refine the hydrogen atoms. The final refinement with anisotropic thermal parameters for the non-hydrogen atoms converged at $R = 0.042$ and $R' = 0.048$, using the weighting scheme $w^{-1} = \sigma^2(F_o) + 0.0005F^2$. Atomic scattering factors used in the refinement were taken from ref. 13. Atomic positional parameters are shown in Table 1.

Crystallographic calculations were performed using the programs of Professor K. Nakatsu, Kwansei Gakuin University, on an ACOS 900S computer at the Research Center of Protein Engineering, Institute for Protein Research, Osaka University. Figures 1 and 2 were drawn with a local version of ORTEP II [14]. See also 'Supplementary material'.

TABLE 1. Atomic coordinates of $[Fe(C_5Me_5)_2][Au(C_3S_5)_2]$ (**1**)

Atom	*x*	*y*	*z*
Au	4164.3(2)	4220.1(2)	3200.3(3)
Fe	8889.8(8)	7711.8(7)	2491.6(9)
S(1)	5011(2)	3961(1)	4534(2)
S(2)	5860(2)	2167(1)	6591(2)
S(3)	6373(2)	124(2)	7573(2)
S(4)	5172(2)	1053(2)	4781(2)
S(5)	4244(2)	2657(1)	2440(2)
S(6)	4102(2)	5781(1)	2131(2)
S(7)	3034(2)	7410(1)	−186(2)
S(8)	1746(3)	8346(2)	−2939(2)
S(9)	2337(2)	6280(1)	−1960(2)
S(10)	3248(2)	4490(1)	92(2)
C(1)	5210(6)	2771(5)	4966(6)
C(2)	5825(6)	1060(5)	6269(7)
C(3)	4877(7)	2243(5)	4119(7)
C(4)	3360(6)	6218(5)	485(7)
C(5)	2333(7)	7399(5)	−1738(7)
C(6)	3029(6)	5693(5)	−341(6)
C(7)	8090(6)	7584(5)	4257(7)
C(8)	7892(6)	8572(5)	3826(7)
C(9)	7225(6)	8866(5)	2514(7)
C(10)	6964(6)	8076(5)	2110(6)
C(11)	7500(6)	7274(5)	3172(7)
C(12)	8691(8)	7007(6)	5610(7)
C(13)	8336(8)	9189(6)	4700(8)
C(14)	6780(8)	9872(5)	1712(8)
C(15)	6238(7)	8087(6)	806(8)
C(16)	7421(8)	6296(5)	3205(9)
C(17)	10816(6)	7077(5)	2944(7)
C(18)	10485(6)	8016(5)	2200(8)
C(19)	9835(7)	8019(6)	940(7)
C(20)	9788(7)	7113(7)	875(8)
C(21)	10398(7)	6531(6)	2136(8)
C(22)	11564(8)	6711(7)	4347(8)
C(23)	10767(8)	8845(7)	2720(12)
C(24)	9341(10)	8901(9)	−185(10)
C(25)	9205(10)	6790(10)	−320(10)
C(26)	10598(9)	5459(6)	2517(12)

Results and discussion

Crystal structure of $[Fe(C_5Me_5)_2][Au(C_3S_5)_2]$ (1)

Geometries of the anion and the cation of **1** are illustrated in Fig. 1 with the atom-labelling scheme. Selected bond lengths and angles are summarized in Table 2.

The C_5 rings of the C_5Me_5 moieties are rotated by approximately 14° away from the ideal D_{5h} symmetry. This is rather similar to $[Fe(C_5Me_5)_2][TCNQI_2]$ (4° rotated) [15]. These findings are in contrast with the essentially staggered form observed for $[Fe(C_5Me_5)_2][C_3(CN)_5]$ and $-[TCNE]\cdot MeCN$ [16], $-[C_4(CN)_6]$ [17], and $-[C_6Cl_2(CN)_2(O)(OH)]$ [18]. The Fe–C, C–C, and C–Me bond lengths range from 2.087(8)–2.118(8), 1.399(15)–1.543(11) and 1.498(9)–1.549(13) Å, respectively, and average 2.089, 1.426 and 1.528 Å, respectively. These values are very close to those of above-described $[Fe(C_5Me_5)_2]^+$ compounds. The Fe atom is located on the C_5 rings 1.707 and 1.720 Å. The Fe–C and Fe–C_5 ring centroid distances are slightly longer than those of $Fe(C_5Me_5)_2$ (av. 2.050(2) and 1.6568 Å, respectively) [19], while C–C and C–Me distances remain essentially the same.

The anion has a square-planar geometry around the gold atom bound with four sulfur atoms. The mean Au–S distance of 2.317 Å is very close to those observed for $[NBu^n_4][Au(C_3S_5)_2]$ (2.322 Å) [1] and other bis(dithiolato)gold(III) complexes; $[NBu^n_4][Au(S_2C_6H_3Me)_2]$ (2.310 Å) [20] and $[Au(S_2CNBu^n_2)_2][Au\{S_2C_2(CN)_2\}_2]$ (2.309 Å) [21]. The S–Au–S angles (88.9 and 91.7°) are also close to those of these complexes (89.6–91.6°). All the atoms of the two Au–C_3S_5 moieties are almost planar (±0.026 and ±0.030 Å) and the dihedral angle between these two planes is 2.3°. The C–S single bond distances (1.709–1.745 Å), the central C=C (1.338(11) and 1.356(11) Å) and terminal C=S double bonds (1.647(7) and 1.657(7) Å) of the $C_3S_5^{2-}$ ligands are close to those of $[NBu^n_4][Au(C_3S_5)_2]$ [1].

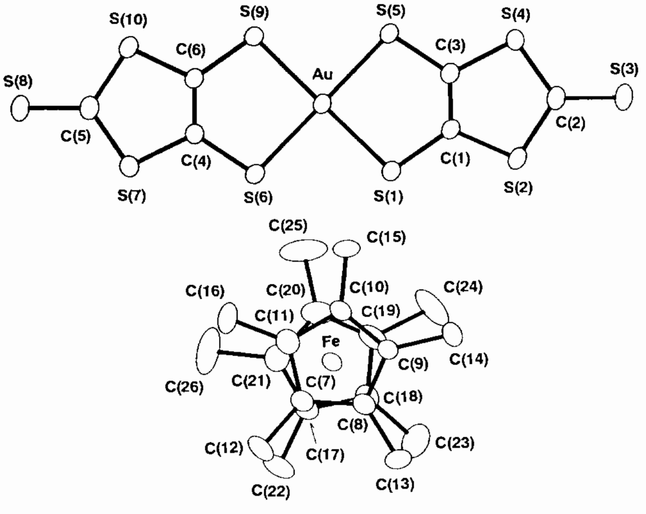

Fig. 1. Molecular structure of the cation and anion moieties of $[Fe(C_5M_5)_2][Au(C_3S_5)_2]$ (**1**), together with the atom-labelling scheme.

TABLE 2. Selected bond distances (Å) and angles (°) in $[Fe(C_5Me_5)_2][Au(C_3S_5)_2]$ (**1**)

Au–S(1)	2.312(2)	S(9)–C(5)	1.729(9)
Au–S(5)	2.319(2)	S(9)–C(6)	1.744(6)
Au–S(6)	2.322(2)	S(10)–C(6)	1.741(8)
Au–S(10)	2.313(2)	C(1)–C(3)	1.356(11)
Fe–C(7)	2.094(7)	C(4)–C(6)	1.338(11)
Fe–C(8)	2.099(7)	C(7)–C(8)	1.436(11)
Fe–C(9)	2.096(6)	C(7)–C(11)	1.453(11)
Fe–C(10)	2.104(7)	C(7)–C(12)	1.498(9)
Fe–C(11)	2.096(9)	C(8)–C(9)	1.414(9)
Fe–C(17)	2.089(7)	C(8)–C(13)	1.540(13)
Fe–C(18)	2.108(9)	C(9)–C(10)	1.427(11)
Fe–C(19)	2.087(8)	C(9)–C(14)	1.523(10)
Fe–C(20)	2.118(8)	C(10)–C(11)	1.434(9)
Fe–C(21)	2.096(7)	C(10)–C(15)	1.500(10)
S(1)–C(1)	1.728(8)	C(11)–C(16)	1.510(13)
S(2)–C(1)	1.745(6)	C(17)–C(18)	1.429(11)
S(2)–C(2)	1.727(8)	C(17)–C(21)	1.400(13)
S(3)–C(2)	1.647(7)	C(18)–C(19)	1.423(11)
S(4)–C(2)	1.718(7)	C(18)–C(23)	1.540(15)
S(4)–C(3)	1.744(7)	C(19)–C(20)	1.399(15)
S(5)–C(3)	1.738(6)	C(19)–C(24)	1.546(13)
S(6)–C(4)	1.744(6)	C(20)–C(21)	1.429(10)
S(7)–C(4)	1.742(7)	C(20)–C(25)	1.546(16)
S(7)–C(5)	1.709(8)	C(21)–C(26)	1.549(13)
S(8)–C(6)	1.657(7)		
S(1)–Au–S(5)	91.7(1)	S(2)–C(2)–S(3)	122.5(5)
S(1)–Au–S(6)	88.9(1)	S(4)–C(3)–C(1)	116.3(5)
S(1)–Au–S(10)	177.9(1)	S(5)–C(3)–C(1)	124.7(6)
S(5)–Au–S(6)	179.1(1)	S(6)–C(4)–C(6)	124.5(5)
S(5)–Au–S(10)	88.1(1)	S(7)–C(5)–S(8)	124.1(5)
S(6)–Au–S(10)	91.4(1)	S(10)–C(6)–C(4)	124.8(5)
Au–S(1)–C(1)	99.9(2)	C(8)–C(7)–C(11)	106.9(6)
C(1)–S(2)–C(2)	98.0(4)	C(7)–C(8)–C(9)	109.1(7)
C(2)–S(4)–C(3)	97.7(4)	C(8)–C(9)–C(10)	108.2(6)
Au–S(5)–C(3)	99.3(3)	C(9)–C(10)–C(11)	108.4(6)
Au–S(6)–C(4)	99.5(3)	C(7)–C(11)–C(10)	107.5(7)
C(4)–S(7)–C(5)	97.6(4)	C(18)–C(17)–C(21)	108.2(6)
C(5)–S(9)–C(6)	97.1(4)	C(17)–C(18)–C(19)	106.3(8)
Au–S(10)–C(6)	99.7(2)	C(18)–C(19)–C(20)	110.0(7)
S(1)–C(1)–C(3)	124.4(5)	C(19)–C(20)–C(21)	106.5(8)
S(2)–C(1)–C(3)	115.2(5)	C(17)–C(21)–C(20)	109.0(8)

The planar anion moieties form dimers through some S–S contacts (3.371(3), 3.502(3), and 3.538(3) Å). The dimer units approach each other through an S–S contact (3.336(3) Å), forming a one-dimensional chain along the *b* axis. The packing diagram of the anion moieties in the crystal is shown in Fig. 2. The one-dimensional array of the anion moieties having some S–S contacts is similar to that of $[NBu^n_4][Au(C_3S_5)_2]$ [1]. The cations are located between the anion arrays. S–S contacts in the crystal phase seem likely to occur in the C_3S_5–Au(III)

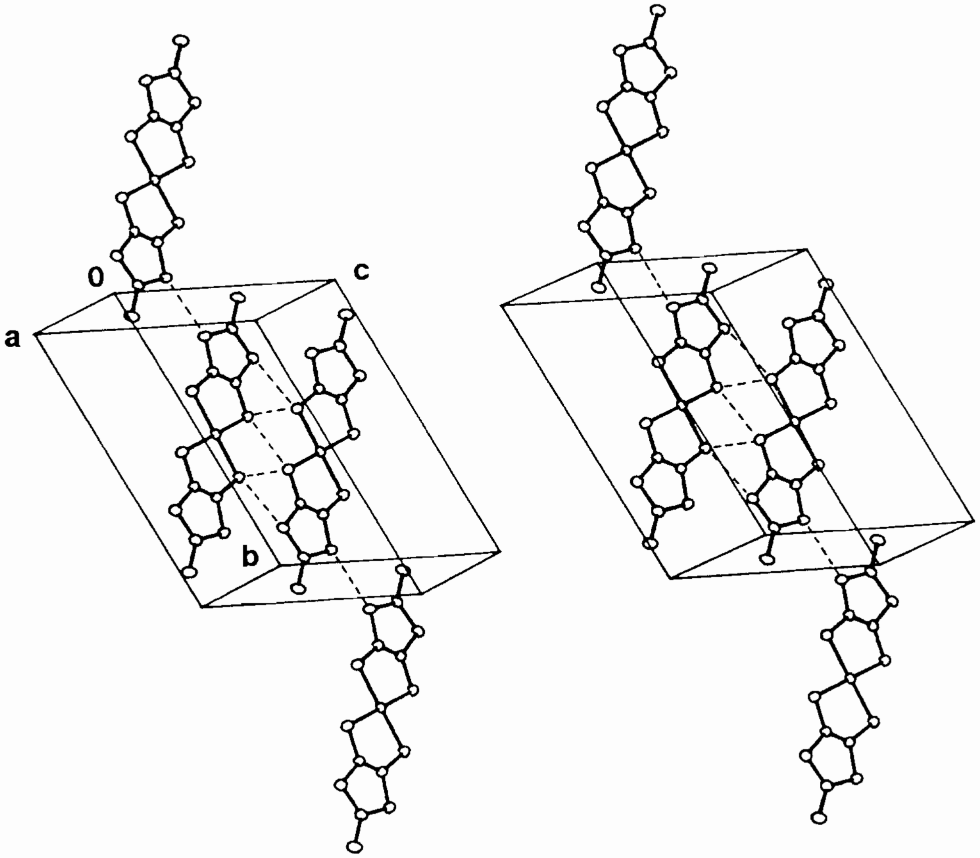

Fig. 2. Stereoview of the packing diagram of the anion moieties of $[Fe(C_5Me_5)_2][Au(C_3S_5)_2]$ (**1**). The dashed lines represent S–S non-bonded contacts less than 3.7 Å.

complexes. This is in contrast with the cases of the metal(II) complexes of $[NBu^n_4]_2[Ni(C_3S_5)_2]$ [5] and $[NBu^n_4]_2[M(C_3S_5)(C_3Se_5)]$ (M = Ni, Pd) [6], in which the anion moieties are arranged separately.

Spectroscopic and electrical properties of the $[Au(C_3S_5)_2]$ anion complexes

$[Fe(C_5Me_5)_2][BF_4]$ reacts with $[NBu^n_4][Au(C_3S_5)_2]$ to give the cation-exchanged species $[Fe(C_5Me_5)_2][Au(C_3S_5)_2]$ (**1**) without any oxidation of the anion moiety. This is in contrast with the finding that a reaction of $[Fe(C_5H_5)_2][PF_6]$ with $[NBu^n_4][Au(C_3S_5)_2]$ in acetonitrile affords the partially oxidized complex, $[Fe(C_5H_5)_2]_{0.25}[Au(C_3S_5)_2]$ [1]. This difference seems to come from the low redox potential of the $[Fe(C_5Me_5)_2]^+$ cation compared with that of the $[Fe(C_5H_5)_2]^+$ cation [22]. However, electrochemical oxidation of the $[Au(C_3S_5)_2]^-$ anion in the presence of $Fe(C_5Me_5)_2$ afforded the partially oxidized anion species **2**.

The powder reflectance spectrum of **1** shows the broad bands at 480 and 780 nm. These bands are essentially the same as those observed for $[NBu^n_4][Au(C_3S_5)_2]$ and $[Fe(C_5Me_5)_2][BF_4]$, respectively. Thus, no significant electronic interaction is assumed between the anion and the cation moieties of **1**. On the other hand, the oxidized species **2** and **3** have exhibited broad bands tailed to longer wavelengths, which seem to be due to interanionic interactions through sulfur—sulfur contacts. They may afford effective electrical conduction pathways, as described below.

Binding energies of Au 4f electrons have been determined by X-ray photoelectron spectra. The values of Au $4f_{5/2}$ electrons of the formally oxidized species (89.9 eV for **2** and **3**) are also very close to those of $[NBu^n_4]$- and $[Fe(C_5Me_5)_2][Au(C_3S_5)_2]$ (90.0 and 90.1 eV, respectively). These findings indicate that the oxidations does not occur on the metal center, but essentially on the $C_3S_5^{2-}$ ligand moieties, as previously reported for other oxidized $[Au(C_3S_5)_2]$ and $[Au(C_3Se_5)_2]$ species [1]. In accordance with this, the oxidized complexes **2** and **3** exhibit broad ESR signals at $g = 2.01$, which are characteristic of the C_3S_5-centered oxidation observed for some oxidized C_3S_5–metal complexes [1, 23, 24].

Electrical conductivities of the complexes measured for compacted pellets and their activation energies are summarized in Table 3. All the complexes behave as

TABLE 3. Electrical conductivities (σ) and activation energies of electrical conduction (E_a) for $[Au(C_3S_5)_2]$ complexes[a]

Complex	$\sigma_{25°C}$ (S cm^{-1})	E_a (eV)
1	2.1×10^{-8}	
$[NBu^n_4][Au(C_3S_5)_2]$[b]	4.9×10^{-8}	
2	0.093	0.061
$[Fe(C_5H_5)_2]_{0.25}[Au(C_3S_5)_2]$[b]	0.10	0.056
3	0.12	0.042

[a]Measured for compacted pellets. [b]Ref. 1.

semiconductors. Complex **1** and $[NBu^n_4][Au(C_3S_5)_2]$ have low conductivities, while **2** and **3** are good electrical conductors. The activation energies determined from the conductivities measured for the temperature range from −30 to +30 °C are very small. Although no crystal structures are known for oxidized $[Au(C_3S_5)_2]$ anion complexes, the oxidized C_3S_5 moieties seem to cause more effective ligand–ligand interactions through sulfur–sulfur contacts in the solid state, resulting in the formation of more extended electron conduction pathways.

Supplementary material

Atomic thermal parameters and observed and calculated structure factors are available from the authors on request.

Acknowledgement

This work was supported by the Grant-in-Aid for Scientific Research on Priority Areas No. 02230220 from the Ministry of Education, Science and Culture, Japanese Government.

References

1 G. Matsubayashi and A. Yokozawa, *J. Chem. Soc., Dalton Trans.,* (1990) 3535.
2 T. Nakamura, H. Tanaka, M. Matsumoto, H. Tachibana, E. Manda and Y. Kawabata, *Chem. Lett.,* (1988) 1667.
3 T. Nakamura, K. Kojima, M. Matsumoto, H. Tachibana, M. Tanaka, E. Manda and Y. Kawabata, *Chem. Lett.,* (1989) 367.
4 M. Bousseau, L. Valade, J.-P. Legros, P. Cassoux, M. Garbauskas and L. V. Interrante, *J. Am. Chem. Soc., 108* (1986) 1908, and refs. therein.
5 O. Lindqvist, L. Sjolin, J. Sieler, G. Steimecke and E. Hoyer, *Acta Chem. Scand., Ser. A, 33* (1979) 445.
6 G. Matsubayashi, S. Tanaka and A. Yokozawa, *J. Chem. Soc., Dalton Trans.,* in press.
7 A. Yokozawa and G. Matsubayashi, *Inorg. Chim. Acta, 186* (1991) 165.
8 K. Ueyama, G. Matsubayashi and T. Tanaka, *Inorg. Chim. Acta, 87* (1984) 143.
9 G. Matsubayashi, K. Kondo and T. Tanaka, *Inorg. Chim. Acta, 69* (1983) 167.
10 T. Nojo, G. Matsubayashi and T. Tanaka, *Inorg. Chim. Acta, 159* (1989) 49.
11 C. T. North, D. C. Philipps and F. C. Matheus, *Acta Crystallogr., Sect. A, 24* (1968) 351.
12 M. Main, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq and M. M. Woolfson, *MULTAN 78,* a system of computer programs of crystal structures from X-ray diffraction data, University of York, UK, 1978.
13 *International Tables for X-Ray Crystallography,* Vol. 4, Kynoch, Birmingham, 1974.
14 C. K. Johnson, *ORTEP II, Rep. ORNL 5138,* Oak Ridge National Laboratory, TN, 1976.
15 J. S. Miller, J. C. Calabrese, R. L. Harlow, D. A Dixson, J. H. Zhang, W. M. Reiff, S. Chittipeddi, M. A. Selover and A. J. Epstein, *J. Am. Chem. Soc., 112* (1990) 5496.
16 J. S. Miller, J. C. Calabrese, H. Rommelmann, S. R. Chittipeddi, J. H. Zhang, W. M. Reiff and A. J. Epstein, *J. Am. Chem. Soc., 109* (1987) 769.
17 J. S. Miller, J. H. Zhang and W. M. Reiff, *J. Am. Chem. Soc., 109* (1987) 4584.
18 E. Gebert, A. H. Reis, Jr., J. S. Miller, H. Rommelmann and A. J. Epstein, *J. Am. Chem. Soc., 104* (1982) 4403.
19 D. P. Freyberg, J. L. Robbins, K. N. Raymond and J. C. Smart, *J. Am. Chem. Soc., 101* (1979) 892.
20 J. H. Noordik and P. T. Beurskens, *J. Cryst. Mol. Struct., 1* (1971) 339.
21 M. A. Mazid, M. T. Razi and P. J. Sadler, *Inorg. Chem., 20* (1981) 2872.
22 S. Fukuzumi, S. Mochizuki and T. Tanaka, *Inorg. Chem., 28* (1989) 2459.
23 Y. Sakamoto, G. Matsubayashi and T. Tanaka, *Inorg. Chim. Acta, 113* (1986) 137.
24 K. Yokoyama, G. Matsubayashi and T. Tanaka, *Polyhedron, 7* (1988) 379.