X-Ray Crystal Structure of Bis(*N*-ethylpyridinium) Bis[4,5-dimercapto-1,3-dithiole-2-thionato(2−)]cuprate(II) and Electrical Properties of its Oxidized Salts†

Gen-etsu Matsubayashi, Kei Takahashi, and Toshio Tanaka *
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565, Japan

A single-crystal *X*-ray structure analysis has been performed for the complex bis(*N*-ethylpyridinium) bis[4,5-dimercapto-1,3-dithiole-2-thionato(2−)]cuprate(II). The crystals are monoclinic, space group *C*2/*m*, with $Z = 4$, $a = 20.04(2)$, $b = 14.56(2)$, $c = 10.19(1)$ Å, and $\beta = 109.2(1)°$. Block-diagonal least-squares refinement, based on 1 882 independent reflections with $|F_o| > 3\sigma(F)$, converged at $R = 0.077$. The geometry around the copper atom is greatly distorted from a square-planar one, with a dihedral angle of 57.3° between the dithiolato ligand planes. While the complex behaves almost as an insulator, with an electrical conductivity of 7.1×10^{-10} S cm^{-1} measured for a compacted pellet at 25 °C, some partially oxidized bis[4,5-dimercapto-1,3-dithiole-2-thionato(2−)]-copper complexes exhibit increased conductivities of 10^{-6}—10^{-5} S cm^{-1}.

Many electrically conducting metal complexes have been investigated, where metal–metal, metal–ligand, and ligand–ligand interactions cause electrical conduction pathways.[1] Recently, some planar bis[4,5-dimercapto-1,3-dithiole-2-thionato(2−)]metal complexes {$[M(dmit)_2]^{n-}$; M = Ni, Pd, or Pt; $n = 0.3$—2; H_2dmit = 4,5-dimercapto-1,3-dithiole-2-thione} were reported to exhibit high conductivities.[2] The dmit ligand in its metal complexes characterises the possibility of two- or three-dimensional interaction through its sulphur atoms. It is noteworthy that [ttf][Ni(dmit)$_2$]$_2$ {ttf = tetrathiafulvalene [2-(1′,3′-dithiol-2′-ylidene)-1,3-dithiole]} was recently reported to exhibit superconductivity even though it was at low temperatures under high pressures.[2b] Structural and electrical properties of dmit complexes containing metals other than Ni, Pd, and Pt have not been reported so far. Since bis(dithiolene)copper(II) complexes are usually found to assume a square-planar geometry,[3] planar bis[4,5-dimercapto-1,3-dithiole-2-thionato(2−)]cuprate(II) complexes may be stacked effectively forming conduction pathways through Cu–Cu, Cu–S, and/or S–S interactions upon oxidation. We have found, however, a significant distortion from square-planar geometry around the copper atom in a $[Cu(dmit)_2]^{2-}$ complex.

This paper reports the *X*-ray crystal structure of bis(*N*-ethylpyridinium) bis[4,5-dimercapto-1,3-dithiole-2-thionato-(2−)]cuprate(II) as well as the spectral and electrical properties of its analogues and partially oxidized complexes.

Experimental

Preparations of $[Cu(dmit)_2]^{2-}$ *Complexes with some Organic Cations, and their Oxidized Species.*—Sodium metal (30 mg, 1.30 mmol) and 4,5-bis(thiobenzoyl)-1,3-dithiole-2-thione[4] (250 mg, 620 µmol) were dissolved in methanol (15 cm^3) to give a dark red solution, to which was added a methanol (20 cm^3) solution of $CuCl_2$ (40 mg, 300 µmol) and *N*-methylpyridinium iodide (140 mg, 620 µmol). The mixture was stirred for 15 min to precipitate dark brown microcrystals of [mpy]$_2$[Cu(dmit)$_2$] (mpy = *N*-methylpyridinium cation) (**1**), which were collected by centrifugation, washed with methanol, and dried *in vacuo* (yield 50%). Similarly, dark brown microcrystals of [epy]$_2$[Cu(dmit)$_2$] (epy = *N*-ethylpyridinium cation) (**2**) were obtained using [epy]I in place of [mpy]I (yield 58%). Recrystallization of the epy salt from a mixture of acetonitrile–methanol (1:1, v/v) afforded dark brown plates, which were used for the *X*-ray crystal analysis.

To an acetonitrile (30 cm^3) solution of (**1**) (55 mg, 85 µmol) was added *N*-methylacridinium perchlorate, [macr][ClO$_4$],[5] (50 mg, 140 µmol) dissolved in the same solvent (10 cm^3) with stirring to give a dark brown precipitate of [macr]$_2$[Cu(dmit)$_2$] (**3**), which was collected by centrifugation, washed with acetonitrile, and dried *in vacuo* (yield 53%). Similarly a dark brown solid of [mpaz]$_{1.8}$[Cu(dmit)$_2$] (**4**) was formed by using [mpaz][MeSO$_4$] (mpaz = *N*-methylphenazinium cation)[5] in place of [macr][ClO$_4$] (yield 70%).

An acetonitrile (60 cm^3) solution of [ttf]$_3$[BF$_4$]$_2$ (ttf = tetrathiafulvalene)[6] (70 mg, 90 µmol) was added dropwise to (**1**) (55 mg, 85 µmol) dissolved in the same solvent (50 cm^3). The mixture was stirred for 30 min to give a black precipitate of [ttf]$_{0.5}$[Cu(dmit)$_2$] (**5**), which was collected by centrifugation, washed with acetonitrile, and dried *in vacuo* [45% yield based on (**1**)].

Finely powdered complex (**1**) (30 mg, 47 µmol) was suspended in a hexane (60 cm^3) solution of iodine (18 mg, 70 µmol). The suspension was stirred for 2 d at room temperature under a nitrogen atmosphere. The resulting solid [mpy]$_2$[Cu(dmit)$_2$]·$I_{2.5}$ (**6**) was collected by filtration and dried *in vacuo*. Similarly, an iodine-oxidized form of the epy salt [epy]$_2$[Cu(dmit)$_2$]·$I_{2.9}$ (**7**) was obtained by using (**2**) in place of (**1**).

Elemental analyses for the complexes obtained are listed in Table 1.

Physical Measurements.—Electronic absorption, powder reflectance,[7] and e.s.r. spectra[8] were measured as described elsewhere. Raman spectra in the solid state were measured by using a cut-off filter for the argon laser (514.5 nm) to avoid the natural scattering of the laser beams, as described previously.[9] Electrical resistivities of compacted pellets were measured by the conventional two-probe technique.[10] Cyclic voltammograms were measured in acetonitrile containing [NBu$^n_4$][ClO$_4$] as a supporting electrolyte, using a conventional cell consisting of two platinum wires as working and counter electrodes, and a saturated calomel electrode (s.c.e.) as reference.

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: G = 10^{-4} T.

Table 1. Elemental analyses* of the $[\mathrm{Cu(dmit)_2}]^{2-}$ complexes

	Analysis (%)		
Complex	C	H	N
(**1**) $[\mathrm{mpy}]_2[\mathrm{Cu(dmit)_2}]$	34.9	3.0	4.05
	(35.7)	(3.0)	(4.15)
(**2**) $[\mathrm{epy}]_2[\mathrm{Cu(dmit)_2}]$	32.9	2.5	4.1
	(33.5)	(2.5)	(4.35)
(**3**) $[\mathrm{macr}]_2[\mathrm{Cu(dmit)_2}]$	47.0	2.95	3.3
	(48.3)	(2.9)	(3.3)
(**4**) $[\mathrm{mpaz}]_{1.8}[\mathrm{Cu(dmit)_2}]$	43.1	2.55	6.4
	(43.7)	(2.5)	(6.25)
(**5**) $[\mathrm{ttf}]_{0.5}[\mathrm{Cu(dmit)_2}]$	19.4	0.4	
	(19.35)	(0.35)	
(**6**) $[\mathrm{mpy}]_2[\mathrm{Cu(dmit)_2}]\cdot\mathrm{I}_{2.5}$	22.45	1.75	2.4
	(22.4)	(1.65)	(2.9)
(**7**) $[\mathrm{epy}]_2[\mathrm{Cu(dmit)_2}]\cdot\mathrm{I}_{2.9}$	23.3	2.0	2.6
	(23.1)	(1.95)	(2.7)

* Calculated values in parentheses.

X-Ray Crystal-structure Determination of $[\mathrm{epy}]_2[\mathrm{Cu(dmit)_2}]$ (**2**).—Accurate cell parameters were determined by least-squares refinement of the angular co-ordinates of 25 independent reflections with 2θ values from 21 to 30°, measured on a Rigaku four-circle automated diffractometer. Intensities were collected in the range $4 < 2\theta < 55°$ for a crystal with approximate dimensions $0.10 \times 0.30 \times 0.48$ mm, using graphite-monochromatized Mo-K_α radiation ($\lambda = 0.710\,69$ Å). An ω–2θ scan mode was used at a 2θ scan rate of 4° min^{-1} and the scan width in 2θ was $(1.0 + 0.35 \tan\theta)°$. No significant intensity variation was observed throughout the data collection. Systematic absences ($hk0$, with $h + k$ odd; $0kl$, with k odd; and $h00$, with h odd) indicated three possible space groups, Cm, $C2$, and $C2/m$. The last proved to be correct, based on the successful analysis. Of 2 382 independent reflections, 1 882 with $|F_o| > 3\sigma(F)$ were used for solving and refining the structure. Lorentz and polarization factors were applied, but no absorption correction was made.

Crystal data. $\mathrm{C_{20}H_{20}CuN_2S_{10}}$, $M = 672.58$, monoclinic, space group $C2/m$, $a = 20.04(2)$, $b = 14.56(2)$, $c = 10.19(1)$ Å, $\beta = 109.2(1)°$, $U = 2\,808(7)$ Å^3, $Z = 4$, $D_c = 1.591(4)$ g cm^{-3}, $F(000) = 1\,372$, and $\mu(\text{Mo-}K_\alpha) = 15.3$ cm^{-1}.

The structure was solved by the conventional heavy-atom technique and atomic parameters were refined by the block-diagonal least-squares method. From Fourier and difference Fourier maps, positions of all the non-hydrogen atoms and hydrogen atoms of the pyridinium rings were determined. Ethyl hydrogen atoms, however, were omitted from the refinement, because their positions were not determined with any certainty. The final refinement, with anisotropic thermal parameters for non-hydrogen atoms and with isotropic thermal parameters for hydrogen atoms, converged at $R = 0.077$ and $R' = 0.087$, using the weighting scheme, $1/w = \sigma^2(F_o) + 0.002F_o^2$. Atomic scattering factors used in the refinement were taken from ref. 11. The fractional atomic co-ordinates with standard deviations are listed in Table 2. The numbering of the atoms is shown in Figure 1.

Crystallographic calculations were performed using the programs of Professor K. Nakatsu, Kwansei Gakuin University, on an ACOS 900S computer at the Crystallographic Research Centre, Institute for Protein Research, Osaka University. Figures for the crystal structures were drawn by the local version of the ORTEP II programs.[12]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Table 2. Atomic co-ordinates ($\times 10^4$; H, $\times 10^3$) for $[\mathrm{epy}]_2[\mathrm{Cu(dmit)_2}]$ (**2**) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Cu	0	2 170(1)	0
S(1)	515(1)	1 624(2)	2 187(2)
S(2)	1 031(1)	2 695(2)	−194(2)
S(3)	2 510(1)	2 403(2)	1 773(3)
S(4)	2 066(1)	1 487(2)	3 825(2)
S(5)	3 606(1)	1 707(2)	4 344(3)
N(1)	8 927(6)	0	1 954(12)
N(2)	5 768(6)	0	2 159(12)
C(1)	1 387(4)	1 853(7)	2 340(7)
C(2)	1 595(4)	2 296(6)	1 370(8)
C(3)	2 774(5)	1 857(7)	3 361(9)
C(4)	8 966(5)	795(7)	2 648(10)
C(5)	9 066(5)	823(7)	4 037(10)
C(6)	9 117(7)	0	4 748(15)
C(7)	8 804(9)	0	433(14)
C(8)	8 022(10)	0	−328(18)
C(9)	5 502(5)	809(7)	2 393(11)
C(10)	4 920(6)	823(8)	2 841(11)
C(11)	4 616(8)	0	3 036(16)
C(12)	6 411(8)	0	1 654(18)
C(13)	7 043(9)	0	2 856(23)
H(4)	895(5)	133(7)	206(10)
H(5)	888(8)	159(12)	436(15)
H(6)	935(6)	0	575(13)
H(9)	583(6)	142(9)	226(13)
H(10)	473(5)	152(7)	297(10)
H(11)	410(8)	0	346(16)

Results and Discussion

Crystal Structure of $[\mathrm{epy}]_2[\mathrm{Cu(dmit)_2}]$ (**2**).—Figure 2 shows the geometry of the $[\mathrm{Cu(dmit)_2}]^{2-}$ anion. Relevant bond lengths and angles for the complex are summarized in Table 3. The copper(II) ion is co-ordinated by four sulphur atoms. The copper–sulphur distances [2.270(3) and 2.273(3) Å] are close to those (2.24—2.29 Å) of analogous bis(dithiolene)copper(II) complexes of the type $[\mathrm{Cu(mnt)_2}]^{2-}$ (mnt = maleonitriledithiolate).[13–18] The copper atom deviates by 0.21 Å (±0.01 Å) from each dmit plane. The geometry around copper is greatly distorted from planar, with a dihedral angle of 57.3° between the dmit planes. This is very uncommon since bis(dithiolene)metal complexes usually assume a planar structure,[3] although non-planarity around metal ions is known to be caused by dimerization *via* metal–sulphur interactions in complexes such as $\mathrm{Co_2[S_2C_2(CF_3)_2]_4}$,[19] $[\mathrm{NBu^n{}_4}]_2[\mathrm{Co_2(S_2C_6Cl_4)_4}]$,[20] $[\mathrm{NBu^n{}_4}]_2[\mathrm{Fe_2(mnt)_4}]$,[21] $[\mathrm{NBu^n{}_4}]_2[\mathrm{Fe_2(edt)_4}]$ (edt = ethane-1,2-dithiolate anion),[22] and $[\mathrm{NEt_4}]_2[\mathrm{Mn_2(edt)_4}]$.[23,24] Only two interesting deviations from planarity in bis(dithiolene)copper(II) complexes have been reported recently; $[\mathrm{mb}]_2[\mathrm{Cu(mnt)_2}]\cdot\mathrm{Me_2CO}$ [mb = methylene blue cation, 3,7-bis(dimethylamino)phenothiazin-5-ium][15] and $[\mathrm{NMe_4}]_2[\mathrm{Cu(mnt)_2}]$[17] exhibit dihedral angles of 47.4 and 41°, respectively. The non-planarity in these complexes is ascribed to the introduction of stacked, large methylene blue molecules and the presence of several short contact distances between the atoms of the anion and the cations, respectively. The present complex, however, involves no significant cation–anion interaction in the crystal, although there exists a close H ⋯ S distance of 2.9 Å. Moreover, the $[\mathrm{Cu(dmit)_2}]^{2-}$ anion is presumably non-planar in solution, as described later. A small distortion (6.1°) from planarity around the metal ion was reported also for $[\mathrm{NBu^n{}_4}][\mathrm{Ni(dmit)_2}]$.[25] Thus, bis[4,5-dimercapto-1,3-dithiole-2-thionato(2−)] metal complexes may preferentially assume distorted geometries.

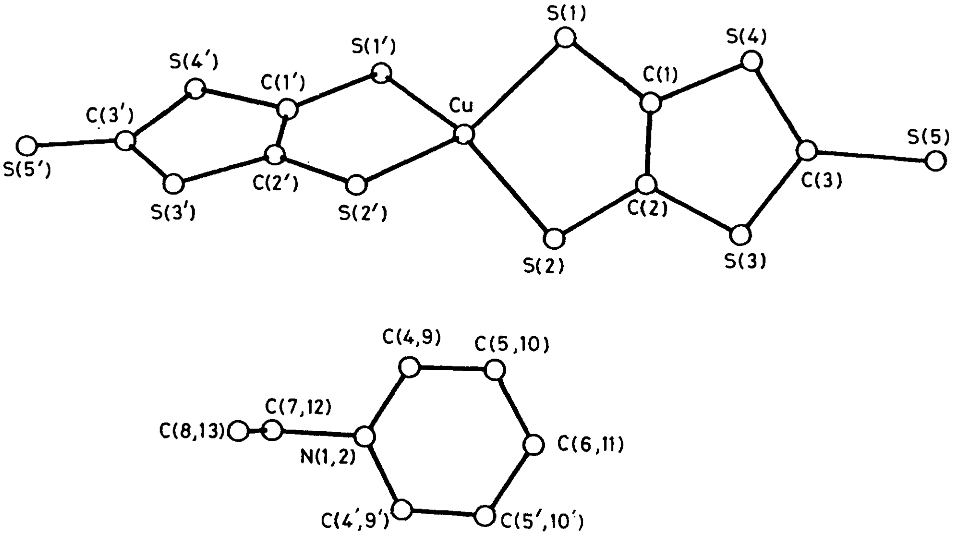

Figure 1. Structural formula of $[epy]_2[Cu(dmit)_2]$ (**2**)

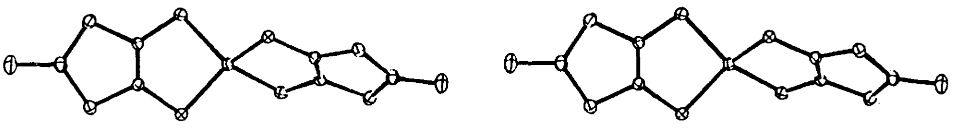

Figure 2. Molecular geometry of the $[Cu(dmit)_2]^{2-}$ anion

Table 3. Selected bond lengths (Å) and angles (°) for $[epy]_2[Cu(dmit)_2]$ (**2**) with e.s.d.s in parentheses

Cu–S(1)	2.270(3)	N(1)–C(4)	1.345(12)
Cu–S(2)	2.273(3)	N(1)–C(7)	1.488(19)
S(1)–C(1)	1.734(9)	N(2)–C(9)	1.347(13)
S(2)–C(2)	1.723(8)	N(2)–C(12)	1.536(24)
S(3)–C(2)	1.748(9)	C(4)–C(5)	1.363(15)
S(3)–C(3)	1.722(10)	C(5)–C(6)	1.387(13)
S(4)–C(1)	1.752(8)	C(7)–C(8)	1.501(24)
S(4)–C(3)	1.722(11)	C(9)–C(10)	1.385(18)
S(5)–C(3)	1.654(9)	C(10)–C(11)	1.387(15)
C(1)–C(2)	1.357(14)	C(12)–C(13)	1.444(22)
S(1)–Cu–S(2)	94.0(1)	C(1)–S(4)–C(3)	98.3(4)
S(1)–Cu–S(1')	130.9(2)	S(3)–C(3)–S(4)	112.1(5)
S(1)–Cu–S(2')	99.5(1)	S(3)–C(3)–S(5)	124.6(6)
S(2)–Cu–S(2')	140.7(1)	C(4)–N(1)–C(7)	120.6(6)
Cu–S(1)–C(1)	98.1(3)	N(1)–C(4)–C(5)	122.3(10)
Cu–S(2)–C(2)	98.3(3)	C(4)–C(5)–C(6)	118.5(10)
S(1)–C(1)–C(2)	124.6(6)	N(1)–C(7)–C(8)	109.0(15)
S(2)–C(2)–C(1)	124.7(6)	C(9)–N(2)–C(12)	118.9(7)
S(3)–C(2)–C(1)	114.9(6)	N(2)–C(9)–C(10)	119.7(11)
S(4)–C(1)–C(2)	115.8(6)	C(9)–C(10)–C(11)	119.5(12)
C(2)–S(3)–C(3)	98.9(5)	N(2)–C(12)–C(13)	108.3(16)

The crystal packing of the complex is shown in Figure 3. There are weak sulphur–sulphur contacts [S(3)–S(3'), 3.613; S(2)–S(3'), 3.78 Å] between the anions to form a one-dimensional anion chain. The closest interchain Cu ··· Cu distance is 6.32 Å, and the closest interchain sulphur–sulphur distances are also large (4.33 Å). This one-dimensional chain arrangement may result in the semi-conductive property of this complex, as described later.

Electronic and E.S.R. Spectra of Complex (**2**).—Figure 4 shows the electronic absorption and powder reflectance spectra of (**2**), together with the reflectance spectrum of its iodine-doped complex. The absorption bands at 310 and 540 nm may be ascribed to local excitations of the dmit ligand, since $Na_2(dmit)$ and $[NBu^n{}_4]_2[Zn(dmit)_2]$ exhibit two absorptions at similar wavelengths; 316 and 514 nm (in methanol), and 300 and 530 nm (in acetonitrile), respectively. The 400 nm band observed for (**2**) is reasonably assigned to a Cu←S charge transfer (c.t.) transition, since $[NEt_4]_2[Cu(mnt)_2]$ exhibits a $d_{xy}(Cu) \leftarrow \pi(mnt)$ c.t. band at 388 nm in acetonitrile,[26] and some copper(II)–thiophenolate complexes, such as $[Cu(L^1)(SC_6H_5)]$,[27] $[Cu_2(L^1)_2(SC_6H_5)]^+$ [L^1 = 3,3'-(trimethylenedinitrilo)bis-(butan-2-one oximate)(1 −) anion],[28] and $[Cu(L^2)(o\text{-}SC_6H_4\text{-}CO_2)]$ (L^2 = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane),[29] display one or two Cu←S c.t. bands in the region 400—430 nm in dichloromethane or in methanol, while both $Na_2(dmit)$ and $[NBu^n{}_4]_2[Zn(dmit)_2]$ do not exhibit a band near 400 nm. The solid-state spectrum of the present complex is essentially the same as the solution spectrum, indicating no significant electronic interaction among the complexes in the solid state.

Figure 5 illustrates the e.s.r. spectra of (**2**) in the solid state and in solution. The g values ($g_{\parallel}$ = 2.092, $g_{\perp}$ = 2.026) observed in the solid-state spectrum are very close to those ($g_{\parallel}$ = 2.090, $g_{\perp}$ = 2.024) of the non-planar mnt complex $[mb]_2[Cu(mnt)_2]\cdot Me_2CO$.[15] These g values are also close to those [g_1 = 2.023, g_2 = 2.026, and g_3 (=$g_{\parallel}$) = 2.086] of the planar mnt complex $[NBu^n{}_4]_2[Cu(mnt)_2]$.[30] As demonstrated for the $[Cu(mnt)_2]^{2-}$ complexes by Manoharan and co-workers,[16] the non-planarity in the dmit complexes may not affect the molecular g values much. Although the solid-state e.s.r. spectrum exhibits no hyperfine structure due to $^{63/65}Cu$ nuclei, the isotropic $^{63/65}Cu$ hyperfine structure is observed (g_0 = 2.051, $|A_0|$ = 66.5 × 10^{-4} cm^{-1}) in the solution

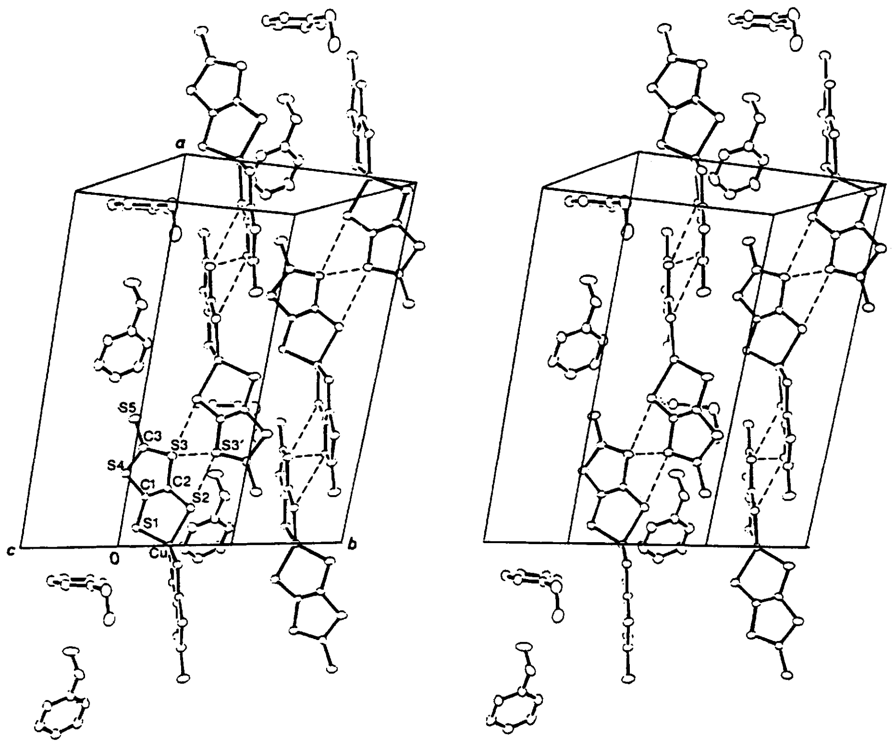

Figure 3. Stereoscopic packing diagram for $[epy]_2[Cu(dmit)_2]$ (**2**)

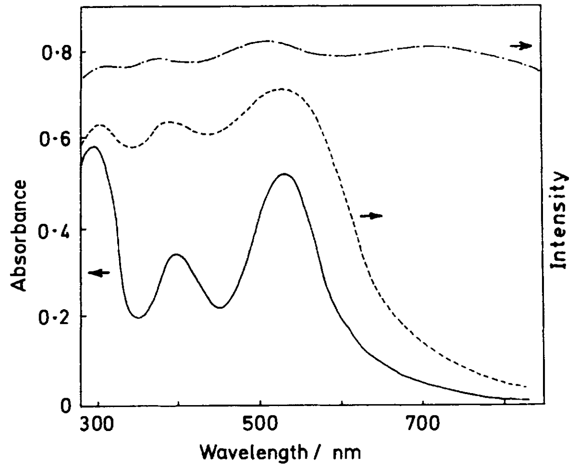

Figure 4. Electronic absorption spectrum of $[epy]_2[Cu(dmit)_2]$ (**2**) in acetonitrile (1.3 × 10^{-4} mol dm^{-3}) (——), and powder reflectance spectra of (**2**) (– – – –) and $[epy]_2[Cu(dmit)_2]\cdot I_{2.9}$ (**7**) (— · — · —)

spectrum. A drastic decrease of $|A_0|$ values in CuS_4 complexes was proposed to be caused by some distortion from a square-planar to a tetrahedral geometry around the copper atom.[31] The present $|A_0|$ value in solution is rather close to that (68.4 × 10^{-4} cm^{-1}) of $[mb]_2[Cu(mnt)_2]\cdot Me_2CO$ containing the non-planar $[Cu(mnt)_2]^{2-}$ anion in the solid state, which is much lower than $|A_0|$ (80.0 × 10^{-4} cm^{-1}) for the planar $[Cu(mnt)_2]^{2-}$ anion.[15] Thus, the present $[Cu(dmit)_2]^{2-}$ complex seems to assume a geometry distorted from square planar in solution also.

Electrical Properties of the Partially Oxidized Bis(dmit)copper Complexes.—A cyclic voltammogram of (**2**) in acetonitrile is

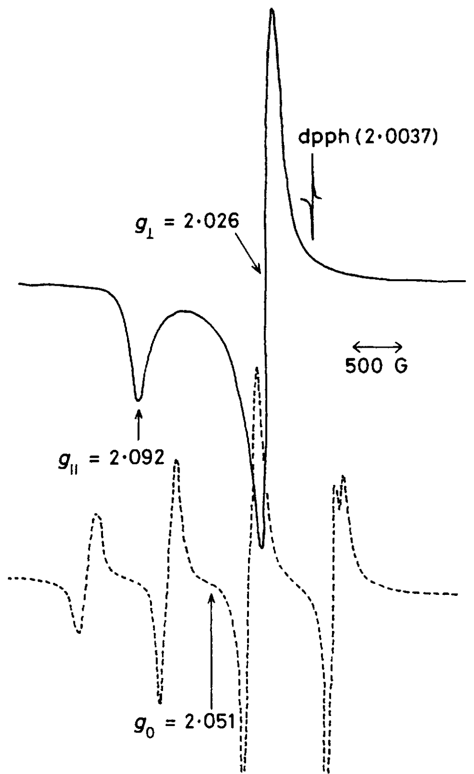

Figure 5. E.s.r. spectra of $[epy]_2[Cu(dmit)_2]$ (**2**) in the solid state (——) and in acetonitrile (– – – –) at room temperature; dpph = diphenylpicrylhydrazyl

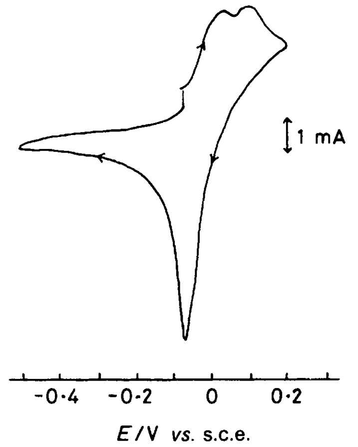

Figure 6. Cyclic voltammogram of $[epy]_2[Cu(dmit)_2]$ (**2**) (3.0×10^{-4} mol dm^{-3}) in acetonitrile containing $[NBu^n{}_4][ClO_4]$ (0.1 mol dm^{-3}); scan rate 0.1 V s^{-1}

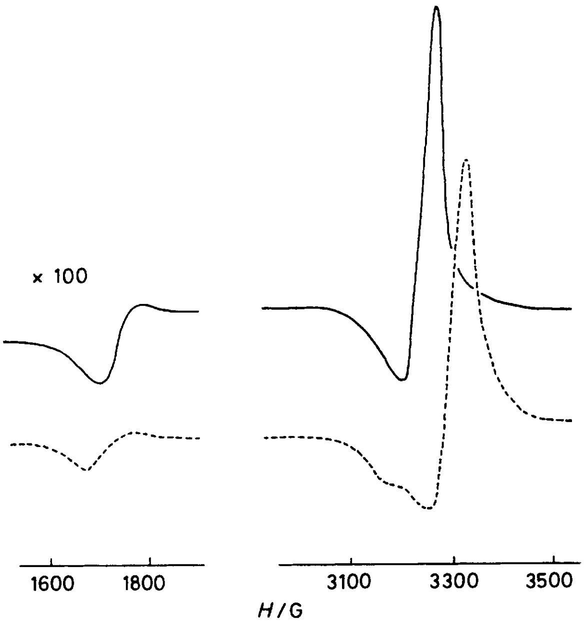

Figure 7. Powder e.s.r. spectra of $[mpaz]_{1.8}[Cu(dmit)_2]$ (**4**) (——) and $[epy]_2[Cu(dmit)_2]\cdot I_{2.9}$ (**7**) at 77 K (- - - -)

depicted in Figure 6, which shows the occurrence of the first (+0.02 V *vs.* s.c.e.) and successive second oxidations (+0.08 V *vs.* s.c.e.) at relatively low potentials, indicating that the $[Cu(dmit)_2]^{2-}$ anion may be easily oxidized. In fact, complexes (**1**) and (**2**) suspended in hexane react with iodine dissolved in the same solvent to yield the iodinated complexes (**6**) and (**7**). Both the complexes exhibit a Raman peak at 108 cm^{-1}, which is reasonably assigned to the characteristic, totally symmetric scattering pattern of the I_3^- ion.[32] Complexes (**4**) and (**5**), which have been obtained by the reactions of (**1**) with the *N*-methylphenazinium and tetrathiafulvalenium cations, respectively, are also partially oxidized.

Figure 7 shows the e.s.r. spectra of the partially oxidized complexes (**4**) and (**7**), which exhibit half bands due to $\Delta M = \pm 2$ near 1 600 G, although the intensities are both extremely weak. Moreover, the reflectance spectra of these partially oxidized complexes show broad bands at long wavelengths [see Figure 4 for complex (**7**)] which are not observed in the solution spectra. These observations suggest an increased interaction between the anions. In accord with this, electrical conductivities of the partially oxidized complexes are significantly increased as described below.

Table 4. Electrical conductivities (σ) and activation energies (E_a) of the complexes; eV $\approx 1.60 \times 10^{-19}$ J

Complex	$\sigma_{25\,°C}$/S cm^{-1}	E_a/eV
(**1**)	5.6×10^{-9}	0.52
(**2**)	7.1×10^{-10}	0.44
(**3**)	7.7×10^{-8}	0.39
(**4**)	1.9×10^{-6}	0.22
(**5**)	4.5×10^{-6}	0.27
(**6**)	3.7×10^{-6}	0.64
(**7**)	1.0×10^{-5}	0.49

All the complexes behave as semiconductors in the temperature range measured: −40 to +40 °C. Table 4 lists the electrical conductivities measured for compacted pellets at 25 °C, and the activation energies. Complexes (**1**)—(**3**) exhibit small conductivities which are presumably due to weak interactions between the $[Cu(dmit)_2]^{2-}$ anions as revealed in the crystal structure of (**2**). In the partially oxidized complexes, however, the interaction between the anions may be strengthened to result in the increase of conductivity by the order of 10^3—10^5.

Acknowledgements

We thank Professor K. Nakatsu, Kwansei Gakuin University, for use of the programs for the structure solution and refinement. This work was partially supported by a Matsuda Research Grant, for which we thank the Matsuda Foundation.

References

1 J. S. Miller (ed.), 'Extended Linear Chain Compounds,' Plenum Press, New York, 1982, vols. 1 and 2; 1983, vol. 3.

2 (*a*) G. C. Papavassiliou, *Z. Naturforsch., Teil B*, 1982, **37**, 825; L. Valade, M. Bousseau, A. Gleizes, and P. Cassoux, *J. Chem. Soc., Chem. Commun.*, 1983, 110; L. Valade, P. Cassoux, A. Gleizes, and L. Interrante, *J. Phys. Colloq. (Paris)*, 1983, **C3**, 1183; L. Valade, J-P. Legros, M. Bousseau, P. Cassoux, M. Garbauskas, and L. V. Interrante, *J. Chem. Soc., Dalton Trans.*, 1985, 783; M. Bousseau, L. Valade, M-F. Bruniquel, P. Cassoux, M. Garbauskas, L. Interrante, and J. Kasper, *Nouv. J. Chim.*, 1984, **8**, 3; R. Kato, T. Mori, A. Kobayashi, Y. Sasaki, and H. Kobayashi, *Chem. Lett.*, 1984, 1; R. Kato, H. Kobayashi, A. Kobayashi, and Y. Sasaki, *ibid.*, 1985, 131; H. Kobayashi, R. Kato, A. Kobayashi, and Y. Sasaki, *ibid.*, p. 191; Y. Sakamoto, G. Matsubayashi, and T. Tanaka, *Inorg. Chim. Acta*, 1986, **113**, 137; (*b*) M. Bousseau, L. Valade, J-P. Legros, P. Cassoux, G. Garbauskas, and L. V. Interrante, *J. Am. Chem. Soc.*, 1986, **108**, 1908.

3 J. A. McCleverty, *Prog. Inorg. Chem.*, 1968, **10**, 49; R. P. Burns and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1979, **22**, 303.

4 G. Steimecke, H. J. Sieler, R. Krimse, and E. Hoyer, *Phosphorus Sulfur*, 1979, **7**, 49.

5 L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, 1962, **84**, 3374.

6 F. Wudl, *J. Am. Chem. Soc.*, 1975, **97**, 1962.

7 K. Ueyama, G. Matsubayashi, and T. Tanaka, *Inorg. Chim. Acta*, 1984, **87**, 143.

8 G. Matsubayashi, K. Kondo, and T. Tanaka, *Inorg. Chim. Acta*, 1983, **69**, 167.

9 G. Matsubayashi, Y. Sakamoto, and T. Tanaka, *J. Chem. Soc., Perkin Trans. 2*, 1985, 947.

10 S. Araki, H. Ishida, and T. Tanaka, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 407.

11 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

12 C. K. Johnson, ORTEP-II, Report ORNL 5138, Oak Ridge National Laboratory, Tennessee, 1976.

13 K. W. Plumbee, B. M. Hoffman, M. T. Ratajack, and C. R. Kannewurf, *Solid State Commun.*, 1974, **15**, 1651.

14 K. W. Plumbee, B. M. Hoffman, J. A. Ibers, and Z. G. Soos, *J. Chem. Phys.*, 1975, **63**, 1926.

15 D. Snaathorst, H. M. Doesburg, J. A. A. J. Perenboom, and C. P. Keijzers, *Inorg. Chem.*, 1981, **20**, 2526.

16 P. Kuppusamy, B. L. Ramakrishna, and P. T. Manoharan, *Inorg. Chem.*, 1984, **23**, 3886.

17 C. Mahadevan and M. Seshasayee, *J. Crystallogr. Spectrosc. Res.*, 1984, **14**, 215.

18 B. L. Ramakrishna, U. Geiser, and R. D. Willett, *Mol. Cryst. Liq. Cryst.*, 1985, **125**, 447.

19 J. H. Enemark and W. N. Lipscomb, *Inorg. Chem.*, 1965, **4**, 1729.

20 M. J. Baker-Hawkes, Z. Dori, R. Eisenberg, and H. B. Gray, *J. Am. Chem. Soc.*, 1968, **90**, 4253.

21 W. C. Hamilton and I. Bernal, *Inorg. Chem.*, 1967, **6**, 2003.

22 M. R. Snow and J. A. Ibers, *Inorg. Chem.*, 1973, **12**, 249.

23 T. Costa, J. R. Dorfman, K. S. Hagen, and R. H. Holm, *Inorg. Chem.*, 1983, **22**, 4091.

24 G. Christou and J. C. Huffman, *J. Chem. Soc., Chem. Commun.*, 1983, 558.

25 O. Lindqvist, L. Andersen, J. Sieler, G. Steimecke, and E. Hoyer, *Acta Chem. Scand., Ser. A*, 1982, **36**, 855.

26 L. Persaud and C. H. Langford, *Inorg. Chem.*, 1985, **24**, 3562.

27 O. P. Andersen, C. M. Perkins, and K. K. Brito, *Inorg. Chem.*, 1983, **22**, 1267.

28 N. Aoi, G. Matsubayashi, and T. Tanaka, *J. Chem. Soc., Dalton Trans.*, 1987, 241.

29 J. L. Hughey, IV, T. G. Fawcett, S. M. Rudich, R. A. Lalancette, J. A. Potenza, and H. J. Schugar, *J. Am. Chem. Soc.*, 1979, **101**, 2617.

30 A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, 1964, **86**, 4580.

31 U. Sakaguchi and A. W. Addison, *J. Am. Chem. Soc.*, 1977, **99**, 5189.

32 D. N. Diel, T. Inabe, J. W. Lyding, K. F. Schoch, jun., C. R. Kannewurf, and T. J. Marks, *J. Am. Chem. Soc.*, 1983, **105**, 1551.

Received 27th May 1987; *Paper* 7/935