

could result from the higher degree of thermal motion present at ambient temperatures as compared to the low temperature at which the cited neutron study was performed. Still, the discrepancies may result from more subtle factors. The possibility of electronic perturbations resulting from interactions between neighboring dimers in FDAH is slight, as the contacts are rather long (*ca* 2.25 to 2.54 Å) and involve two crystallographically independent molecules. A further possibility is that the observed differences result from perturbations attributable to the presence of an 'extra' carboxylate group on the second ring in FDAH.

Ligation of the FCA<sup>-</sup> anion to dimetal centers results in considerable changes in its molecular dimensions. These observations will be reported in detail in the near future (Cotton *et al.*, 1984).

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## Structure of the 2/1 Complex Dibenzotetrathiafulvalenium Hexabromodicuprate(II),\* 2C<sub>14</sub>H<sub>8</sub>S<sub>4</sub><sup>+</sup>·Cu<sub>2</sub>Br<sub>6</sub><sup>2-</sup>

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**Abstract.**  $M_r = 1215.49$ , triclinic,  $P\bar{1}$ ,  $a = 9.982$  (1),  $b = 12.122$  (1),  $c = 7.893$  (1) Å,  $\alpha = 83.70$  (1),  $\beta = 112.80$  (1),  $\gamma = 104.97$  (1)°,  $V = 850.4$  (1) Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 2.37$ ,  $D_m = 2.36$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu(\text{Cu } K\alpha) = 140.45$  cm<sup>-1</sup>,  $F(000) = 580$ ,  $T = 293$  K,  $R = 0.039$  for 2678 observed reflections. Cation radicals are stacked to form columns along **c** [interplanar distance 3.5 (5) Å]. Shortest contacts between adjacent cations in a column are S...S 3.391 (2) Å. The central C=C bond of the cation is 1.397 (6) Å.

**Introduction.** Organic charge-transfer radical salts consisting of the electron donor TTF (tetrathiafulvalene) and an electron acceptor such as TCNQ (tetracyano-*p*-quinodimethane) display high electrical

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conductivities (Cohen, Coleman, Garito & Heeger, 1974). The crystal structures of the organic conductors are composed of characteristic columns in which the donor cation and acceptor anion radicals are stacked separately. Electrons and holes are delocalized in the respective columns. This causes high anisotropy in the solid-state properties of the organic conductors, such as electrical, optical and magnetic ones. Many compounds analogous to TTF have been synthesized to obtain the radical salts with high electrical conductivity. Dibenzotetrathiafulvalene (DBTTF) is one of them and the direct oxidation of DBTTF by halogens and metal halides was reported to yield radical salts such as (DBTTF)<sub>2</sub>I<sub>3</sub> (Shibaeva, Rozenberg, Aldoshina, Lubovskaya & Khidekel, 1979), (DBTTF)<sub>8</sub>(SnCl<sub>6</sub>)<sub>3</sub> and (DBTTF)<sub>3</sub>(SnBr<sub>6</sub>) (Shibaeva, Rozenberg & Lubovskaya, 1980), and (DBTTF)<sub>2</sub>(Cu<sub>2</sub>Cl<sub>6</sub>) (Honda, Katayama, Tanaka & Tanaka, 1985). In this paper, we report the crystal structure of the complex of DBTTF with cupric bromide.

\* Alternative nomenclature: bis(2,2'-bi-1,3-benzodithiolyli-denium) hexabromodicuprate(II).

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**Experimental.** Crystal prepared using the closed-system evaporation crystallizer, transferring DBTTF and  $\text{CuBr}_2$  from solid sources to an acetonitrile solution. Dark-red plate-like crystal  $0.13 \times 0.05 \times 0.20$  mm.  $D_m$  measured by flotation. Rigaku automated four-circle diffractometer. Cell dimensions from 20 selected reflections with  $28^\circ < \theta < 31^\circ$ . 2975 measured reflections,  $2\theta_{\max} = 126^\circ$ ,  $-11 \leq h \leq 11$ ,  $-14 \leq k \leq 14$ ,  $0 \leq l \leq 9$ ,  $R_{\text{int}} = 0.017$ . Three standard reflections after every 100 reflections (decay less than 4%). Structure solved by the Monte-Carlo direct method (Furusaki, 1979) with the aid of *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) using 2678 non-zero unique reflections, and refined on  $F^2$  by full-matrix least-squares program with analytical absorption correction (Katayama, Sakabe & Sakabe, 1972); transmission factors 0.16 to 0.50. Isotropic extinction factor (Coppens & Hamilton, 1970),  $g = 1.58 \times 10^{-3}$ . Non-H atoms assigned anisotropic temperature factors. All H atoms located from difference Fourier map and refined with isotropic temperature factors equivalent to that for bonded C atoms.  $R = 0.039$ ,  $S = 2.12$ ,  $w = 1/\sigma^2(F^2)$ ,  $(\Delta/\sigma)_{\max} = 0.394$  for x of H(16),  $\Delta\rho_{\max} = 0.9 \text{ e } \text{Å}^{-3}$ . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). *ORTEP* (Johnson, 1965) employed for drawing molecular structure, and *PLUTO78* (Motherwell, 1976) for crystal structure projection. All calculations made on a FACOM M-382 computer at the computation center of Nagoya University.

**Discussion.** The atomic parameters are given in Table 1.\* The projection of the structure along the  $c$  axis is shown in Fig. 1. The cation radicals are stacked to form columns along the  $c$  axis with an interplanar distance of about 3.5 (5) Å. Shortest contacts between adjacent cations in a column are found between S(1) and S(13) with a distance of 3.391 (2) Å (see Table 2). Fig. 2 shows the bond lengths and bond angles of the DBTTF cation and  $\text{Cu}_2\text{Br}_6^{2-}$  dianion. The length of the central C=C bond in the DBTTF cation is longer than that of the neutral DBTTF molecule [1.336 (2) Å] (Emge, Wiygul, Chappell, Bloch, Ferrais, Cowan & Kistenmacher, 1982) and is comparable with those of other DBTTF cations (Shibaeva, Rozenberg, Aldoshina, Lubovskaya & Khidekel, 1979; Shibaeva, Rozenberg & Lubovskaya, 1980; Honda, Katayama, Tanaka & Tanaka, 1985). Furthermore, the outer S—C bonds like S(1)—C(8) are slightly longer than the inner S—C bonds like S(1)—C(2). The  $\text{Cu}_2\text{Br}_6^{2-}$  anion has two types of Cu—Br bond. The longer Cu—Br bonds [2.433 (1) and

2.416 (1) Å] interconnect the Cu atoms in the planar  $\text{Cu}_2\text{Br}_6^{2-}$  anion and the shorter Cu—Br bonds [2.357 (1) and 2.369 (1) Å] are those to the terminal Br atoms Br(21) and Br(22). The bridging Br atoms and the Cu atoms are located about centers of symmetry in the direction of the  $b$  axis.

Table 1. Positional parameters ( $\times 10^5$ ) and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{3}{2}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	$x$	$y$	$z$	$B_{\text{eq}}(\text{Å}^2 \times 10^2)$
Cu(10)	7408 (6)	64160 (5)	-6951 (7)	378 (3)
Br(20)	2167 (6)	55057 (3)	19338 (6)	469 (2)
Br(21)	16124 (6)	82174 (3)	7427 (7)	530 (3)
Br(22)	11662 (6)	70871 (3)	-34033 (6)	534 (2)
S(1)	58116 (10)	30413 (7)	50243 (14)	413 (3)
C(2)	47117 (44)	38670 (34)	34658 (53)	384 (10)
S(3)	28084 (11)	33163 (9)	26901 (15)	439 (3)
C(4)	16288 (53)	11383 (38)	36825 (66)	460 (12)
C(5)	18390 (56)	1501 (38)	46915 (71)	498 (13)
C(6)	32538 (60)	354 (40)	58571 (75)	535 (15)
C(7)	45092 (57)	8953 (40)	60029 (74)	502 (14)
C(8)	43231 (44)	18935 (34)	49922 (56)	394 (11)
C(9)	28884 (50)	20156 (34)	38403 (56)	409 (11)
S(11)	71985 (10)	55350 (7)	35437 (14)	415 (3)
C(12)	53012 (46)	49340 (35)	28436 (53)	390 (10)
S(13)	41354 (11)	57178 (9)	12961 (14)	434 (3)
C(14)	52804 (56)	78056 (41)	-93 (65)	475 (13)
C(15)	64928 (60)	86596 (38)	-263 (68)	514 (14)
C(16)	79491 (54)	85743 (38)	10174 (66)	481 (13)
C(17)	82287 (54)	76341 (38)	21201 (65)	450 (12)
C(18)	70143 (47)	67698 (34)	21849 (53)	392 (11)
C(19)	55554 (49)	68551 (34)	11074 (54)	401 (11)

Table 2. Selected intermolecular distances (Å)

S(1)—S(13 <sup>h</sup> )	3.391 (2)	Cu(10)—S(1 <sup>l</sup> )	4.455 (1)
S(3)—S(11 <sup>l</sup> )	3.421 (2)	Cu(10)—S(13 <sup>lll</sup> )	3.425 (1)
S(13)—S(11 <sup>h</sup> )	3.868 (2)	Cu(10)—S(3 <sup>ll</sup> )	3.361 (1)
S(13)—S(13 <sup>ll</sup> )	3.907 (3)	Cu(10)—S(11 <sup>l</sup> )	4.580 (1)

Symmetry code

- |                           |                          |
|---------------------------|--------------------------|
| (i) $1 - x, 1 - y, 1 - z$ | (iv) $-1 + x, y, -1 + z$ |
| (ii) $1 - x, 1 - y, -z$   | (v) $-x, 1 - y, -z$      |
| (iii) $x, y, z$           |                          |

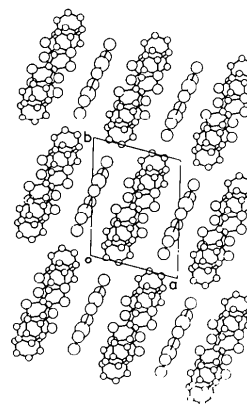


Fig. 1. Projection of the structure along the  $c$  axis.

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39970 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

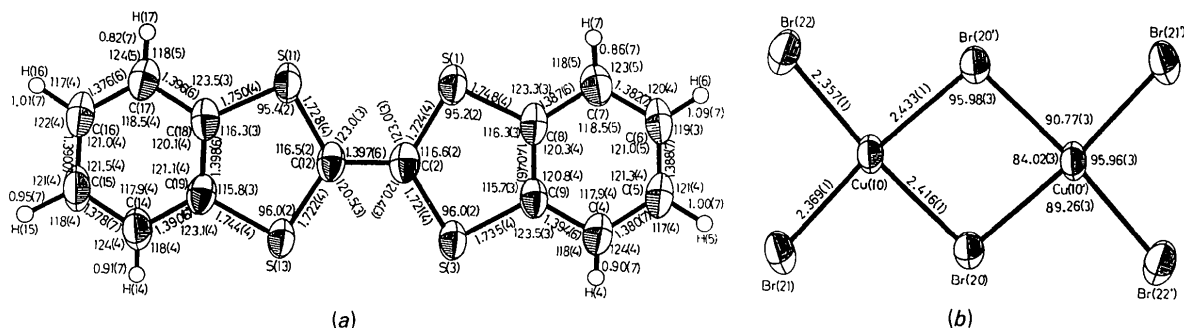


Fig. 2. Molecular dimensions (distances in Å, angles in °) for the DBTTF cation (a) and the  $Cu_2Br_6^{2-}$  anion (b). Additional angles: Br(22)—Cu(10)—Br(20) 173.26 (3), Br(21)—Cu(10)—Br(20') 174.77 (4)°.

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## Structures of $\alpha$ - and $\beta$ -Copper(II) Pipecolinate Dihydrate, Diaquabis-(2-piperidinecarboxylato)copper(II), $[Cu(C_6H_{10}NO_2)_2(H_2O)_2]$

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**Abstract.**  $M_r = 356.0$ .  $\alpha$  form:  $P2_1/c$ ,  $a = 11.723$  (4),  $b = 5.749$  (3),  $c = 11.174$  (3) Å,  $\beta = 104.11$  (3)°,  $V = 730.4$  (5) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.62$ ,  $D_m = 1.60$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71073$  Å,  $\mu = 15.9$  cm<sup>-1</sup>,  $F(000) = 374$ ,  $wR = 0.032$  for 1413 observed [ $I > 3\sigma(I)$ ] reflections.  $\beta$  form:  $P2_1/n$ ,  $a = 5.875$  (2),  $b = 18.618$  (5),  $c = 7.014$  (2) Å,  $\beta = 106.40$  (3)°,  $V = 736.0$  (4) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.61$ ,  $D_m = 1.60$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71073$  Å,  $\mu = 15.7$  cm<sup>-1</sup>,  $F(000) = 374$ ,  $wR = 0.031$  for 1370 observed reflections; for the standard space group  $P2_1/c$ :  $a = 5.875$  (2),  $b = 18.618$  (5),  $c = 10.342$  (3) Å,  $\beta = 139.42$  (3)°. The Cu atoms have distorted octahedral

coordination, the pipecolinate radical acting as a bidentate ligand, bonded through the equatorial imino N and the carboxylate O, which are *cis* to each other. The two water molecules occupy the axial positions, at greater distance from the Cu. Distances and angles in the two forms are similar, but there are significant variances. The copper–water bond length is greater in the  $\beta$  form (2.611 vs 2.401 Å), and the torsion angles in the piperidine ring are larger in the  $\alpha$  form. The difference in the structures lies in the tilt angles of the molecules relative to the symmetry elements of the space group.