S(11)—C(15)	1.722 (4)	C(26)—C(27)	1.355 (5)
S(11)—C(16)	1.745 (4)	C(28)—C(29)	1.511 (5)
S(12)—C(15)	1.726 (4)	S(31)—C(35)	1.753 (4)
S(12)—C(17)	1.737 (4)	S(31)—C(36)	1.758 (4)
S(13)—C(16)	1.729 (4)	S(32)—C(35)	1.749 (4)
S(13)—C(18)	1.805 (4)	S(32)—C(37)	1.753 (4)
S(14)—C(17)	1.741 (4)	S(33)—C(36)	1.746 (4)
S(14)—C(19)	1.815 (4)	S(33)—C(38)	1.811 (4)
C(15)—C(25)	1.376 (5)	S(34)—C(37)	1.749 (4)
C(16)—C(17)	1.359 (5)	S(34)—C(39)	1.807 (4)
C(18)—C(19)	1.507 (5)	C(36)—C(37)	1.345 (5)
S(21)—C(25)	1.730 (4)	C(38)—C(39)	1.508 (6)
S(21)—C(26)	1.742 (4)	C(35)—C(35$^{\rm i}$)	1.349 (1)
Br(1)—Cu—Br(2)	89.9 (1)	S(21)—C(26)—S(23)	114.8 (2)
Cl(1′)—Cu—Cl(2′)	90.1 (2)	S(21)—C(26)—C(27)	116.2 (3)
C(15)—S(11)—C(16)	96.2 (2)	S(23)—C(26)—C(27)	129.0 (3)
C(15)—S(12)—C(17)	96.2 (2)	S(22)—C(27)—S(24)	114.9 (2)
C(16)—S(13)—C(18)	100.9 (2)	S(22)—C(27)—C(26)	117.0 (3)
C(17)—S(14)—C(19)	101.3 (2)	S(24)—C(27)—C(26)	128.1 (3)
S(11)—C(15)—S(12)	114.8 (2)	S(23)—C(28)—C(29)	114.6 (3)
S(11)—C(15)—C(25)	121.3 (3)	S(24)—C(29)—C(28)	112.9 (3)
S(12)—C(15)—C(25)	123.8 (3)	C(35)—S(31)—C(36)	95.4 (2)
S(11)—C(16)—S(13)	114.2 (2)	C(35)—S(32)—C(37)	95.2 (2)
S(11)—C(16)—C(17)	116.2 (3)	C(36)—S(33)—C(38)	100.5 (2)
S(13)—C(16)—C(17)	129.6 (3)	C(37)—S(34)—C(39)	101.8 (2)
S(12)—C(17)—S(14)	116.1 (2)	S(31)—C(35)—S(32)	114.9 (2)
S(12)—C(17)—C(16)	116.6 (3)	S(31)—C(35)—C(35$^{\rm i}$)	122.5 (3)
S(14)—C(17)—C(16)	127.3 (3)	S(32)—C(35)—C(35$^{\rm i}$)	122.6 (3)
S(13)—C(18)—C(19)	112.3 (3)	S(31)—C(36)—S(33)	114.6 (2)
S(14)—C(19)—C(18)	113.8 (3)	S(31)—C(36)—C(37)	116.7 (3)
C(25)—S(21)—C(26)	96.0 (2)	S(33)—C(36)—C(37)	128.7 (3)
C(25)—S(22)—C(27)	95.7 (2)	S(32)—C(37)—S(34)	113.6 (2)
C(26)—S(23)—C(28)	101.7 (2)	S(32)—C(37)—C(36)	117.7 (3)
C(27)—S(24)—C(29)	100.8 (2)	S(34)—C(37)—C(36)	128.6 (3)
C(15)—C(25)—S(21)	121.3 (3)	S(33)—C(38)—C(39)	113.8 (3)
C(15)—C(25)—S(22)	123.5 (3)	S(34)—C(39)—C(38)	113.7 (3)
S(21)—C(25)—S(22)	115.2 (2)		

Symmetry code: (i) $-x+1, -y+1, -z+1$.

The atomic coordinates given by Mori, Sakai, Saito & Inokuchi (1987) were used as starting values for the refinement. All non-H atoms were refined anisotropically. H atoms were placed at calculated positions (C—H = 1.0 Å); these positions were allowed to vary during the last few cycles. Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: *SDP* (Enraf–Nonius, 1985). Program used to refine structure: *SHELXS*86 (Sheldrick, 1985).

This work was supported by the SERC (UK), CNRS (France), NATO and the British Council (Alliance programme).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates, and plots of the structure and the crystal packing have been deposited with the IUCr (Reference: MU1086). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$(BEDT-TTF)_3[CuBr_4]$

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(*Received* 13 *September* 1993; *accepted* 19 *May* 1994)

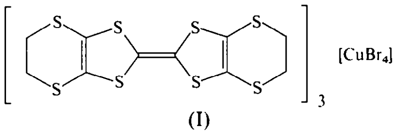
Abstract

The crystal structure of the title compound, tris-[3,4,3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene] tetrabromocuprate(2−), $(C_{10}H_8S_8)_3[CuBr_4]$, is classified as the α phase and contains two independent BEDT-TTF [BEDT-TTF = 3,4,3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene] molecules (*A* and *B*) stacked as *ABBABB* along the *c* axis. The dihedral angle between the *A* and *B* molecules is 5.3 (1)° and between the stacks is 67.1 (2)°. The shortest intermolecular distances observed between molecules in adjacent columns are S···S 3.485 (2) and S···C 3.428 (4) Å, and between anions and cations Br···S 3.777 (1) Å. Layers of BEDT-TTF molecules are separated by pseudo-square-planar $[CuBr_4]^{2-}$ anions. The BEDT-TTF molecules are almost planar and the ethylene groups are ordered with low thermal parameters.

Comment

Mori, Sakai, Saito & Inokuchi (1987) reported the structure of a mixed-valence organic–inorganic composite $[(BEDT\text{-}TTF^{3/4+})_4(BEDT\text{-}TTF^0)_2][Cu^IBr_2]$-

$[\mathrm{Cu^{II}Br_4}]$, with properties similar to those of the title compound. However, the magnetic susceptibility at 300 K exceeds that expected for the above composition (Kurmoo *et al.*, 1993; Susuki, Yamaura, Sugiyasu, Enoki & Saito, 1993). Mori *et al.* (1987) remarked on the ambiguities in the structural model since it was refined with a fixed occupancy of 0.75 for the Br-atom sites. We have therefore determined the structure of our crystal (and that of the isomorphous $\mathrm{CuCl_2Br_2}$ salt; Hebrard *et al.*, 1994) and found a stoichiometry of $(\mathrm{BEDT\text{-}TTF})_3[\mathrm{CuBr_4}]$. The volume of the unit cell found by Mori *et al.* (1987) is smaller than that of the $[\mathrm{CuBr_4}]$ salt of our work. Mori's sample was electrocrystallized by oxidation of both BEDT-TTF and $\mathrm{Cu^IBr_2^-}$ in a chlorine-containing solvent, so it is probable that his crystal contained some Cl (Rosseinsky *et al.*, 1988), thus reducing the observed electron density at the Br sites. Our crystals were prepared in a non-chlorinated solvent. In the present structure determination, the Br-atom site occupancies were refined to yield ordered $\mathrm{CuBr_4}$ units (Fig. 1) with Cu—Br distances of 2.407 (2) and 2.421 (2) Å, both within the expected range for $\mathrm{Cu^{II}}$—Br bonds (Willett, Place & Middleton, 1988). The structure of the BEDT-TTF layers (Fig. 2) is exactly that found by Mori *et al.* (1987). The dimensions of the BEDT-TTF molecules correspond to charges of +1 on *B* and 0 on *A*, *i.e.* $(A^0B^+B^+)$-$[\mathrm{CuBr_4}]^{2-}$, in agreement with the physical properties. To our knowledge this is the first example of a planar $[\mathrm{CuBr_4}]^{2-}$ anion, although we have evidence that it becomes Jahn–Teller distorted below 60 K (Kurmoo *et al.*, 1993).



(I)

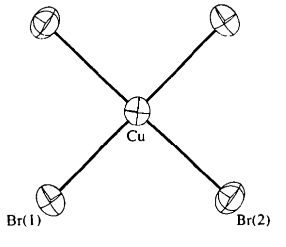


Fig. 1. An *ORTEP*II (Johnson, 1976) view of the planar $[\mathrm{CuBr_4}]^{2}$ anion. Displacement ellipsoids are shown at the 50% probability level.

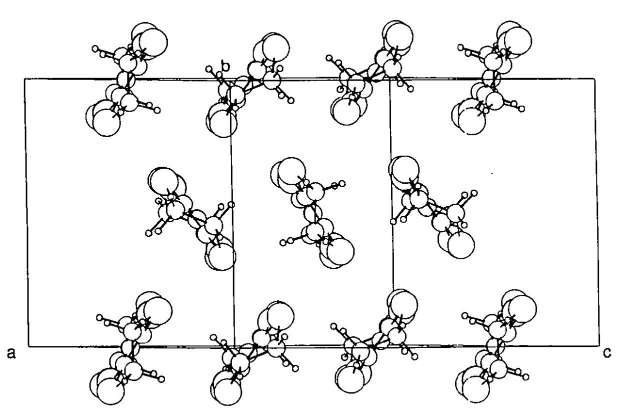


Fig. 2. Projection along the molecular axis of BEDT-TTF (molecule *A*).

Experimental

The title compound was prepared by electrocrystallization as described by Kurmoo, Kanazawa & Day (1991).

Crystal data

$(\mathrm{C_{10}H_8S_8})_3[\mathrm{CuBr_4}]$
$M_r = 1537.2$
Monoclinic
$P2_1/c$
$a = 17.001$ (3) Å
$b = 10.140$ (2) Å
$c = 14.178$ (3) Å
$\beta = 102.75$ (3)°
$V = 2383.9$ (10) Å^3
$Z = 2$
$D_x = 2.14$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 8$–28°
$\mu = 5.063$ mm^{-1}
$T = 296$ K
Plate
0.8 × 0.5 × 0.5 mm
Black

Data collection

CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical
$T_{\min} = 0.348$, $T_{\max} = 1.000$
7866 measured reflections
6331 independent reflections
3201 observed reflections [$I > 3\sigma(I)$]

$R_{\mathrm{int}} = 0.01$
$\theta_{\max} = 29°$
$h = -22 \rightarrow 22$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 18$
3 standard reflections
frequency: 120 min
intensity variation: none

Refinement

Refinement on F
$R = 0.034$
$wR = 0.037$
$S = 0.97$
3201 reflections
271 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F) + 0.005F^2]$

$(\Delta/\sigma)_{\max} = 0.8$
$\Delta\rho_{\max} = 1.0$ e Å^{-3}
$\Delta\rho_{\min} = -0.9$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{\mathrm{eq}} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
Cu	0	1/2	0	1.94 (3)
Br(1)	−0.02071 (3)	0.33062 (5)	0.11096 (3)	3.19 (2)
Br(2)	−0.02585 (3)	0.66714 (5)	0.11134 (3)	3.08 (2)

S(11)	0.33371 (7)	0.0973 (1)	0.28839 (8)	2.4 (1)
S(12)	0.35470 (7)	−0.1341 (1)	0.17584 (8)	2.7 (1)
S(13)	0.15972 (7)	0.1191 (1)	0.21790 (9)	3.2 (1)
S(14)	0.18234 (7)	−0.1633 (1)	0.08249 (8)	2.6 (1)
C(15)	0.3987 (3)	−0.0197 (4)	0.2609 (3)	2.1 (2)
C(16)	0.2468 (2)	0.0353 (4)	0.2126 (3)	1.9 (2)
C(17)	0.2568 (2)	−0.0733 (4)	0.1596 (3)	1.8 (2)
C(18)	0.0841 (2)	0.0005 (4)	0.1635 (3)	2.4 (2)
C(19)	0.0966 (2)	−0.0524 (4)	0.0695 (3)	2.1 (2)
S(21)	0.51910 (7)	0.0966 (1)	0.39283 (8)	2.6 (1)
S(22)	0.54725 (7)	−0.1350 (1)	0.28315 (9)	2.8 (1)
S(23)	0.68451 (7)	0.1207 (1)	0.50615 (8)	2.8 (1)
S(24)	0.71959 (7)	−0.1589 (1)	0.37375 (9)	2.8 (1)
C(25)	0.4787 (3)	−0.0200 (4)	0.3053 (3)	2.2 (2)
C(26)	0.6170 (2)	0.0351 (4)	0.4178 (3)	1.9 (2)
C(27)	0.6302 (2)	−0.0735 (4)	0.3659 (3)	2.1 (2)
C(28)	0.7720 (3)	0.0141 (5)	0.5264 (3)	2.6 (2)
C(29)	0.7924 (3)	−0.0406 (5)	0.4358 (3)	2.8 (2)
S(31)	0.39397 (7)	0.3753 (1)	0.49644 (9)	2.8 (1)
S(32)	0.41676 (7)	0.6252 (1)	0.39875 (9)	3.0 (1)
S(33)	0.21883 (7)	0.3589 (1)	0.41770 (8)	2.7 (1)
S(34)	0.24652 (8)	0.6586 (1)	0.30291 (9)	3.1 (1)
C(35)	0.4606 (2)	0.4995 (5)	0.4783 (3)	2.3 (2)
C(36)	0.3071 (3)	0.4489 (4)	0.4242 (3)	2.1 (2)
C(37)	0.3184 (3)	0.5616 (4)	0.3807 (3)	2.3 (2)
C(38)	0.1555 (3)	0.4345 (5)	0.3123 (3)	2.8 (2)
C(39)	0.1540 (3)	0.5824 (5)	0.3156 (3)	2.9 (2)

Table 2. *Selected geometric parameters* (Å, °)

Br(1)—Cu	2.407 (2)	S(23)—C(26)	1.734 (5)
Br(2)—Cu	2.421 (2)	S(23)—C(28)	1.810 (5)
S(11)—C(15)	1.723 (5)	S(24)—C(27)	1.731 (5)
S(11)—C(16)	1.741 (4)	S(24)—C(29)	1.807 (5)
S(12)—C(15)	1.721 (5)	C(26)—C(27)	1.370 (6)
S(12)—C(17)	1.742 (4)	C(28)—C(29)	1.508 (7)
S(13)—C(16)	1.723 (4)	S(31)—C(35)	1.750 (5)
S(13)—C(18)	1.805 (5)	S(31)—C(36)	1.766 (5)
S(14)—C(17)	1.738 (4)	S(32)—C(35)	1.755 (5)
S(14)—C(19)	1.818 (5)	S(32)—C(37)	1.758 (5)
C(15)—C(25)	1.367 (6)	S(33)—C(36)	1.741 (5)
C(16)—C(17)	1.365 (6)	S(33)—C(38)	1.808 (5)
C(18)—C(19)	1.495 (6)	S(34)—C(37)	1.756 (5)
S(21)—C(25)	1.742 (5)	S(34)—C(39)	1.797 (5)
S(21)—C(26)	1.739 (5)	C(36)—C(37)	1.332 (6)
S(22)—C(25)	1.726 (5)	C(38)—C(39)	1.501 (7)
S(22)—C(27)	1.739 (5)	C(35)—C(35^{i})	1.343 (8)
Br(1)—Cu—Br(2)	90.00 (2)	S(21)—C(26)—S(23)	114.8 (2)
C(15)—S(11)—C(16)	96.4 (2)	S(21)—C(26)—C(27)	116.2 (3)
C(15)—S(12)—C(17)	96.3 (2)	S(23)—C(26)—C(27)	129.0 (3)
C(16)—S(13)—C(18)	101.0 (2)	S(22)—C(27)—S(24)	115.7 (3)
C(17)—S(14)—C(19)	101.3 (2)	S(22)—C(27)—C(26)	116.5 (3)
S(11)—C(15)—S(12)	114.9 (3)	S(24)—C(27)—C(26)	127.8 (3)
S(11)—C(15)—C(25)	121.3 (3)	S(23)—C(28)—C(29)	114.8 (3)
S(12)—C(15)—C(25)	123.8 (3)	S(24)—C(29)—C(28)	113.4 (3)
S(11)—C(16)—S(13)	114.5 (2)	C(35)—S(31)—C(36)	95.5 (2)
S(11)—C(16)—C(17)	116.1 (3)	C(35)—S(32)—C(37)	94.7 (2)
S(13)—C(16)—C(17)	129.4 (3)	C(36)—S(33)—C(38)	99.8 (2)
S(12)—C(17)—S(14)	116.1 (2)	C(37)—S(34)—C(39)	101.5 (2)
S(12)—C(17)—C(16)	116.4 (3)	S(31)—C(35)—S(32)	114.8 (3)
S(14)—C(17)—C(16)	127.5 (3)	S(31)—C(35)—C(35^{i})	123.2 (5)
S(13)—C(18)—C(19)	113.1 (3)	S(32)—C(35)—C(35^{i})	122.0 (5)
S(14)—C(19)—C(18)	113.6 (3)	S(31)—C(36)—S(33)	114.2 (2)
C(25)—S(21)—C(26)	96.4 (2)	S(31)—C(36)—C(37)	116.3 (3)
C(25)—S(22)—C(27)	96.6 (2)	S(33)—C(36)—C(37)	129.5 (4)
C(26)—S(23)—C(28)	101.9 (2)	S(32)—C(37)—S(34)	113.2 (3)
C(27)—S(24)—C(29)	101.3 (2)	S(32)—C(37)—C(36)	118.5 (4)
C(15)—C(25)—S(21)	121.5 (3)	S(34)—C(37)—C(36)	128.3 (4)
C(15)—C(25)—S(22)	124.1 (4)	S(33)—C(38)—C(39)	114.1 (3)
S(21)—C(25)—S(22)	114.4 (3)	S(34)—C(39)—C(38)	113.9 (4)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

The atomic coordinates given by Mori *et al.* (1987) were used as starting values for the refinement and the atom-labelling scheme employed is the same as that used by Hebrard *et al.* (1994). All non-H atoms were refined anisotropically. H atoms were placed at calculated positions (C—H = 1.0 Å); these positions were allowed to vary during the last few cycles. Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: *SDP* (Enraf–Nonius, 1985). Program used to refine structure: *SHELXS*86 (Sheldrick, 1985).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates, and plots of the structure and the crystal packing have been deposited with the IUCr (Reference: MU1087). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Chloro[tri(*p*-tolyl)phosphine]gold(I)

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(*Received* 25 *April* 1994; *accepted* 5 *July* 1994)

Abstract

The Au atom in each of the two molecules that comprise the asymmetric unit of chloro[tris(4-methylphenyl)phosphine]gold(I), $[AuCl(C_{21}H_{21}P)]$, ex-