Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *XP*. Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: CR1121). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# $(BEDT\text{-}TTF)_3[CuBr_2Cl_2]$

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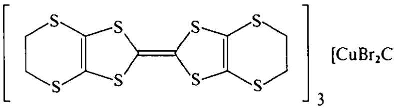
## Abstract

The structure of the title compound, tris[3,4,3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene] dibromodichlorocuprate(2−), $(C_{10}H_8S_8)_3[CuBr_2Cl_2]$, consists of alternate layers of BEDT-TTF molecules [BEDT-TTF = 3,4,3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene] and pseudo-square-planar $[CuBr_2Cl_2]^{2-}$ anions. Two crystallographically independent BEDT-TTF molecules (*A* and *B*) are observed with approximate charges of 0 and +1, respectively. The BEDT-TTF molecules are stacked in an *ABBABB* fashion with a dihedral angle of 67° between the stacks, as in the *α* phase; short S···S contacts result in two-dimensional conducting layers.

## Comment

Considerable efforts are being devoted to the search for superconductors with higher transition temperatures (*Proceedings of the International Conference on Synthetic Metals*, 1993). Among the compounds studied are the salts of organic electron donors such as BEDT-TTF, which provides some of the highest $T_c$'s among the organic chalcogenides. Several studies of the effect of the shape, size and charge of the counter anions have developed guidelines for the synthesis of conducting polytypes. Of particular interest, due to the interplay between superconductivity and magnetism, are the salts containing transition metal anions with a magnetic moment (Kurmoo *et al.*, 1993). We report here the crystal structure of one member of this family, which contains a $d^9$ ion, $(BEDT\text{-}TTF)_3[CuBr_2Cl_2]$, (I).



(I)

The title compound is isostructural with $(BEDT\text{-}TTF)_3[CuBr_4]$ (Guionneau *et al.*, 1994) and consists of BEDT-TTF layers separated by layers of $[CuBr_2Cl_2]^{2-}$ anions. Apart from the halogen atoms all of the atoms are ordered. The refined occupancies of the sites for the Cl and the Br atoms show statistical disorder such that each halide site is approximately 50% Cl and 50% Br. The mean Cu—Cl [2.311 (3) Å] and Cu—Br [2.391 (3) Å] dis-

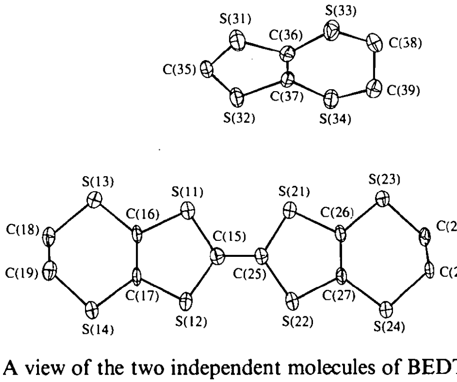


Fig. 1. A view of the two independent molecules of BEDT-TTF in the unit cell, showing displacement ellipsoids at the 50% probability level. The second half of the top molecule is generated by an inversion centre.

tances lie between the average values considered typical for $Cu^{II}$—Cl and $Cu^{II}$—Br bonds (Halvorson, Patterson & Willett, 1990; Willett, 1991). The coordination geometry for the anion is unusual, as one would expect a Jahn–Teller distorted geometry as observed for $(BEDT\text{-}TTF)_3[CuCl_4].H_2O$ (Day *et al.*, 1992).

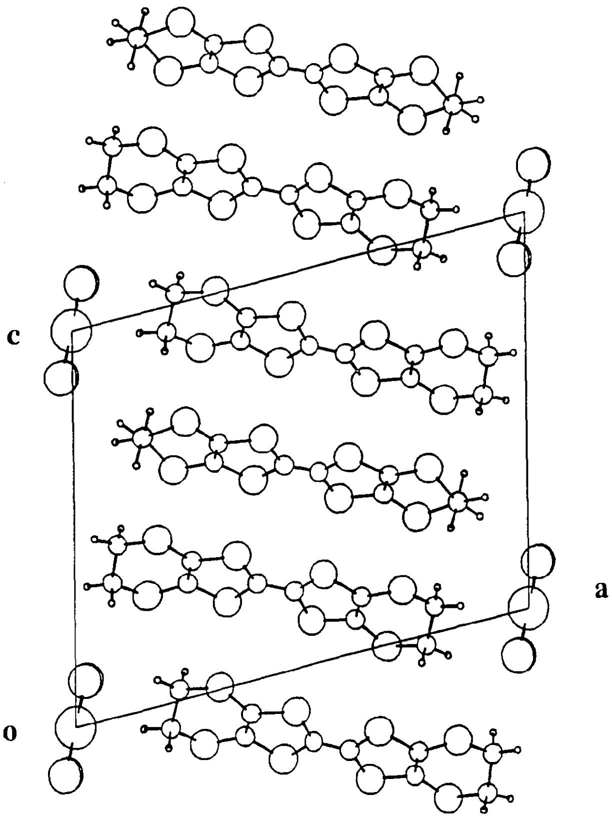


Fig. 2. A projection of the structure along **b**, showing the layers of BEDT-TTF and $[CuBr_2Cl_2]^{2-}$ ions.

## Experimental

Crystals of the title compound were obtained by electrocrystallization of BEDT-TTF and $[(C_2H_5)_4N]_2[CuBr_2Cl_2]$ in benzonitrile (Kurmoo, Kanazawa & Day, 1991).

*Crystal data*

$(C_{10}H_8S_8)_3[CuBr_2Cl_2]$
$M_r = 1448.3$
Monoclinic
$P2_1/c$
$a = 16.895$ (3) Å
$b = 10.108$ (4) Å
$c = 14.150$ (4) Å
$\beta = 102.60$ (2)°
$V = 2358$ (2) Å$^3$
$Z = 2$
$D_x = 2.04$ Mg m$^{-3}$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 12\text{–}25°$
$\mu = 3.434$ mm$^{-1}$
$T = 296$ K
Plate
0.2 × 0.2 × 0.03 mm
Black

*Data collection*

CAD-4 diffractometer
$\omega\text{–}2\theta$ scans
Absorption correction: empirical
$T_{min} = 0.573$, $T_{max} = 1.000$
7988 measured reflections
5416 independent reflections
3437 observed reflections [$I > 3\sigma(I)$]

$R_{int} = 0.017$
$\theta_{max} = 28°$
$h = -22 \rightarrow 22$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 18$
3 standard reflections
frequency: 120 min
intensity variation: none

*Refinement*

Refinement on $F$
$R = 0.036$
$wR = 0.034$
$S = 0.95$
3437 reflections
273 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F) + 0.005F^2]$

$(\Delta/\sigma)_{max} = 0.8$
$\Delta\rho_{max} = 0.9$ e Å$^{-3}$
$\Delta\rho_{min} = -0.8$ 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$^2$)

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

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Cu | 0 | 1/2 | 0 | 2.34 (2) |
| Br(1)* | −0.01984 (4) | 0.32965 (8) | 0.10958 (5) | 3.33 (3) |
| Cl(1′)* | −0.0189 (1) | 0.3353 (2) | 0.1060 (1) | 4.0 (1) |
| Br(2)* | −0.02517 (4) | 0.66382 (8) | 0.11201 (5) | 3.26 (3) |
| Cl(2′)* | −0.0237 (1) | 0.6587 (3) | 0.1083 (2) | 4.0 (1) |
| S(11) | 0.33294 (5) | 0.0975 (1) | 0.28930 (6) | 2.50 (4) |
| S(12) | 0.35394 (5) | −0.1353 (1) | 0.17682 (7) | 2.79 (4) |
| S(13) | 0.15790 (5) | 0.1196 (1) | 0.21864 (7) | 3.36 (5) |
| S(14) | 0.18058 (5) | −0.1651 (1) | 0.08414 (6) | 2.69 (4) |
| C(15) | 0.3984 (2) | −0.0195 (4) | 0.2616 (2) | 2.2 (1) |
| C(16) | 0.2456 (2) | 0.0345 (4) | 0.2134 (2) | 2.1 (1) |
| C(17) | 0.2557 (2) | −0.0748 (4) | 0.1613 (2) | 1.9 (1) |
| C(18) | 0.0817 (2) | −0.0003 (4) | 0.1664 (2) | 2.7 (2) |
| C(19) | 0.0945 (2) | −0.0541 (4) | 0.0715 (3) | 2.7 (2) |
| S(21) | 0.51928 (5) | 0.0966 (1) | 0.39333 (6) | 2.70 (4) |
| S(22) | 0.54745 (5) | −0.1356 (1) | 0.28302 (7) | 2.95 (4) |
| S(23) | 0.68612 (5) | 0.1211 (1) | 0.50542 (7) | 2.79 (4) |
| S(24) | 0.72093 (5) | −0.1593 (1) | 0.37272 (7) | 2.83 (4) |
| C(25) | 0.4793 (2) | −0.0200 (4) | 0.3065 (2) | 2.2 (1) |
| C(26) | 0.6179 (2) | 0.0349 (4) | 0.4177 (2) | 2.1 (1) |
| C(27) | 0.6309 (2) | −0.0726 (4) | 0.3659 (2) | 2.2 (2) |
| C(28) | 0.7733 (2) | 0.0138 (4) | 0.5255 (2) | 2.7 (2) |
| C(29) | 0.7941 (2) | −0.0398 (4) | 0.4342 (2) | 2.7 (2) |
| S(31) | 0.39359 (5) | 0.3750 (1) | 0.49763 (7) | 2.93 (4) |
| S(32) | 0.41584 (5) | 0.6251 (1) | 0.39887 (7) | 3.03 (4) |
| S(33) | 0.21716 (5) | 0.3582 (1) | 0.41969 (7) | 2.82 (4) |
| S(34) | 0.24459 (5) | 0.6584 (1) | 0.30403 (7) | 3.14 (4) |
| C(35) | 0.4603 (2) | 0.4998 (4) | 0.4782 (2) | 2.5 (1) |
| C(36) | 0.3065 (2) | 0.4476 (4) | 0.4254 (2) | 2.3 (1) |
| C(37) | 0.3170 (2) | 0.5624 (4) | 0.3817 (2) | 2.3 (1) |
| C(38) | 0.1525 (2) | 0.4330 (4) | 0.3143 (2) | 2.8 (2) |
| C(39) | 0.1510 (2) | 0.5821 (4) | 0.3176 (3) | 3.0 (2) |

* Site occupancy = 0.5.

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

| | | | |
|---|---|---|---|
| Br(1)—Cu | 2.389 (1) | S(22)—C(25) | 1.723 (4) |
| Cl(1′)—Cu | 2.309 (2) | S(22)—C(27) | 1.746 (4) |
| Br(1)···Cl(1′) | 0.080 (2) | S(23)—C(26) | 1.733 (4) |
| Br(2)—Cu | 2.394 (1) | S(23)—C(28) | 1.801 (4) |
| Cl(2′)—Cu | 2.313 (2) | S(24)—C(27) | 1.740 (4) |
| Br(2)···Cl(2′) | 0.081 (3) | S(24)—C(29) | 1.810 (4) |

| | | | |
|---|---|---|---|
| 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$^{\mathrm{i}}$) | 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$^{\mathrm{i}}$) | 122.5 (3) |
| S(14)—C(17)—C(16) | 127.3 (3) | S(32)—C(35)—C(35$^{\mathrm{i}}$) | 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).

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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: 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 $\alpha$ 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-TTF$^{3/4+}$)$_4$(BEDT-TTF$^0$)$_2$][Cu$^{\mathrm{I}}$Br$_2$]-

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