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Structure of Di[3,4;3',4'-bis(ethylenedithio)-2,2',5,5'-tetrathiafulvalenium] Dichlorocuprate(I), (BEDT-TTF)₂CuCl₂

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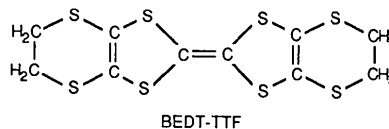
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Abstract. 2C₁₀H₈S₈^{1/2+}·CuCl₂⁻, *M_r* = 903·8, monoclinic, *P*2/*c*, *a* = 7·941 (2), *b* = 6·676 (2), *c* = 30·586 (9) Å, β = 97·47 (2)°, *V* = 1607·7 (6) Å³, *Z* = 2, *D_x* = 1·87 Mg m⁻³, λ(Mo *K*α) = 0·71073 Å, μ = 1·87 mm⁻¹, *F*(000) = 910, *T* = 298 K, *R*(*F*) = 0·049 for 1897 observed reflections. The structure consists of layers (within the *ab* plane) of partially oxidized BEDT-TTF molecules separated by isolated, linear CuCl₂⁻ anions along the *c* direction. Within the layers, transverse, or interstack intermolecular S··S contacts along the *b* direction are shorter than the intrastack distances (along *a*). The electrical conductivity is thermally activated, with *E_a* = 0·15 eV and σ_{300 K} = 0·003 (Ωcm)⁻¹.

Introduction. Superconductivity has been observed in a number of (BEDT-TTF)₂X charge-transfer salts with linear triatomic monovalent anions, including β-(BEDT-TTF)₂I₃ (*T_c* ≈ 1·5 K at ambient pressure; Yagubskii, Shchegolev, Laukhin, Kononovich, Kartsovnik, Zvarykina & Buravov, 1984; Williams, Emge, Wang, Beno, Copps, Hall, Carlson & Crabtree, 1984), β-(BEDT-TTF)₂IBr₂ (*T_c* ≈ 2·8 K, Williams, Wang, Beno, Emge, Sowa, Copps, Behroozi, Hall, Carlson & Crabtree, 1984), and β-(BEDT-TTF)₂AuI₂ (*T_c* ≈ 5 K, Wang, Beno, Geiser, Firestone, Webb,

Núñez, Crabtree, Carlson, Williams, Azevedo, Kwak & Schirber, 1985). Other BEDT-TTF salts have metallic conductivity, e.g. β-(BEDT-TTF)₂I₂Br (Emge, Wang, Beno, Leung, Firestone, Jenkins, Cook, Carlson, Williams, Venturini, Azevedo & Schirber, 1985), or behave as semiconductors, viz β-(BEDT-TTF)₂ICl₂ (Emge, Wang, Leung, Rust, Cook, Jackson, Carlson, Williams, Whangbo, Venturini, Schirber, Azevedo & Ferraro, 1986; Kobayashi, Kato, Kobayashi, Saito, Tokumoto, Anzai & Ishiguro, 1986). Anion size and symmetry are some of the factors that determine if a salt becomes a superconductor at low temperatures (Emge, Leung, Beno, Wang, Firestone, Webb, Carlson, Williams, Venturini, Azevedo & Schirber, 1986).



Most BEDT-TTF charge-transfer salts consist of layers of donor radical molecules, separated by counteranions. Within the layers, stacking is usually observed. Short intermolecular S··S contacts (compared with the van der Waals radii sum, 3·6 Å; Bondi, 1964) are involved in the electrical conduction pathways. The details of the packing, as determined in part by the cation–anion interactions, influence the electronic band structure, and thus the electrical properties.

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Experimental. Crystals of (BEDT-TTF)₂CuCl₂ prepared by electrocrystallization (Pt electrodes, 0.61 μA cm⁻², 295 K) of 2.0 mM BEDT-TTF and 0.1 M [N(n-C₄H₉)₄]CuCl₂ in 1,1,2-trichloroethane. [N(n-C₄H₉)₄]CuCl₂ synthesized by heating dehydrated [N(n-C₄H₉)₄]Cl and freshly prepared CuCl in an oil bath at 363 K (Nilsson, 1983). Small black blocks 0.15 × 0.14 × 0.08 mm. Nicolet P3/F automated four-circle diffractometer. Unit-cell dimensions determined from a least-squares refinement of the setting angles of 25 reflections (17 < 2θ < 24°). Intensity data collected using the ω-scan technique (1° width) with variable scan rates of 1 to 12° min⁻¹ to sinθ/λ = 0.595 Å⁻¹ (h = 0 to 9, k = -7 to 7, l = -32 to 32). Three standard reflections, measured at an interval of 96 reflections, small (4%) random variations. Data corrected for Lorentz and polarization factors, and absorption effects using a Gaussian integration procedure; T_{min} = 0.776, T_{max} = 0.876. 6331 reflections collected, averaged to 2848 unique and allowed reflections, R_{int}(F_o) = 0.061, R_{int}(wF_o) = 0.024, 1897 with I > 2σ(I) used for refinement. Space group indicated by systematic absences, confirmed by successful structure solution and least-squares refinement. Structure solved by direct methods using MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) which provided positions for the CuCl₂⁻ anion, seven S and seven C atoms of the radical cation. Structure completed using Fourier methods. Atomic scattering factors including anomalous contributions from *International Tables for X-ray Crystallography* (1974). All computations carried out with a modified version of the *UCLA Crystallographic Package* (Strouse, 1978). The calculated electron density showed double maxima for the exocyclic C atoms C(7) and C(10) which were refined as two disordered, partially occupied positions. The site occupancies, *f*, of C(7) and C(7'), and of C(10) and C(10') were refined, but constrained to add to 1.0 for both pairs. Common isotropic thermal parameters were refined for C(7) and C(7'), and C(10) and C(10'), respectively. All other atoms were refined with anisotropic thermal parameters. H atoms not located. 177 parameters varied. Σw(|F_o| - |F_c|)² minimized, where w = 1/σ²(F_o) and σ(F_o) = [σ²(F_o) + (0.02F_o)²]^{1/2}/(2F_o), with the value of σ(F_o) based on counting statistics. Δ/σ ≤ 0.03 in final least-squares cycle which resulted in the agreement factors R(F_o) = 0.049, wR(F_o) = 0.050, and S = 1.93. No extinction correction applied. A difference Fourier synthesis based on the structure factors derived from the final parameter values produced random variations of ±0.3 e Å⁻³ with the largest peaks 0.4–0.6 e Å⁻³ associated with S(8) and the disordered ethylene-group C atoms. Electrical conductivity measured on a single crystal along an arbitrary direction within the *ab* plane in the temperature range 220–300 K, four-probe technique with phase-sensitive

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters*

The complete temperature factor is exp[-8π²U_{eq}sin²θ/λ²], where U_{eq} = (Σ_iΣ_jU_{ij}a_i^{*}a_j^{*}a_i^{*}a_j^{*})/3 (i, j = 1, 2, 3) in units of Å².

	x	y	z	U _{eq} (× 10 ⁴)
Cu	0.5000	0.0000	0.5000	524 (5)
Cl	0.6492 (3)	0.2393 (3)	0.48408 (7)	662 (8)
S(1)	0.1195 (3)	0.7823 (3)	0.69302 (6)	500 (7)
S(2)	0.0616 (2)	0.3633 (3)	0.66907 (5)	435 (7)
S(3)	0.3109 (3)	0.6474 (3)	0.78830 (6)	479 (7)
S(4)	0.2667 (3)	0.2269 (3)	0.76284 (6)	471 (7)
S(5)	-0.0007 (4)	0.9415 (3)	0.60509 (7)	817 (10)
S(6)	-0.0720 (3)	0.4400 (3)	0.57599 (6)	503 (7)
S(7)	0.5248 (2)	0.5687 (3)	0.87287 (6)	450 (7)
S(8)	0.4898 (3)	0.0742 (3)	0.84069 (7)	765 (10)
C(1)	0.1514 (8)	0.5339 (9)	0.7083 (2)	367 (23)
C(2)	0.2340 (8)	0.4770 (10)	0.7479 (2)	364 (23)
C(3)	0.0385 (9)	0.7318 (11)	0.6383 (2)	439 (26)
C(4)	0.0115 (8)	0.5402 (10)	0.6273 (2)	389 (25)
C(5)	0.4158 (8)	0.4712 (10)	0.8240 (2)	356 (24)
C(6)	0.3982 (9)	0.2802 (11)	0.8117 (2)	428 (25)
C(7)	-0.0607 (16)	0.8412 (17)	0.5509 (4)	459 (28)†
C(7')	-0.1585 (30)	0.8405 (33)	0.5654 (7)	459†
C(8)	-0.1566 (13)	0.6633 (13)	0.5476 (3)	848 (40)
C(9)	0.5635 (11)	0.3475 (12)	0.9078 (2)	647 (33)
C(10)	0.4715 (18)	0.1617 (16)	0.8952 (3)	435 (27)†
C(10')	0.5765 (36)	0.1651 (35)	0.8908 (7)	435†

† C(7), C(7'), C(10), and C(10') were refined isotropically, with U[C(7')] = U[C(7)], and U[C(10')] = U[C(10)]. The occupancy factors, *f*, of C(7) and C(10) were refined to f[C(7)] = 1 - f[C(7')] = 0.654 (13), and f[C(10)] = 1 - f[C(10')] = 0.681 (15).

detection at 1.5 μA and 37 Hz. Thermally activated conductivity with E_a = 0.15 eV and σ₃₀₀ ≈ 0.003 (Ω cm)⁻¹.

Discussion. Final positional and equivalent isotropic thermal parameters are presented in Table 1.* Bond lengths, angles, and intermolecular S...S and S...Cl distances less than 3.8 Å are given in Table 2. The atomic numbering of the BEDT-TTF donor radical cation (formal charge ½+) is shown in Fig. 1. The central part of the molecule [S(1)–S(8), C(1)–C(6)] is almost planar, although a boat-shaped distortion is noticeable: C(1), C(2) and S(1)–S(4) are ≈ 0.2 Å below, C(3)–C(6) less than 0.1 Å above, and S(5)–S(8) 0.1–0.3 Å above the least-squares plane through all 14 atoms. Both exocyclic ethylene groups exhibit conformational disorder, as evidenced by the electron density double maxima around C(7) and C(10), and by the large anisotropic temperature factors of C(8), C(9), and the adjacent S atoms S(5)–S(8). Further indication of disorder is given by the ethylene C–C bond lengths which are up to 0.2 Å shorter than normal C–C single bonds (1.54 Å). The other bond lengths and angles are in their expected ranges.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43559 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Several crystal structures containing the linear CuCl_2^- anion have been reported (Newton, Caughman & Taylor, 1970, 1974; Marsh & Trotter, 1971; Kaiser, Brauer, Schröder, Taylor & Rasmussen, 1974; Siiman, Huber & Post, 1977; Huber, Post & Siiman, 1978; Francisco, de Almeida Santos, Lechat & Massabni, 1981; Clegg, Garner, Nicholson & Raithby, 1983; Sakurai, Kobayashi, Masuda, Tsuboyama & Tsuboyama, 1983; Asplund, Jagner & Nilsson, 1983; Tsuboyama, Kobayashi, Sakurai & Tsuboyama, 1984;

Andersson & Jagner, 1985). $\text{Cu}-\text{Cl}$ bond lengths of $2.05-2.10 \text{ \AA}$, and $\text{Cl}-\text{Cu}-\text{Cl}$ angles of $175-180^\circ$ are usually observed, in agreement with the present findings: $d(\text{Cu}-\text{Cl}) = 2.084(2) \text{ \AA}$, linear by symmetry.

The crystal packing (see Fig. 2) consists of layers of BEDT-TTF molecules parallel to the ab plane. The layers are separated by the dichlorocuprate(I) anions, and there are two layers per unit cell along the crystallographic c direction. Within the layers, the molecules are arranged uniformly along the b direction with short intermolecular separations ($\text{S}\cdots\text{S} < 3.60 \text{ \AA}$). Along the a axis the BEDT-TTF donor radical cations are loosely stacked. Two cations form the repeat distance, and the stacking sequence alternates considerably. Whereas, from a given cation, a number of intermolecular $\text{S}\cdots\text{S}$ contacts between 3.6 and 3.8 \AA exist to one of the neighbours along the crystallographic a direction, none are observed to the opposite neighbor. This alternation is accompanied by zigzag displacement of the molecules from the stacking direction. The Cl atoms of the counteranion are therefore able to approach the donor radical cations quite closely: the shortest $\text{S}\cdots\text{Cl}$ distances are 3.60 \AA , equal to the sum of the van der Waals radii (1.8 and $1.7-1.9 \text{ \AA}$, respectively; Bondi, 1964). Because of the interrupted packing along the stacking axis (a), metallic conduction along that direction is not expected. The crystal structure does not rule out electrical conductivity along the transverse (b) direction, but the measurement indicates that the conduction is thermally activated. $(\text{BEDT-TTF})_2\text{CuCl}_2$ is, therefore, a semiconductor. Unfortunately, the small crystal size prohibits the measurement of the conductivity anisotropy. Electronic-band-structure calculations (Whangbo, 1986) have confirmed the quasi one-dimensional nature of this material, with the dominating dispersion along the crystallographic b axis.

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Table 2. Interatomic distances (\AA) and angles ($^\circ$)

E.s.d.'s are in parentheses.

$\text{Cu}-\text{Cl}$	2.084 (2)	$\text{C}(5)-\text{C}(6)$	1.331 (9)
$\text{C}(1)-\text{S}(1)$	1.733 (6)	$\text{C}(6)-\text{S}(4)$	1.745 (7)
$\text{C}(1)-\text{S}(2)$	1.740 (6)	$\text{C}(6)-\text{S}(8)$	1.743 (7)
$\text{C}(1)-\text{C}(2)$	1.353 (8)	$\text{C}(7)-\text{S}(5)$	1.793 (11)
$\text{C}(2)-\text{S}(3)$	1.732 (6)	$\text{C}(7)-\text{S}(5)$	1.76 (2)
$\text{C}(2)-\text{S}(4)$	1.742 (7)	$\text{C}(7)-\text{C}(8)$	1.407 (14)
$\text{C}(3)-\text{S}(1)$	1.747 (7)	$\text{C}(7)-\text{C}(8)$	1.30 (2)
$\text{C}(3)-\text{S}(5)$	1.733 (7)	$\text{C}(8)-\text{S}(6)$	1.810 (8)
$\text{C}(3)-\text{C}(4)$	1.333 (9)	$\text{C}(9)-\text{S}(7)$	1.825 (7)
$\text{C}(4)-\text{S}(2)$	1.747 (7)	$\text{C}(9)-\text{C}(10)$	1.466 (13)
$\text{C}(4)-\text{S}(6)$	1.755 (6)	$\text{C}(9)-\text{C}(10')$	1.33 (2)
$\text{C}(5)-\text{S}(3)$	1.741 (6)	$\text{C}(10)-\text{S}(8)$	1.789 (11)
$\text{C}(5)-\text{S}(7)$	1.753 (6)	$\text{C}(10')-\text{S}(8)$	1.71 (2)
$\text{S}(1)-\text{C}(1)-\text{S}(2)$	114.0 (3)	$\text{C}(6)-\text{C}(5)-\text{S}(7)$	128.1 (5)
$\text{C}(2)-\text{C}(1)-\text{S}(1)$	123.2 (5)	$\text{S}(4)-\text{C}(6)-\text{S}(8)$	116.0 (4)
$\text{C}(2)-\text{C}(1)-\text{S}(2)$	122.7 (5)	$\text{C}(5)-\text{C}(6)-\text{S}(4)$	117.7 (5)
$\text{C}(1)-\text{S}(1)-\text{C}(3)$	95.6 (3)	$\text{C}(5)-\text{C}(6)-\text{S}(8)$	126.3 (5)
$\text{C}(1)-\text{S}(2)-\text{C}(4)$	95.5 (3)	$\text{C}(3)-\text{S}(5)-\text{C}(7)$	104.2 (4)
$\text{S}(3)-\text{C}(2)-\text{S}(4)$	114.5 (3)	$\text{C}(3)-\text{S}(5)-\text{C}(7')$	98.7 (7)
$\text{C}(1)-\text{C}(2)-\text{S}(3)$	122.6 (5)	$\text{C}(4)-\text{S}(6)-\text{C}(8)$	100.9 (4)
$\text{C}(1)-\text{C}(2)-\text{S}(4)$	122.9 (5)	$\text{C}(5)-\text{S}(7)-\text{C}(9)$	103.1 (3)
$\text{C}(2)-\text{S}(3)-\text{C}(5)$	95.7 (3)	$\text{C}(6)-\text{S}(8)-\text{C}(10)$	97.9 (4)
$\text{C}(2)-\text{S}(4)-\text{C}(6)$	94.7 (3)	$\text{C}(6)-\text{S}(8)-\text{C}(10')$	105.6 (8)
$\text{S}(1)-\text{C}(3)-\text{S}(5)$	114.9 (4)	$\text{S}(5)-\text{C}(7)-\text{C}(8)$	117.3 (8)
$\text{C}(4)-\text{C}(3)-\text{S}(1)$	117.0 (5)	$\text{S}(5)-\text{C}(7)-\text{C}(8)$	126 (2)
$\text{C}(4)-\text{C}(3)-\text{S}(5)$	128.1 (5)	$\text{S}(6)-\text{C}(8)-\text{C}(7)$	119.8 (7)
$\text{S}(2)-\text{C}(4)-\text{S}(6)$	114.8 (4)	$\text{S}(6)-\text{C}(8)-\text{C}(7')$	125 (1)
$\text{C}(3)-\text{C}(4)-\text{S}(2)$	116.8 (5)	$\text{S}(7)-\text{C}(9)-\text{C}(10)$	119.4 (6)
$\text{C}(3)-\text{C}(4)-\text{S}(6)$	128.4 (5)	$\text{S}(7)-\text{C}(9)-\text{C}(10')$	122 (1)
$\text{S}(3)-\text{C}(5)-\text{S}(7)$	115.3 (4)	$\text{S}(8)-\text{C}(10)-\text{C}(9)$	115.0 (8)
$\text{C}(6)-\text{C}(5)-\text{S}(3)$	116.5 (5)	$\text{S}(8)-\text{C}(10')-\text{C}(9)$	129 (2)
Intermolecular $\text{S}\cdots\text{S}$ and $\text{S}\cdots\text{Cl}$ distances (\AA)			
$\text{S}(1)-\text{S}(3')$	3.650 (3)	$\text{S}(5)-\text{S}(6^{\text{II}})$	3.472 (3)
$\text{S}(1)-\text{S}(4^{\text{II}})$	3.754 (3)	$\text{S}(7)-\text{S}(8^{\text{II}})$	3.516 (3)
$\text{S}(2)-\text{S}(5^{\text{III}})$	3.428 (3)	$\text{S}(6)-\text{Cl}^{\text{IV}}$	3.603 (3)
$\text{S}(2)-\text{S}(4^{\text{I}})$	3.657 (3)	$\text{S}(7)-\text{Cl}^{\text{V}}$	3.649 (3)
$\text{S}(3)-\text{S}(8^{\text{II}})$	3.480 (3)		

Symmetry code: (i) $-x, y, \frac{1}{2}-z$; (ii) $x, 1+y, z$; (iii) $x, -1+y, z$; (iv) $-1+x, y, z$; (v) $x, 1-y, \frac{1}{2}+z$.

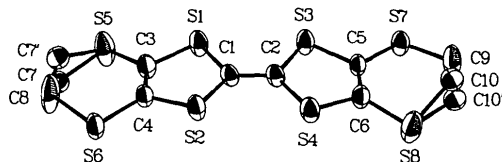


Fig. 1. BEDT-TTF molecule (without H atoms) and atomic-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

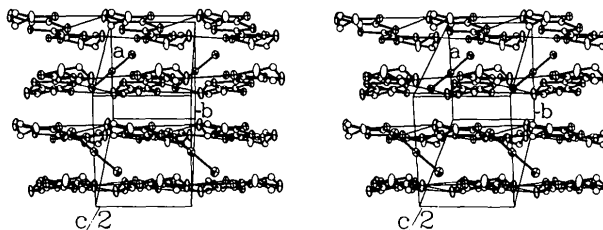


Fig. 2. Packing diagram of $(\text{BEDT-TTF})_2\text{CuCl}_2$, showing one of the BEDT-TTF molecular layers. For clarity, only half a unit cell along the c axis is shown. Intermolecular $\text{S}\cdots\text{S}$ distances less than 3.60 \AA are indicated with thin lines.

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Tetraaquabis(5-nitrotetrazolato-*N*²)nickel(II)

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Abstract. $[\text{Ni}(\text{CN}_5\text{O}_2)_2(\text{H}_2\text{O})_4]$, $M_r = 358.8$, orthorhombic, *Cmca*, $a = 6.872$ (2), $b = 16.522$ (3), $c = 11.900$ (3) Å, $V = 1351.12$ Å³, $Z = 4$, $D_x = 1.76$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 14.17$ cm⁻¹, $F(000) = 728$, $T = 293$ K. Final $R = 0.0471$ for 450 unique observed reflections. The Ni atom has octahedral coordination, site symmetry $2/m$ (C_{2h}), being bonded to two N atoms of different 5-nitrotetrazole rings in *trans* position [Ni–N = 2.105 (6) Å]; the nitro

substituents are not involved in the bonding to the metal. The coordination is completed by four equatorial water molecules [Ni–O = 2.125 (5) Å].

Introduction. Complexes containing the anions of 5-substituted tetrazoles (see below) as ligands exhibit explosive properties (Butler, 1977), and some have been used as primers (McGuhane, 1979). The anions of 5-substituted tetrazoles are ambidentate and can coor-