The Tl—N distances in (1) of 2·568 (4) and 2·587 (5) Å are typical of covalent bonding between these atoms. In hydridotris(3-*tert*-butyl-1-pyrazolyl)-thallium(I) (which has crystallographic mirror symmetry; Cowley *et al.*, 1989) the corresponding distances are 2·582 (6) and 2·587 (9) Å. The Tl—N distances in (*N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane)thallium(I) hexafluorophosphate are 2·59 (2)–2·63 (1) Å (Weighardt, Kleine-Boymann, Nuber & Weiss, 1986). The acute N—Tl—N angles of 75·2 (2) and 78·2 (2)° are due to steric demands of the pyrazolyl ligand; the values in the *tert*-butyl derivative are 75·2 (2) and 78·3 (2)°.

The van der Waals radius of a Tl atom given by Bondi (1964) is 1·96 Å; the Tl···Tl separation of 3·8636 (4) Å in (1) thus probably implies that there is little significant interaction between the two Tl atoms in this crystal structure; closer approach of the thallium atoms is precluded in any case as it would lead to unacceptably short intermolecular contacts between the phenyl rings of the two molecules. The packing in the 3-*tert*-butyl derivative is quite different from that reported here, presumably because of the greater bulk of the *tert*-butyl groups. In [{η^5-$(PhCH_2)_5C_5$}Tl] a quasi dimer is formed about an inversion centre with Tl···Tl 3·632 Å (Schumann, Janiak, Khan & Zuckermann, 1988). Maroni & Spiro (1968) claim that normal coordinate analysis of the IR and Raman spectra of $Tl_4(OR)_4$ derivatives fails to predict the observed spectrum unless some Tl···Tl bonding is assumed; the only X-ray data available are from an incomplete analysis using two-dimensional data of $Tl_4(OMe)_4$ where Tl···Tl separations in the range 3·81–3·86 Å are reported (Dahl, Davis, Wampler & West, 1962).

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Structure and Conductivity of a New Phase of Di[3,4;3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalenium] Dichlorocuprate(I); β-(BEDT-TTF)$_2$CuCl$_2$

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Abstract. β-$(C_{10}H_8S_8)_2[CuCl_2]$, $M_r = 903\cdot8$, triclinic, $P\bar{1}$, $a = 6\cdot623\ (2)$, $b = 9\cdot723\ (2)$, $c = 12\cdot658\ (3)$ Å, $\alpha = 85\cdot98\ (2)$, $\beta = 79\cdot72\ (2)$, $\gamma = 79\cdot95\ (2)°$, $V = 789\cdot0\ (4)$ Å^3, $Z = 1$, $D_x = 1\cdot90$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 19\cdot01$ cm^{-1}, $F(000) = 455$, room temperature, $R(F) = 0\cdot049$, $wR(F) = 0\cdot057$ for 1382 unique reflections. The structure consists of layers of partially oxidized BEDT-TTF cations [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene] separated along the **c** direction by discrete, linear $CuCl_2^-$ anions. Intermolecular S···S distances shorter than the sum of the van der Waals radii (3·6 Å) are found

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Table 1. *Positional parameters and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

	x	y	z	B_{eq}
Cu	0·000	0·000	0·000	4·56 (5)
Cl	0·0916 (4)	−0·2021 (3)	0·0629 (2)	4·72 (6)
S1	0·4181 (3)	0·2584 (3)	0·4593 (2)	2·73 (5)
S2	0·0238 (3)	0·1756 (2)	0·4382 (2)	2·79 (5)
S3	0·1798 (3)	0·4604 (2)	0·6499 (2)	2·57 (5)
S4	−0·2139 (3)	0·3786 (2)	0·6268 (2)	2·74 (5)
S5	0·6692 (3)	0·0759 (3)	0·2904 (2)	4·36 (6)
S6	0·1962 (3)	−0·0107 (3)	0·2600 (2)	3·77 (6)
S7	0·0084 (3)	0·6274 (3)	0·8403 (2)	3·03 (5)
S8	−0·4635 (3)	0·5282 (3)	0·8097 (2)	3·34 (5)
C1	0·151 (1)	0·2776 (9)	0·5017 (7)	2·3 (2)
C2	0·052 (1)	0·3620 (9)	0·5824 (7)	2·2 (2)
C3	0·426 (1)	0·1386 (9)	0·3618 (7)	2·7 (2)
C4	0·243 (1)	0·1022 (9)	0·3511 (7)	2·4 (2)
C5	−0·037 (1)	0·5221 (9)	0·7443 (7)	2·2 (2)
C6	−0·219 (1)	0·4851 (9)	0·7316 (7)	2·3 (2)
C7	0·622 (1)	−0·091 (1)	0·2586 (8)	4·4 (3)
C8	0·453 (1)	−0·085 (1)	0·1973 (9)	4·5 (3)
C9	−0·226 (1)	0·625 (1)	0·9357 (9)	6·3 (3)
C10	−0·418 (1)	0·652 (1)	0·8952 (9)	5·1 (3)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $B_{eq} = (4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Expression for β thermal parameters: $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

only between interstack BEDT-TTF molecules. Four-probe conductivity measurements indicate that the crystal is a semiconductor, with a relatively small bandgap of 45 meV.

Introduction. Salts of BEDT-TTF are of particular interest because of their unusual solid state properties. The organic superconductors with highest T_c known to date, such as κ-(BEDT-TTF)$_2$ [Cu(NCS)$_2$] (Saito, Urayama, Yamochi & Oshima, 1988), κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br and κ-(BEDT-TTF)$_2$ Cu[N(CN)$_2$]Cl (Wang *et al.*, 1991; Kini *et al.*, 1990) belong to this class.

The present paper is one in a continuing series describing products of electrocrystallization reactions, aimed at the synthesis of novel salts and the study of the relationship between structure and properties. Previous papers in this series concern (BEDT-TTF)$_2$HgBr$_4$(TCE) (Bu, Coppens & Naughton, 1990), (BEDT-TTF)$_2$Cd$_2$I$_6$ (Bu, Su & Coppens, 1991) and γ-(BEDT-TTF)$_2$PF$_6$ (Bu, Coppens, Lederle & Naughton, 1991).

Experimental. Crystals of β-(BEDT-TTF)$_2$CuCl$_2$ were prepared by electrocrystallization in a mixed solvent of 1,1,2-trichloroethane (TCE) and 10% volume absolute ethanol containing 1 m*M* BEDT-TTF, 2 m*M* CuCl, 2 m*M* NaN$_3$, 10 m*M* 15-crown-5. A current of 0·8 μA was applied to a 30 ml solution and needle-like crystals were collected on a disk platinum anode after 10 d.

Table 2. *Bond distances* (Å) *and angles* (°)

Cu—Cl	2·098 (3)	S6—C4	1·75 (1)
S1—C1	1·736 (7)	S6—C8	1·791 (9)
S1—C3	1·74 (1)	S7—C5	1·74 (1)
S2—C1	1·73 (1)	S7—C9	1·79 (1)
S2—C4	1·736 (8)	S8—C6	1·742 (7)
S3—C2	1·735 (9)	S8—C10	1·77 (1)
S3—C5	1·743 (7)	C1—C2	1·36 (1)
S4—C2	1·734 (7)	C3—C4	1·35 (1)
S4—C6	1·73 (1)	C5—C6	1·35 (1)
S5—C3	1·734 (8)	C7—C8	1·46 (2)
S5—C7	1·79 (1)	C9—C10	1·43 (1)
C1—S1—C3	95·2 (4)	S1—C3—C4	117·1 (6)
C1—S2—C4	95·7 (4)	S5—C3—C4	126·8 (7)
C2—S3—C5	95·8 (4)	S2—C4—S6	114·6 (5)
C2—S4—C6	95·4 (4)	S2—C4—C3	116·8 (7)
C3—S5—C7	98·9 (4)	S6—C4—C3	128·5 (6)
C4—S6—C8	102·9 (5)	S3—C5—S7	115·3 (5)
C5—S7—C9	99·4 (5)	S3—C5—C6	115·9 (7)
C6—S8—C10	101·7 (4)	S7—C5—C6	128·7 (6)
S1—C1—S2	115·2 (5)	S4—C6—S8	113·9 (5)
S1—C1—C2	121·9 (7)	S4—C6—C5	117·8 (6)
S2—C1—C2	122·9 (6)	S8—C6—C5	128·3 (7)
S3—C2—S4	114·8 (5)	S5—C7—C8	114·7 (7)
S3—C2—C1	123·3 (6)	S6—C8—C7	117·6 (8)
S4—C2—C1	121·9 (7)	S7—C9—C10	117·3 (8)
S1—C3—S5	116·2 (5)	S8—C10—C9	117·6 (8)
Intermolecular S···S distances less than 3·6 Å			
S2—S5^{i}	3·545 (4)	S5—S6^{ii}	3·402 (3)
S3—S8^{ii}	3·542 (4)	S7—S8^{ii}	3·421 (3)

Symmetry codes: (i) $x - 1, y, z$; (ii) $x + 1, y, z$.

A single crystal of β-(BEDT-TTF)$_2$CuCl$_2$, 0·38 × 0·05 × 0·03 mm, was mounted on a glass fiber. Unit-cell dimensions were determined from a least-squares refinement of the setting angles of 23 reflections ($20 < 2\theta < 32°$). Room-temperature data were collected on a MicroVAX-controlled CAD-4 diffractometer with the $\theta/2\theta$ scan technique and graphite-monochromatized Mo $K\alpha$ radiation. Three standard reflections monitored throughout the data collection showed less than 3% change in intensity. 3038 reflections with $1 < \theta < 25°$ [$0·025 < (\sin\theta/\lambda) < 0·59$ Å^{-1}] were measured ($h = 0,7$; $k = -11,11$; $l = -15,15$) and averaged to give 2772 unique reflections, the internal agreement factor $R(F) = 0·025$. Data were reduced using the VAX *SDP* (Enraf-Nonius, 1985) package. Numerical absorption corrections were applied. The transmission factors ranged from 0·91 to 0·96. The structure was solved based on the centrosymmetric space group $P\bar{1}$ using *MULTAN*11/82 from the *SDP* package. Cu and S atoms were located on *E* maps, additional atoms were found on the subsequent difference Fourier maps. The centrosymmetry was suggested by the intensity statistics and confirmed by the successful refinement. 1382 unique reflections with $I > 3\sigma(I)$ were used in the final full-matrix refinement with anisotropic thermal parameters for all non-H atoms. The positions of H atoms were calculated with a C—H distance of 0·95 Å and included in the structure-factor calculation. 178 variables were refined, minimizing the function $\sum[w(|F_{\rm obs}| - k|F_{\rm calc}|)^2]$, where $w = 1/\sigma^2(F)$; $\sigma(F) = \sigma(F^2)/2F$; $\sigma(F^2) = [\sigma^2_{\rm counting} + (0{\cdot}02|F|^2)^2]^{1/2}$. Scattering factors (including anomalous contributions) were taken from *International Tables for X-ray Crystallography* (1974). Parameter shifts in the final least-squares cycle were smaller than 0·02σ. For 1382 reflections, $R(F) = 0{\cdot}049$, $wR(F) = 0{\cdot}057$, $S = 2{\cdot}58$. Largest peaks (+0·66, −0·67 e Å^{-3}) in the final difference Fourier synthesis are near the Cu and Cl atoms.

Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1,* while bond lengths and angles are given in Table 2. Fig. 1 shows the atomic labeling scheme for the BEDT-TTF molecule and Figs. 2 and 3 are packing diagrams for the unit cell and one of the BEDT-TTF molecular layers, respectively.

Discussion. The unit cell contains two BEDT-TTF molecules and one $CuCl_2^-$ anion. BEDT-TTF cations form layers parallel to the *ab* plane. $CuCl_2^-$ ions are located between BEDT-TTF layers in the $z = 0$ plane. Within BEDT-TTF layers, short intermolecular S···S distances (less than 3·6 Å) are found only between stacks, the shortest being 3·402 (3) Å. Within the BEDT-TTF stacks, pairs of molecules are related by the *b* packing mode [a shift in the direction perpendicular to the long molecular axis (Williams *et al.*, 1987)], whereas the *a* mode (a shift parallel to the long axis) relates the two molecules within a pair (Fig. 3). This structural feature is different from that of α-(BEDT-TTF)$_2$CuCl$_2$ reported by Geiser, Wang, Hammond, Firestone, Beno & Williams (1987) and Kurmoo *et al.* (1988), in which the BEDT-TTF molecules within pairs are rotated by 31° with respect to one another. The latter packing mode is described as the *c* mode in terms of the same classification. The cell parameters and the

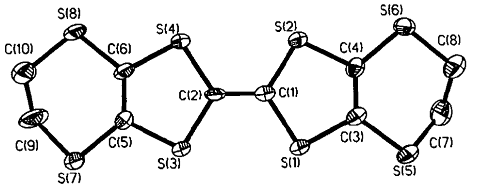

Fig. 1. Molecular diagram of BEDT-TTF showing the labeling of the atoms. Thermal ellipsoids are drawn at the 50% level.

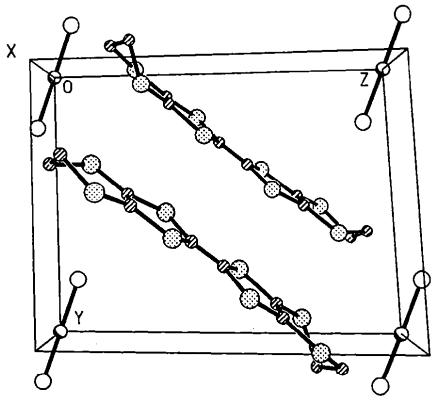

Fig. 2. Packing diagram of (BEDT-TTF)$_2$CuCl$_2$ projected along the *a* axis.

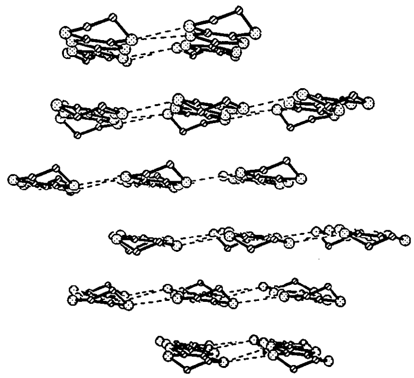

Fig. 3. The packing diagram showing one of the BEDT-TTF molecular layers. Intermolecular S···S distances less than 3·6 Å are indicated with dashed lines.

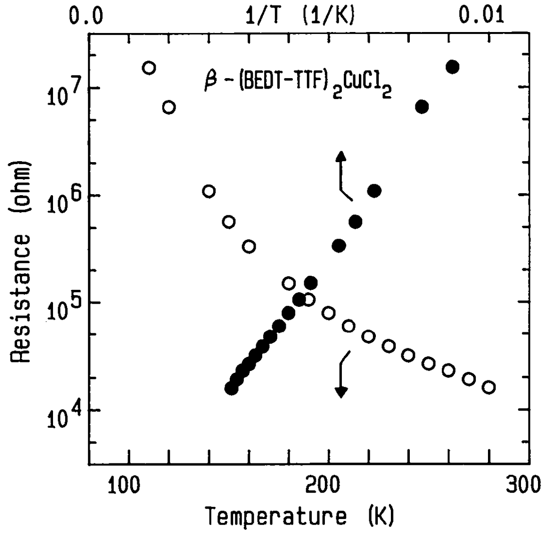

Fig. 4. Resistivity *vs* temperature *T* (open circles), and *vs* 1/*T* (closed circles).

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54196 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

packing mode of β-(BEDT-TTF)$_2$CuCl$_2$ are very similar to those of β-(BEDT-TTF)$_2$ICl$_2$ and β-(BEDT-TTF)$_2$BrICl (Emge *et al.*, 1986). We note that Kurmoo, Talham, Day, Howard, Stringer, Obertelli & Friend (1988) report that they found no evidence for the β-phase, which is the subject of this study, either by chemical or electrochemical crystal growth.

The $CuCl_2^-$ anion is linear as required by symmetry. The Cu—Cl distance, 2·098 (3) Å, is in close agreement with that in $[N(C_4H_9)_2][CuCl_2]$ (Asplund, Jagner & Nilsson, 1983), α-(BEDT-TTF)$_2$CuCl$_2$ (Geiser *et al.*, 1987) and (BEDT-TTF)CuCl$_2$ (Kawamoto, Tanaka & Tanaka, 1987).

Four-probe conductivity measurements were made on two different single crystals of the same batch of β-(BEDT-TTF)$_2$CuCl$_2$. Fig. 4 shows the resistance of one of these samples in the needle direction (crystallographic *a* axis) in the temperature range of 100 to 290 K. The room-temperature conductivity is approximately $10^{-2}\,\Omega^{-1}\text{cm}^{-1}$. Linear dependence of the log *R vs* 1/*T* plot indicates standard semiconductivity behaviour with a relatively small gap of 45 meV.

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Structure of a Binuclear Disulfido–Vanadium Complex, $[V_2(\mu\text{-}\eta^2\text{-}S_2)_2(Et_2NCS_2)_4]$

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Abstract. Di[bis(diethyldithiocarbamato)(μ-η^2-disulfido)vanadium], $C_{20}H_{40}N_4S_{12}V_2$, $M_r = 823·22$, triclinic, $P\bar{1}$, $a = 11·071\ (7)$, $b = 12·161\ (6)$, $c = 6·714\ (4)$ Å, $\alpha = 102·62\ (4)$, $\beta = 95·14\ (4)$, $\gamma = 97·17\ (5)$°, $V = 868·8$ Å^3, $Z = 1$, $D_x = 1·57$ g cm^{-3}, λ(Mo *Kα*) 0·71069 Å, $\mu = 12·4$ cm^{-1}, $F(000) = 426$, room temperature, final $R = 0·058$ for 1346 unique reflections with $(F_o)^2 > 3\sigma(F_o)^2$. The environment of the V atom in the title compound is of a distorted tetragonal prism geometry. The single V—V bond distance is 2·884 (4)Å.

Introduction. Vanadium compounds are of special interest for their wide range of applications in biological systems, new materials and catalysis. Among sulfido–vanadium complexes reported, only a few

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