

Bis(ethylenedithio)tetrathiafulvalenium–tetrachloridocobaltate(II) (3/2)

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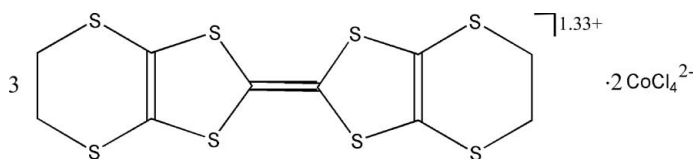
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.022$ Å; R factor = 0.100; wR factor = 0.281; data-to-parameter ratio = 17.9.

The structure of the electrochemically crystallized title compound, $(\text{C}_{10}\text{H}_8\text{S}_8)_3[\text{CoCl}_4]_2$, consists of two types of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) radical cation stacks separated by sheets of tetrahedral $[\text{CoCl}_4]^{2-}$ anions. One of the BEDT-TTF molecules is generated by inversion. There are short $\text{S}\cdots\text{S}$ contacts between the stacks in the a direction and short $\text{C}-\text{H}\cdots\text{Cl}$ contacts between the radical cations and the anions.

Related literature

For related literature, see: Mori (1998, 1999); Mori *et al.* (1999, 2002); Shibaeva & Yagubskii (2004); Varma *et al.* (1987); Williams *et al.* (1984).



Experimental

Crystal data

 $(\text{C}_{10}\text{H}_8\text{S}_8)_3[\text{CoCl}_4]_2$
 $M_r = 1555.39$

 Triclinic, $P\bar{1}$
 $a = 6.7904$ (19) Å

 $b = 9.6402$ (18) Å

 $c = 20.499$ (4) Å

 $\alpha = 86.280$ (14)°

 $\beta = 89.967$ (19)°

 $\gamma = 78.456$ (19)°

 $V = 1311.9$ (5) Å³
 $Z = 1$

 Mo $K\alpha$ radiation

 $\mu = 2.03$ mm⁻¹
 $T = 293$ (2) K

 $0.22 \times 0.18 \times 0.10$ mm

Data collection

Bruker P4 diffractometer

 Absorption correction: ψ scan

(XSCANS; Bruker, 1996)

 $T_{\min} = 0.652$, $T_{\max} = 0.816$

6527 measured reflections

5159 independent reflections

 1927 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.094$

97 standard reflections

every 3 reflections

intensity decay: 1%

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.100$
 $wR(F^2) = 0.281$
 $S = 0.92$

5159 reflections

289 parameters

8 restraints

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.91$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.06$ e Å⁻³
Table 1

Selected bond lengths (Å).

Co1—Cl1	2.296 (5)	Co1—Cl3	2.259 (5)
Co1—Cl2	2.265 (5)	Co1—Cl4	2.276 (5)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1A \cdots Cl1 ⁱ	0.97	2.55	3.494 (16)	165
C1—H1B \cdots Cl2 ⁱⁱ	0.97	2.83	3.591 (16)	136
C10—H10A \cdots Cl4 ⁱⁱⁱ	0.97	2.78	3.57 (2)	139

 Symmetry codes: (i) $-x + 1, -y + 1, -z + 2$; (ii) $-x, -y + 1, -z + 2$; (iii) $x - 1, y + 1, z$.

Data collection: XSCANS (Bruker, 1996); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2784).

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Bis(ethylenedithio)tetrathiafulvalenium-tetrachloridocobaltate(II) (3/2)

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Comment

There is a large variety of quasi-two-dimensional organic conductors based on the radical cation salts of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) which also is abbreviated to ET. They show a wealth of structural modifications, but the conducting properties of the radical salts are essentially determined by the packing patterns of their BEDT-TTF layers (Shibaeva & Yagubskii, 2004). So, according to packing patterns of the BEDT-TTF layers in the various crystal structure, it is customary classified as α , β , δ , χ and so on. (Mori, 1998; Mori, 1999; Mori *et al.*, 1999)

In the title structure, (I), the unit cell contains three ET donors and two anions. Since one BEDT-TTF molecule (ETA) and $[\text{CoCl}_4]^{2-}$ anion are on general positions, and the other BEDT-TTF molecule (ETB) is positioned on an inversion center, the crystallographically independent molecules are 1.5 ET molecules and one $[\text{CoCl}_4]^{2-}$ anion (Fig. 1). The $[\text{CoCl}_4]^{2-}$ anion shows a slightly distorted tetrahedral configuration (Table 1). The two independent ET molecules have different molecular configuration. In the ETA, the terminal ethylene C2 and C9 atoms extend from the molecular plane with deviations of -0.499 (16) Å and -0.579 (18) Å, but C1 and C10 atoms [with deviations of 0.169 (17) Å and 0.057 (19) Å] almost share the same plane with the rest of the molecule. ETA shows a boat conformation in which C2 and C9 are on the both sides of the molecular plane. Otherwise, ETB shows a chair conformation in which C11 and C12 deviate from the molecular plane by 0.658 (18) Å and 0.02 (2) Å respectively and the inversion center positioned on the middle of the C15—C15A bond. The dihedral angle between the molecular planes of ETA and ETB is 16.88 (16)° and their molecular planes make angles of 43.93 (10)° and 27.10 (13)° with $[010]$ directions respectively.

ETA and ETB form stack A and stack B along the b axis in a face to face manner with different intra-stack packing modes. In the stack A, ETA molecules are dimerized and the intra-stack packing mode alternates between the ROB [ring over bond, ET molecules stack on top of each other with a relative displacement between stacking molecules along their long in-plane axes] and ROA [ring over atom, ET molecules stack on above or below with a large displacement between stacking molecules along their short in-plane axes] modes, as defined by Williams *et al.* (1984). The mean interplanar distance in the dimerized ET molecules is 3.606 Å and between the dimerized is 3.082 Å. There are three kinds of intra-dimer S...S short distances within each dimer shorter than the combined van der Waals radii of two sulfur atoms (3.60 Å), but there are no obvious inter-dimer S...S short contacts between the dimers. Stack B contains only ETB molecules overlapped with ROB mode, and there are no intrastack S...S short contacts. The mean interplanar distance in stack B is 4.392 Å.

Stack A and Stack B form layer A and layer B in the ab plane respectively and these layers are interleaved by the inorganic anions. In layer A, one ET molecule has four pairs of inter-stack S...S short contacts between the stacks in the a -direction [$\text{S1}\cdots\text{S2} = 3.518$ (6) Å, $\text{S1}\cdots\text{S4} = 3.562$ (6) Å, $\text{S7}\cdots\text{S8} = 3.549$ (6) Å] as shown in Fig. 2. Combined with intra-stack S...S short contacts within Stack A, it is suggested that the possibility of a quasi-two-dimensional interaction in the ab -plane. In contrast to the layer A, there are no S...S distance are shorter than the sum of van der Waals radii of two sulfur atoms in the layer B, which indicates the absence of any intermolecular interaction in the layer B.

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Between layer A and layer B, there are layers of $[\text{CoCl}_4]^{2-}$ anions, which engage in ionic donor-anion interactions. The anions sandwich the layers A and layers B along the c axis. The $[\text{CoCl}_4]^{2-}$ anions are situated in the so called 'anion cavity', which is bonded by the terminal ethylene groups of the ET cations. Short C—H \cdots Cl interactions (Table 2) probably stabilize the crystal structure.

Among the molecular conductors based on the ET, there are three major determinant of packing of a crystal: (1) the ET network packing motif; (2) the anion layer motif; and (3) the interatomic environment at the interface of the donor and anion layers. For the larger size of the ET and fractional charge on it, the coulomb interaction between the ET cations and anions is inferior to the π - π interaction. In the title crystal, the ET molecules form poly-ET cations by the π - π interaction and $[\text{CoCl}_4]^{2-}$ anions fill the cavity formed by the ethylene groups of the surrounding ET molecules to balance charge. Hence, the 'anion cavity' is mainly determined by the ET packing motif where the 'anion cavity' is a trigonal channel along the [100] directions. If the size of anion is not enough to fill the anion cavity, the solvent molecules will be crystallized in the crystal to stabilize the structure, such as TCE(1,1,2-trichloroethane) molecules in the crystal α -ET₃(CoCl₄)(TCE)(Mori *et al.*, 2002). In the crystal α -ET₃(CoCl₄)(TCE), the oxidation on ET molecules is lower than that in the title compound, where only one $[\text{CoCl}_4]^{2-}$ anion is needed to balance charge, so the TCE solvent molecules are filled in the 'anion cavity' together. At the same time, if some of the anions are replaced by the other anion with same geometry, size and charge, the crystal structure will be an isomorphic structure, for example, β -(ET)₃(CoCl₄)_{1.34}(GaCl₄)_{0.66}, α -ET₃(CoCl₄)_{0.38}(CoCl₄)_{0.62}(TCE) (Mori *et al.*, 2002). On the other hand, the oxidation on ET molecules and the interaction between the anions and the ethylene groups of the ET will significant affect the packing motif of the ET cations, so the ET packing motif of the title crystal belongs to β' and ET₃(CoCl₄)(TCE) belongs to α . But the 'anion cavity' formed by the ET cations as above two packing motif are nearly same.

Experimental

BEDT-TTF was synthesized following the method of Varma *et al.* (1987) and recrystallized from CHCl₃. K₂CoCl₄.6H₂O was synthesized by metathesis of CoCl₂.6H₂O and KCl in a molar ratio of 1:2 in water and recrystallized before use. All solvent were distilled before use.

Electrochemical crystal growth was carried out in conventional H-shaped cells with Pt electrodes in a constant temperature of 295 (2) K at a current of 0.2 μ A. Each cell contained 7 mg of BEDT-TTF and 99.3 mg of K₂CoCl₄.6H₂O together with 40 mg of 18-crown-6 in 35 mL of TCE(1,1,2-trichloroethane) under an inert atmosphere (N₂). Black needles of (I) were obtained after three months.

Refinement

The electrocrystallization process is a 'self-assembly' process which is difficult to control. The tendency to grow as bundles of fine needles has hampered our efforts to get a better crystal. The low quality of the crystal was the reason for low bond precision, but the obtained structure information of the title compound is meaningful.

The H atoms were geometrically placed (C—H = 0.97Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$.

Figures

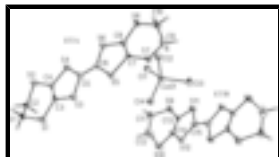


Fig. 1. Molecular structure of (I) with displacement ellipsoids for the non-hydrogen atoms at the 30% probability level. The unlabelled atoms of the ETB molecule are generated by the symmetry operation (1-x, 1-y, 1-x).

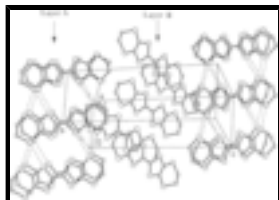


Fig. 2. A packing diagram of (I), with short S...S contacts indicated by dashed lines. The anions and H atoms are omitted for clarity.

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Crystal data

(C₁₀H₈S₈)₃[CoCl₄]₂

M_r = 1555.39

Triclinic, *P* $\bar{1}$

Hall symbol: -P 1

a = 6.7904 (19) Å

b = 9.6402 (18) Å

c = 20.499 (4) Å

α = 86.280 (14)°

β = 89.967 (19)°

γ = 78.456 (19)°

V = 1311.9 (5) Å³

Z = 1

*F*₀₀₀ = 778

D_x = 1.969 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 31 reflections

θ = 5.0–12.4°

μ = 2.03 mm⁻¹

T = 293 (2) K

Prism, black

0.22 × 0.18 × 0.10 mm

Data collection

Bruker P4
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 293(2) K

/w scans

Absorption correction: ψ scan
(XSCANS; Bruker, 1996)

*T*_{min} = 0.652, *T*_{max} = 0.816

6527 measured reflections

5159 independent reflections

1927 reflections with *I* > 2 σ (*I*)

*R*_{int} = 0.094

θ _{max} = 26.0°

θ _{min} = 2.0°

h = -8→1

k = -11→11

l = -25→25

97 standard reflections

every 3 reflections

intensity decay: 1%

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.100$	H-atom parameters constrained
$wR(F^2) = 0.281$	$w = 1/[\sigma^2(F_o^2) + (0.1192P)^2]$
$S = 0.92$	where $P = (F_o^2 + 2F_c^2)/3$
5159 reflections	$(\Delta/\sigma)_{\max} < 0.001$
289 parameters	$\Delta\rho_{\max} = 0.91 \text{ e } \text{\AA}^{-3}$
8 restraints	$\Delta\rho_{\min} = -1.06 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.271 (3)	0.0230 (19)	0.6376 (9)	0.068 (6)
H11A	0.2624	0.0986	0.6671	0.081*
H11B	0.1845	-0.0397	0.6542	0.081*
C12	0.487 (2)	-0.0600 (19)	0.6370 (11)	0.085 (7)
H12A	0.4917	-0.1379	0.6090	0.102*
H12B	0.5226	-0.1013	0.6809	0.102*
C1	0.557 (2)	0.4107 (18)	1.1811 (8)	0.051 (5)
H1A	0.6758	0.3413	1.1952	0.061*
H1B	0.5116	0.4665	1.2180	0.061*
C2	0.397 (2)	0.3341 (16)	1.1632 (8)	0.041 (4)
H2A	0.3816	0.2680	1.1997	0.049*
H2B	0.4443	0.2784	1.1265	0.049*
C3	0.397 (2)	0.5999 (16)	1.0767 (7)	0.035 (4)
C4	0.218 (2)	0.5659 (13)	1.0853 (7)	0.029 (3)
C5	0.161 (2)	0.7692 (15)	0.9978 (7)	0.035 (4)
C6	0.076 (2)	0.8723 (13)	0.9480 (7)	0.023 (3)
C7	0.023 (2)	1.0697 (16)	0.8548 (7)	0.035 (4)

C8	-0.155 (2)	1.0292 (14)	0.8635 (7)	0.034 (4)
C9	-0.106 (3)	1.2069 (19)	0.7415 (9)	0.061 (6)
H9A	-0.0977	1.2849	0.7099	0.073*
H9B	-0.0827	1.1209	0.7181	0.073*
C10	-0.304 (3)	1.228 (2)	0.7659 (9)	0.069 (6)
H10A	-0.3953	1.2454	0.7286	0.082*
H10B	-0.3260	1.3151	0.7888	0.082*
C13	0.350 (2)	0.2161 (15)	0.5480 (7)	0.035 (4)
C14	0.542 (2)	0.1863 (16)	0.5711 (8)	0.040 (4)
C15	0.485 (3)	0.4319 (15)	0.5147 (9)	0.045 (4)
Cl1	0.0026 (7)	0.7913 (4)	0.7470 (2)	0.0460 (11)
Cl2	-0.2946 (7)	0.5703 (5)	0.6666 (2)	0.0563 (13)
Cl3	0.0831 (8)	0.7338 (5)	0.5751 (2)	0.0546 (13)
Cl4	0.2378 (7)	0.4170 (4)	0.6910 (2)	0.0529 (12)
Co01	0.0140 (4)	0.6252 (2)	0.67099 (11)	0.0402 (6)
S1	0.6258 (6)	0.5265 (5)	1.1162 (2)	0.0508 (13)
S2	0.1496 (6)	0.4391 (4)	1.1417 (2)	0.0426 (11)
S3	0.4092 (6)	0.7397 (4)	1.0199 (2)	0.0373 (10)
S4	0.0217 (6)	0.6592 (4)	1.0356 (2)	0.0351 (10)
S5	0.2191 (6)	0.9787 (4)	0.9081 (2)	0.0371 (10)
S6	-0.1704 (6)	0.9004 (4)	0.9241 (2)	0.0370 (10)
S7	0.0938 (6)	1.1928 (4)	0.7998 (2)	0.0388 (11)
S8	-0.3763 (6)	1.0934 (5)	0.8193 (2)	0.0439 (11)
S9	0.1832 (8)	0.0971 (5)	0.5591 (2)	0.0572 (14)
S10	0.6771 (8)	0.0341 (5)	0.6107 (3)	0.0673 (16)
S11	0.2669 (7)	0.3772 (5)	0.5071 (2)	0.0536 (13)
S12	0.6655 (6)	0.3251 (4)	0.5600 (2)	0.0450 (12)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.089 (17)	0.062 (13)	0.058 (13)	-0.042 (13)	0.003 (12)	0.028 (10)
C12	0.104 (18)	0.063 (13)	0.098 (17)	-0.053 (14)	-0.022 (14)	0.035 (12)
C1	0.038 (10)	0.046 (10)	0.060 (12)	0.004 (9)	-0.018 (9)	0.028 (9)
C2	0.028 (9)	0.030 (9)	0.060 (11)	-0.002 (7)	-0.011 (8)	0.018 (8)
C3	0.047 (10)	0.037 (9)	0.025 (8)	-0.024 (8)	-0.011 (8)	0.012 (7)
C4	0.039 (9)	0.014 (7)	0.031 (8)	-0.006 (7)	-0.001 (7)	0.011 (6)
C5	0.039 (10)	0.029 (8)	0.042 (9)	-0.023 (8)	-0.015 (8)	0.014 (7)
C6	0.024 (8)	0.017 (7)	0.028 (8)	-0.005 (6)	-0.003 (7)	-0.007 (6)
C7	0.027 (9)	0.032 (8)	0.040 (10)	0.007 (7)	0.007 (8)	0.008 (7)
C8	0.040 (10)	0.018 (7)	0.044 (10)	-0.008 (7)	-0.001 (8)	0.010 (7)
C9	0.065 (13)	0.054 (12)	0.074 (13)	-0.048 (11)	-0.022 (11)	0.025 (10)
C10	0.040 (12)	0.090 (16)	0.074 (14)	-0.023 (12)	-0.020 (11)	0.035 (12)
C13	0.041 (10)	0.029 (8)	0.036 (9)	-0.010 (8)	-0.013 (8)	0.013 (7)
C14	0.031 (9)	0.030 (8)	0.060 (11)	-0.016 (7)	-0.013 (8)	0.026 (8)
C15	0.043 (10)	0.021 (8)	0.069 (12)	-0.009 (8)	0.000 (9)	0.011 (8)
Cl1	0.058 (3)	0.028 (2)	0.053 (3)	-0.013 (2)	-0.001 (2)	0.0053 (18)
Cl2	0.053 (3)	0.047 (3)	0.071 (3)	-0.020 (2)	-0.004 (3)	0.013 (2)

supplementary materials

C13	0.071 (3)	0.045 (3)	0.050 (3)	-0.021 (2)	0.003 (2)	0.013 (2)
C14	0.047 (3)	0.031 (2)	0.077 (3)	-0.006 (2)	-0.002 (2)	0.016 (2)
Co01	0.0444 (15)	0.0261 (11)	0.0492 (14)	-0.0093 (11)	-0.0038 (12)	0.0124 (10)
S1	0.030 (2)	0.044 (3)	0.076 (3)	-0.011 (2)	-0.013 (2)	0.028 (2)
S2	0.035 (2)	0.032 (2)	0.060 (3)	-0.014 (2)	-0.002 (2)	0.024 (2)
S3	0.032 (2)	0.038 (2)	0.044 (2)	-0.0170 (19)	-0.005 (2)	0.0166 (18)
S4	0.030 (2)	0.027 (2)	0.048 (3)	-0.0129 (18)	-0.0060 (19)	0.0179 (17)
S5	0.030 (2)	0.031 (2)	0.050 (3)	-0.0120 (18)	-0.004 (2)	0.0195 (18)
S6	0.030 (2)	0.030 (2)	0.053 (3)	-0.0170 (18)	-0.007 (2)	0.0143 (18)
S7	0.033 (2)	0.035 (2)	0.047 (3)	-0.011 (2)	-0.002 (2)	0.0167 (19)
S8	0.034 (2)	0.043 (2)	0.053 (3)	-0.012 (2)	-0.010 (2)	0.019 (2)
S9	0.060 (3)	0.052 (3)	0.065 (3)	-0.034 (3)	-0.014 (3)	0.030 (2)
S10	0.058 (3)	0.030 (2)	0.105 (4)	0.003 (2)	-0.008 (3)	0.030 (3)
S11	0.041 (3)	0.044 (3)	0.075 (3)	-0.019 (2)	-0.015 (2)	0.031 (2)
S12	0.035 (2)	0.038 (2)	0.062 (3)	-0.015 (2)	-0.009 (2)	0.018 (2)

Geometric parameters (Å, °)

C11—C12	1.527 (10)	C7—C8	1.35 (2)
C11—S9	1.772 (17)	C7—S7	1.723 (14)
C11—H11A	0.9700	C7—S5	1.774 (15)
C11—H11B	0.9700	C8—S6	1.717 (14)
C12—S10	1.782 (9)	C8—S8	1.735 (16)
C12—H12A	0.9700	C9—C10	1.42 (2)
C12—H12B	0.9700	C9—S7	1.786 (17)
C1—C2	1.49 (2)	C9—H9A	0.9700
C1—S1	1.803 (16)	C9—H9B	0.9700
C1—H1A	0.9700	C10—S8	1.791 (17)
C1—H1B	0.9700	C10—H10A	0.9700
C2—S2	1.818 (15)	C10—H10B	0.9700
C2—H2A	0.9700	C13—C14	1.36 (2)
C2—H2B	0.9700	C13—S11	1.708 (14)
C3—C4	1.333 (19)	C13—S9	1.771 (15)
C3—S3	1.738 (14)	C14—S12	1.719 (14)
C3—S1	1.747 (16)	C14—S10	1.720 (15)
C4—S4	1.739 (14)	C15—C15 ⁱ	1.46 (3)
C4—S2	1.756 (13)	C15—S12	1.672 (17)
C5—C6	1.416 (18)	C15—S11	1.679 (16)
C5—S3	1.708 (15)	Co1—C11	2.296 (5)
C5—S4	1.708 (13)	Co1—C12	2.265 (5)
C6—S6	1.706 (14)	Co1—C13	2.259 (5)
C6—S5	1.720 (13)	Co1—C14	2.276 (5)
C12—C11—S9	112.6 (14)	S6—C8—S8	115.0 (9)
C12—C11—H11A	109.1	C10—C9—S7	117.0 (15)
S9—C11—H11A	109.1	C10—C9—H9A	108.0
C12—C11—H11B	109.1	S7—C9—H9A	108.0
S9—C11—H11B	109.1	C10—C9—H9B	108.0
H11A—C11—H11B	107.8	S7—C9—H9B	108.0
C11—C12—S10	117.6 (12)	H9A—C9—H9B	107.3

C11—C12—H12A	107.9	C9—C10—S8	119.3 (14)
S10—C12—H12A	107.9	C9—C10—H10A	107.5
C11—C12—H12B	107.9	S8—C10—H10A	107.5
S10—C12—H12B	107.9	C9—C10—H10B	107.5
H12A—C12—H12B	107.2	S8—C10—H10B	107.5
C2—C1—S1	114.6 (12)	H10A—C10—H10B	107.0
C2—C1—H1A	108.6	C14—C13—S11	117.8 (11)
S1—C1—H1A	108.6	C14—C13—S9	123.2 (11)
C2—C1—H1B	108.6	S11—C13—S9	119.0 (9)
S1—C1—H1B	108.6	C13—C14—S12	113.9 (11)
H1A—C1—H1B	107.6	C13—C14—S10	130.2 (11)
C1—C2—S2	117.9 (11)	S12—C14—S10	115.8 (9)
C1—C2—H2A	107.8	C15 ⁱ —C15—S12	121.2 (17)
S2—C2—H2A	107.8	C15 ⁱ —C15—S11	122.1 (17)
C1—C2—H2B	107.8	S12—C15—S11	116.7 (8)
S2—C2—H2B	107.8	C13—Co01—C12	110.4 (2)
H2A—C2—H2B	107.2	C13—Co01—C14	110.28 (19)
C4—C3—S3	116.7 (12)	C12—Co01—C14	106.69 (18)
C4—C3—S1	129.2 (11)	C13—Co01—C11	105.49 (17)
S3—C3—S1	114.1 (8)	C12—Co01—C11	107.4 (2)
C3—C4—S4	116.9 (10)	C14—Co01—C11	116.55 (19)
C3—C4—S2	128.5 (12)	C3—S1—C1	103.6 (7)
S4—C4—S2	114.6 (8)	C4—S2—C2	99.8 (7)
C6—C5—S3	122.8 (10)	C5—S3—C3	95.1 (7)
C6—C5—S4	120.8 (11)	C5—S4—C4	95.0 (7)
S3—C5—S4	116.3 (8)	C6—S5—C7	95.2 (7)
C5—C6—S6	123.3 (10)	C6—S6—C8	96.0 (7)
C5—C6—S5	120.7 (11)	C7—S7—C9	98.3 (8)
S6—C6—S5	116.0 (8)	C8—S8—C10	101.3 (8)
C8—C7—S7	131.0 (12)	C13—S9—C11	97.4 (8)
C8—C7—S5	114.8 (11)	C14—S10—C12	103.2 (8)
S7—C7—S5	114.2 (9)	C15—S11—C13	94.8 (7)
C7—C8—S6	118.0 (12)	C15—S12—C14	96.2 (7)
C7—C8—S8	127.0 (11)		
S9—C11—C12—S10	61 (2)	C3—C4—S4—C5	-3.4 (14)
S1—C1—C2—S2	-63.6 (17)	S2—C4—S4—C5	175.8 (9)
S3—C3—C4—S4	3.4 (18)	C5—C6—S5—C7	178.4 (12)
S1—C3—C4—S4	-178.5 (10)	S6—C6—S5—C7	-2.0 (9)
S3—C3—C4—S2	-175.7 (9)	C8—C7—S5—C6	0.7 (14)
S1—C3—C4—S2	2(2)	S7—C7—S5—C6	-178.4 (9)
S3—C5—C6—S6	178.5 (9)	C5—C6—S6—C8	-178.0 (13)
S4—C5—C6—S6	2.7 (19)	S5—C6—S6—C8	2.4 (9)
S3—C5—C6—S5	-1.9 (18)	C7—C8—S6—C6	-2.0 (14)
S4—C5—C6—S5	-177.7 (8)	S8—C8—S6—C6	177.8 (9)
S7—C7—C8—S6	179.7 (10)	C8—C7—S7—C9	-18.6 (19)
S5—C7—C8—S6	0.9 (18)	S5—C7—S7—C9	160.3 (10)
S7—C7—C8—S8	0(3)	C10—C9—S7—C7	49.3 (16)
S5—C7—C8—S8	-178.9 (9)	C7—C8—S8—C10	-3.3 (18)

supplementary materials

S7—C9—C10—S8	-64 (2)	S6—C8—S8—C10	176.9 (10)
S11—C13—C14—S12	4.6 (19)	C9—C10—S8—C8	35.6 (19)
S9—C13—C14—S12	-174.7 (9)	C14—C13—S9—C11	34.6 (17)
S11—C13—C14—S10	-176.7 (11)	S11—C13—S9—C11	-144.8 (10)
S9—C13—C14—S10	4(3)	C12—C11—S9—C13	-64.9 (14)
C4—C3—S1—C1	-8.6 (18)	C13—C14—S10—C12	-17 (2)
S3—C3—S1—C1	169.6 (9)	S12—C14—S10—C12	161.7 (11)
C2—C1—S1—C3	37.9 (15)	C11—C12—S10—C14	-17 (2)
C3—C4—S2—C2	-17.8 (17)	C15 ⁱ —C15—S11—C13	177 (2)
S4—C4—S2—C2	163.1 (9)	S12—C15—S11—C13	-5.1 (12)
C1—C2—S2—C4	49.0 (14)	C14—C13—S11—C15	0.1 (15)
C6—C5—S3—C3	-176.9 (13)	S9—C13—S11—C15	179.5 (11)
S4—C5—S3—C3	-0.9 (11)	C15 ⁱ —C15—S12—C14	-175 (2)
C4—C3—S3—C5	-1.4 (14)	S11—C15—S12—C14	7.2 (12)
S1—C3—S3—C5	-179.9 (9)	C13—C14—S12—C15	-6.9 (15)
C6—C5—S4—C4	178.4 (13)	S10—C14—S12—C15	174.3 (11)
S3—C5—S4—C4	2.3 (11)		

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1A \cdots Cl1 ⁱⁱ	0.97	2.55	3.494 (16)	165
C1—H1B \cdots Cl2 ⁱⁱⁱ	0.97	2.83	3.591 (16)	136
C10—H10A \cdots Cl4 ^{iv}	0.97	2.78	3.57 (2)	139

Symmetry codes: (ii) $-x+1, -y+1, -z+2$; (iii) $-x, -y+1, -z+2$; (iv) $x-1, y+1, z$.

Fig. 1

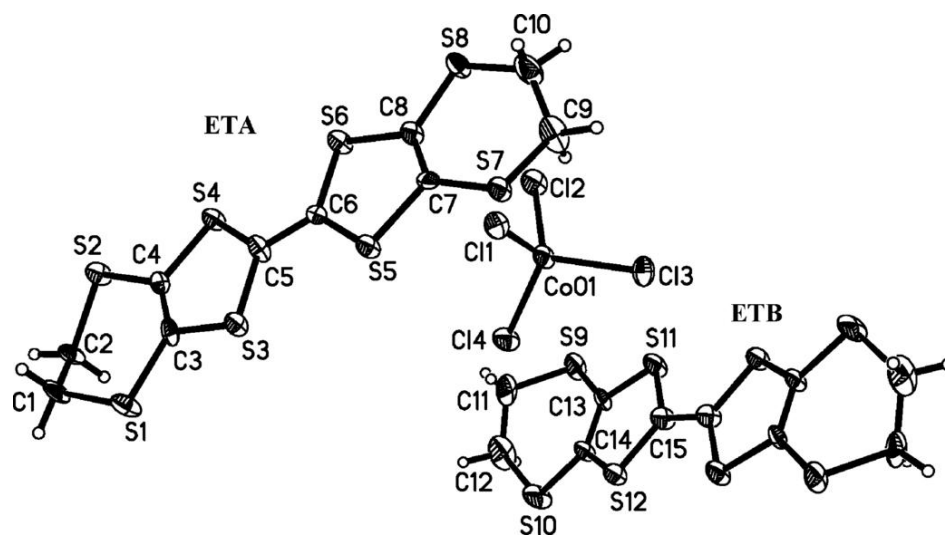


Fig. 2

