Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis[tetrakis(methylsulfanyl)tetrathiafulvalenium] oxalate dichloride

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.004 Å
R factor = 0.039
wR factor = 0.093
Data-to-parameter ratio = 21.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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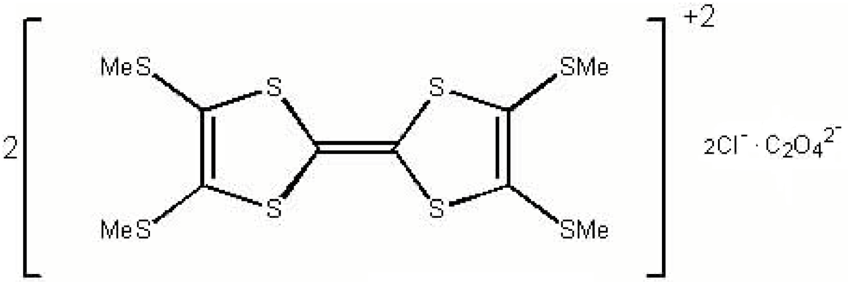
Received 18 April 2005
Accepted 3 May 2005
Online 14 May 2005

The title compound, $2C_{10}H_{12}S_8^{2+}\cdot C_2O_4^{2-}\cdot 2Cl^-$, displays packing *via* hydrogen bonds. The oxalate anion possesses exact $\overline{1}$ and approximate D_{2h} symmetry. Cationic columns of stacked donor molecules have weaker lateral interactions, forming layers. The Cl^- and $C_2O_4^{2-}$ anions form anionic layers. The two layers alternate in the crystal structure.

Comment

Tetrathiafulvalene (TTF) and its derivatives have received much attention over many years (Narita *et al.*, 1976; Andreu *et al.*, 2000). Since the first organic conductor was synthesized in 1973 and the first superconductor in 1979, they have been widely used to prepare charge-transfer salts for good transport properties (Williams *et al.*, 1992). Recently, both transport and magnetic properties have been postulated through the introduction of paramagnetic ions (Kumai *et al.*, 1997; Kikuchi *et al.*, 2002).



(I)

Tetramethylthiotetrathiafulvalene (TTM-TTF) is a popular molecule used in the synthesis of charge-transfer salts, for example $(C_{10}H_{12}S_8)[AuCl_4]_2$, $(C_{10}H_{12}S_8)_2[Cu_2Cl_6]$ and $(C_{10}H_{12}S_8)[C_4(CN)_6]$ (Katayama *et al.*, 1985). Their structural polymorphism is prolific and their physical properties, which are determined by weak intermolecular interactions, are varied. The physical properties of these compounds are of great interest to chemists in the synthesis of new systems. The wealth of crystal structures makes these compounds very interesting crystallographically. We report here the preparation and crystal structure of the title compound, (I), a new TTM-TTF–halogen–oxalic acid salt.

There is one TTM-TTF cation, a Cl^- anion and one half of a $C_2O_4^{2-}$ anion in the asymmetric unit of (I). The molecular configuration is shown in Fig. 1. The centrosymmetric oxalate anion possesses approximate D_{2h} symmetry. The main atoms (except H atoms) in the donor molecule are almost in one plane. The largest torsion angle (C8—S6—C4—S2) is −20.7 (2)°.

doi:10.1107/S1600536805014121

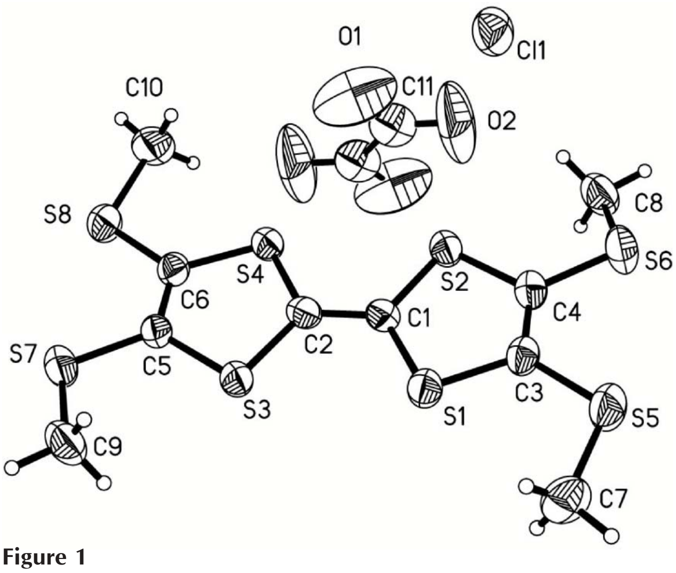


Figure 1
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Unlabelled atoms are related by the symmetry operator $(-x, 1-y, 1-z)$.

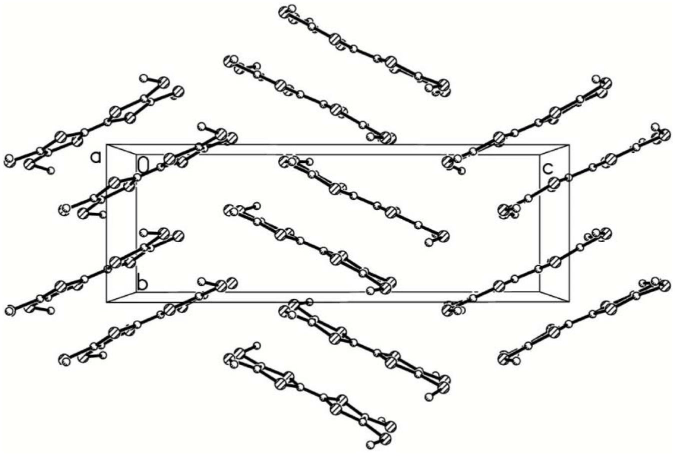


Figure 2
The donor packing of (I), viewed along the *a* axis.

A donor packing diagram is shown in Fig. 2. The cations stack along the *b* axis to form columns, with two different but symmetry-related orientations of the molecular plane, inclined at 50.87 (1)° to each other. In each column, all cations are almost parallel and stack in a face-to-face mode, but they are strongly dimerized along the stacking direction, with substantial lateral displacement between each dimer and the next. Weaker lateral interactions between adjacent columns link them into donor layers (*A*).

The Cl^- and $C_2O_4^{2-}$ anions form an anion layer (*B*) parallel to the *bc* plane. The $C_2O_4^{2-}$ anion and two Cl^- anions form a unit. The shortest O···O distance along the *b* axis is 4.91 (6) Å, and the shortest Cl···Cl distance along the *c* axis is 5.69 (6) Å.

Layers *A* and *B* pack alternately along the *a* axis in the crystal structure (Figs. 3 and 4). Some hydrogen-bond contacts exist between the donor and anion layers.

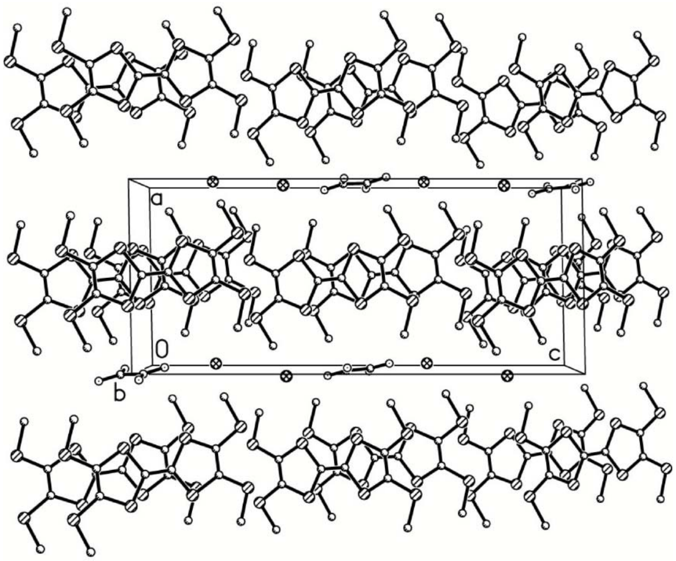


Figure 3
The packing of (I), viewed along the *b* axis.

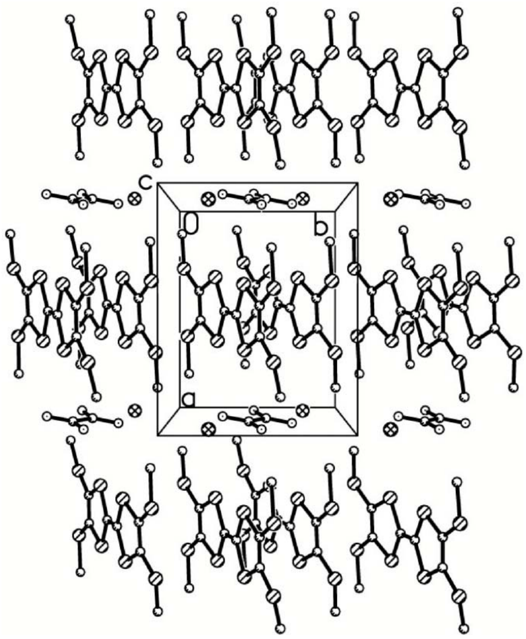


Figure 4
The packing of (I), viewed along the *c* axis.

Experimental

The title compound was an unexpected product of electrocrystallization. Two-compartment cells with platinum electrodes (l = 2 cm, d = 1 mm) were used. The donor, (I) (20 mg), in CH_2Cl_2 (32 ml) with $(Me_4N)^{3+}(FeC_2O_4)_3^{2-}$ (81.5 mg) as electrolyte was electrocrystallized at constant voltage (2.5 V) for two weeks. Black thin needle and block crystals were obtained at the anode. The block crystals were suitable for single-crystal X-ray diffraction analysis. They were collected and washed with acetone.

Crystal data

$2C_{10}H_{12}S_8^{2+}\cdot C_2O_4^{2-}\cdot 2Cl^-$
$M_r = 936.28$
Monoclinic, $P2_1/c$
$a = 10.0277$ (2) Å
$b = 7.9202$ (2) Å
$c = 23.2669$ (6) Å
$\beta = 90.985$ (1)°
$V = 1847.62$ (8) Å^3
$Z = 2$

$D_x = 1.683$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 473
$\theta = 3.3$–$27.5°$
$\mu = 1.11$ mm^{-1}
$T = 296$ (2) K
Block, black
0.18 × 0.17 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min} = 0.825$, $T_{\max} = 0.897$
24 473 measured reflections

4255 independent reflections
2090 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.076$
$\theta_{\max} = 27.7°$
$h = -12 \rightarrow 13$
$k = -10 \rightarrow 10$
$l = -30 \rightarrow 30$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.093$
$S = 0.91$
4255 reflections
199 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0398P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.42$ e Å^{-3}
$\Delta\rho_{\min} = -0.53$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.715 (3)	S6—C8	1.787 (3)
S1—C3	1.736 (3)	S7—C5	1.735 (3)
S2—C1	1.725 (3)	S7—C9	1.792 (3)
S2—C4	1.739 (3)	S8—C6	1.742 (3)
S3—C2	1.725 (3)	S8—C10	1.790 (3)
S3—C5	1.741 (3)	O1—C11	1.205 (5)
S4—C2	1.727 (3)	O2—C11	1.201 (5)
S4—C6	1.733 (3)	C1—C2	1.387 (4)
S5—C3	1.733 (3)	C3—C4	1.355 (4)
S5—C7	1.774 (3)	C5—C6	1.360 (4)
S6—C4	1.741 (3)		
C1—S1—C3	95.64 (13)	C4—C3—S5	121.5 (2)
C1—S2—C4	95.55 (14)	C4—C3—S1	116.8 (2)
C2—S3—C5	95.57 (13)	S5—C3—S1	121.67 (16)
C2—S4—C6	95.36 (13)	C3—C4—S2	116.3 (2)
C3—S5—C7	103.46 (14)	C3—C4—S6	121.9 (2)
C4—S6—C8	103.27 (14)	S2—C4—S6	121.71 (16)
C5—S7—C9	103.57 (13)	C6—C5—S7	122.5 (2)
C6—S8—C10	102.34 (14)	C6—C5—S3	116.1 (2)
C2—C1—S1	122.4 (2)	S7—C5—S3	121.35 (15)
C2—C1—S2	122.0 (2)	C5—C6—S4	117.2 (2)
S1—C1—S2	115.54 (16)	C5—C6—S8	121.3 (2)
C1—C2—S3	122.4 (2)	S4—C6—S8	121.41 (16)
C1—C2—S4	122.1 (2)	O2—C11—C11$^{\rm i}$	119.9 (6)
S3—C2—S4	115.45 (16)	O1—C11—C11$^{\rm i}$	117.2 (6)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8B···Cl1	0.96	2.61	3.543 (4)	165
C8—H8A···Cl1$^{\rm ii}$	0.96	2.66	3.454 (3)	141
C7—H7A···Cl1$^{\rm iii}$	0.96	2.85	3.780 (3)	163
C9—H9A···Cl1$^{\rm iv}$	0.96	2.69	3.594 (3)	157
C9—H9A···Cl1$^{\rm iv}$	0.96	2.69	3.594 (3)	157
C8—H8C···S7$^{\rm v}$	0.96	2.87	3.744 (4)	152

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

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.96 Å and $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(C).

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Bruker, 1998); software used to prepare material for publication: *SHELXL97*.

This work was supported by grant No. CMS-CX200314 from ICCAS and by the Natural Science Foundation of China (grant No. 20343001). The authors thank Professor Dr Zhe-Ming Wang for the X-ray data collection.

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