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2,3,4,5-Tetrakis[(2-hydroxyethyl)thio]-tetrathiafulvalene tetrafluoroborate

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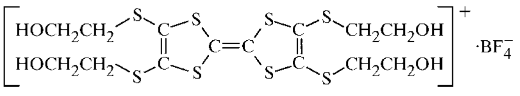
The title complex, $C_{14}H_{20}O_4S_8^{+}\cdot BF_4^{-}$, is a charge-transfer complex with typical charges for the donor and anion of +1 and −1, respectively. Two centrosymmetrically related donors form a face-to-face π-dimer with a strong intermolecular S···S interaction. These π-dimers stack along the *a* axis to form a donor column. The structure is extensively hydrogen bonded.

Comment

The structures of many charge-transfer complexes with the donor containing a tetrathiafulvalene (TTF) unit have been reported (Endres, 1981, 1987; Bechgarrd *et al.*, 1977; Katayama *et al.*, 1985). Studies of the relationship between physical properties and structure have shown the co-existence of high electric conductivity and non-covalent interactions in complexes, such as hydrogen bonds and enhanced van der Waals forces. We have prepared a new charge-transfer complex, (I), with the possibility of hydrogen bonding between donor and acceptor components. The title complex is a charge-transfer complex with one donor and one BF_4^{-} anion in the asymmetric unit. In the donor, bond distances and angles at S are dependent on the hybridization state of the C atoms to which S is bonded, so S—C*sp*^{3} is longer that S—C*sp*^{2} and angles are wider in the case of an *sp*^{2}-hydridized C atom. The S—C*sp*^{3} bond distance is longer than reported values on derivatives of TTF and S—C*sp*^{2} bond distances are similar (Saitoh *et al.*, 1995; Katayama *et al.*, 1985; Brunn *et al.*, 1987; Endres, 1981). C═C bond distances in the TTF core are in the same range as in TTF$^+$ cores. C—C bond distances in the 2-hydroxyethyl groups are similar to C—C bond distances in the ethyl group in BEDT—TTF (Saitoh *et al.*, 1995). C—O bond distances range from 1.385 (6) to 1.433 (7) Å. With the exception of the four 2-hydroxyethyl groups, all the atoms in the donor are close to coplanar with a deviation of 0.20 Å, owing to a charge-transfer interaction between donor and anion. All four 2-hydroxyethyl groups depart from this plane in the same direction and form a U-type structure not reported previously (Batsanov *et al.*, 1995).



(I)

Parallel pairs of donors related by a centre of symmetry lie face-to-face and form an X-type donor dimer with a strong π–π interaction. Donor dimers stack along the *a* axis to form a donor column. The intermolecular S···S contacts in the π-dimer are significantly shorter than the sum of van der Waals radii, 3.7 Å, but no strong intermolecular contacts exist between dimers in a column. The anion is tetrahedral with bond distances and angles similar to reported values (Hursthouse *et al.*, 1995; Saitoh *et al.*, 1995). Owing to the —OH group in the donor and strongly electronegative element in the anion, a lot of hydrogen bonds of types O—H···F and O—H···O exist in the title complex. This phase is an insulator at room temperature, corresponding to the theory of Pierles distortion in low-dimensional conductors. Experiments on physical properties are in progress.

Experimental

Crystals were obtained by electrocrystallization of 10 mg 2,3,4,5-tetrakis[(2-hydroxyethyl)thio]tetrathiafulvalene dissolved in 50 ml 1,1,2-trichloromethane with 4.96 mg KBF_4 and 7.1 mg dibenzo-18-crown-6 in an H-shaped tube. A constant current of 1.0 µA was applied to the supernatant using platinum electrodes for two weeks.

Crystal data

$C_{14}H_{20}O_4S_8^{+}\cdot BF_4^{-}$
$M_r = 595.59$
Triclinic, $P\overline{1}$
$a = 9.7070$ (5) Å
$b = 11.5750$ (6) Å
$c = 11.5920$ (7) Å
$\alpha = 71.333$ (3)°
$\beta = 85.678$ (4)°
$\gamma = 73.601$ (3)°
$V = 1183.58$ (11) Å^3

$Z = 2$
$D_x = 1.671$ Mg m^{-3}
Mo *K*α radiation
Cell parameters from 3980 reflections
$\theta = 0.912$–25.42°
$\mu = 0.806$ mm^{-1}
$T = 293$ (2) K
Block, dark green
0.25 × 0.15 × 0.10 mm

Data collection

MacScience DIP 2030 K image-plate system diffractometer
ω scans
3980 measured reflections
3980 independent reflections

3623 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 25.42°$
$h = -11 \rightarrow 0$
$k = -13 \rightarrow 13$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.149$
$S = 1.075$
3980 reflections
284 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0676P)^2 + 1.9465P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.804$ e Å^{-3}
$\Delta\rho_{\min} = -0.465$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.715 (4)	F2—B1	1.358 (5)
S1—C3	1.736 (4)	F3—B1	1.349 (5)
S2—C1	1.727 (4)	F4—B1	1.321 (5)
S2—C4	1.751 (4)	O1—C8	1.387 (6)
S3—C2	1.722 (4)	O2—C10	1.414 (6)
S3—C5	1.740 (4)	O3—C12	1.421 (5)
S4—C2	1.715 (4)	O4—C14	1.434 (6)
S4—C6	1.738 (4)	C1—C2	1.403 (5)
S5—C3	1.754 (4)	C3—C4	1.361 (5)
S5—C7	1.811 (5)	C5—C6	1.361 (6)
S6—C4	1.734 (3)	C7—C8	1.497 (7)
S6—C9	1.825 (4)	C9—C10	1.494 (6)
S7—C5	1.742 (4)	C11—C12	1.511 (6)
S7—C11	1.821 (4)	C13—C14	1.456 (8)
S8—C6	1.748 (4)	S4—S1$^{\rm i}$	3.356 (1)
S8—C13	1.820 (5)	S3—S2$^{\rm i}$	3.456 (1)
F1—B1	1.333 (5)		
C1—S1—C3	95.98 (17)	C4—C3—S1	116.7 (3)
C1—S2—C4	95.67 (17)	C4—C3—S5	125.7 (3)
C2—S3—C5	95.67 (18)	S1—C3—S5	117.5 (2)
C2—S4—C6	95.78 (17)	C3—C4—S6	124.9 (3)
C3—S5—C7	102.11 (19)	C3—C4—S2	115.9 (3)
C4—S6—C9	101.87 (18)	S6—C4—S2	119.1 (2)
C5—S7—C11	102.88 (18)	C6—C5—S3	116.3 (3)
C6—S8—C13	103.4 (2)	C6—C5—S7	123.2 (3)
F4—B1—F1	111.5 (5)	S3—C5—S7	120.3 (2)
F4—B1—F3	109.0 (4)	C5—C6—S4	116.5 (3)
F1—B1—F3	111.7 (4)	C5—C6—S8	124.2 (3)
F4—B1—F2	108.4 (4)	S4—C6—S8	119.2 (2)
F1—B1—F2	106.2 (4)	C8—C7—S5	114.9 (4)
F3—B1—F2	109.9 (4)	O1—C8—C7	110.7 (4)
C2—C1—S1	122.8 (3)	C10—C9—S6	107.3 (3)
C2—C1—S2	122.0 (3)	O2—C10—C9	109.0 (4)
S1—C1—S2	115.18 (19)	C12—C11—S7	107.4 (3)
C1—C2—S4	122.9 (3)	O3—C12—C11	108.3 (4)
C1—C2—S3	121.5 (3)	C14—C13—S8	115.8 (4)
S4—C2—S3	115.59 (19)	O4—C14—C13	110.3 (4)

Symmetry code: (i) $1 - x, 1 - y, 2 - z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2$\cdots$O4$^{\rm i}$	0.820	2.089	2.891 (5)	165.6
O1—H1$\cdots$F3$^{\rm i}$	0.820	2.145	2.930 (5)	142.6
O1—H1$\cdots$F4$^{\rm i}$	0.820	2.546	3.224 (7)	152.8
O3—H3$\cdots$O1$^{\rm ii}$	0.820	1.932	2.748 (6)	173.8
O4—H4$\cdots$F2$^{\rm iii}$	0.820	2.104	2.875 (6)	156.5

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

Data collection: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); cell refinement: *DENZO* and *SCALEPACK*; data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

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