Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* ($Å^2$)

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
S1	0.07281 (9)	0.3649 (1)	−0.2415 (2)	0.0463 (3)
S5	0.1992 (1)	0.3395 (1)	0.2372 (3)	0.0568 (4)
P	0.000	0.000	0.000	0.0392 (6)
C1	0.0294 (5)	0.500	−0.385 (1)	0.040 (2)
C3	0.1399 (3)	0.4370 (5)	0.0133 (8)	0.039 (1)
C7	0.2906 (5)	0.4387 (7)	0.400 (2)	0.116 (3)
F1	0.0038 (5)	0.000	0.258 (1)	0.208 (7)
F2	−0.0858 (6)	−0.0880 (8)	−0.047 (1)	0.203 (3)

Table 2. *Geometric parameters* (Å, °)

S1—C1	1.715 (4)	P—F2	1.529 (8)
S1—C3	1.743 (5)	C1—C1	1.396 (9)
S5—C3	1.728 (5)	C3—C3	1.353 (8)
S5—C7	1.772 (7)	C7—C7	1.32 (1)
P—F1	1.513 (8)		
C1—S1—C3	95.8 (3)	S1—C1—S1	115.6 (4)
C3—S5—C7	101.6 (3)	S1—C1—C1	122.1 (2)
F1—P—F2	90.6 (4)	S1—C3—S5	116.3 (3)
F1—P—F2	89.4 (4)	S1—C3—C3	116.4 (3)
F2—P—F2	180	S5—C3—C3	127.3 (3)
F2—P—F2	76.3 (4)	S5—C7—C7	126.9 (6)
F2—P—F2	103.7 (4)		

Data collection: Enraf–Nonius CAD-4 software. Data reduction: Enraf–Nonius (1985) *SDP*. Program(s) used to solve structure: Enraf–Nonius *SDP*. Program(s) used to refine structure: Enraf–Nonius *SDP*. Molecular graphics: Nicolet X-ray products. Software used to prepare material for publication: Enraf–Nonius *SDP*.

Structure solved by direct methods and subsequent difference Fourier methods. Anisotropic thermal parameters for all non-H atoms. H atoms were not included in the structure-factor calculation because of the disorder of two terminal ethylene groups. Refinements in the space groups *C*2 and *Cm* did not give any improvement in the apparent disorder, and resulted in severe convergence problems. The weighting scheme was $w=1/\sigma^2(F)$ where $\sigma(F)=\sigma(F^2)/2F$ and $\sigma(F^2)=[\sigma^2_{\text{counting}}+(0.02|F|^2)^2]^{1/2}$.

Support of this work by the Petroleum Research fund administered by the American Chemical Society (PRF21392-AC6-C) and the National Science Foundation (CHE9021069) is gratefully acknowledged.

Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55143 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1002]

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Williams, J. M., Wang, H. H., Emge, T. J., Geiser, U., Beno, M. A., Leung, P. C. W., Carlson, K. D., Thorn, R. J., Schultz, A. J. & Whangbo, M. H. (1987). *Progress in Inorganic Chemistry*, Vol. 35, edited by S. Lippard, pp. 51-218. New York: John Wiley.

Acta Cryst. (1992). C**48**, 1563–1565

Structure of ζ-(BEDT-TTF)$_2$PF$_6$.C$_4$H$_8$O$_2$

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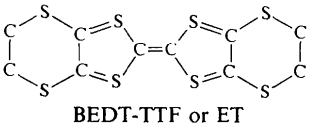
Abstract

The structure consists of sheets of partially oxidized BEDT-TTF molecules [BEDT-TTF, or ET = 3,4;3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene] separated by PF_6^- and tetrahydrofuran solvent molecules along the crystallographic *a* axis. The structure is isomorphous with the corresponding (BEDT-TTF)$_2$ClO$_4$.C$_4$H$_8$O$_2$ [Kobayashi, Kato, Mori, Kobayashi, Sasaki, Saito, Enoki & Inokuchi (1984). *Chem. Lett.* p. 179]. There are two orientations for the chair-shaped tetrahydrofuran molecule.

Comment

Because of their unusual transport properties, salts of BEDT-TTF have attracted considerable attention (Williams *et al.*, 1987). Of particular interest are the organomineral salts, which show the highest superconducting transition temperatures in the BEDT-TTF family or in other organic salts. We report here on the crystal structure of a newly synthesized salt, ζ-(ET)$_2$PF$_6$.



BEDT-TTF or ET

Crystals were prepared by the electrochemical oxidation of BEDT-TTF in a tetrahydrofuran solution containing 0.5 m*M* ET, 0.09 *M* [CH$_3$(CH$_2$)$_3$]$_4$NPF$_6$ and [CH$_3$(CH$_2$)$_3$]$_4$Hg(SCN)$_3$ with a constant current of 0.2 μA.

Three phases of (ET)$_2$PF$_6$ have been reported (Kobayashi, Kato *et al.*, 1983; Kobayashi, Mori *et al.*, 1983; Bu, Coppens, Lederle & Naughton, 1992). Only the title compound contains solvent molecules. Tetrahydrofuran molecules are located on a inversion center and are disordered with two possible positions. As a result of the weak diffracting power of the crystal, only a small fraction of the reflections (about 23%) were observed. The reflection profile analysis showed that reflections with large *l* but small *h* and *k* often overlap, which suggested the highly mosaic nature of the crystal. The poor crystal quality is largely responsible for the high *R* factors.

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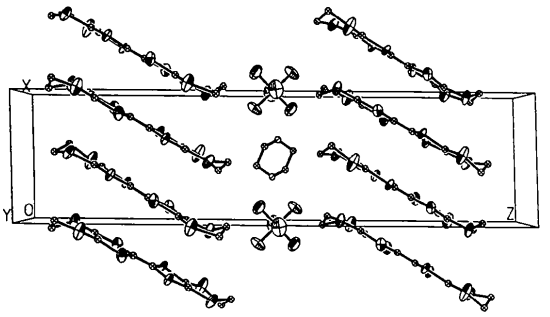

Fig. 1. Packing diagram of the unit cell projected along the *b* axis. The six-membered rings are tetrahydrofuran molecules drawn in two orientations. Thermal ellipsoids drawn at the 50% level. S, P and F were refined anisotropically.

Experimental

Crystal data

$2C_{10}H_8S_8^{1/2+}.PF_6^-.C_4H_8O$
M_r = 986.5
Monoclinic
$P2/c$
a = 8.293 (1) Å
b = 6.703 (1) Å
c = 33.020 (8) Å
β = 91.87 (2)°
V = 1832 (1) Å^3
Z = 2
D_x = 1.79 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 12–18°
μ = 1.004 mm^{-1}
T = 293 K
Thin plate
0.40 × 0.30 × 0.03 mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
5920 measured reflections
5568 independent reflections
1253 observed reflections [$I>3\sigma(I)$]
R_{int} = 0.044

θ_{max} = 30°
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 9$
$l = -43 \rightarrow 43$
3 standard reflections
frequency: 300 min
intensity variation: 1.7%

Refinement

Refinement on F
Final R = 0.119
wR = 0.141
S = 3.39
1253 reflections
226 parameters
H-atom parameters not refined

$(\Delta/\sigma)_{max}$ = 0.01
$\Delta\rho_{max}$ = 0.13 e Å^{-3}
$\Delta\rho_{min}$ = −0.05 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Data collection: Enraf–Nonius CAD-4 software. Data reduction: Enraf–Nonius (1985) *SDP*. Program(s) used to solve structure: Enraf–Nonius *SDP*. Program(s) used to refine structure: Enraf–Nonius *SDP*. Molecular graphics: Nicolet X-ray products. Software used to prepare material for publication: Enraf–Nonius *SDP*.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
S1	0.3698 (8)	0.4208 (9)	0.1989 (2)	0.037 (2)
S2	0.3102 (7)	0.0022 (9)	0.2173 (2)	0.029 (2)
S3	0.192 (1)	0.546 (1)	0.2798 (2)	0.053 (3)
S4	0.1389 (9)	0.1268 (8)	0.2990 (2)	0.041 (2)
S5	0.5302 (10)	0.3453 (10)	0.1220 (2)	0.050 (3)
S6	0.471 (1)	−0.1569 (9)	0.1467 (3)	0.070 (3)
S7	0.016 (1)	0.7057 (9)	0.3489 (3)	0.059 (3)
S8	−0.031 (1)	0.2070 (9)	0.3751 (2)	0.049 (3)
P1	0.000 (0)	0.0000 (0)	0.0000 (0)	0.050 (3)
F1	−0.001 (3)	0.231 (2)	−0.0045 (8)	0.089 (8)
F2	−0.136 (2)	0.010 (3)	0.0326 (5)	0.074 (7)
F3	0.134 (2)	0.020 (3)	0.0362 (5)	0.076 (7)
O	0.355 (7)	0.556 (9)	0.493 (2)	0.10 (2)
C1	0.290 (3)	0.252 (3)	0.2312 (7)	0.031 (5)
C2	0.212 (3)	0.308 (4)	0.2648 (8)	0.041 (6)
C3	0.440 (4)	0.249 (4)	0.1654 (9)	0.046 (7)
C4	0.425 (3)	0.052 (4)	0.1731 (8)	0.044 (7)
C5	0.083 (2)	0.502 (3)	0.3234 (6)	0.024 (4)
C6	0.049 (3)	0.298 (3)	0.3351 (7)	0.025 (5)
C7	0.535 (4)	0.140 (5)	0.088 (1)	0.068 (9)
C8	0.595 (4)	−0.058 (4)	0.1087 (9)	0.055 (8)
C9	−0.050 (4)	0.600 (6)	0.397 (1)	0.068 (9)
C10	0.010 (4)	0.416 (5)	0.4089 (9)	0.056 (8)
C11	0.590 (6)	0.583 (7)	0.480 (1)	0.10 (1)
C12	0.439 (5)	0.560 (6)	0.463 (1)	0.09 (1)

Table 2. *Geometric parameters* (Å, °)

S1—C1	1.70 (2)	S7—C5	1.71 (2)
S1—C3	1.71 (3)	S7—C9	1.83 (4)
S2—C1	1.74 (2)	S8—C6	1.61 (2)
S2—C4	1.80 (3)	S8—C10	1.82 (3)
S3—C2	1.68 (3)	C1—C2	1.36 (4)
S3—C5	1.75 (2)	C3—C4	1.35 (4)
S4—C2	1.78 (3)	C5—C6	1.45 (3)
S4—C6	1.83 (2)	C7—C8	1.57 (5)
S5—C3	1.76 (3)	C9—C10	1.38 (5)
S5—C7	1.77 (4)	P1—F1	1.55 (2)
S6—C4	1.70 (3)	P1—F2	1.58 (2)
S6—C8	1.77 (3)	P1—F3	1.61 (2)
C1—S1—C3	96. (1)	S2—C4—S6	113. (1)
C1—S2—C4	95. (1)	S2—C4—C3	113. (2)
C2—S3—C5	98. (1)	S6—C4—C3	133. (2)
C2—S4—C6	98. (1)	S3—C5—S7	117. (1)
C3—S5—C7	104. (2)	S3—C5—C6	119. (2)
C4—S6—C8	102. (1)	S7—C5—C6	124. (2)
C5—S7—C9	103. (1)	S4—C6—S8	119. (1)
C6—S8—C10	98. (1)	S4—C6—C5	109. (2)
S1—C1—S2	116. (1)	S8—C6—C5	131. (2)
S1—C1—C2	122. (2)	S5—C7—C8	113. (2)
S2—C1—C2	122. (2)	S6—C8—C7	116. (2)
S3—C2—S4	115. (2)	S7—C9—C10	118. (3)
S3—C2—C1	124. (2)	S8—C10—C9	117. (2)
S4—C2—C1	121. (2)	F1—P1—F2	91. (1)
S1—C3—S5	116. (2)	F1—P1—F3	89. (1)
S1—C3—C4	120. (2)	F2—P1—F3	88.9 (9)
S5—C3—C4	124. (2)		

Structure solved by direct methods and subsequent difference Fourier methods. No absorption correction applied. Anisotropic thermal parameters for S, P and F. The weighting scheme was $w=1/\sigma^2(F)$ where $\sigma(F)=\sigma(F^2)/2F$ and $\sigma(F^2)=[\sigma^2_{counting}+(0.02|F|^2)^2]^{1/2}$.

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Structure of $(BEDT\text{-}TTF)_4Hg_2I_6(I_8)$

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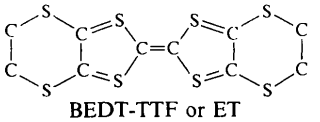
(*Received* 16 *December* 1991; *accepted* 11 *May* 1992)

Abstract

The structure consists of two-dimensional sheets containing both BEDT-TTF [BEDT-TTF, or ET = 3,4;3′4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene] and centrosymmetric I_8 anions. These mixed (ET)-(I_8) sheets are separated by $Hg_2I_6^{2-}$ anions along the *c* axis. Dimers of ET molecules are tilted towards adjacent dimers, similar to the arrangement in κ-phase ET salts.

Comment

Because of their unusual transport properties, salts of BEDT-TTF have attracted considerable attention (Williams *et al.*, 1987). Of particular interest are the organomineral salts, which show the highest superconducting transition temperatures in the BEDT-TTF family or in other organic salts. We report here on the crystal structure of a newly synthesized salt, $(ET)_4Hg_2I_6(I_8)$.



BEDT-TTF or ET

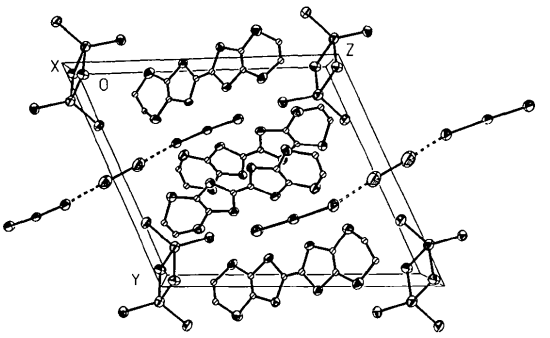


Fig. 1. Packing diagram of the unit cell projected down the *a* axis. Thermal ellipsoids are drawn at the 50% level.

Experimental

Crystal data

$4C_{10}H_8S_8^+.Hg_2I_6^{2-}.I_8^{2-}$	D_x = 2.77 Mg m^{-3}
M_r = 3716.6	Mo $K\alpha$ radiation
Triclinic	λ = 0.71073 Å
$P\bar{1}$	Cell parameters from 25 reflections
a = 8.892 (1) Å	θ = 10-18°
b = 15.627 (2) Å	μ = 8.981 mm^{-1}
c = 17.840 (2) Å	T = 293 K
α = 66.169 (9)°	Needle
β = 79.791 (9)°	0.30 × 0.08 × 0.03 mm
γ = 85.810 (9)°	Black
V = 2231.7 (5) Å^3	
Z = 1	

Data collection

Enraf-Nonius CAD-4 diffractometer	3378 observed reflections [$I > 3\sigma(I)$]
$\theta/2\theta$ scans	R_{int} = 0.034
Absorption correction: by integration from crystal shape	θ_{max} = 23°
T_{min} = 0.47, T_{max} = 0.81	h = 0 → 9
6672 measured reflections	k = −17 → 17
5716 independent reflections	l = −19 → 19
	3 standard reflections
	frequency: 300 min
	intensity variation: −1.4%

Refinement

Refinement on F	$(\Delta/\sigma)_{max}$ = 0.01
Final R = 0.070	$\Delta\rho_{max}$ = 3.6 e Å^{-3}
wR = 0.089	$\Delta\rho_{min}$ = −2.4 e Å^{-3}
S = 3.77	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)
3378 reflections	
297 parameters	
H-atom parameters not refined	

Data collection: Enraf-Nonius CAD-4 software. Data reduction: Enraf-Nonius (1985) *SDP*. Program(s) used to solve structure: Enraf-Nonius *SDP*. Program(s) used to refine structure: Enraf-Nonius *SDP*. Molecular graphics: Nicolet X-ray products. Software used to prepare material for publication: Enraf-Nonius *SDP*.

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