Structure of ε-(BEDT-TTF)PF₆

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Abstract

The structure consists of columns of BEDT-TTF [BEDT-TTF, or ET = 3,4;3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetra-thiafulvalene] isolated by columns of $PF_6{}^-$. The shortest intermolecular S—S distances are found to be 3.618(2) Å, which is comparable to the sum of the van der Waals radii (3.6 Å).

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, ε-(ET)PF₆.

BEDT-TTF or ET
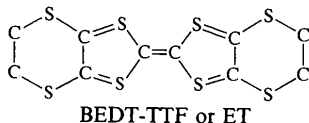
Crystals were prepared by the electrochemical oxidation of BEDT-TTF in a mixed solvent of 1,1,2-trichloroethane and 10% *v/v* absolute ethanol containing 1 m*M* ET, 2 m*M* CuSCN, 2 m*M* KF, 10 m*M* 18-crown-6 and 0.1 *M* [CH₃(CH₂)₃]₄NPF₆ with a constant current of 0.8 μA. Two phases with the same stoichiometry, but different morphology, were obtained. Crystals of ε-(ET)PF₆ are chunky hexagon-shaped while the other phases are needle-like.

Three phases of (ET)₂PF₆ have been reported (Kobayashi, Kato *et al.*, 1983; Kobayashi, Mori *et al.*, 1983; Bu, Coppens, Lederle & Naughton, 1992), all of which consist of layers of BEDT-TTF molecules.

Even though it is common for ET molecules to be located on an inversion center, the title compound is the only ET salt in which ET molecules are located on a 2/*m* site. Since both ET molecules and PF₆⁻ are located on 2/*m* sites, the terminal ethylene groups of ET molecules and PF₆⁻ anions are disordered as demonstrated by their larger-than-normal mean-square displacement parameters. The structural disorder of the ethylene groups and PF₆⁻ anions explains the relatively high *R* factors.
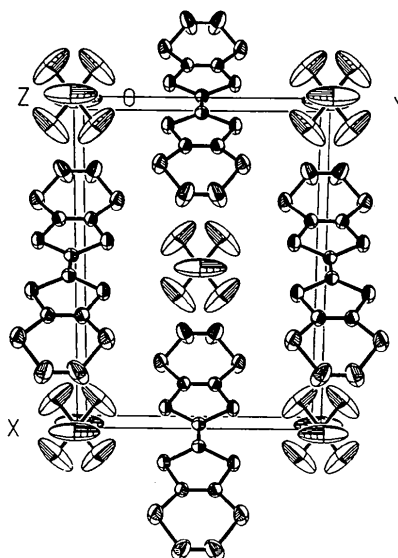
Fig. 1. Packing diagram of the unit cell projected along the *c* axis. Thermal ellipsoids are drawn at the 50% level.

Experimental

Crystal data

$C_{10}H_8S_8{}^+.PF_6{}^-$	Mo *Kα* radiation
$M_r = 529.65$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 21
$C2/m$	reflections
$a = 14.527\,(1)$ Å	$\theta = 10{-}18°$
$b = 10.735\,(2)$ Å	$\mu = 1.105$ mm⁻¹
$c = 5.9233\,(6)$ Å	$T = 293$ K
$\beta = 105.559\,(8)°$	Chunky hexagon
$V = 889.8\,(4)$ Å³	$0.28 \times 0.25 \times 0.15$ mm
$Z = 2$	Black
$D_x = 1.98$ Mg m⁻³	

Data collection

Enraf-Nonius CAD-4	1013 observed reflections
diffractometer	$[I > 3\sigma(I)]$
$\theta/2\theta$ scans	$R_{int} = 0.020$
Absorption correction:	$\theta_{max} = 30°$
by integration from crystal	$h = 0 \rightarrow 20$
shape	$k = 0 \rightarrow 15$
$T_{min} = 0.56$, $T_{max} = 0.82$	$l = -8 \rightarrow 8$
1419 measured reflections	3 standard reflections
1372 independent reflections	frequency: 300 min
	intensity variation: −1.9%

Refinement

Refinement on *F*	$(\Delta/\sigma)_{max} = 0.01$
Final $R = 0.082$	$\Delta\rho_{max} = 0.63$ e Å⁻³
$wR = 0.114$	$\Delta\rho_{min} = -0.37$ e Å⁻³
$S = 6.4$	Atomic scattering factors
1013 reflections	from *International Tables*
62 parameters	*for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)
H-atom parameters not refined	

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Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* ($\mathring{A}^2$)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	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* ($\mathring{A}$, °)

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 $\sigma(F^2)=[\sigma_{counting}^2+(0.02|F|^2)^2]^{1/2}$.

References

Bu, X., Coppens, P., Lederle, B. & Naughton, M. (1992). *Acta Cryst.* C48, 516–519.

Enraf–Nonius (1985). *Structure Determination Package.* Enraf–Nonius, Delft, The Netherlands.

Kobayashi, H., Kato, R., Mori, T., Kobayashi, A., Sasaki, Y., Saito, G., & Inokuchi, H. (1983). *Chem. Lett.* p. 759.

Kobayashi, H., Mori, T., Kato, R., Kobayashi, A., Sasaki, Y., Saito, G. & Inokuchi, H. (1983). *Chem. Lett.* p. 581.

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.

Structure of ζ-(BEDT-TTF)₂PF₆.C₄H₈O₂

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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)₂ClO₄.C₄H₈O₂ [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)₂PF₆.

BEDT-TTF or ET
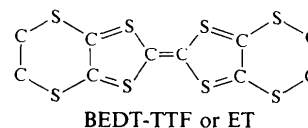
Crystals were prepared by the electrochemical oxidation of BEDT-TTF in a tetrahydrofuran solution containing 0.5 m*M* ET, 0.09 *M* [CH₃(CH₂)₃]₄NPF₆ and [CH₃(CH₂)₃]₄Hg(SCN)₃ with a constant current of 0.2 μA.

Three phases of (ET)₂PF₆ 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.