Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.025$
ω–2θ scans	$\theta_{max} = 27°$
Absorption correction:	$h = 0 \to 11$
none	$k = -14 \to 13$
5635 measured reflections	$l = -16 \to 15$
5302 independent reflections	2 standard reflections
2451 observed reflections	frequency: 120 min
$[I>2\sigma(I)]$	intensity variation: none

Refinement

Refinement on F	$w = \sigma^{-2}(F)$
Final $R = 0.044$	$(\Delta/\sigma)_{max} = 0.33$
$wR = 0.047$	$\Delta\rho_{max} = 2.0$ e Å^{-3}
$S = 1.9$	$\Delta\rho_{min} = -2.2$ e Å^{-3}
2451 reflections	Atomic scattering factors
362 parameters	from *International Tables*
All H-atom parameters re-	*for X-ray Crystallogra-*
fined except those of H25,	*phy* (1974, Vol. IV, Tables
H42, H43 and H45	2.2B and 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^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}
C1	−0.0552 (10)	0.0166 (8)	−0.3618 (6)	0.030
C2	−0.0797 (10)	0.1314 (8)	−0.3474 (7)	0.033
C3	−0.0227 (10)	0.2141 (7)	−0.4184 (7)	0.034
C4	0.0360 (10)	0.1722 (7)	−0.5060 (7)	0.032
C9	−0.0207 (10)	−0.0402 (7)	−0.4618 (6)	0.027
C11	0.1269 (11)	0.0831 (9)	−0.1473 (7)	0.042
C12	0.1119 (14)	0.1323 (9)	−0.0433 (7)	0.051
C13	0.2355 (15)	0.2202 (10)	0.0306 (8)	0.056
C14	0.3771 (16)	0.2630 (11)	0.0005 (10)	0.070
C15	0.3946 (14)	0.2213 (12)	−0.1055 (11)	0.069
C16	0.2703 (13)	0.1295 (11)	−0.1760 (9)	0.062
C21	−0.3621 (12)	0.0331 (9)	−0.2586 (9)	0.051
C22	−0.4541 (15)	−0.0198 (12)	−0.3587 (11)	0.071
C23	−0.5897 (19)	−0.1218 (16)	−0.3714 (18)	0.094
C24	−0.6422 (19)	−0.1654 (13)	−0.2856 (18)	0.091
C25	−0.5550 (18)	−0.1141 (15)	−0.1865 (14)	0.092
C26	−0.4159 (16)	−0.0138 (12)	−0.1690 (10)	0.071
C31	0.0522 (11)	0.4611 (8)	−0.2522 (7)	0.039
C32	0.1607 (12)	0.4271 (9)	−0.1967 (8)	0.046
C33	0.2249 (13)	0.4927 (11)	−0.0899 (9)	0.056
C34	0.1853 (17)	0.5904 (12)	−0.0398 (11)	0.070
C35	0.0793 (18)	0.6260 (14)	−0.0958 (12)	0.080
C36	0.0109 (13)	0.5623 (10)	−0.1997 (10)	0.058
C41	0.3294 (11)	0.3744 (8)	−0.4520 (8)	0.043
C42	0.3739 (12)	0.5041 (8)	−0.4035 (8)	0.045
C43	0.4928 (14)	0.5598 (10)	−0.3190 (10)	0.060
C44	0.5705 (15)	0.4896 (13)	−0.2808 (11)	0.070
C45	0.5288 (14)	0.3591 (12)	−0.3317 (10)	0.074
C46	0.4103 (14)	0.3027 (11)	−0.4159 (10)	0.057
Se1	−0.04145 (12)	−0.05939 (9)	−0.23912 (7)	0.041
Se2	−0.17859 (12)	0.18551 (9)	−0.23080 (8)	0.043
Se3	−0.04317 (13)	0.38087 (9)	−0.39957 (8)	0.047
Se4	0.16730 (12)	0.29549 (9)	−0.57532 (8)	0.041

Table 2. *Geometric parameters* (Å)

C1—C2	1.372 (12)	C21—Se2	1.922 (10)
C1—C9	1.427 (12)	C22—C23	1.37 (3)
C1—Se1	1.936 (9)	C23—C24	1.35 (4)
C2—C3	1.434 (12)	C24—C25	1.34 (3)
C2—Se2	1.924 (9)	C25—C26	1.37 (3)
C3—C4	1.360 (13)	C31—C32	1.375 (14)
C3—Se3	1.929 (8)	C31—C36	1.397 (14)
C4—C9*	1.424 (11)	C31—Se3	1.904 (9)
C4—Se4	1.937 (9)	C32—C33	1.386 (15)
C9—C9*	1.447 (12)	C33—C34	1.344 (18)
C11—C12	1.372 (13)	C34—C35	1.37 (3)
C11—C16	1.372 (16)	C35—C36	1.358 (19)
C11—Se1	1.913 (9)	C41—C42	1.379 (13)
C12—C13	1.367 (15)	C41—C46	1.384 (16)
C13—C14	1.36 (2)	C41—Se4	1.911 (10)
C14—C15	1.385 (19)	C42—C43	1.352 (15)
C15—C16	1.365 (17)	C43—C44	1.361 (18)
C21—C22	1.368 (17)	C44—C45	1.396 (19)
C21—C26	1.413 (18)	C45—C46	1.348 (17)

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

The title compound was initially prepared by persubstitution of octafluoronaphthalene with phenylselenide anion (Robertson, 1984), and was identified spectroscopically in the first instance.

The structure was solved by a manual Patterson solution. Calculations were performed with the *GX* package (Mallinson & Muir, 1985), which includes local modifications of *ORTEP* (Johnson 1971).

References

Barbour, R. H., Freer, A. A. & MacNicol, D. D. (1983). *J. Chem. Soc. Chem. Commun.* pp. 362–363.

Gilmore, C. J., MacNicol, D. D., Mallinson, P. R., Murphy, A. & Russell, M. A. (1984). *J. Incl. Phenom.* 1, 295–299.

Johnson, C. K. (1971). *ORTEPII.* Report ORNL-3794. 2nd revision, and supplementary instructions. Oak Ridge National Laboratory, Tennessee, USA.

MacNicol, D. D., Mallinson, P. R. & Robertson, C. D. (1985). *J. Chem. Soc. Chem. Commun.* pp. 1649–1651.

Mallinson, P. R. & Muir, K. W. (1985). *J. Appl. Cryst.* 18, 51–53.

Robertson, C. D. (1984). BSc thesis, Glasgow Univ., Scotland.

Structure of δ-(BEDT-TTF)PF₆

Xianhui Bu, Ivana Cisarova and Philip Coppens

Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14214, USA

Abstract

The structure consists of two-dimensional sheets of BEDT-TTF [BEDT-TTF, or ET = 3,4;3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene] separated by PF₆⁻ along the crystallographic *b* axis. Intermolecular S—S
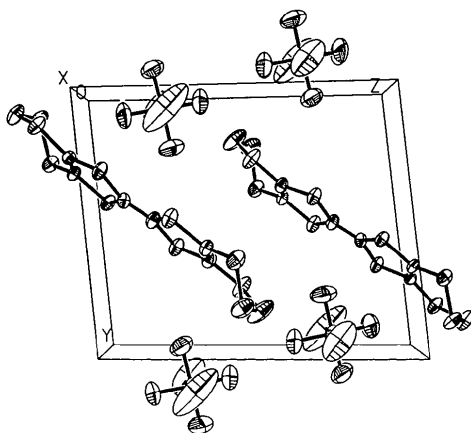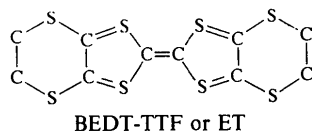
Fig. 1. Packing diagram of the unit cell projected along the *a* axis. Ellipsoids are 50% probability surfaces.

distances shorter than the sum of the van der Waals radii (3.6 Å) are found between both interstack and intrastack BEDT-TTF molecules.

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, δ-(ET)PF$_6$.

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 mM ET, 2 mM CuSCN, 2 mM KF, 10 mM 18-crown-6 and 0.1 M [CH$_3$(CH$_2$)$_3$]$_4$NPF$_6$ with a constant current of 0.8 μA. Two phases with the same stoichiometry, but different morphology, were obtained. Crystals of δ-(ET)PF$_6$ are needle-like while the other phases are chunky hexagon-shaped.

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).

Experimental

Crystal data

C$_{10}$H$_8$S$_8$$^+$.PF$_6^-$
M_r = 529.65
Triclinic

D_x = 1.99 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å

$P\bar{1}$
a = 6.4253 (6) Å
b = 10.7241 (8) Å
c = 13.049 (1) Å
α = 84.084 (6)°
β = 82.435 (7)°
γ = 87.378 (7)°
V = 886.1 (2) Å^3
Z = 2

Cell parameters from 25 reflections
θ = 10–18°
μ = 1.110 mm^{-1}
T = 293 K
Needle
0.35 × 0.08 × 0.04 mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: by integration from crystal shape
T_{min} = 0.92, T_{max} = 0.96
3418 measured reflections
3115 independent reflections

1950 observed reflections
[$I > 3\sigma(I)$]
R_{int} = 0.017
θ_{max} = 25°
h = 0 → 5
k = −9 → 9
l = −11 → 11
3 standard reflections frequency: 300 min intensity variation: −1.1%

Refinement

Refinement on F
Final R = 0.042
wR = 0.054
S = 2.55
1950 reflections
226 parameters
H-atom parameters not refined

$(\Delta/\sigma)_{max}$ = 0.01
$\Delta\rho_{max}$ = 0.71 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 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)

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

	x	*y*	*z*	U_{eq}
S1	0.2067 (2)	0.4287 (1)	0.0915 (1)	0.0318 (3)
S2	0.6306 (2)	0.3247 (1)	0.0973 (1)	0.0342 (4)
S3	0.2626 (2)	0.5893 (1)	0.2834 (1)	0.0361 (4)
S4	0.6883 (2)	0.4867 (1)	0.2847 (1)	0.0369 (4)
S5	0.1146 (2)	0.2858 (1)	−0.0771 (1)	0.0371 (4)
S6	0.6254 (2)	0.1656 (1)	−0.0714 (1)	0.0380 (4)
S7	0.2684 (2)	0.7327 (2)	0.4640 (1)	0.0480 (4)
S8	0.7766 (2)	0.6287 (2)	0.4578 (1)	0.0444 (4)
P	0.0607 (3)	0.0896 (2)	0.2794 (1)	0.0464 (5)
F1	0.0940 (7)	−0.0533 (4)	0.2625 (3)	0.083 (1)
F2	0.000 (1)	0.0637 (5)	0.3973 (3)	0.114 (2)
F3	−0.1736 (8)	0.0737 (7)	0.2674 (5)	0.159 (2)
F4	0.025 (1)	0.2308 (5)	0.2938 (5)	0.151 (3)
F5	0.111 (2)	0.1140 (6)	0.1617 (4)	0.209 (4)
F6	0.2865 (8)	0.0962 (7)	0.2950 (6)	0.232 (3)
C1	0.4349 (8)	0.4238 (5)	0.1484 (4)	0.028 (1)
C2	0.4589 (8)	0.4926 (5)	0.2296 (4)	0.031 (1)
C3	0.2947 (7)	0.3247 (5)	0.0026 (4)	0.027 (1)
C4	0.4911 (8)	0.2745 (5)	0.0047 (4)	0.026 (1)
C5	0.4011 (8)	0.6347 (5)	0.3785 (4)	0.032 (1)
C6	0.6005 (8)	0.5889 (5)	0.3775 (4)	0.032 (1)
C7	0.2067 (9)	0.1261 (5)	−0.0923 (5)	0.042 (2)
C8	0.4282 (9)	0.1182 (6)	−0.1452 (5)	0.045 (2)
C9	0.476 (1)	0.8116 (7)	0.5106 (6)	0.072 (2)
C10	0.692 (1)	0.7914 (6)	0.4615 (5)	0.055 (2)

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

S1—C1	1.725 (5)	S8—C6	1.735 (6)
S1—C3	1.717 (5)	S8—C10	1.807 (7)
S2—C1	1.720 (5)	P—F1	1.571 (4)
S2—C4	1.737 (6)	P—F2	1.535 (5)
S3—C2	1.719 (5)	P—F3	1.553 (6)
S3—C5	1.739 (6)	P—F4	1.548 (5)
S4—C2	1.719 (5)	P—F5	1.526 (5)
S4—C6	1.738 (5)	P—F6	1.497 (6)
S5—C3	1.745 (5)	C1—C2	1.381 (8)
S5—C7	1.808 (6)	C3—C4	1.352 (7)
S6—C4	1.737 (5)	C5—C6	1.350 (7)
S6—C8	1.809 (6)	C7—C8	1.501 (7)
S7—C5	1.728 (5)	C9—C10	1.467 (9)
S7—C9	1.812 (8)		
C1—S1—C3	95.8 (2)	S1—C1—S2	114.9 (3)
C1—S2—C4	96.0 (2)	S1—C1—C2	122.9 (4)
C2—S3—C5	96.0 (3)	S2—C1—C2	122.2 (4)
C2—S4—C6	95.7 (3)	S3—C2—S4	115.2 (3)
C3—S5—C7	98.3 (3)	S3—C2—C1	122.7 (4)
C4—S6—C8	103.4 (3)	S4—C2—C1	122.1 (4)
C5—S7—C9	103.9 (3)	S1—C3—S5	116.5 (3)
C6—S8—C10	97.0 (3)	S1—C3—C4	117.6 (4)
F1—P—F2	93.6 (3)	S5—C3—C4	125.8 (4)
F1—P—F3	86.6 (3)	S2—C4—S6	114.7 (3)
F1—P—F4	178.6 (3)	S2—C4—C3	115.8 (4)
F1—P—F5	85.9 (3)	S6—C4—C3	129.4 (4)
F1—P—F6	90.4 (3)	S3—C5—S7	116.5 (3)
F2—P—F3	87.8 (3)	S3—C5—C6	116.2 (4)
F2—P—F4	87.3 (3)	S7—C5—C6	127.2 (5)
F2—P—F5	177.5 (5)	S4—C6—S8	118.0 (3)
F2—P—F6	90.0 (4)	S4—C6—C5	116.8 (4)
F3—P—F4	92.5 (4)	S8—C6—C5	125.1 (4)
F3—P—F5	89.8 (4)	S5—C7—C8	112.6 (4)
F3—P—F6	176.1 (4)	S6—C8—C7	114.9 (4)
F4—P—F5	93.1 (3)	S7—C9—C10	118.0 (5)
F4—P—F6	90.6 (4)	S8—C10—C9	114.7 (5)
F5—P—F6	92.4 (5)		

Structure solved by direct methods and subsequent difference Fourier methods. Anisotropic thermal parameters for all non-H atoms. H atoms were calculated with a C—H distance of 0.95 Å and included in the structure-factor calculation only. The weighting scheme was $w=1/\sigma^2(F)$ where $\sigma(F)=\sigma(F^2)/2F$ and $\sigma(F^2)=[\sigma^2_{counting}+(0.02|F|^2)^2]^{1/2}$.

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 (BEDT-TTF)2N(CN)2

XIANHUI BU AND PHILIP COPPENS

Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14214, USA

BARBARA LEDERLE AND MICHAEL J. NAUGHTON

Department of Physics and Astronomy, State University of New York at Buffalo, Buffalo, NY 14214, USA
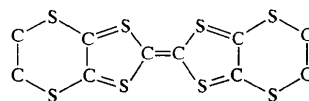
Abstract

The structure consists of layers of partially oxidized BEDT-TTF donor molecules [BEDT-TTF, or ET = 3,4;-3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene] separated by dicyanamide anions along the crystallographic *c* axis. Dicyanamide anions are located between BEDT-TTF sheets. The salt showed semiconducting behavior as measured by the four-probe conductivity method.

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)2N(CN)2.

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
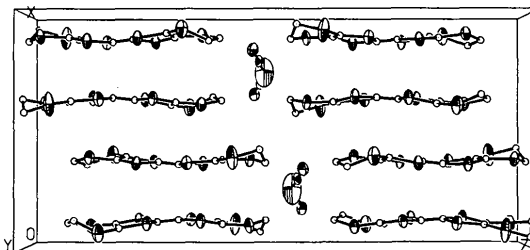

Fig.1. Packing diagram of the unit cell projected along the *b* axis. Thermal ellipsoids are drawn at the 50% level.

© 1992 International Union of Crystallography