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Structures of 3,4-Dimethyl-2,2′,5,5′-tetrathiafulvalene Perrhenate, (DMTTF)ReO$_4$, and 3′,4′-Dimethyl-3,4-tetramethylene-2,5-dithia-2′,5′-diselenafulvalene Hexafluorophosphate, (CHDTDMDSF)PF$_6$

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Abstract

The two compounds (DMTTF)ReO$_4$ (1) [DMTTF = 2-(1,3-dithiol-2-ylidene)-4,5-dimethyl-1,3-dithiole cation] and (CHDTDMDSF)PF$_6$ (2) [CHDTDMDSF = 2-(4,5-dimethyl-1,3-diselenol-2-ylidene)-4,5,6,7-tetrahydro-1,3-benzodithiole cation] contain unsymmetrically substituted tetrathiafulvalene (TTF) derivatives. They present similar crystal structures which are characterized by alternating organic dimers and inorganic pairs of anions. The values of the central C—C bond lengths are 1.39 (1) and 1.40 (1) Å for (1) and (2), respectively. Strong intradimer contacts are observed: S1···S2 = 3.379 (2) Å for (1) and Se1···S2 = 3.460 (3) and Se2···S1 = 3.435 (3) Å for (2).

Comment

The single crystals of (DMTTF)ReO$_4$ (1) and (CHDTDMDSF)PF$_6$ (2) were obtained by electro-oxidation, on a platinum electrode, of DMTTF or CHTMDTDSF (10^{-3} M) in a tetrahydrofuran solution containing (Bu$_4$N)ReO$_4$ or (Bu$_4$N)PF$_6$ (0.1 M) as supporting electrolytes.

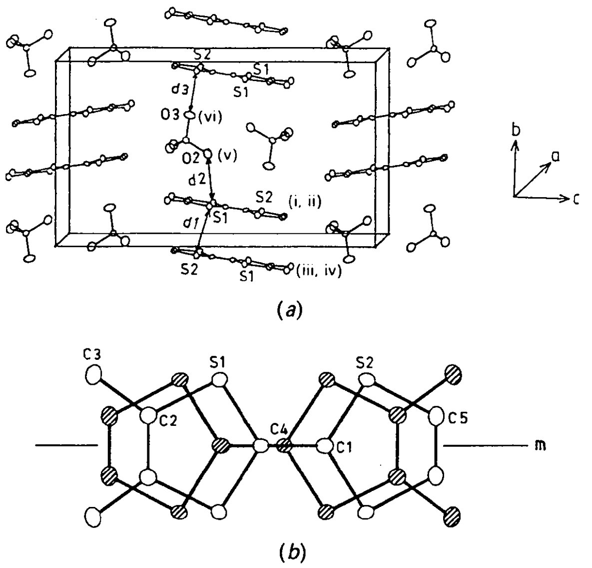

Fig. 1. (*a*) Crystal structure projection of (1) in the (100) plane, showing the alternate packing of the organic dimers and the pairs of inorganic anions, with $d1(\mathrm{S1^{i}\cdots S2^{iii}}) = 3.379\ (2)$, $d2(\mathrm{S1^{i}\cdots O2^{v}}) = 3.683\ (9)$, $d3(\mathrm{S2^{i}\cdots O3^{vi}}) = 3.495\ (9)$, $(\mathrm{S2^{i}\cdots O1^{vii}}) = 2.973\ (6)$ Å [symmetry code: (i) $1 + x, y, z$; (ii) $1 - x, y, z$; (iii) $1 - x, -y, 1 - z$; (iv) $1 + x, -y, 1 - z$; (v) $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$; (vi) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (vii) $\frac{3}{2} + x, y, \frac{1}{2} - z$]. (*b*) Atomic numbering scheme and intra-dimer overlap.

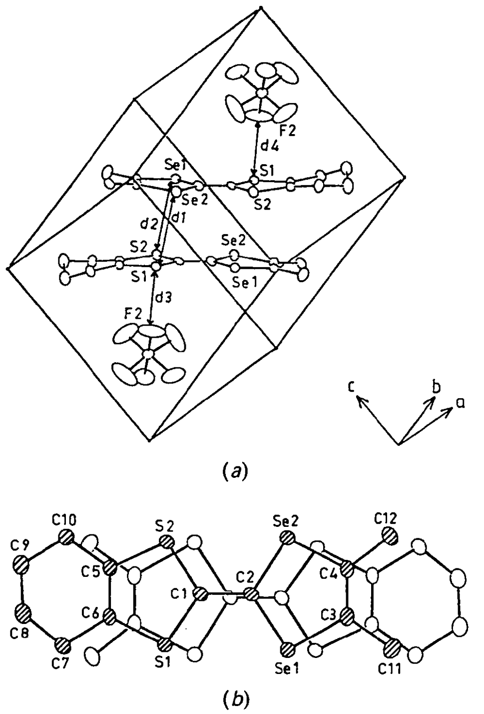

Fig. 2. (*a*) Crystal structure projection of (2) in the (101) plane, showing the alternate packing of the organic dimers and the pairs of inorganic anions, with *d*1 = 3.460 (3), *d*2 = 3.435 (3), *d*3 = 3.164 (8) and *d*4 = 3.300 (11) Å. (*b*) Atomic numbering scheme and intra-dimer overlap.

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Final atomic coordinates and isotropic thermal parameters for non-H atoms are given in Tables 1 and 3, for (1) and (2), respectively, bond lengths and bond angles are given in Tables 2 and 4. The atomic numbering and the intermolecular interactions are given in Figs. 1 and 2, which present also *ORTEP* (Johnson, 1965) drawings of the crystal structures of (1) and (2), respectively.

The values of the central C—C bond lengths are 1.39 (1) Å and 1.40 (1) Å for (1) and (2), respectively, indicating that the organic molecules are fully oxidized and thus complete charge transfer for the two salts. The shortest intra-dimer S···S contacts and anion–cation interactions are given in Figs. 1 and 2.

Experimental

Compound (1)

Crystal data

$C_8H_8S_4.ReO_4$
$M_r = 482.61$
Orthorhombic
Cmca
$a = 10.107$ (4) Å
$b = 12.359$ (5) Å
$c = 20.861$ (13) Å
$V = 2605.8$ Å^3
$Z = 8$
$D_x = 2.460$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5$-$10°$
$\mu = 10.067$ mm^{-1}
$T = 293$ K
Parallelepiped
0.5 × 0.5 × 0.4 mm
Black

Data collection

Enraf-Nonius CAD-4 diffractometer
θ-2θ scans
Absorption correction: empirical
$T_{\min} = 0.8840$, $T_{\max} = 1.2268$
1225 measured reflections
1225 independent reflections

907 observed reflections $[I > 3\sigma(I)]$
$R_{\text{int}} = 0.00$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 14$
$l = -24 \rightarrow 24$
3 standard reflections
frequency: 60 min
intensity variation: <2%

Refinement

Refinement on F
Final $R = 0.031$
$wR = 0.051$
$S = 1.347$
907 reflections
86 parameters
H-atom parameters not refined
$w = 4F_o^2/[\sigma(I)^2 + (0.07|F_o|^2)^2]$
$(\Delta/\sigma)_{\max} = 0.0$

$\Delta\rho_{\max} = 0.974$ e Å^{-3}
$\Delta\rho_{\min} = -1.755$ e Å^{-3}
Extinction correction: $|F_c|(1+gI_c)^{-1}$
Extinction coefficient: $g = 1.3975 \times 10^{-7}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{\text{eq}} = \tfrac{4}{3}\textstyle\sum_i\sum_j B_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
S1	0.1433 (2)	0.1550 (1)	0.44440 (8)	2.43 (3)
S2	0.1438 (2)	0.1096 (1)	0.59659 (8)	2.36 (3)
C1	0.000	0.1426 (7)	0.4879 (4)	1.9 (2)
C2	0.0671 (7)	0.1764 (5)	0.3707 (3)	2.5 (1)
C3	0.1542 (7)	0.1875 (6)	0.3137 (3)	3.2 (1)
C4	0.000	0.1255 (6)	0.5538 (4)	2.0 (2)
C5	0.0649 (7)	0.0904 (5)	0.6692 (3)	2.6 (1)
Re	0.000	−0.00054 (3)	−0.13656 (2)	2.95 (1)
O1	−0.1363 (6)	0.0335 (6)	−0.1798 (3)	5.0 (1)
O2	0.000	0.0718 (8)	−0.0676 (5)	6.9 (3)
O3	0.000	−0.1377 (8)	−0.1249 (5)	7.1 (3)

Table 2. *Bond lengths* (Å) *and angles* (°) *for* (1)

S1—C1	1.716 (5)	C2—C3	1.486 (9)
S1—C2	1.739 (6)	C5—C5	1.31 (1)
S2—C4	1.716 (5)	Re—O1	1.701 (6)
S2—C5	1.729 (7)	Re—O2	1.69 (1)
C1—C4	1.39 (1)	Re—O3	1.71 (1)
C2—C2	1.36 (1)		
C1—S1—C2	96.1 (3)	S2—C4—S2	115.7 (5)
C4—S2—C5	94.6 (4)	S2—C4—C1	122.1 (3)
S1—C1—S1	115.2 (5)	S2—C5—C5	117.5 (5)
S1—C1—C4	122.4 (2)	O1—Re—O1	108.3 (3)
S1—C2—C2	116.3 (5)	O1—Re—O2	108.7 (3)
S1—C2—C3	117.3 (5)	O1—Re—O3	108.7 (3)
C2—C2—C3	126.3 (6)	O2—Re—O3	113.7 (5)

Compound (2)

Crystal data

$C_{12}H_{14}S_2Se_2.PF_6$
$M_r = 525.26$
Triclinic
$P\bar{1}$
$a = 9.682$ (14) Å
$b = 9.698$ (4) Å
$c = 9.926$ (2) Å
$\alpha = 81.947$ (30)°
$\beta = 80.837$ (53)°
$\gamma = 68.364$ (74)°
$V = 852.0$ Å^3
$Z = 2$

$D_x = 2.047$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5$-$10°$
$\mu = 4.67$ mm^{-1}
$T = 293$ K
Parallelepiped
0.3 × 0.2 × 0.15 mm
Black

Data collection

Enraf-Nonius CAD-4 diffractometer
θ-2θ scans
Absorption correction: empirical
$T_{\min} = 0.7179$, $T_{\max} = 1.2045$
3191 measured reflections
2799 independent reflections

1821 observed reflections $[I > 3\sigma(I)]$
$R_{\text{int}} = 0.034$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 11$
$k = -10 \rightarrow 11$
$l = -11 \rightarrow 11$
3 standard reflections
frequency: 60 min
intensity variation: <2%

Refinement

Refinement on F
Final $R = 0.051$

$\Delta\rho_{\max} = 0.918$ e Å^{-3}
$\Delta\rho_{\min} = -0.353$ e Å^{-3}

$wR = 0.071$
$S = 1.617$
1821 reflections
209 parameters
H-atom parameters not refined
$w = 4F_o^2/[\sigma(I)^2+(0.07|F_o|^2)^2]$
$(\Delta/\sigma)_{\max} = 0.09$

Extinction correction: $|F_c|(1+gI_c)^{-1}$
Extinction coefficient: $g = 1.6287 \times 10^{-7}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å²) *for* (2)

$B_{\rm eq} = \frac{4}{3}\sum_i\sum_j B_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$B_{\rm eq}$
Se1	0.6690 (1)	0.3465 (1)	0.3014 (1)	2.99 (2)
Se2	0.3638 (1)	0.6108 (1)	0.2748 (1)	3.36 (2)
S1	0.4882 (2)	0.1941 (2)	0.5592 (2)	2.53 (5)
S2	0.2103 (2)	0.4406 (3)	0.5299 (3)	3.02 (5)
C1	0.3977 (9)	0.3612 (9)	0.4721 (9)	2.5 (2)
C2	0.4689 (9)	0.4302 (9)	0.364 (1)	2.9 (2)
C3	0.6569 (9)	0.496 (1)	0.156 (1)	3.0 (2)
C4	0.527 (1)	0.609 (1)	0.1451 (9)	3.2 (2)
C5	0.1987 (9)	0.2960 (9)	0.6492 (9)	2.8 (2)
C6	0.3322 (9)	0.1816 (9)	0.665 (1)	2.8 (2)
C7	0.343 (1)	0.044 (1)	0.761 (1)	3.7 (2)
C8	0.190 (1)	0.041 (1)	0.804 (1)	5.1 (3)
C9	0.068 (1)	0.180 (1)	0.831 (1)	5.6 (3)
C10	0.051 (1)	0.300 (1)	0.720 (1)	4.0 (3)
C11	0.803 (1)	0.476 (1)	0.061 (1)	5.1 (3)
C12	0.493 (1)	0.735 (1)	0.034 (1)	3.9 (2)
P	0.1570 (3)	0.1430 (3)	0.2747 (3)	3.74 (6)
F1	0.0210 (8)	0.161 (1)	0.199 (1)	9.6 (3)
F2	0.2880 (9)	0.1271 (9)	0.354 (1)	12.1 (3)
F3	0.263 (1)	0.090 (1)	0.148 (1)	16.2 (4)
F4	0.173 (1)	−0.0180 (9)	0.311 (1)	15.3 (4)
F5	0.045 (1)	0.205 (2)	0.392 (1)	15.7 (5)
F6	0.145 (1)	0.298 (1)	0.219 (2)	16.9 (4)

Table 4. *Bond lengths* (Å) *and angles* (°) *for* (2)

Se1—C2	1.844 (8)	C5—C6	1.37 (1)
Se1—C3	1.880 (9)	C5—C10	1.48 (1)
Se2—C2	1.853 (8)	C6—C7	1.51 (1)
Se2—C4	1.868 (9)	C7—C8	1.49 (2)
S1—C1	1.715 (7)	C8—C9	1.46 (1)
S1—C6	1.729 (9)	C9—C10	1.47 (2)
S2—C1	1.725 (8)	P—F1	1.56 (1)
S2—C5	1.729 (9)	P—F2	1.55 (1)
C1—C2	1.40 (1)	P—F3	1.51 (1)
C3—C4	1.34 (1)	P—F4	1.51 (1)
C3—C11	1.53 (1)	P—F5	1.48 (1)
C4—C12	1.50 (1)	P—F6	1.50 (1)
C2—Se1—C3	92.9 (4)	C5—C6—C7	122.4 (8)
C2—Se2—C4	93.4 (4)	C6—C7—C8	108.9 (7)
C1—S1—C6	96.3 (4)	C7—C8—C9	119. (1)
C1—S2—C5	97.2 (4)	C8—C9—C10	115. (1)
S1—C1—S2	114.3 (5)	C5—C10—C9	110.9 (8)
S1—C1—C2	123.5 (6)	F1—P—F2	178.2 (5)
S2—C1—C2	122.2 (5)	F1—P—F3	90.3 (6)
Se1—C2—Se2	116.1 (5)	F1—P—F4	87.7 (6)
Se1—C2—C1	122.7 (5)	F1—P—F5	86.3 (6)
Se2—C2—C1	121.1 (5)	F1—P—F6	88.9 (7)
Se1—C3—C4	119.1 (7)	F2—P—F3	91.5 (6)
Se1—C3—C11	115.0 (6)	F2—P—F4	92.5 (6)
C4—C3—C11	125.9 (8)	F2—P—F5	91.9 (6)
Se2—C4—C3	118.3 (7)	F2—P—F6	91.2 (7)
Se2—C4—C12	114.4 (6)	F3—P—F4	85.7 (7)
C3—C4—C12	127.3 (8)	F3—P—F5	175.2 (6)
S2—C5—C6	114.9 (7)	F3—P—F6	87.5 (7)
S2—C5—C10	119.7 (6)	F4—P—F5	97.5 (8)
C6—C5—C10	125.4 (8)	F4—P—F6	172.4 (8)
S1—C6—C5	117.1 (7)	F5—P—F6	89.1 (8)
S1—C6—C7	120.3 (6)		

Data collection: Enraf-Nonius CAD-4 software (Enraf-Nonius, 1985). Cell refinement: Enraf-Nonius software. Data reduction: Enraf-Nonius *SDP* (Frenz, 1985). Program(s) used to solve structures: Enraf-Nonius *SDP*. Program(s) used to refine structures: Enraf-Nonius *SDP*. Software used to prepare material for publication: Enraf-Nonius *SDP*. Absorption correction was performed using the *DIFABS* procedure (Walker & Stuart, 1983). The structures were solved by direct methods and successive difference Fourier syntheses. H atoms were placed in computed positions (C—H = 1 Å, $B_{\rm eq}$ = 4 Å²). All calculations were performed on a MicroVAX 3100 using the *SDP* programs.

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55933 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1033]

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Acta Cryst. (1993). C**49**, 1189–1192

Structure of Anthracenediylidene-bis-(1,3-dithiole)–Tetracyanoquinodimethane–Bis(cyanoformyl)phenyl-malononitrile Ylide Monohydrate: (Ext-TTF^{2+}).TCNQ.(Y$^-$)$_2$.(H$_2$O)

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Abstract

The crystal structure of the title compound is built from four kinds of molecule: one 7,7,8,8-tetracyano-*p*-quinodimethane [TCNQ: 2,2′-(2,5-cyclohexadiene-

0108-2701/93/061189-04$06.00