Structure of Tris(3,3',4,4'-tetramethyl-2,2',5,5'-tetraselenafulvalenium) Phosphododecatungstate: (TMTSF)$_3$PW$_{12}$O$_{40}$

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Abstract. $3C_{10}H_{12}Se_4^+ \cdot PW_{12}O_{40}^{3-}$ $M_r = 4221.29$, monoclinic, $P2_1/n$, $a = 11.733$ (5), $b = 18.461$ (5), $c = 16.223$ (6) Å, $\beta = 98.05$ (4)°, $V = 3479.2$ Å^3, $Z = 2$, $D_x = 4.03$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 265.07$ cm^{-1}, $F(000) = 1495$, $T = 293$ K, $R = 0.053$ based on 3152 observed reflections with $I \geq 3\sigma(I)$. The crystal structure is built from PW$_{12}$O$_{40}$ units located at the origin of the lattice and stacks of fully oxidized TMTSF molecules parallel to the [100] direction. Criss-cross and ring-over-double-bond types of overlap are observed within the organic stack. The Se···Se [3.633 (6) and 3.613 (5) Å] contacts between molecules of the B type are significantly shorter than the corresponding (4 Å) van der Waals separation. The contacts between molecules A and B are Se2···Se5 = 3.898 (5) and Se3···Se5 = 3.909 (5) Å. Additionally, the Se···O contacts range from 3.00 to 3.31 Å indicating strong organic–inorganic interactions.

Experimental. The title compound was obtained on a platinum wire electrode by anodic oxidation of the organic donor (2.10^{-3} M) in a mixture of dimethylformamide (85%) and dichloromethane (15%) under low constant current ($I = 0.95$ μA) in the presence of (Et$_4$N)$_3$PW$_{12}$O$_{40}$ (10^{-2} M) as supporting electrolyte. A black needle crystal with approximate dimensions $0.08 \times 0.08 \times 0.15$ mm was selected for intensity data collection using an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Cell dimensions from least-squares refinement from setting angles of 25 centred reflections ($\theta \leq 15°$). 5752 independent reflections were measured in the range $2 \leq 2\theta \leq 50°$ with $0 \leq h \leq 13$, $0 \leq k \leq 22$, $-19 \leq l \leq 19$. The θ–2θ mode was used with scan width $\Delta\omega = (1 + 0.35\tan\theta)°$ and counter aperture $\Delta l = (2.0 + 0.6\tan\theta)$ mm. Three standard reflections measured every hour showed no fluc-

tuation in intensities. 3152 reflections with $I \geq 3\sigma(I)$. The intensities were corrected for Lorentz and polarization effects. The absorption correction was applied based on ψ-scan data obtained at the conclusion of intensity-data collection. The minimum and maximum absorption factors were 0.81 and 1.54, with an average value of 0.97. The space group $P2_1/n$ was determined on the basis of systematic extinctions ($h0l$, $h + l = 2n + l$ and $0k0$, $k = 2n + 1$) and successful refinements. The structure was solved by direct methods and successive difference Fourier syntheses. H atoms placed at computed positions (C—H = 1.0 Å). Full-matrix least-squares anisotropic (β_{ij}) refinement on F (H atoms isotropic, not refined). The O atoms of the disordered PO$_4$ group and the O8, C7, C11 and C15 atoms were refined isotropically. Final $R = 0.053$, $wR = 0.072$, $w = 4F_o^2/[\sigma^2(F_o^2) - (0.07F_o^2)^2]$, $S = 1.58$, $(\Delta/\sigma)_{min} = 0.01$, $\Delta\rho_{max} = 2.37$ e Å^{-3}; refined secondary-extinction value $g = 3.8568 \times 10^{-8}$. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed on a PDP11/60 and a MicroVAX 3100 computer using the *SDP* programs (B. A. Frenz & Associates, Inc., 1985).

Final atomic parameters are given in Table 1,† bond distances and angles in Table 2. The atomic numbering is shown in Fig. 1. The crystal structure represented in Fig. 2 is built from PW$_{12}$O$_{40}$ units located at the origin of the lattice, and stacks of TMTSF molecules.

Related literature. The title compound was prepared as part of our investigations on charge-transfer salts comprising organic donors derived from TTF (tetra-

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Table 1. Atomic coordinates and equivalent isotropic temperature factors (Å²)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	y	B_{eq}
W1	0.2152 (1)	−0.06833 (8)	0.15749 (8)	2.52 (3)
W2	−0.1516 (1)	0.07007 (7)	0.15758 (8)	1.89 (2)
W3	−0.0784 (1)	−0.11723 (7)	0.15696 (8)	2.02 (3)
W4	0.1413 (1)	0.11867 (7)	0.15476 (8)	2.28 (3)
W5	0.0771 (1)	−0.18702 (6)	0.00123 (8)	2.08 (3)
W6	0.2949 (1)	0.04654 (7)	−0.00117 (8)	2.16 (3)
Se1	0.1526 (4)	−0.0498 (2)	0.3944 (2)	3.49 (8)
Se2	0.1872 (3)	−0.0520 (2)	0.5896 (2)	2.74 (7)
Se3	0.1281 (3)	0.1276 (2)	0.5905 (2)	2.96 (8)
Se4	0.0935 (4)	0.1274 (2)	0.3961 (2)	3.42 (8)
Se5	0.5467 (3)	−0.0761 (2)	0.3968 (2)	3.36 (8)
Se6	0.4611 (3)	0.0840 (2)	0.3947 (2)	3.46 (8)
P	0.0	0.0	0.0	1.3 (2)
O1	0.193 (2)	−0.147 (1)	0.080 (1)	4.2 (6)
O2	0.318 (2)	−0.102 (1)	0.230 (1)	3.1 (5)
O3	0.075 (2)	−0.098 (2)	0.199 (2)	5.6 (7)
O4	0.305 (2)	−0.025 (1)	0.083 (2)	6.0 (7)
O5	0.192 (3)	0.023 (1)	0.193 (2)	8.0 (8)
O6	−0.115 (2)	−0.024 (1)	0.201 (2)	4.0 (6)
O7	0.157 (2)	−0.149 (1)	−0.081 (2)	5.0 (6)
O8	0.000 (2)	0.099 (1)	0.205 (2)	4.1 (6)*
O9	−0.227 (2)	0.103 (2)	0.233 (2)	4.6 (6)
O10	0.269 (2)	−0.028 (1)	−0.080 (1)	4·1 (6)
O11	−0.218 (2)	−0.111 (1)	0.085 (2)	4.7 (6)
O12	−0.115 (2)	−0.172 (1)	0.229 (2)	4.0 (6)
O13	−0.025 (2)	−0.184 (2)	0.086 (2)	5.3 (6)
O14	0.251 (2)	0.114 (1)	0.080 (2)	6.7 (7)
O15	0.209 (2)	0.173 (1)	0.229 (2)	3.9 (6)
O16	0.057 (2)	0.185 (1)	0.083 (1)	4.3 (6)
O17	0·106 (2)	−0.275 (1)	0.001 (1)	2.6 (4)*
O18	0.432 (2)	0.071 (1)	−0.001 (2)	3.5 (5)
O19	0.021 (4)	−0.063 (2)	−0.054 (3)	2.5 (8)*
O20	−0.036 (3)	0.066 (2)	−0.056 (2)	1.4 (7)*
O21	−0.089 (4)	−0.015 (3)	0.052 (3)	4 (1)*
O22	0.123 (3)	0.020 (2)	0.059 (2)	1.3 (7)*
C1	0.149 (3)	0.002 (2)	0.490 (2)	3.8 (8)
C2	0.203 (3)	−0.136 (2)	0.452 (2)	3.4 (8)
C3	0.212 (3)	−0.139 (2)	0.526 (2)	2.4 (7)
C4	0.132 (2)	0.071 (1)	0.496 (2)	1.8 (6)
C5	0.086 (3)	0.216 (2)	0.533 (2)	3.0 (8)
C6	0.074 (3)	0.213 (2)	0.455 (2)	2.5 (7)
C7	0.213 (4)	−0.198 (2)	0.392 (3)	4.6 (9)*
C8	0.252 (3)	−0.199 (2)	0.589 (3)	4.6 (9)
C9	0.046 (4)	0.282 (2)	0.398 (4)	6 (1)
C10	0.085 (3)	0.275 (2)	0.591 (2)	3.5 (9)
C11	0.503 (3)	0.001 (2)	0.457 (2)	2.3 (6)*
C12	0.541 (3)	−0.025 (2)	0.298 (2)	3.1 (8)
C13	0.506 (3)	0.044 (2)	0.299 (2)	2.9 (7)
C14	0.576 (3)	−0.061 (2)	0.220 (3)	6 (1)
C15	0.501 (4)	0.097 (2)	0.227 (3)	4.5 (9)*

* Refined isotropically

Table 2. Bond distances (Å) and bond angles (°)

W1—O1	1.92 (3)	W6—O18	1.67 (2)
W1—O2	1.68 (2)	P—O19	1.50 (4)
W1—O3	1.94 (3)	P—O20	1.55 (4)
W1—O4	1.88 (3)	P—O21	1.46 (5)
W1—O5	1.81 (3)	P—O22	1.65 (3)
W2—O6	1.90 (2)	Se1—C1	1.83 (4)
W2—O7	1.91 (3)	Se1—C2	1.90 (3)
W2—O8	1.91 (2)	Se2—C1	1.90 (4)
W2—O9	1.72 (3)	Se2—C3	1.95 (3)
W2—O10	1.90 (2)	Se3—C4	1.86 (3)
W3—O3	1.87 (2)	Se3—C5	1.92 (3)
W3—O6	1.94 (2)	Se4—C4	1.92 (3)
W3—O11	1.87 (2)	Se4—C6	1.88 (3)
W3—O12	1.65 (2)	Se5—C11	1.83 (3)
W3—O13	1.86 (3)	Se5—C12	1.85 (3)
W4—O5	1.95 (3)	Se6—C11	1.87 (3)
W4—O8	1.98 (3)	Se6—C13	1.86 (3)
W4—O14	1.89 (3)	C1—C4	1.29 (4)
W4—O15	1.67 (2)	C2—C3	1.19 (5)
W4—O16	1.87 (2)	C2—C7	1.52 (5)
W5—O1	1.87 (2)	C3—C8	1.55 (5)
W5—O7	1.87 (3)	C5—C6	1.25 (5)
W5—O13	1.95 (3)	C5—C10	1.44 (5)
W5—O16	1.94 (2)	C6—C9	1.58 (6)
W5—O17	1.65 (2)	C11—C11	1.41 (4)
W6—O4	1.90 (3)	C12—C13	1.34 (5)
W6—O10	1.87 (2)	C12—C14	1.53 (6)
W6—O11	1.94 (3)	C13—C15	1.51 (6)
W6—O14	1.94 (3)		

O1—W1—O2	101.0 (1)	O10—W6—O11	88.0 (1)
O1—W1—O3	89.0 (1)	O10—W6—O14	155.0 (1)
O1—W1—O4	86.0 (1)	O10—W6—O18	105.0 (1)
O1—W1—O5	154.0 (1)	O11—W6—O14	87.0 (1)
O2—W1—O3	102.0 (1)	O11—W6—O18	101.0 (1)
O2—W1—O4	101.0 (1)	O14—W6—O18	100.0 (1)
O2—W1—O5	104.0 (1)	O19—P—O20	109.0 (2)
O3—W1—O4	157.0 (1)	O20—P—O21	109.0 (2)
O3—W1—O5	89.0 (1)	O20—P—O22	108.0 (2)
O4—W1—O5	86.0 (1)	O21—P—O22	110.0 (2)
O6—W2—O7	158.0 (1)	W1—O1—W5	139.0 (1)
O6—W2—O8	87.0 (1)	W1—O3—W3	138.0 (2)
O6—W2—O9	100.0 (1)	W1—O4—W6	141.0 (2)
O6—W2—O10	89.0 (1)	W1—O5—W4	143.0 (2)
O7—W2—O8	90.0 (1)	W2—O6—W3	136.0 (1)
O7—W2—O9	102.0 (1)	W2—O7—W5	141.0 (1)
O7—W2—O10	85.6 (9)	W2—O8—W4	132.0 (1)
O8—W2—O9	99.0 (1)	W2—O10—W6	142.0 (2)
O8—W2—O10	158.0 (1)	W3—O11—W6	139.0 (1)
O9—W2—O10	103.0 (1)	W3—O13—W5	138.0 (2)
O3—W3—O6	87.0 (1)	W4—O14—W6	138.0 (1)
O3—W3—O11	158.0 (1)	W4—O16—W5	139.0 (1)
O3—W3—O12	101.0 (1)	C1—Se1—C2	94.1 (1)
O3—W3—O13	88.0 (1)	C1—Se2—C3	91.0 (1)
O6—W3—O11	87.6 (9)	G4—Se3—C5	96.0 (1)
O6—W3—O12	101.0 (1)	C4—Se4—C6	93.0 (1)
O6—W3—O13	159.0 (1)	C11—Se5—C12	95.0 (1)
O11—W3—O12	101.0 (1)	C11—Se6—C13	92.0 (1)
O11—W3—O13	90.0 (1)	Se1—C1—C4	127.0 (3)
O12—W3—O13	100.0 (1)	Se2—C1—C4	119.0 (3)
O5—W4—O8	86.0 (1)	Se1—C2—C3	120.0 (3)
O5—W4—O14	87.0 (1)	Se1—C2—C7	112.0 (3)
O5—W4—O15	103.0 (1)	C3—C2—C7	128.0 (3)
O5—W4—O16	155.0 (1)	Se2—C3—C2	121.0 (3)
O8—W4—O14	160.0 (1)	Se2—C3—C8	107.0 (2)
O8—W4—O15	99.0 (1)	C2—C3—C8	132.0 (3)
O8—W4—O16	89.0 (1)	Se3—C4—Se4	111.0 (1)
O14—W4—O15	101.0 (1)	Se3—C4—C1	129.0 (3)
O14—W4—O16	89.0 (1)	Se4—C4—C1	119.0 (3)
O15—W4—O16	102.0 (1)	Se3—C5—C6	116.0 (3)
O1—W5—O7	87.0 (1)	Se3—C5—C10	111.0 (3)
O1—W5—O13	88.2 (9)	C6—C5—C10	133.0 (3)
O1—W5—O16	156.0 (1)	Se4—C6—C5	123.0 (3)
O1—W5— 17	105.0 (1)	Se4—C6—C9	114.0 (3)
O7—W5—O13	156.0 (1)	C5—C6—C9	122.0 (3)
O7—W5—O16	86.0 (1)	Se5—C11—Se6	115.0 (2)
O7—W5—O17	104.0 (1)	Se5—C11—C11	125.0 (2)
O13—W5—O16	89.0 (1)	Se6—C11—C11	120.0 (2)
O13—W5—O17	100.0 (1)	Se5—C12—C13	117.0 (3)
O16—W5—O17	99.0 (1)	Se5—C12—C14	121.0 (3)
O4—W6—O10	88.0 (1)	C13—C12—C14	122.0 (3)
O4—W6—O11	156.0 (1)	Se6—C13—C12	121.0 (3)
O4—W6—O14	87.0 (1)	Se6—C13—C15	113.0 (3)
O4—W6—O18	103.0 (1)	C12—C13—C15	126.0 (3)

thiafulvalene) and inorganic acceptors derived from the polyoxometallates (Ouahab, Bencharif & Grandjean, 1988; Triki, Ouahab, Padiou & Grandjean, 1989). The structural features of the $[PW_{12}O_{40}]^{3-}$ anion are in good agreement with those reported for a fully ordered unit (Brown, Noe-Spirlet, Busing & Levy, 1977). It is well known that the α-Keggin type of anion has the acentric T_d symmetry group. However, as in the present work, some centric (because of orientational disorder) anions have been reported (Attanasio, Bonamico, Fares, Imperatori & Suber, 1990; Evans & Pope, 1984).

The organic stack is constituted by the packing of two independent TMTSF molecules denoted A and B (Fig. 1). Molecule A is centred at the $(\frac{1}{2},0,\frac{1}{2})$ centre of inversion and molecule B is in general position. Molecule B overlaps with another centrosymmetrically related B molecule in a ring-
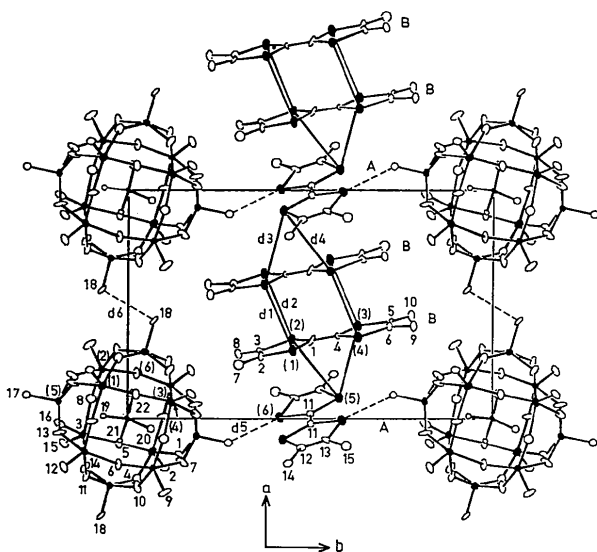
Fig. 1. Constituent molecules and atomic numbering. Numbers in parentheses correspond to W and Se atoms. The intermolecular contacts (Å) are given: $d^1(Se1\cdots Se3^i) = 3.633$ (6), $d^2(Se2\cdots Se4^i) = 3.613$ (5), $d^3(Se3\cdots Se5^{ii}) = 3.909$ (5), $d^4(Se2\cdots Se5^{ii}) = 3.898$ (5), $d^5(Se6\cdots O17^{iii}) = 3.27$ (2), $d^6(O18\cdots O18^{iv}) = 3.06$ (3). Symmetry code: (i) $-x$, $-y$, $1-z$; (ii) $1-x$, $-y$, $1-z$; (iii) $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; (iv) $1-x$, $-y$, $-z$.

Fig. 2. Stereoscopic view of the crystal structure.

over-double-bond fashion to form dimers. The latter are separated along the [100] direction by molecule A. The overlaps between molecules A and B are of the criss-cross type (Fig. 2). This arrangement results in short Se···Se (3.60 Å) contacts between molecules of the B type. The contacts between molecules A a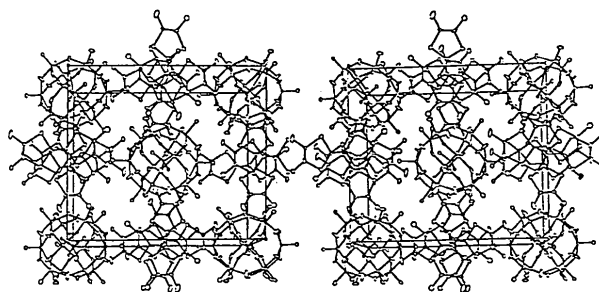nd B are equal to 3.90 Å (see Fig. 1). Additionally, strong organic–inorganic interactions are observed: $Se1\cdots O3 = 3.29$ (3), $Se2\cdots O9(-x, -y, 1-z) = 3.00$ (2), $Se3\cdots O12$ $(-x, -y, 1-z) = 3.06$ (2), $Se4\cdots O15 = 3.31$ (3), $Se5\cdots O17$ $(\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z) = 3.25$ (2), $Se6\cdots O17$ $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z) = 3.27$ (2) Å.

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Structure of Tetraethylammonium Permanganate

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Abstract. $(C_2H_5)_4N^+.MnO_4^-$, $M_r = 249.19$, monoclinic, $P2_1/c$, $a = 7.512$ (1), $b = 11.103$ (1), $c = 14.764$ (2) Å, $\beta = 91.44$ (1)°, $V = 1230.9$ (3) Å^3, $Z = 4$, $D_x = 1.34$ g cm^{-3}, $\lambda(Mo\ K\alpha_1) = 0.7093$ Å, $\mu = 10.2$ cm^{-1}, $F(000) = 528$, $T = 295$ K, final $R = 0.047$ for 983 reflections [$F_o > 3\sigma(F_o)$]. The average Mn—O bond length in the title permanganate is 1.610 (6) Å which is similar to the values reported for the potassium and caesium salts.

Experimental. The crystals of the title compound were obtained accidentally from the reaction mixture of $MnCl_2$ and $KMnO_4$ in aqueous solution containing tetraethylammonium bromide. X-ray data for a black oblique crystal (0.2 × 0.2 × 0.07 mm) mounted on the top of a glass fiber were collected on an

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