

## Structure of Bis(2,3,6,7-tetramethyl-1,4,5,8-tetrathiafulvalenium) Hexatungstate and Hexamolybdate; (TMTTF)<sub>2</sub>M<sub>6</sub>O<sub>19</sub>, M = W, Mo

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(Received 21 June 1990; accepted 2 January 1991)

**Abstract.**  $2[\text{C}_{10}\text{H}_{12}\text{S}_4]^+ \cdot [\text{W}_6\text{O}_{19}]^{2-}$ , (1),  $M_r = 1928.02$ , triclinic,  $P\bar{1}$ ,  $a = 8.469$  (7),  $b = 13.337$  (10),  $c = 16.776$  (10) Å,  $\alpha = 94.35$  (5),  $\beta = 95.68$  (6),  $\gamma = 98.95$  (7)°,  $V = 1854.5$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 3.452$  g cm<sup>-3</sup>,  $F(000) = 1736$ ,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 194.50$  cm<sup>-1</sup>,  $T = 293$  K,  $R = 0.035$  based on 4184 observed reflections with  $I \geq 3\sigma(I)$ .  $2[\text{C}_{10}\text{H}_{12}\text{S}_4]^+ \cdot [\text{Mo}_6\text{O}_{19}]^{2-}$ , (2),  $M_r = 1400.55$ , triclinic,  $P\bar{1}$ ,  $a = 8.421$  (7),  $b = 13.268$  (10),  $c = 16.740$  (8) Å,  $\alpha = 94.54$  (6),  $\beta = 95.69$  (5),  $\gamma = 99.03$  (8)°,  $V = 1829.7$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.542$  g cm<sup>-3</sup>. Only the structure of (1) has been determined since the two compounds are isostructural. The fully oxidized organic molecules overlap in an eclipsed fashion and form isolated dimers. Intra-dimer contacts S1...S3 (3.447), S2...S4 (3.320), S5...S8 (3.482) and S6...S7 (3.406 Å) are observed. There are no significant S...S inter-dimer contacts (>4 Å). Anion...cation interactions are also observed through O...S contacts: O1...S1 (3.103), O6...S2 (3.085), O12...S7 (2.997) and O18...S8 (3.099 Å).

**Introduction.** Using the classical electro-oxidation method, we have synthesized two isomorphous radical cation salts composed of TMTTF (tetramethyl-tetrathiafulvalene) and  $M_6O_{19}^{2-}$  dianions  $\{[M_6O_{19}]^{2-} = \text{hexatungstate } (M = \text{W}), \text{ hexamolybdate } (M = \text{Mo})\}$ . These salts have been prepared as part of our program aimed to investigate new organic donor inorganic acceptor (ODIA) charge transfer salts (Ouahab, Bencharif & Grandjean, 1988; Triki, Ouahab, Padiou & Grandjean, 1989). The prototypical organic donor TMTTF and its selenium analog (TMTSF) are the key molecules of the Bechgaard salts, among which the first organic superconductors were discovered (Bechgaard, Jacobsen, Mortensen, Pedersen & Thorup, 1980). The  $M_6O_{19}^{2-}$  dianions are the members of the group of discrete isopolymetal-

lates, having a Lindquist type of structure (Lindquist, 1953), which are known for their electron acceptor capabilities (Pope & Varga, 1966). The two salts are isostructural and it is the structure of the (TMTTF)<sub>2</sub>W<sub>6</sub>O<sub>19</sub> salt which is reported here.

**Experimental.** The compounds have been obtained on a platinum wire electrode by anodic oxidation of DMF (DMF = *N,N*-dimethylformamide) solutions of the organic donor (TMTTF) ( $2 \times 10^{-3}$  M), under low constant current ( $I = 1.2$  μA), in the presence of the tetrabutylammonium salts of the  $[M_6O_{19}]^{2-}$  dianions ( $10^{-2}$  M) as supporting electrolyte. The latter were prepared according to the literature procedure (Che, Fournier & Launay, 1979; Sanchez, Livage, Launay & Fournier, 1983).

Black crystal with dimensions  $0.25 \times 0.10 \times 0.10$  mm selected for intensity data collection. Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation,  $\theta$ - $2\theta$  scan. Cell dimensions from least-squares refinement of 25 centered reflections ( $\theta \leq 14^\circ$ ). Three standard reflections measured every hour: no fluctuations in intensities. 7681 reflections were recorded in the range  $2 \leq 2\theta \leq 50^\circ$  with ( $0 < h < 10$ ,  $-16 < k < 16$ ,  $-20 < l < 20$ ). Lorentz-polarization correction. An empirical absorption correction was performed using the DIFABS (Walker & Stuart, 1983) procedure. The min. and max. correction factors were 0.791 and 1.240. The structure was solved by the heavy-atom method and successive difference Fourier syntheses. 4184 independent reflections with  $I \geq 3\sigma(I)$ , after averaging of the symmetry related reflections ( $R_{\text{int}} = 0.051$ ), were used for the refinements. H atoms placed at computed positions ( $\text{C}-\text{H} = 1$  Å;  $B_{\text{eq}} = 4$  Å<sup>2</sup>). Full-matrix least-squares anisotropic ( $\beta_{ij}$ ) refinement on  $F^2$ , H atoms isotropic, not refined;  $R = 0.035$ ,  $wR = 0.045$ ,  $w = 4F_o^2/[\sigma^2(F_o^2) + (0.06F_o^2)^2]$ ,  $S = 1.132$ ,  $(\Delta/\sigma)_{\text{max}} = 0.05$ ,  $\Delta\rho_{\text{max}} = 1.801$  e Å<sup>-3</sup>. Scattering factors from *International Tables for X-ray*

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Table 1. Atomic coordinates and equivalent isotropic temperature factors

$$B_{\text{eq}} = (4/3) \sum_i \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$B_{\text{eq}} (\text{\AA}^2)$
W1	0-12838 (8)	0-10185 (5)	0-11384 (4)	2.04 (1)
W2	-0-22864 (8)	0-07475 (5)	0-01071 (4)	2.05 (1)
W3	0-09704 (8)	0-12498 (5)	-0-08069 (4)	1.90 (1)
O1	-0-392 (2)	0-1303 (9)	0-0182 (8)	3.4 (3)
O2	-0-103 (1)	0-1615 (8)	-0-0551 (8)	2.3 (2)
O3	0-181 (1)	0-1816 (8)	0-0261 (6)	2.4 (2)
O4	0-222 (1)	0-1756 (9)	0-1966 (7)	3.5 (3)
O5	-0-079 (1)	0-1434 (8)	0-1012 (7)	2.5 (2)
O6	0-170 (2)	0-2146 (8)	-0-1407 (7)	2.6 (2)
O7	-0-261 (1)	-0-0379 (9)	0-0751 (7)	2.7 (2)
O8	0-023 (1)	-0-0173 (8)	0-1581 (6)	2.4 (2)
O9	0-287 (1)	0-0209 (8)	0-0828 (7)	2.6 (2)
O10	0	0	0	1.8 (3)
W11	0-24450 (8)	0-40068 (5)	0-48658 (4)	2.19 (1)
W22	0-58955 (8)	0-37745 (5)	0-41749 (4)	2.13 (1)
W33	0-57448 (8)	0-41798 (5)	0-61138 (4)	2.14 (1)
O11	0-062 (1)	0-327 (1)	0-4780 (8)	4.0 (3)
O12	0-651 (1)	0-2884 (9)	0-3557 (6)	2.9 (2)
O13	0-509 (1)	0-4666 (8)	0-3428 (7)	2.8 (2)
O14	0-352 (1)	0-3568 (9)	0-5797 (6)	2.6 (2)
O15	0-364 (1)	0-3231 (9)	0-4227 (7)	3.1 (3)
O16	0-237 (1)	0-4860 (8)	0-4007 (6)	2.2 (2)
O17	0-629 (1)	0-3341 (8)	0-5232 (6)	2.3 (2)
O18	0-627 (1)	0-3587 (9)	0-6933 (6)	3.3 (3)
O19	0-225 (1)	0-5179 (8)	0-5554 (7)	2.5 (2)
O20	0-500	0-500	0-500	2.2 (3)
S1	0-2768 (5)	0-6381 (3)	-0-0126 (3)	2.75 (9)
S2	0-2630 (5)	0-4194 (3)	-0-0354 (2)	2.36 (8)
S3	0-0931 (5)	0-3929 (3)	0-1256 (3)	2.91 (9)
S4	0-0904 (5)	0-6104 (3)	0-1469 (3)	2.59 (8)
C1	0-144 (2)	0-509 (1)	0-091 (1)	2.5 (3)
C2	0-215 (2)	0-524 (1)	0-022 (1)	2.6 (3)
C3	0-369 (2)	0-591 (1)	-0-093 (1)	2.7 (3)
C4	0-363 (2)	0-491 (1)	-0-1019 (9)	2.1 (3)
C5	0-023 (2)	0-438 (1)	0-2119 (9)	2.5 (3)
C6	0-019 (2)	0-540 (1)	0-2234 (9)	2.3 (3)
C7	0-452 (2)	0-670 (1)	-0-143 (1)	3.9 (4)
C8	0-430 (2)	0-432 (1)	-0-167 (1)	3.1 (4)
C9	-0-031 (2)	0-359 (2)	0-268 (1)	3.7 (4)
C10	-0-034 (2)	0-597 (2)	0.290 (1)	4.5 (5)
S5	0-7246 (5)	-0-1080 (3)	0-4714 (3)	2.69 (9)
S6	0-8017 (5)	0-1128 (3)	0-4787 (3)	2.68 (9)
S7	0-5602 (5)	-0-0880 (3)	0-6356 (2)	2.34 (8)
S8	0-6445 (5)	0-1317 (3)	0-6460 (3)	2.78 (9)
C11	0-651 (2)	0-018 (1)	0-594 (1)	2.3 (3)
C12	0-719 (2)	0-010 (1)	0-5221 (9)	2.2 (3)
C13	0-835 (2)	-0-057 (1)	0-399 (1)	2.9 (4)
C14	0-876 (2)	0-045 (1)	0-4025 (9)	2.4 (3)
C15	0-512 (2)	-0-020 (1)	0-7184 (9)	2.2 (3)
C16	0-554 (2)	0-082 (1)	0-727 (1)	2.6 (3)
C17	0-880 (3)	-0-133 (2)	0-338 (1)	4.4 (5)
C18	0-970 (2)	0-108 (1)	0-346 (1)	3.4 (4)
C19	0-422 (2)	-0-081 (1)	0-779 (1)	3.2 (4)
C20	0-531 (2)	0-153 (1)	0-795 (1)	3.3 (4)

Table 2. Bond distances ( $\text{\AA}$ ) with e.s.d.'s in parentheses

W1—O3	1.929 (11)	W33—O17	1.923 (11)
W1—O4	1.689 (11)	W33—O18	1.693 (12)
W1—O5	1.915 (11)	W33—O20	2.319 (1)
W1—O8	1.934 (11)	S1—C2	1.69 (2)
W1—O9	1.934 (12)	S1—C3	1.75 (2)
W1—O10	2.326 (1)	S2—C2	1.76 (2)
W2—O1	1.681 (12)	S2—C4	1.72 (2)
W2—O2	1.932 (11)	S3—C1	1.70 (2)
W2—O5	1.950 (10)	S3—C5	1.72 (2)
W2—O7	1.918 (12)	S4—C1	1.73 (2)
W2—O9	1.918 (10)	S4—C6	1.75 (2)
W2—O10	2.328 (1)	C1—C2	1.37 (2)
W3—O2	1.913 (11)	C3—C4	1.33 (3)
W3—O3	1.913 (10)	C3—C7	1.52 (3)
W3—O6	1.704 (11)	C4—C8	1.51 (2)
W3—O7	1.944 (12)	C5—C6	1.36 (2)
W3—O8	1.945 (9)	C5—C9	1.51 (3)
W3—O10	2.329 (1)	C6—C10	1.46 (3)
W11—O11	1.687 (11)	S5—C12	1.74 (2)
W11—O14	1.907 (11)	S5—C13	1.72 (2)
W11—O15	1.903 (12)	S6—C12	1.69 (2)
W11—O16	1.905 (11)	S6—C14	1.74 (2)
W11—O19	1.911 (11)	S7—C11	1.73 (2)
W11—O20	2.335 (1)	S7—C15	1.72 (2)
W22—O12	1.693 (12)	S8—C11	1.71 (2)
W22—O13	1.938 (12)	S8—C16	1.75 (2)
W22—O15	1.946 (11)	C11—C12	1.39 (2)
W22—O17	1.920 (11)	C13—C14	1.35 (2)
W22—O19	1.925 (9)	C13—C17	1.50 (3)
W22—O20	2.326 (1)	C14—C18	1.51 (2)
W33—O13	1.932 (12)	C15—C16	1.34 (2)
W33—O14	1.938 (10)	C15—C19	1.54 (2)
W33—O16	1.923 (10)	C16—C20	1.47 (3)

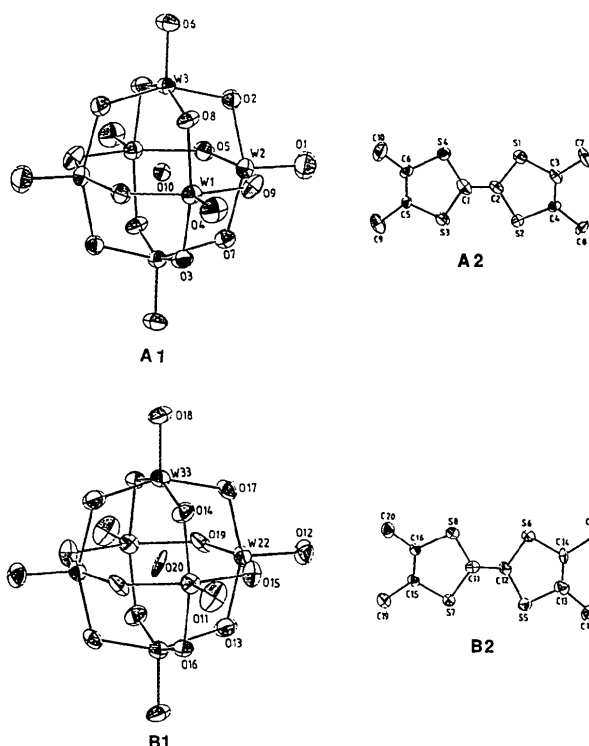


Fig. 1. The constituent molecules and atomic labeling scheme.

*Crystallography* (1974, Vol. IV). All the calculations were performed on a PDP11/60 using the *SDP* (B. A. Frenz & Associates, Inc., 1985) programs.

**Discussion.** Final atomic positional and thermal parameters are given in Table 1\* and bond lengths in Table 2. The atomic numbering is shown in Fig. 1. The unit cell contains two independent  $(\text{TMTTF})_2\text{W}_6\text{O}_{19}$  blocks, *A* and *B*.

\* Lists of structure factors, anisotropic thermal parameters, least-squares planes, bond angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53867 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

In the  $\text{W}_6\text{O}_{19}^{2-}$  units, each W atom is surrounded by a distorted octahedron consisting of one central  $\text{O}_c$  (e.g. O10), one terminal  $\text{O}_t$  (e.g. O1) and four

bridging  $O_b$  atoms (e.g. O2, O5, O7, O9). Their structures are formed by the condensation of six  $WO_6$  octahedra sharing a common vertex. The two independent  $W_6O_{19}^{2-}$  units,  $A_1$  and  $B_1$  (Fig. 1), are centered at the 0,0,0 and  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$  positions. The general structural features of these  $[W_6O_{19}]^{2-}$  units [av. W—W 3.291 (1), W— $O_i$  1.691 (12), W— $O_b$  1.926 (12) and W— $O_c$  2.327 (1) Å] are essentially identical and in good agreement with the previously reported data for such a unit in  $[(C_4H_9)_4N]_2W_6O_{19}$  (Fuchs, Freiwald & Hartl, 1978). The charge on the TMTTF has been assumed to be +1 based on a comparison (Table 3) of the geometrical parameters with those found for a variety of oxidation states of

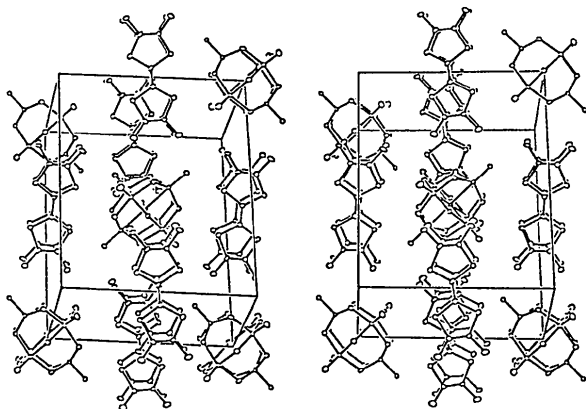


Fig. 2. Stereoscopic view of the crystal structure.  $a$  is into the plane of the paper,  $b$  is horizontal and  $c$  is vertical.

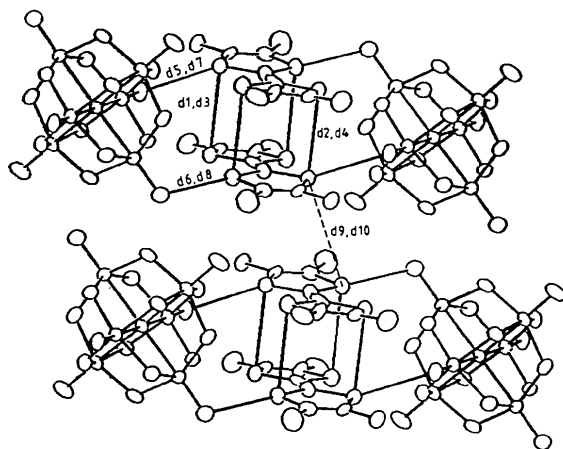
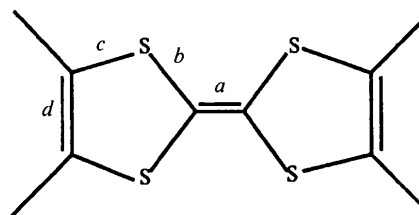


Fig. 3. Projection of the structure showing isolated TMTTF dimers.  $d1(S1-S3^i) = 3.447$  (6),  $d2(S2-S4^i) = 3.320$  (6),  $d3(S5-S8^{ii}) = 3.482$  (6),  $d4(S6-S7^{ii}) = 3.406$  (6),  $d5(O1-S1^i) = 3.103$  (13),  $d6(O6-S2) = 3.085$  (11),  $d7(O12-S7^{ii}) = 2.997$  (12),  $d8(O18-S8) = 3.099$  (14),  $d9(S1-S2^{iii}) = 4.100$ , and  $d10(S5-S6^{iv}) = 4.024$  Å. Symmetry code: (i)  $-x, 1-y, -z$ ; (ii)  $1-x, -y, 1-z$ ; (iii)  $1-x, 1-y, z$ ; (iv)  $2-x, y, 1-z$ .

Table 3. Comparison of the averaged intramolecular distances (Å) for various observed charges on the TMTTF molecule



Compound	Charge	$a$	$b$	$c$	$d$
(TMTTF) <sub>2</sub> Br	+ $\frac{1}{2}$	1.349 (12)	1.739 (7)	1.744 (7)	1.323 (2)
(TMTTF) <sub>2</sub> Mo <sub>2</sub> Cl <sub>14</sub>	+1	1.379 (4)	1.715 (3)	1.737 (3)	1.347 (5)
(TMTTF) <sub>2</sub> W <sub>6</sub> O <sub>19</sub> (A <sub>2</sub> )	+1	1.37 (2)	1.72 (2)	1.73 (2)	1.34 (2)
(TMTTF) <sub>2</sub> W <sub>6</sub> O <sub>19</sub> (B <sub>2</sub> )	+1	1.39 (2)	1.72 (2)	1.73 (2)	1.35 (2)
(TMTTF)(ClO <sub>4</sub> ) <sub>2</sub>	+2	1.452 (3)	1.681 (3)	1.711 (3)	1.364 (5)

that molecule, *i.e.* TMTTF<sup>0.5+</sup> (Galigné, Liautard, Peytavin, Brun, Fabre, Torrelles & Giral, 1978), TMTTF<sup>+</sup> (Ouahab, Batail, Perrin & Garrigou-Lagrange, 1986) and TMTTF<sup>2+</sup> (Shibaeva, 1984). In agreement with this result, the 2:1 stoichiometry of these salts suggests that the TMTTF molecules are fully oxidized. The organic molecules  $A_2$  and  $B_2$  (Fig. 1) with their centrosymmetrically related partners form isolated dimers centered at centers of symmetry at  $0, \frac{1}{2}, 0$  and  $\frac{1}{2}, 0, \frac{1}{2}$ . The interdimer overlap of the TMTTF molecules is of the eclipsed type (Fig. 2) and results in short S...S contacts (< 3.60 Å). The interdimer S...S contacts are > 4 Å. Finally, strong anion-cation interactions are observed through short O...S (< 3.20 Å) contacts (Fig. 3).

## References

- B. A. FRENZ & ASSOCIATES, INC. (1985). *SDP - Structure Determination Package*. College Station, Texas, USA, and Enraf-Nonius, Delft, The Netherlands.
- BECHGAARD, K., JACOBSEN, C. S., MORTENSEN, K., PEDERSEN, H. J. & THORUP, N. (1980). *Solid State Commun.* **33**, 1119-1125.
- CHE, M., FOURNIER, M. & LAUNAY, J. P. (1979). *J. Chem. Phys.* **71**, 1954-1960.
- FUCHS, V. J., FREIWAJD, W. & HARTL, H. (1978). *Acta Cryst.* **B34**, 1764-1770.
- GALIGNÉ, J. L., LIAUTARD, B., PEYTAVIN, S., BRUN, G., FABRE, J. M., TORREILLES, E. & GIRAL, L. (1978). *Acta Cryst.* **B34**, 620-624.
- LINDQUIST, I. (1953). *Ark. Kemi*, **5**, 247-250.
- OUAHAB, L., BATAIL, P., PERRIN, C. & GARRIGOU-LAGRANGE, C. (1986). *Mat. Res. Bull.* **21**, 1223-1230.
- OUAHAB, L., BENCHARIF, M. & GRANDJEAN, D. (1988). *C. R. Acad. Sci.* **307**, 749-751.
- POPE, M. T. & VARGA, G. M. (1966). *Inorg. Chem.* **5**, 1249-1254.
- SANCHEZ, C., LIVAGE, J., LAUNAY, J. P. & FOURNIER, M. (1983). *J. Am. Chem. Soc.* **105**, 6817-6823.
- SHIBAeva, R. P. (1984). *Kristallografiya*, **29**, 480-483.
- TRIKI, S., OUAHAB, L., PADIOU, J. & GRANDJEAN, D. (1989). *J. Chem. Soc. Chem. Commun.* pp. 1068-1070.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158-166.