dioxo- and (oxo)peroxomolybdenum complexes containing organic ligands have been investigated rather extensively by X-ray studies (*e.g.* Hawkins, Dewan & Sharpless, 1986; Dengel, Griffith, Powell & Skapski, 1987), only few structural studies have been performed on corresponding W and Cr complexes (Stomberg & Olsen, 1985; Yang, Dzugan & Goedken, 1985; Venturello, D'Aloisio, Bart & Ricci, 1985). The structure of the corresponding oxoperoxotungsten Schiff-base complex $WO(O_2)$-[(2-salicylidenamino)phenolato(2 −)][tris(dimethylamino)phosphine oxide], and a comparative study of the two compounds will be reported elsewhere (Terheijden, Kraaykamp, Timmer, Meinema & Spek, 1989).

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Structure of Bis(3′,4′-dimethyltetrathiafulvalen-3-yl)ethylenium Hexafluoroarsenate Hemibutyronitrile Solvate

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Abstract. $C_{18}H_{18}S_8^+.AsF_6^-.\frac{1}{2}C_4H_7N$, $M_r = 715{\cdot}35$, triclinic, $P\bar{1}$, $a = 7{\cdot}133\,(3)$, $b = 14{\cdot}718\,(3)$, $c = 14{\cdot}778\,(3)$ Å, $\alpha = 68{\cdot}75\,(2)$, $\beta = 79{\cdot}46\,(3)$, $\gamma = 73{\cdot}12\,(3)°$, $V = 1378{\cdot}4\,(7)$ Å^3, $Z = 2$, $D_x = 1{\cdot}724$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 18{\cdot}62$ cm^{-1}, $F(000) = 724$, $T = 298$ K, final $R = 0{\cdot}0853$ for 1602 observed unique reflections. The organic cations are planar, stacked along the a axis in a zigzag stack with overlaps 'double bond over ring'. AsF_6^- and the disordered solvent molecules are situated between the organic stacks. Crystals of the compound exhibit semiconducting behaviour.

Experimental. Crystals were prepared by electrochemical oxidation of $C_{18}H_{18}S_8$ in a 4:1 mixture of chlorobenzene and butyronitrile containing n-Bu_4NAsF_6 (0·100 M) (Lerstrup & Bechgaard, 1990). The size of the crystal used was 0·007 × 0·087 × 0·20 mm. The X-ray data were measured with an Enraf–Nonius CAD-4 diffractometer. The lattice parameters were derived from setting angles of 22 reflections, $8{\cdot}8 < \theta < 15{\cdot}9°$. Intensity data were collected with ω scans [$\Delta\omega = (0{\cdot}70 + 0{\cdot}35\tan\theta)°$] using graphite-monochromated Mo $K\alpha$ radiation, max. counting time was 8 min, $|h| \le 8$, $|k| \le 16$, $|l| \le 16$,

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Table 1. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$)

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U/U_{eq}
S(1)	−1041 (10)	3350 (4)	8405 (4)	38 (3)
S(2)	−1083 (10)	4681 (4)	6373 (4)	40 (3)
S(3)	460 (10)	2716 (4)	5653 (4)	39 (3)
S(4)	472 (10)	1401 (4)	7710 (4)	43 (3)
S(5)	3728 (9)	−1752 (4)	4654 (4)	34 (2)
S(6)	3832 (10)	−494 (4)	2619 (4)	42 (3)
S(7)	5285 (10)	−2419 (4)	1948 (4)	42 (3)
S(8)	5392 (10)	−3745 (4)	3952 (4)	38 (3)
C(1)	−1700 (33)	4642 (15)	8202 (15)	38 (6)
C(2)	−1758 (36)	5221 (16)	7302 (16)	51 (6)
C(3)	−623 (31)	3447 (14)	7181 (14)	27 (6)
C(4)	−3 (36)	2630 (14)	6905 (14)	41 (6)
C(5)	1292 (33)	1401 (14)	5879 (15)	37 (6)
C(6)	1218 (31)	818 (14)	6813 (15)	35 (6)
C(7)	−2210 (36)	4966 (16)	9085 (16)	53 (6)
C(8)	−2246 (36)	6398 (13)	6940 (16)	48 (6)
C(9)	1855 (34)	1079 (15)	4981 (15)	38 (6)
C(10)	3057 (31)	−452 (14)	4425 (17)	34 (6)
C(11)	3088 (35)	124 (15)	3462 (15)	40 (6)
C(12)	4265 (29)	−1690 (14)	3456 (13)	27 (6)
C(13)	4918 (30)	−2524 (15)	3140 (14)	32 (6)
C(14)	6044 (35)	−3734 (14)	2158 (16)	40 (6)
C(15)	6060 (34)	−4326 (15)	3046 (17)	42 (6)
C(16)	2503 (33)	−100 (14)	5290 (13)	29 (6)
C(17)	6577 (33)	−4006 (16)	1231 (15)	44 (6)
C(18)	6627 (36)	−5468 (15)	3418 (17)	52 (6)
As	8192 (6)	2418 (2)	1896 (2)	67 (2)
F(1)	6477 (31)	3496 (13)	1812 (15)	141 (7)
F(2)	6377 (32)	1768 (12)	2387 (15)	131 (6)
F(3)	7929 (36)	2559 (14)	756 (14)	149 (6)
F(4)	8300 (41)	2297 (15)	3101 (13)	172 (6)
F(5)	9725 (31)	1318 (12)	2085 (16)	153 (7)
F(6)	9898 (35)	3077 (17)	1538 (18)	166 (7)
C(19)	4559 (36)	1406 (19)	485 (17)	71 (6)*
C(20)	6473 (36)	633 (19)	336 (17)	71 (6)*
C(21)	6008 (36)	−159 (19)	17 (17)	71 (6)*
C(22)	7925 (36)	−923 (19)	−149 (17)	71 (6)*
N	3125 (36)	2010 (19)	549 (17)	71 (6)*

* Isotropic temperature factors.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

S(1)—C(1)	1·74 (2)	C(2)—C(8)	1·57 (3)
S(1)—C(3)	1·74 (2)	C(3)—C(4)	1·34 (3)
S(2)—C(2)	1·75 (2)	C(5)—C(6)	1·34 (3)
S(2)—C(3)	1·75 (2)	C(5)—C(9)	1·52 (3)
S(3)—C(4)	1·78 (2)	C(9)—C(16)	1·57 (3)
S(3)—C(5)	1·77 (2)	C(10)—C(11)	1·37 (3)
S(4)—C(4)	1·74 (2)	C(10)—C(16)	1·49 (3)
S(4)—C(6)	1·75 (2)	C(12)—C(13)	1·40 (3)
S(5)—C(10)	1·75 (2)	C(14)—C(15)	1·29 (3)
S(5)—C(12)	1·72 (2)	C(14)—C(17)	1·52 (3)
S(6)—C(11)	1·72 (2)	C(15)—C(18)	1·52 (3)
S(6)—C(12)	1·72 (2)	As—F(1)	1·68 (2)
S(7)—C(13)	1·69 (2)	As—F(2)	1·73 (2)
S(7)—C(14)	1·78 (2)	As—F(3)	1·66 (2)
S(8)—C(13)	1·74 (2)	As—F(4)	1·74 (2)
S(8)—C(15)	1·76 (2)	As—F(5)	1·63 (2)
C(1)—C(2)	1·30 (3)	As—F(6)	1·67 (2)
C(1)—C(7)	1·50 (3)		

C(1)—S(1)—C(3)	96 (1)	S(6)—C(11)—C(10)	117 (2)
C(2)—S(2)—C(3)	94 (1)	S(5)—C(12)—S(6)	115 (1)
C(4)—S(3)—C(5)	96 (1)	S(5)—C(12)—C(13)	125 (2)
C(4)—S(4)—C(6)	96 (1)	S(6)—C(12)—C(13)	120 (1)
C(10)—S(5)—C(12)	96 (1)	S(7)—C(13)—S(8)	116 (1)
C(11)—S(6)—C(12)	96 (1)	S(7)—C(13)—C(12)	123 (2)
C(13)—S(7)—C(14)	95 (1)	S(8)—C(13)—C(12)	122 (2)
C(13)—S(8)—C(15)	95 (1)	S(7)—C(14)—C(15)	118 (2)
S(1)—C(1)—C(2)	117 (2)	S(7)—C(14)—C(17)	114 (2)
S(1)—C(1)—C(7)	117 (2)	C(15)—C(14)—C(17)	129 (2)
C(2)—C(1)—C(7)	127 (2)	S(8)—C(15)—C(14)	116 (2)
S(2)—C(2)—C(1)	119 (2)	S(8)—C(15)—C(18)	116 (2)
S(2)—C(2)—C(8)	115 (2)	C(14)—C(15)—C(18)	128 (2)
C(1)—C(2)—C(8)	126 (2)	C(9)—C(16)—C(10)	112 (2)
S(1)—C(3)—S(2)	114 (1)	F(1)—As—F(2)	89 (1)
S(1)—C(3)—C(4)	121 (2)	F(1)—As—F(3)	90 (1)
S(2)—C(3)—C(4)	124 (2)	F(1)—As—F(4)	87 (1)
S(3)—C(4)—S(4)	114 (1)	F(1)—As—F(5)	174 (1)
S(3)—C(4)—C(3)	122 (2)	F(1)—As—F(6)	89 (1)
S(4)—C(4)—C(3)	124 (2)	F(2)—As—F(3)	94 (1)
S(3)—C(5)—C(6)	116 (2)	F(2)—As—F(4)	84 (1)
S(3)—C(5)—C(9)	116 (2)	F(2)—As—F(5)	86 (1)
C(6)—C(5)—C(9)	128 (2)	F(2)—As—F(6)	174 (1)
S(4)—C(6)—C(5)	118 (2)	F(3)—As—F(4)	176 (1)
C(5)—C(9)—C(16)	110 (2)	F(3)—As—F(5)	94 (1)
S(5)—C(10)—C(11)	115 (2)	F(3)—As—F(6)	92 (1)
S(5)—C(10)—C(16)	117 (2)	F(4)—As—F(5)	89 (1)
C(11)—C(10)—C(16)	128 (2)	F(4)—As—F(6)	90 (1)
		F(5)—As—F(6)	96 (1)

$(\sin\theta/\lambda_{max}) = 0·572$ Å^{-1}. A total of 5933 reflections were measured, of which 4214 were unique, $R_{int} = 0·0315$. 1602 reflections with $I > 3\sigma(I)$ were used for structure refinement. Three standards were measured for intensity and orientation control after every 200 reflections, no fading was observed. The data were corrected for absorption effects (Gaussian integration) with $\mu = 18·62$ cm^{-1}, and transmission in the range 0·8661–0·9855. The structure was determined and refined using *SHELX*76 (Sheldrick, 1976) with complex atomic scattering factors from *International Tables for X-ray Crystallography* (1974). *ORTEP* (Johnson, 1965) and *PLUTO* (Motherwell & Clegg, 1978) were used for illustrations.

After least-squares refinements (on F) with all atoms anisotropic the H atoms appeared. They were fixed with all C—H distances 1·07 Å and with $U_{iso} = 0·04$ Å^2. The methyl groups were refined as rigid groups. The solvent molecule, butyronitrile, C_4H_7N was found to be disordered with a site occupation of 0·5 corresponding to an equal distribution on two inversion-related positions. The molecule was refined as a rigid body with C—C distances of 1·54 Å and a C—N distance of 1·16 Å. A total of 336 parameters were refined, $R = 0·085$, $wR = 0·109$, $w = (\sigma^2 + 0·0010|F_o|^2)^{-1}$, $S = 2·62$, $(\Delta/\sigma)_{max} = 0·035$ for positional parameters in the final refinement cycle. In final difference density maps $(\Delta\rho)_{max} = 0·53$ and $(\Delta\rho)_{min} = -1·5$ e Å^{-3}, except near the disordered butyronitrile.

Final positional and equivalent isotropic thermal parameters are given in Table 1.* Fig. 1 shows the numbering of the atoms. Bond lengths and angles are listed in Table 2. The $C_{18}H_{18}S_8^+$ cation is planar, the angle between the normal to the molecular plane and the a axis is 1·5°. The organic molecules are stacked along the a axis. The two independent interplanar distances are both 3·56 (2) Å. The shortest intermolecular S···S distance within a stack is 3·82 (1) Å. The shortest intermolecular S···S distance between stacks is 3·94 (1) Å. Both distances are larger than

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52463 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

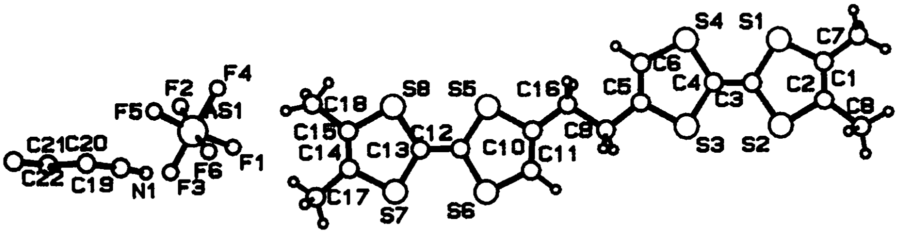

Fig. 1. Constituents with atomic numbering.

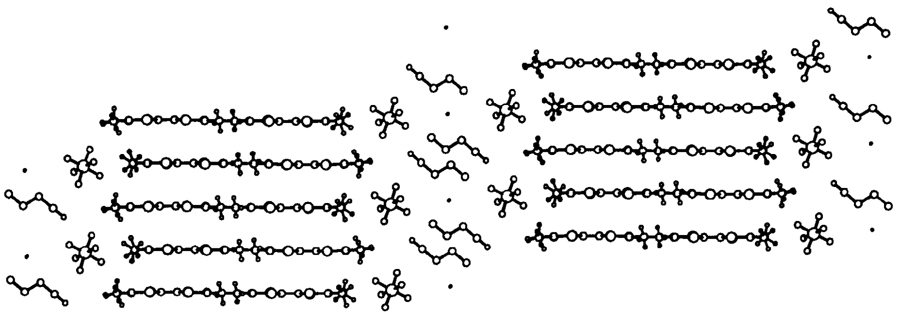

Fig. 2. Side view of the stacks and AsF_6^- ions with C_4H_7N in the two half-occupied positions.

the van der Waals contact distance of 3·60 Å. No S···F distances shorter than 3·27 Å (the van der Waals distance) are found. The AsF_6^- ion is regularly shaped. Fig. 2 is a side view of the stacks with the AsF_6^- ions and the two half-occupied positions of C_4H_7N.

Related literature. The packing arrangement and the intermolecular S···S distances are similar to those observed in tetramethyltetrathiafulvalene (TMTTF) salts (Liautard, Peytavin, Brun & Maurin 1983).

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Structure of *trans*-Tribromomethoxobis(triphenylphosphine)osmium(IV)

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Abstract. $[OsBr_3(CH_3O)\{P(C_6H_5)_3\}_2]$, $M_r = 985·53$, monoclinic, $P2_1/c$, $a = 12·796$ (4), $b = 16·389$ (7), $c = 16·873$ (4) Å, $\beta = 102·04$ (3)°, $V = 3461$ (4) Å^3, $Z = 4$, $D_x = 1·89$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 72·38$ cm^{-1}, $F(000) = 1896$, $T = 296$ K, $R = 0·040$, 3500 unique observed reflections. The compound was

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