Fig. 1. Constituents with atomic numbering.
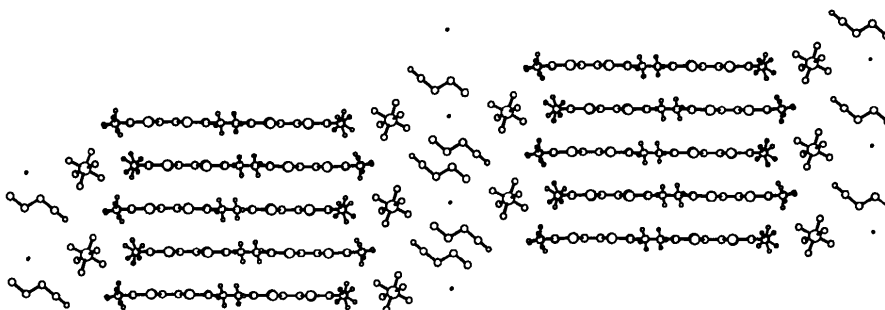

Fig. 2. Side view of the stacks and AsF₆⁻ ions with C₄H₇N in the two half-occupied positions.

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 C₄H₇N.

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).

References

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
LERSTRUP, K. & BECHGAARD, K. (1990). Proceedings of International Symposium on the Physics and Chemistry of Organic Superconductors, Tokyo, Japan, 27–30 August 1989. Berlin: Springer-Verlag. To be published.
LIAUTARD, B., PEYTAVIN, S., BRUN, G. & MAURIN, M. (1983). J. Phys. Paris Colloq. C3, 44, 951–956.
MOTHERWELL, W. D. S. & CLEGG, W. (1978). PLUTO. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
SHELDRICK, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.

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

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Abstract. [OsBr₃(CH₃O){P(C₆H₅)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) Å³, $Z = 4$, $D_x = 1·89$ 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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prepared by reflux of a mixture of bis(tetra-*n*-butylammonium) hexabromoosmate(IV), triphenylphosphine, phthalic acid, and phthalic anhydride in dichloromethane. The six-coordinate Os atom is bonded to *trans*-triphenylphosphine molecules, three bromo ligands, and one methoxide group. The Os—Br bond *trans* to the methoxide group is significantly shorter [2·471 (2) Å] than the two remaining Os—Br bonds [2·492 (2) and 2·494 (2) Å].

Experimental. Compound (I) prepared by combining bis(tetra-*n*-butylammonium) hexabromoosmate(IV) (0·8749 g, 0·7578 mmol), triphenylphosphine (0·6013 g, 2·2925 mmol), phthalic acid (0·5119 g, 3·0811 mmol), and phthalic anhydride (0·2679 g, 1·8087 mmol) in 50 ml of dichloromethane solvent.

(I)
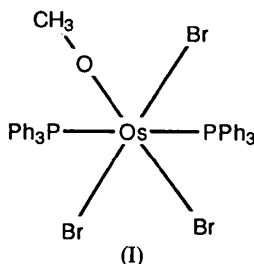
Mixture refluxed for 72 h, white solid present throughout the reflux. Solution filtered and filtrate reduced to dryness by rotary evaporation, solid residue dissolved in methyl alcohol and layered with ethyl ether. A mixture of solids obtained including maroon-red crystals (the major product and the title compound), a noncrystalline orange-red material, small green, and small yellow crystals. Crystal used for data collection 0·20 × 0·15 × 0·05 mm, maroon-red, platy, with large {001} basal pinacoid bounded by {010} side pinacoid and {110} prism. Rigaku AFC5S diffractometer, graphite-monochromated Mo $K\alpha$ radiation, ω–2θ scans, scan speed 6° min^{-1}, maximum of three scan repetitions to obtained $\sigma F/F$ < 0·10. Lattice parameters from least-squares fit of 25 strong reflections in 2θ range 28–37°. A total of 6084 unique reflections measured (*h* 0 to 17, *k* 0 to 21, *l* −22 to 22), 2584 reflections considered unobserved with $I < 3\sigma(I)$, data set comprised 3500 observed reflections, [(sinθ)/λ]$_{max}$ = 0·60 Å^{-1}. R_{int} (based on F^2) = 0·053 for 299 pairs of equivalent reflections. Three standard reflections ($1\bar{1}1$, $\bar{1}32$, $1\bar{4}2$) changed by −0·7, 0·1, and 0·2%, respectively; no decay correction applied. Data corrected for Lorentz, polarization and absorption (analytical correction, transmission range 0·22–0·68). Direct methods provided the locations of most of the non-H atomic positions, remainder obtained from difference Fourier syntheses. Full-matrix least-squares refinement was performed to minimize $\Sigma w(|F_o|$ −

Table 1. *Positional and equivalent isotropic thermal parameters for the non-*H *atoms and their e.s.d.'s*

$$B_{eq} = (8\pi^2/3)[U_{22} + (1/\sin^2\beta)(U_{11} + U_{33} + 2U_{13}\cos\beta)].$$

	x	*y*	*z*	B_{eq}(Å²)
Os(1)	0·27326 (4)	0·05070 (3)	0·26372 (3)	2·13 (2)
Br(1)	0·2033 (1)	−0·08800 (7)	0·22801 (9)	3·60 (6)
Br(2)	0·3112 (1)	0·04371 (9)	0·41458 (8)	3·92 (6)
Br(3)	0·2533 (1)	0·09279 (7)	0·11927 (8)	3·17 (5)
P(1)	0·4532 (2)	0·0040 (2)	0·2682 (2)	2·4 (1)
P(2)	0·0953 (2)	0·0975 (2)	0·2696 (2)	2·6 (1)
C(1)	0·5034 (9)	−0·0870 (6)	0·3306 (8)	2·8 (5)
C(2)	0·443 (1)	−0·1294 (7)	0·3735 (8)	3·9 (6)
C(3)	0·486 (1)	−0·1962 (8)	0·420 (1)	4·7 (7)
C(4)	0·586 (1)	−0·2211 (8)	0·4194 (9)	4·4 (7)
C(5)	0·645 (1)	−0·1807 (8)	0·375 (1)	4·7 (7)
C(6)	0·606 (1)	−0·1131 (8)	0·330 (1)	4·0 (6)
C(7)	0·495 (1)	−0·0249 (6)	0·1747 (7)	2·6 (5)
C(8)	0·426 (1)	−0·0744 (7)	0·1204 (8)	3·5 (6)
C(9)	0·462 (1)	−0·1068 (7)	0·0544 (9)	4·5 (7)
C(10)	0·560 (1)	−0·0849 (9)	0·039 (1)	4·8 (8)
C(11)	0·624 (1)	−0·037 (1)	0·091 (1)	4·4 (7)
C(12)	0·596 (1)	−0·0069 (8)	0·1591 (9)	4·0 (6)
C(13)	0·548 (1)	0·0846 (7)	0·3117 (8)	2·9 (5)
C(14)	0·596 (1)	0·0823 (8)	0·3919 (9)	3·9 (6)
C(15)	0·668 (1)	0·1444 (9)	0·425 (1)	5·4 (8)
C(16)	0·688 (1)	0·2057 (9)	0·378 (1)	5·5 (8)
C(17)	0·638 (1)	0·2098 (8)	0·296 (1)	6·0 (9)
C(18)	0·567 (1)	0·1488 (8)	0·2629 (9)	3·8 (6)
C(19)	0·100 (1)	0·1958 (7)	0·3218 (8)	3·4 (5)
C(20)	0·120 (1)	0·2669 (8)	0·2831 (9)	4·4 (7)
C(21)	0·128 (1)	0·3415 (8)	0·325 (1)	4·8 (7)
C(22)	0·116 (1)	0·341 (1)	0·403 (1)	5·8 (9)
C(23)	0·098 (1)	0·274 (1)	0·442 (1)	5·9 (9)
C(24)	0·089 (1)	0·1986 (7)	0·4012 (8)	3·8 (6)
C(25)	−0·003 (1)	0·1155 (7)	0·1751 (7)	2·9 (5)
C(26)	−0·069 (1)	0·1807 (8)	0·161 (1)	5·4 (7)
C(27)	−0·146 (1)	0·190 (1)	0·090 (1)	6·6 (9)
C(28)	−0·156 (1)	0·130 (1)	0·032 (1)	6 (1)
C(29)	−0·091 (1)	0·0655 (9)	0·0433 (9)	4·9 (7)
C(30)	−0·014 (1)	0·0570 (8)	0·1142 (8)	3·7 (6)
C(31)	0·016 (1)	0·0325 (7)	0·3231 (8)	3·1 (5)
C(32)	0·056 (1)	−0·0347 (8)	0·3682 (9)	4·2 (7)
C(33)	−0·004 (1)	−0·0816 (8)	0·411 (1)	4·7 (7)
C(34)	−0·108 (1)	−0·059 (1)	0·408 (1)	5·7 (8)
C(35)	−0·151 (1)	0·008 (1)	0·362 (1)	7 (1)
C(36)	−0·089 (1)	0·053 (1)	0·322 (1)	5·2 (7)
O(1)	0·3302 (6)	0·1775 (4)	0·2798 (5)	3·2 (4)
C(37)	0·370 (1)	0·2273 (8)	0·349 (1)	5·1 (7)

Table 2. *Selected bond distances* (Å), *bond angles* (°), *and their e.s.d.'s*

Os(1)	P(1)	2·413 (3)		P(1)	C(7)	1·83 (1)
Os(1)	P(2)	2·424 (3)		P(1)	C(13)	1·84 (1)
Os(1)	Br(1)	2·471 (2)		P(1)	C(1)	1·86 (1)
Os(1)	Br(2)	2·492 (2)		P(2)	C(19)	1·83 (1)
Os(1)	Br(3)	2·494 (2)		P(2)	C(31)	1·83 (1)
Os(1)	O(1)	2·200 (7)		P(2)	C(25)	1·84 (1)
O(1)	C(37)	1·43 (2)				

O(1)	Os(1)	P(1)	90·4 (2)		Br(2)	Os(1)	Br(3)	165·70 (5)
O(1)	Os(1)	P(2)	89·2 (2)		C(37)	O(1)	Os(1)	133·8 (8)
O(1)	Os(1)	Br(1)	173·1 (2)		C(7)	P(1)	C(13)	104·1 (6)
O(1)	Os(1)	Br(2)	85·9 (2)		C(7)	P(1)	C(1)	98·7 (5)
O(1)	Os(1)	Br(3)	79·8 (2)		C(7)	P(1)	Os(1)	120·2 (4)
P(1)	Os(1)	P(2)	176·0 (1)		C(13)	P(1)	C(1)	103·3 (5)
P(1)	Os(1)	Br(1)	90·62 (8)		C(13)	P(1)	Os(1)	109·2 (4)
P(1)	Os(1)	Br(2)	88·41 (9)		C(1)	P(1)	Os(1)	119·1 (4)
P(1)	Os(1)	Br(3)	91·18 (9)		C(19)	P(2)	C(31)	103·8 (6)
P(2)	Os(1)	Br(1)	90·29 (8)		C(19)	P(2)	C(25)	102·8 (6)
P(2)	Os(1)	Br(2)	87·57 (9)		C(19)	P(2)	Os(1)	111·3 (4)
P(2)	Os(1)	Br(3)	92·68 (9)		C(31)	P(2)	C(25)	99·8 (5)
Br(1)	Os(1)	Br(2)	100·96 (5)		C(31)	P(2)	Os(1)	117·3 (4)
Br(1)	Os(1)	Br(3)	93·33 (5)		C(25)	P(2)	Os(1)	119·7 (4)

$|F_c|)^2$ where $w = [1/\sigma^2(|F_o|)]$ and $p = 0·05$ [details of σ calculation given in Robinson, Hinckley & Kibala (1988)]. After ansitropic convergence, ring-H atoms placed in geometrically assumed positions (C—H = 0·95 Å) and model again refined to convergence.

Methyl-H sites located from difference Fourier synthesis, mathematically optimized (tetrahedral geometry, C—H = 0·95 Å), and fixed. Final stage of refinement performed with 397 variables including all non-H positional and anisotropic thermal parameters, and one scale factor. Convergence yielded $R = 0\cdot040$, $wR = 0\cdot047$, $S = 1\cdot05$ and $(\Delta/\sigma)_{max} = 0\cdot02$. When all (6084) reflections are included, $R = 0\cdot114$ and $wR = 0\cdot057$. Final difference synthesis produced $\Delta\rho_{max} = 1\cdot06$ and $\Delta\rho_{min} = -0\cdot96$ e Å^{-3}, both in the vicinity of the Os atom. Atomic scattering factors and anomalous-dispersion corrections from Cromer & Waber (1974). Positional and equivalent isotropic thermal parameters are listed in Table 1, selected interatomic distances and angles are given in Table 2.* Fig. 1 illustrates the molecular configuration, thermal motion and atom-numbering scheme. All computer programs from the *TEXSAN* crystal-structure-analysis package (Molecular Structure Corporation, 1985).

Related literature. This compound is one of a group of materials prepared in a study of the reactions of the hexabromoosmate ion with triphenylphosphine (Hinckley, Matusz, Kibala & Robinson, 1987;

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* Lists of structure factors, H-atom coordinates, phenyl-ring bond distances and angles, intermolecular distances, torsion angles, anisotropic thermal parameters and selected least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52326 (51 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
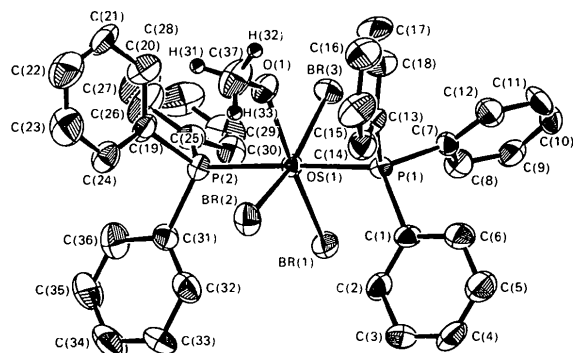

Fig. 1. Molecular configuration and atom-numbering scheme, thermal ellipsoids at the 50% probability level. Ring-H atoms omitted to improve clarity.

Hinckley, Ikuo & Robinson, 1988; Robinson, Hinckley & Ikuo, 1988).

References

CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, p.71 (scattering factors), p.148 (anomalous dispersion). Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

HINCKLEY, C. C., IKUO, A. & ROBINSON, P. D. (1988). *Acta Cryst.* C44, 1827–1829.

HINCKLEY, C. C., MATUSZ, M., KIBALA, P. A. & ROBINSON, P. D. (1987). *Acta Cryst.* C43, 1880–1882.

Molecular Structure Corporation (1985). *TEXSAN. Structure Analysis Package.* MSC, 3304 Longmire Drive, College Station, TX 77840, USA.

ROBINSON, P. D., HINCKLEY, C. C. & IKUO, A. (1988). *Acta Cryst.* C44, 1491–1492.

ROBINSON, P. D., HINCKLEY, C. C. & KIBALA, P. A. (1988). *Acta Cryst.* C44, 1365–1368.

Structure of $(Se_2N_2C-C_6H_4-CN_2Se_2)^{2+}.2SbF_6^-.3C_6H_5CN$

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Abstract. *P*-Di(1,2,3,5,-diselenadiazolium-4-yl)benzene hexafluoroantimonate benzonitrile solvate, $C_8H_4N_4Se_2^{2+}.2SbF_6^-.3C_7H_5N$, $M_r = 1252\cdot8$, triclinic, $P\bar{1}$, $a = 6\cdot829$ (2), $b = 13\cdot981$ (6), $c = 21\cdot320$ (9) Å, $\alpha = 72\cdot26$ (4), $\beta = 89\cdot03$ (3), $\gamma = 88\cdot78$ (3)°, $V = 1938$ (2) Å^3, $Z = 2$, $D_x = 2\cdot15$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 52\cdot1$ cm^{-1}, $F(000) = 1176$, $T = 293$ K, $R = 0\cdot049$ for 1975 reflections with $F_o^2 > 3\sigma(F_o^2)$. The unit cell contains four anions and six solvent molecules in general positions and two cations each located on crystallographic inversion centers. In the Se_2N_2C rings the Se—Se, Se—N, and