Structure of Dibromotetrakis(dimethyl sulfoxide)osmium(II)

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Abstract. [OsBr$_2$(C$_2$H$_6$OS)$_4$], M_r = 662·52, tetragonal, $I4/m$, a = 9·178 (2), c = 11·126 (2) Å, V = 937·2 (4) Å^3, Z = 2, D_x = 2·35 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 114·66 cm^{-1}, $F(000)$ = 628, T = 296 K, R = 0·024 for 425 unique reflections. Crystals were prepared by warming a solution of bis(tetra-*n*-butylammonium) hexabromoosmate(IV) and dimethyl sulfoxide. The molecule has $4/m$ symmetry with the Os atom at the $4/m$ intersection, S and O atoms on the symmetry plane, and the *trans*-Br atoms on the fourfold axis. All Me$_2$SO ligands are S-bonded to the Os atom. Principal distances and angles are Os–Br = 2·555 (1), Os–S = 2·351 (2), S–O = 1·487 (6), S–C = 1·784 (6) Å, Os–S–C = 115·8 (2), Os–S–O = 113·5 (2), O–S–C = 105·2 (3) and C–S–C' = 99·8 (5)°.

Experimental. Preparation by dissolution of 50 mg of bis(tetra-*n*-butylammonium) hexabromoosmate(IV) in 2 ml of dimethyl sulfoxide and heating at 323 K for two weeks. Color of solution changed from wine-red to orange, solution cooled slowly to 253 K, pale-yellow crystals separated by filtration. Crystal used for data collection 0·17 × 0·22 × 0·30 mm, pale-yellow fragment cut from larger tetragonal dipyramid. Rigaku AFC-5S diffractometer, graphite-monochromated Mo $K\alpha$ radiation, ω–2θ scans, scan speed 6° min^{-1}, maximum of three scan repetitions to obtain $\sigma F/F$ < 0·10. Lattice parameters from least-squares fit of 25 strong reflections in 2θ range 49–50°. 441 reflections measured (h, k 0 to 10, l 0 to 13), 16 reflections considered unobserved with [$I < 3\sigma(I)$], data set composed of 425 unique reflections, (sinθ/λ)$_{max}$ = 0·60 Å^{-1}. Three standard reflections (101, 0$\bar{1}$1, 110)

changed by −1·2, −1·1 and 0·5%, respectively; no decay correction applied. Data corrected for Lorentz, polarization and absorption (empirical ψ scan correction, three reflections, transmission range 0·43–1·00). Systematic absences indicated space group $I4$, $I\bar{4}$, or $I4/m$; structure solved in $I\bar{4}$ and later converted to $I4/m$ when the plane of symmetry normal to the fourfold axis became apparent. Direct methods used to locate the Os, Br and S atomic sites, C and O positions from difference Fourier synthesis. Full-matrix least-squares refinement was performed to minimize $\sum w(|F_o| - |F_c|)^2$ where $w = [1/\sigma^2(|F_o|)]$. Methyl H atomic sites located from difference Fourier synthesis but failed to refine to reasonable positions. H atoms geometrically optimized from difference Fourier peak positions and fixed (C–H = 0·95 Å, tetrahedral H–C–H and H–C–S angles), all H atom B's set at 1·2 × B_{eq} of associated C atom. Regeneration of H positions and refinement to convergence repeated until shifts became insignificant. Final refinement performed with 27 variables including all non-H positional and anisotropic thermal parameters, and one scale factor. Convergence yielded R = 0·024, wR = 0·034, S = 1·14 and (Δ/σ)$_{max}$ = 0·01. Final difference synthesis produced ($\Delta\rho$)$_{max}$ = 1·33 and ($\Delta\rho$)$_{min}$ = −0·69 e Å^{-3}, located near S(1) and Os(1), respectively. Atomic scattering factors and anomalous-dispersion corrections from Cromer & Waber (1974). Positional and thermal parameters are listed in Table 1, selected interatomic distances and angles are given in Table 2.†

† Lists of structure factors, H-atom coordinates, intermolecular distances, and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51742 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

$$B_{eq} = (8\pi^2/3)(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Os	0	0	$\frac{1}{4}$	1·34 (2)
Br	0	0	0·2704 (1)	2·56 (4)
S	−0·2536 (2)	0·0363 (2)	$\frac{1}{4}$	2·16 (8)
O	−0·3385 (6)	−0·1017 (7)	$\frac{1}{4}$	3·8 (3)
C	−0·3242 (8)	0·1395 (9)	0·3773 (5)	3·3 (3)

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

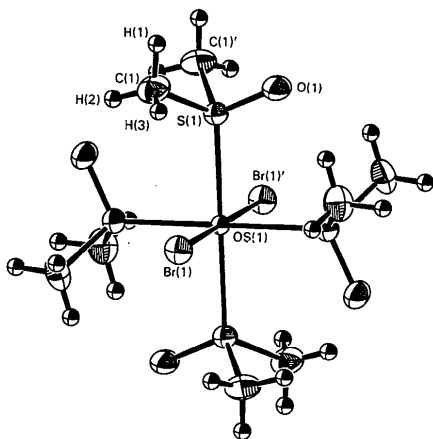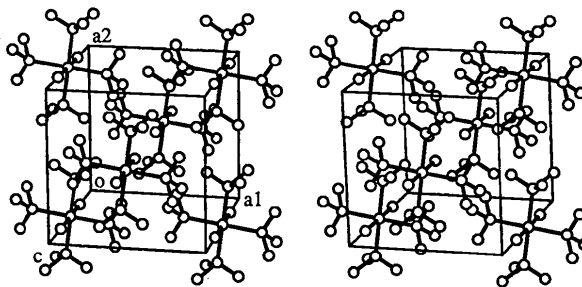| Os—Br	2·555 (1)	S—O	1·487 (6)
Os—S	2·351 (2)	S—C	1·784 (6)
O—S—C	105·2 (3)	C—S—C'	99·8 (5)
Os—S—O	113·5 (2)	Os—S—C	115·8 (2)

Fig. 1. Molecular structure and numbering scheme, thermal ellipsoids at the 50% probability level. H atoms shown with isotropic B's of $1 \cdot 0 \text{Å}^2$. Primed and unprimed atoms are related by a plane of symmetry.

Fig. 2. Stereoscopic illustration of the molecular packing.

Fig. 1 illustrates the molecular configuration, thermal motion and atom-numbering scheme, while Fig. 2 displays the molecular packing. All computer programs from the *TEXSAN* crystal structure analysis package (Molecular Structure Corporation, 1985).

Related literature. Although Os(Me₂SO) compounds have been previously reported (Antonov, Kukushkin, Konnov & Ionin, 1978) the title compound is apparently the first to be structurally characterized. It is isomorphous with [RuBr₂(Me₂SO)₄] (Oliver & Riley, 1984).

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Bis[bis(trimethylsilyl)cyclopentadienyl](chloro)uranium(III) Bis(2,6-dimethylphenylisocyanide)

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Abstract. [U(C₁₁H₂₁Si₂)₂Cl](C₉H₉N)₂, $M_r = 954 \cdot 77$, monoclinic, $P2_1/n$, $a = 16 \cdot 000$ (4), $b = 22 \cdot 806$ (4), $c = 13 \cdot 093$ (3) Å, $\beta = 92 \cdot 85$ (2)°, $V = 4771 \cdot 7$ Å⁻³, $Z = 4$, $D_x = 1 \cdot 33 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71073$ Å, $\mu = 34 \cdot 0 \text{ cm}^{-1}$, $F(000) = 1916$, $T = 296$ K, $R = 0 \cdot 031$ for 4116 $[F^2 > 2\sigma(F^2)]$ of 8437 total unique data. The U atom is five coordinate with distances: U—Cl 2·6865 (20); U—Cp 2·505, 2·508; U—C(isocyanide) 2·654 (9), 2·681 (9); ⟨U—C(cyclopentadiene)⟩ 2·781 (11) Å.