A Tetrahedral Osmyl Thiosulphato Complex: the X-Ray Crystal Structure of $(Bu^n{}_4N)_2[OsO_2(S_2O_3)_2]$

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In the title compound osmium(VI) has unusual distorted tetrahedral geometry, with two oxo and two *S*-bonded thiosulphato ligands; Raman, IR and ^{17}O NMR spectra show that this structure is maintained in solution.

Most oxo-osmium(VI) ('osmyl') complexes are octahedral with a *trans* arrangement of the oxo ligands. There are only two authenticated examples of tetrahedral osmyl complexes, both with organic ligands {[OsO$_2$(mesityl)$_2$][1] and [OsO$_2$(xylyl)$_2$][2]}. We report here the first osmyl species in which there is tetrahedral geometry in a purely inorganic anion, $[OsO_2(S_2O_3)_2]^{2-}$, the first osmium complex of the ambidentate thiosulphato ligand. We demonstrate also that this unusual structure is maintained in solution.

Green crystals of the complex were made by reaction of OsO_4 (1 mmol) in water (25 cm^3) with $Na_2S_2O_3$ (2 mmol) with addition of excess of $Bu^n{}_4N(HSO_4)$. Crystallisation was achieved from dichloromethane–toluene.†

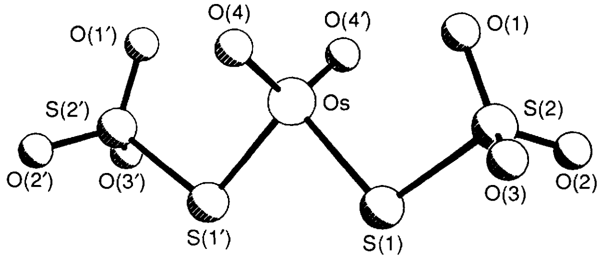

Fig. 1 The molecular structure of the $[OsO_2(S_2O_3)]^{2-}$ anion. Selected bond lengths (Å) and angles (°) Os–S(1) 2.218(1), Os–O(4) 1.692(3), S(1)–S(2) 2.152(1); O(4)–Os–O(4') 127.2(2), S(1)–Os–S(1') 89.2(1), S(1)–Os–O(4) 108.4(1), S(1)–Os–O(4') 108.5(1), Os–S(1)–S(2) 101.1(1).

The X-ray crystal structure‡ shows the anion to have crystallographic *C*2 symmetry (Fig. 1). The coordination about osmium is distorted tetrahedral with the O–Os–O angle significantly enlarged at 127.2(2)° and that for S–Os–S appreciably contracted at 89.2(1)°; the remaining S–Os–O angles are all equal [108.5(1)°]. The Os=O and Os–S distances are 1.692(3) and 2.218(1) Å respectively and the non-bonded S(1)···S(1)' separation is 3.12 Å. The thiosulphate groups function as monodentate sulphur donors [S(2)–S(1) 2.152(1) Å], the closest approach to the metal of the SO_3 oxygen atoms being 3.01 Å, too large for any bonding to occur. The Os–O distance is slightly shorter than those found in conventional

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† Satisfactory elemental analyses were obtained.

‡ *Crystal data*: $C_{32}H_{72}N_2O_8OsS_4$, M = 931.4, monoclinic, a = 25.556(6), b = 9.677(2), c = 18.256(3) Å, β = 108.94(1)°, V = 4270 Å^3, space group *C*2/*c*, Z = 4 (the molecule is disposed about a 2-fold axis), D_c = 1.45 g cm^{-3}, μ = 78 cm^{-1}. Data were measured on a Nicolet R3m diffractometer with Cu-Kα radiation (graphite monochromator) using ω-scans. The structure was solved by the heavy atom method and refined anisotropically using absorption-corrected data to give R = 0.026, R_w = 0.028 for 2749 independent observed reflections [$|F_o|>3\sigma(|F_o|)$, $2\theta\leqslant116°$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

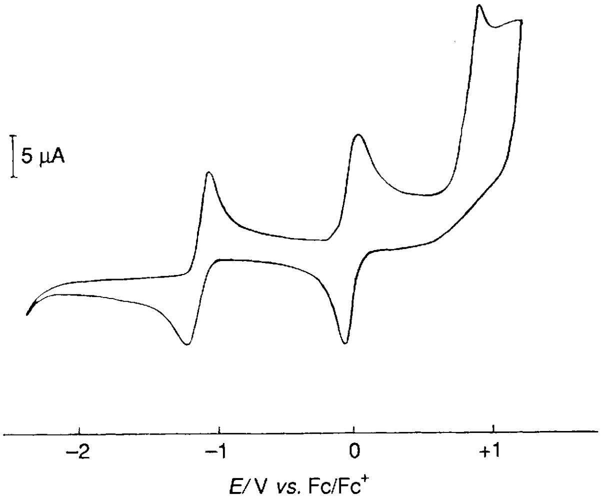

Fig. 2 Cyclic voltammogram of $(Bu^n{}_4N)_2[OsO_2(S_2O_3)_2]$ in dichloroethane with $Bu^n{}_4NPF_6$ as supporting electrolyte and ferrocene as internal reference (0.00 V). The sweep rate was 100 mV s^{-1}.

octahedral *trans* osmyl complexes (*ca.* 1.75 Å), but is similar to those found in $[OsO_2(mesityl)_2]$ [mean 1.695(5) Å[1]] and in $[OsO_2(xylyl)_2]$ [mean 1.692(5) Å[2]]; however the O–Os–O angle is substantially less in our complex.

The complex is diamagnetic. The X-ray photoelectron spectrum shows an osmium $4f_{7/2}$ binding energy of 54.1 eV, typical of oxo-osmium(VI) complexes.[3] Cyclic voltammetry of the complex in dichloroethane (Fig. 2) shows a reversible one-electron reduction ($E_{1/2} = -1.10$ V, $\Delta E = 85$ mV) signifying reduction to an osmium(V) dioxo complex. The Raman and IR spectra of the solid show bands typical[4] of *S*-bonded thiosulphate and the profiles of the spectra are little changed from solid to solution in CH_2Cl_2, suggesting retention of the structure of the anion in solution. In the latter the bands due to the *cis*-OsO_2 stretching vibrations are clearly distinguishable; both are observed in the Raman and IR as expected; the symmetric stretch $\nu^s(OsO_2)$ is strong and polarised in the Raman at 931 cm^{-1}, weak in the IR, while the asymmetric $\nu^{as}(OsO_2)$ mode is strong in the IR at 915 cm^{-1} and weak in the Raman, again as expected for *cis*-oxo ligands. The high values of $\nu^s(SO_3)$ and $\nu^{as}(SO_3)$ in the Raman (1011 and 1223 cm^{-1}) also typify[4] *S*-bonding of thiosulphate. The ^{17}O NMR (natural abundance) spectrum of a saturated solution of the complex in CD_2Cl_2 shows only two peaks in an approximate 1 : 3 ratio at δ 825.9 and 241.0 ppm (relative to $H_2{}^{17}O$); these we assign to the osmyl oxo ligands and thiosulphate oxygen atoms respectively, and this also confirms the *S*-bonded structure (in $Os^{17}O_4$, ^{17}O resonates at 784.9 ppm and in aqueous $S_2O_3{}^{2-}$ it lies[5] at δ 222.8 ppm).

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