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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{s-O}) = 0.005$ Å
 R factor = 0.023
 wR factor = 0.053
Data-to-parameter ratio = 15.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Trisodium dihydroxotetraoxoosmate(VII),
 $\text{Na}_3[\text{OsO}_4(\text{OH})_2]$ $\text{Na}_3[\text{OsO}_4(\text{OH})_2]$ contains osmium(VII) coordinated octahedrally by four oxide and two hydroxide groups. The $\text{OsO}_4(\text{OH})_2$ octahedra form zigzag chains parallel to $[010]$, linked by hydrogen bridges. Two O atoms, one Na and the Os atom lie on a mirror plane.Received 30 January 2006
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Comment

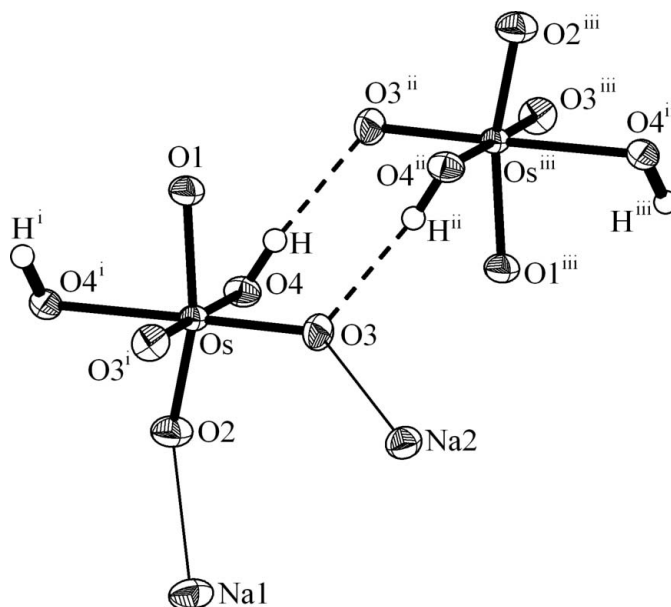
During recent years an increasing interest in osmium oxides has been registered, mainly due to their magnetic or electronic characteristics. Recently, for example, superconductivity was observed in KO_2O_6 (Yonezawa *et al.*, 2004). However, the number of crystal structures, especially of compounds containing osmium in higher oxidation states, is still very limited. In the course of our systematic investigations of oxoosmates with monovalent metals (Ahlert *et al.*, 2003, Mogare *et al.*, 2005) we have obtained single crystals of $\text{Na}_3[\text{OsO}_4(\text{OH})_2]$.The crystal structure of the title compound consists of $\text{OsO}_4(\text{OH})_2$ octahedra with the two OH groups coordinated in *cis* positions. The octahedron is distorted in such a way that the edge formed by the OH groups is considerably longer [3.068 (8) Å] than the remaining ones [2.491 (6)–2.767 (6) Å], and the Os atom is shifted off-center due to the longer bond lengths to the hydroxide ligands (see Table 1). The Os—O

Figure 1
Detail of the crystal structure of $\text{Na}_3[\text{OsO}_4(\text{OH})_2]$. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines represent the hydrogen bonds. [Symmetry codes: (i) $x, \frac{1}{2} - y, z$; (ii) $2 - x, -y, 1 - z$; (iii) $2 - x, -\frac{1}{2} + y, 1 - z$.]

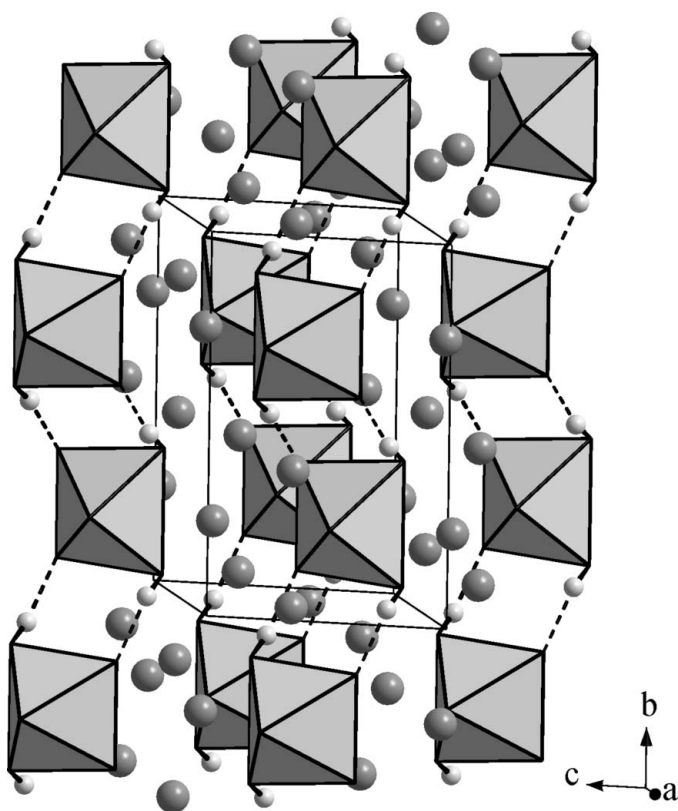


Figure 2
The crystal structure of $\text{Na}_3[\text{OsO}_4(\text{OH})_2]$, viewed approximately along $[\bar{1}00]$, showing the Na and H atoms and OsO_6 octahedra. Dashed lines represent the hydrogen bonds.

distances vary depending upon their functionality. The shortest Os—O distances are found to atoms O1 and O2 which are not involved in hydrogen bonding, while O3 is involved as an acceptor in the $\text{O}3^{\text{ii}} \cdots \text{H}—\text{O}4$ hydrogen bond to the neighbouring OsO_6 octahedron (Table 2) and shows a slightly longer bond length to the Os atom.

The hydroxide groups form hydrogen bonds to two neighbouring octahedra; thus each octahedron participates in four bonds. The hydrogen bonds, shown in Fig. 1, are unsymmetrical and nearly linear. The octahedra which are connected by these hydrogen bonds form zigzag chains parallel to $[010]$, as illustrated in Fig. 2. The chains of OsO_6 octahedra are separated by sodium cations coordinated by a square pyramid of five (Na1) and an irregular polyhedron of six O atoms (Na2).

Among many postulated (hydroxy/oxo)osmates, few of them have been structurally characterized (Nevskii *et al.*, 1982*a*; Nevskii & Porai-Koshits, 1983; Jewiss *et al.*, 1985; Murmann & Barnes, 2002). Within this family, only one sodium compound, formulated as $\text{Na}_2[\text{OsO}_4(\text{OH})_2] \cdot \text{H}_2\text{O}$, has been published (Nevskii *et al.*, 1982*b*), without the location of H atoms. Although this reported compound contains osmium in the oxidation state +VIII, the shape of the OsO_6 octahedron is very similar to that found in the title compound, *i.e.* with one considerably longer edge and an off-center Os atom with similar bond lengths. Nevertheless, the three-dimensional arrangement of the octahedra and the most

probable arrangement of hydrogen bonds is completely different.

Experimental

Single crystals of $\text{Na}_3[\text{OsO}_4(\text{OH})_2]$ were prepared *via* reaction of sodium hydroxide and osmium powder in the molar ratio 3:1 under an elevated oxygen pressure. The mixture was annealed in gold crucibles and placed in stainless steel autoclaves for 48 h (Linke & Jansen, 1997). The reaction temperature and oxygen pressure were 673 K and 28 MPa, respectively. The crystals were of irregular shape with edge lengths up to 0.5 mm. The X-ray powder pattern shows weak reflections of an unknown phase in an amount close to the detection limit.

Crystal data

$\text{Na}_3[\text{OsO}_4(\text{OH})_2]$
 $M_r = 357.19$
Monoclinic, $P2_1/m$
 $a = 5.7605$ (5) Å
 $b = 9.2995$ (7) Å
 $c = 5.9485$ (5) Å
 $\beta = 118.168$ (2)°
 $V = 280.92$ (4) Å³
 $Z = 2$

$D_x = 4.223$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 1930 reflections
 $\theta = 3.9–34.4^\circ$
 $\mu = 22.89$ mm⁻¹
 $T = 293$ (2) K
Block, black
0.25 × 0.13 × 0.08 mm

Data collection

Bruker SMART APEX CCD diffractometer
 ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1998)
 $T_{\text{min}} = 0.042$, $T_{\text{max}} = 0.160$
3488 measured reflections

871 independent reflections
814 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.065$
 $\theta_{\text{max}} = 30.0^\circ$
 $h = -8 \rightarrow 8$
 $k = -13 \rightarrow 13$
 $l = -8 \rightarrow 8$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.053$
 $S = 1.03$
871 reflections
57 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0209P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.94$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.62$ e Å⁻³
Extinction correction: SHELXL97
Extinction coefficient: 0.0032 (9)

Table 1

Selected geometric parameters (Å, °).

Os—O1	1.775 (5)	Na1—O3 ^v	2.577 (5)
Os—O2	1.784 (5)	Na1—O3 ^{vi}	2.577 (5)
Os—O3	1.807 (4)	Na1—O1 ^{iv}	2.945 (6)
Os—O3 ⁱ	1.807 (4)	Na2—O4 ^{vii}	2.309 (4)
Os—O4	2.152 (4)	Na2—O3	2.376 (5)
Os—O4 ⁱ	2.152 (4)	Na2—O1 ^{iv}	2.388 (4)
O4—O3 ⁱⁱ	2.910 (5)	Na2—O3 ^{viii}	2.390 (5)
Na1—O2	2.291 (6)	Na2—O4 ⁱⁱⁱ	2.436 (5)
Na1—O4 ⁱⁱⁱ	2.383 (5)	Na2—O2 ^{vii}	2.689 (5)
Na1—O4 ^{iv}	2.383 (5)		
O1—Os—O2	151.3 (3)	O1—Os—O4	82.13 (16)
O3—Os—O4 ⁱ	178.54 (15)	O2—Os—O4	77.90 (16)
O3 ⁱ —Os—O4	178.54 (15)	O3—Os—O4	88.19 (18)
O1—Os—O3 ⁱ	98.92 (17)	O1—Os—O4 ⁱ	82.13 (16)
O2—Os—O3 ⁱ	100.76 (17)	O2—Os—O4 ⁱ	77.90 (16)
O1—Os—O3	98.92 (17)	O3 ⁱ —Os—O4 ⁱ	88.19 (18)
O2—Os—O3	100.76 (17)	O4—Os—O4 ⁱ	91.0 (2)
O3 ⁱ —Os—O3	92.6 (3)		

Symmetry codes: (i) $x, -y + \frac{1}{2}, z$; (ii) $-x + 2, -y, -z + 1$; (iii) $x - 1, -y + \frac{1}{2}, z$; (iv) $x - 1, y, z$; (v) $x - 1, y, z - 1$; (vi) $x - 1, -y + \frac{1}{2}, z - 1$; (vii) $x, y, z + 1$; (viii) $-x + 1, -y, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O4-H\cdots O3^{ii}$	0.84 (6)	2.08 (6)	2.910 (5)	169 (5)

Symmetry code: (ii) $-x + 2, -y, -z + 1$.

The H atoms were located in a difference Fourier map after anisotropic refinement of all non-H atoms and refined without any constraints in the final refinement, resulting in plausible O—H bond distances. The highest peak and the deepest hole in the final difference Fourier map are 0.82 and 0.86 Å, respectively, from the Os atom.

Data collection: *SMART32* (Bruker, 2000); cell refinement: *SAINT32* (Bruker, 2000); data reduction: *SAINT32*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

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