Co-ordination Chemistry of Higher Oxidation States. Part 13.[1] Synthesis and Properties of Alkali-metal Hydroxo-oxo-osmate(VIII) Compounds and the Molecular Structure of $Cs[O_4Os(\mu\text{-}OH)OsO_4]$ †

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The reaction of concentrated aqueous solutions of caesium or rubidium hydroxide with osmium tetraoxide, in various ratios produced the osmates(VIII), $M_2[OsO_4(OH)_2]$, $M[OsO_4(OH)]$, and $M[O_4Os(OH)OsO_4]$ (M = Rb or Cs). Potassium and sodium hydroxide produced only $K_2[OsO_4(OH)_2]$ and $Na_2[OsO_4(OH)_2]\cdot 2H_2O$, respectively. Vibrational spectra show the $[OsO_4(OH)_2]^{2-}$ ions to have *cis*-octahedral structures. The structure of the title complex was established by a single-crystal *X*-ray study and shown to be monoclinic, space group *Cc*, with $a = 14.304(4)$, $b = 5.798(1)$, $c = 10.527(4)$ Å, $\beta = 109.92(3)°$, and $Z = 4$. The structure was refined to $R = 0.059$ from 710 reflections. The anion contains distorted trigonal-bipyramidal co-ordination (O_5) about the osmium atoms, which are linked *via* a single bent hydroxo-bridge Os–O(H)–Os, 133(1)°. The terminal Os=O bonds lie in the range 1.62(4)—1.77(3) Å and Os–OH 2.21(2) and 2.22(2) Å. Vibrational spectra are reported for $M[OsO_4(OH)]$, $M[O_4Os(OH)OsO_4]$ (M = Cs or Rb), and for barium and strontium osmates(VIII), and possible structures proposed.

Although osmium tetraoxide is the most important compound of osmium, its reactions with alkalis have been little studied. Early workers[2] reported no acidic properties, although recent measurements[3] show that in water very small amounts of the weak acid $H[OsO_4(OH)]$ are present: $K = [OsO_4(OH)^-][H^+]/[OsO_4][H_2O] \sim 10^{-13}$. Tschugaeff[4,5] and Krauss and Wilken[6] reported unstable complexes with alkali-metal hydroxides, including $2KOH\cdot OsO_4$, $2MOH\cdot OsO_4$, $MOH\cdot OsO_4$ (M = Cs or Rb) and $CsOH\cdot 2OsO_4$, but not all were obtained pure and there are inconsistencies in the few reported properties.[7-9] We have recently studied[10] the related fluoro-oxo-osmates(VIII) $[OsO_4F_2]^{2-}$ and $[OsO_3F_3]^-$, and report here a reinvestigation of the reactions of OsO_4 with hydroxides of Group 1A and 2A. During our studies, Russian workers reported[11-13] *X*-ray structures of three osmate(VIII) compounds.

Results and Discussion

$M_2[OsO_4(OH)_2]$.—The reactions of alkali-metal hydroxides, MOH (M = Cs, Rb, K, or Na), with OsO_4 in a >2:1 mol ratio in a small quantity of water produced dark red crystalline solids, $M_2[OsO_4(OH)_2]$. The solids are stable in sealed containers, but slowly lose OsO_4 in air, probably due to reaction with CO_2, and are extensively hydrolysed in water unless excess MOH is present. They are readily reduced by organic compounds; ethanol for example, converts them into the well known dark purple tetrahydroxo-oxo-osmates(VI), $M_2[OsO_2(OH)_4]$.[9,14] The solubilities in water increase in the order Cs < Rb < K < Na.

The i.r. spectra ‡ (Table 1) of $M_2[OsO_4(OH)_2]$ and of the deuteriated caesium salt, $Cs_2[OsO_4(OD)_2]$, contain three or four strong absorptions in the range *ca.* 850—750 cm^{-1} assignable as ν(Os=O) consistent with a *cis* arrangement of the oxo-groups [*cis* (C_{2v}) = $2A_1 + B_1 + B_2$, *trans* (D_{4h}) = E_u]. The spectra also contain medium intensity bands at *ca.* 3 500—3 300 cm^{-1} and *ca.* 1 050—970 cm^{-1} which shift on deuteriation to *ca.* 2 600 cm^{-1} and *ca.* 750—800 cm^{-1}, readily assigned to ν(OH) and δ(OH) respectively of co-ordinated hydroxo-groups.[8] Two further bands at *ca.* 460 and 480 cm^{-1}, only slightly affected by deuteriation, are the ν(Os–OH) vibrations. The spectrum of the sodium salt also shows absorptions due to lattice water (Table 1), consistent with the analytical data which indicate a dihydrate. The i.r. spectrum of the potassium salt is very different from that reported in ref. 9 and the latter appears to be the spectrum of the Os^{VI} complex $K_2[OsO_2(OH)_4]$. The i.r. spectra of $M_2[OsO_2(OH)_4]$ are given in Table 1 for comparison. Confirmation of the *cis* geometry of the $[OsO_4(OH)_2]^{2-}$ ion has recently been obtained by *X*-ray studies[11,12] of the Na and Li § salts. The *cis* arrangement of the oxo-groups is consistent with the prediction of Griffith[8] for d^0 systems, which is based upon a more equal utilisation of the metal $d\pi$ orbitals. The $[OsO_4F_2]^{2-}$ ion also has *cis* fluoro-groups.[10]

$M[OsO_4(OH)]$ *and* $M[Os_2O_8(OH)]$ (M = Rb *or* Cs).—A 1:1 mol ratio of RbOH or CsOH and OsO_4 in a small amount of water produces an orange-yellow solution, from which orange-yellow solids of stoicheiometry $M[OsO_4(OH)]$ are obtained on cooling. A 1:2 mol ratio MOH : OsO_4 yields yellow $M[Os_2O_8(OH)]$. Use of KOH in these reactions produces similar colours, but on concentration of the solutions only red $K_2[OsO_4(OH)_2]$ crystallises. The structure of $Cs[Os_2O_8(OH)]$ has been established by a single-crystal *X*-ray study (below), which shows the presence of $[O_4Os(\mu\text{-}OH)OsO_4]^-$ anions with a single non-linear hydroxo-bridge, and trigonal-bipyramidal (t.b.p.) co-ordination about each osmium. If coupling between the OsO_4 units is small, three i.r.-active ν(Os=O) vibrations are expected for local C_{3v} symmetry ($2A_1 + E$), and the spectra

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† Caesium μ-hydroxo-bis[tetraoxo-osmate(VIII)].

Supplementary data available (No. SUP 56072, 3 pp.): isotropic and anisotropic thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

‡ Raman spectra of $M_2[OsO_4(OH)_2]$ were obtained, but the intensities of the main bands changed rapidly with time, and some blackening of the samples occurred, indicating decomposition in the laser beam. The ν(OsO) vibrations were coincident with those in the i.r. spectra, but in view of this decomposition the data have not been quoted.

§ Not prepared in the present study.

Table 1. Infrared spectroscopic data[a]

Compound	Colour	ν(OH)	δ(OH)	ν(OsO)	ν(Os–OH)	δ(OsO)
$Na_2[OsO_4(OH)_2]\cdot 2H_2O$	Dark red	3 540, 3 450 (br)	1 650 (br), 995 (sh), 980	845, 800 (sh), 780, 740	495, 460	360, 328 (br)
$K_2[OsO_4(OH)_2]$	Dark red	3 300 (br)	1 020, 980	845, 820, 780, 750	500, 450	360, 340, 320
$Rb_2[OsO_4(OH)_2]$	Dark red	3 500	1 025, 975	830, 800 (br), 768	480, 460	360, 330 (br)
$Cs_2[OsO_4(OH)_2]$	Dark red	3 500	1 025, 975	828, 800 (br), 755	478, 450	355, 340, 320
$Cs_2[OsO_4(OD)_2]$		2 590	790, 740 (?)	830, 800 (br), 760	475, 445	355, 340, 332
$Rb[OsO_4(OH)]$	Yellow-orange	3 540	1 035	930 (sh), 905, 880, 850 (sh)	490	352, 338, 300, 250
$Cs[OsO_4(OH)]$	Yellow-orange	3 540	1 038	928 (sh), 910, 882 (br)	485	350, 338, 300, 250
$Cs[OsO_4(OD)]$		2 620	765	930 (sh), 910, 880 (br)	470	340, 300, 250, 240
$Rb[Os_2O_8(OH)]$	Yellow	3 540	1 040	925 (sh), 908, 880	490	350, 338, 300, 250
$Cs[Os_2O_8(OH)]$	Yellow	3 550	1 038	928 (sh), 910, 875 (br)	485	350, 340, 300, 248
$Cs[Os_2O_8(OD)]$		2 620	778	930 (sh), 910, 880, 860 (sh)	470	340, 300, 250 (br)
'$Sr[OsO_4(OH)_2]\cdot 3H_2O$'[b]	Red-brown	3 575 (sh), 3 560, 3 400, 3 330	1 630, 1 060, 960	890, 870, 816	545, 478	363, 340, 230
'$Sr[OsO_4(OD)_2]\cdot 3D_2O$'[b]		2 630, 2 520, 2 485	1 170 (br), 770 (sh), 730	890, 875, 820	565, 480	365, 345, 230
'$Ba[OsO_4(OH)_2]\cdot 2H_2O$'[b]	Red-brown	3 560, 3 400, 3 340	1 630, 1 040, 940	870, 860 (sh), 820	535, 460	365, 340
$K_2[OsO_2(OH)_4]$	Purple	3 300	1 110	820	520	310
$Rb_2[OsO_2(OH)_4]$	Purple	3 300	1 085	815	520	310
$Cs_2[OsO_2(OH)_4]$	Purple	3 350	1 050	810	510	300

[a] Frequencies in cm^{-1}; Nujol mulls. [b] See text for discussion of the formulations.

(Table 1) show two or three bands at *ca.* 930—870 cm^{-1}, essentially unaffected by deuteriation. The distorted t.b.p. amine adducts $OsO_4\cdot L$[15] [*e.g.* L = quinuclidine (qncd)] have ν(Os=O) at *ca.* 930—900 cm^{-1}. The medium intensity band at *ca.* 490 cm^{-1}, which shifts by 20 cm^{-1} to lower frequency in the deuteriated analogue, is assigned to ν_{asym}[Os–O(H)–Os]. Several bands <360 cm^{-1} are attributable to δ(OsO) and although ν_{sym}[Os–O(H)–Os] is expected in this region, it has not been unambiguously identified; the band at *ca.* 250 cm^{-1} is a likely candidate {*cf.* the single hydroxo-bridge in $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$ in which the bridge vibrations are assigned[16] at 570 and 294 cm^{-1}}.

The nature of the anions in the $M[OsO_4(OH)]$ compounds is less clear. The diffuse reflectance electronic spectra (Figure 1) of $M[OsO_4(OH)]$ and $M[O_4Os(\mu\text{-}OH)OsO_4]$ are essentially identical, but quite different from that of the six-co-ordinate $M_2[OsO_4(OH)_2]$, so that $M[OsO_4(OH)]$ contain five-co-ordinate osmium. More importantly, except for minor differences in relative intensities, the i.r. spectra of $M[OsO_4(OH)]$ and $M[O_4Os(OH)OsO_4]$ are identical (Table 1), inconsistent with six-co-ordinate osmium, *e.g.* $[O_4Os(\mu\text{-}OH)_2OsO_4]^{2-}$. The two remaining possibilities are that the i.r. spectra of t.b.p. monomers $[OsO_4(OH)]^-$ and dimers $[O_4Os(OH)OsO_4]^-$ are effectively identical, or that the compounds $M[OsO_4(OH)]$ are really 'double salts,' $M[O_4Os(OH)OsO_4]\cdot MOH$. An attempt to grow crystals of $Cs[OsO_4(OH)]$ for an *X*-ray study produced crystals of $Cs[O_4Os(OH)OsO_4]$, although since Os^{VIII} is labile and interconversion of the osmates in solution is rapid, this is inconclusive.

Structure of $Cs[O_4Os(\mu\text{-}OH)OsO_4]$.—The structure of the anion is shown in Figure 2, and selected bond lengths and angles are given in Table 2. The anion consists of two OsO_4 units linked by a single OH bridge with Os–O(H)–Os 133(1)°. The co-ordination about each osmium is very distorted t.b.p., containing an essentially linear axial unit O=Os–OH. The osmium atoms lie out of the trigonal planes (by 0.27 and 0.28 Å) towards the terminal oxygens [O_{eq}–Os–O(H) 78(1)—82(1)°]. An alternative description would be to view the anion as derived from two T_d OsO_4 groups, one face of each tetrahedron having opened out to accommodate the OH group.

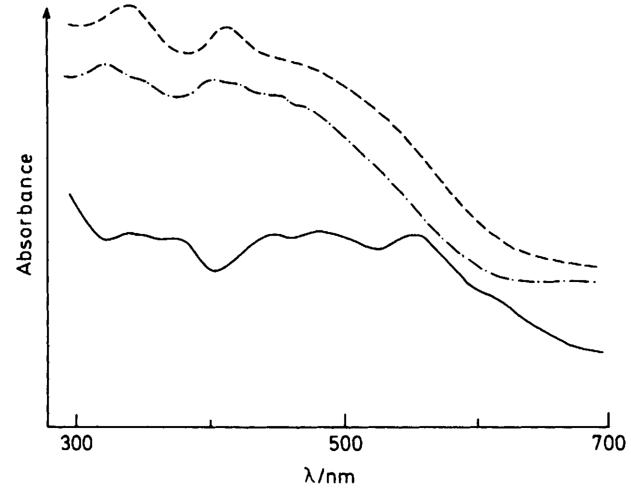


Figure 1. Electronic spectra of caesium osmate(VIII) compounds in the solid state: $Cs[O_4Os(OH)OsO_4]$ (– · – · –); $Cs[OsO_4(OH)]$(– – – –); $Cs_2[OsO_4(OH)_2]$ (——)

The Os=O bonds lie in the range 1.62(4)—1.77(3) Å (av. 1.69 Å), which compare well with those in OsO_4 (av. 1.712 Å),[17] and

Table 2. Bond lengths (Å) and angles (°) for $Cs[Os_2O_8(OH)]$

Os(1)–O(1)	1.67(3)	Os(2)–O(5)	2.21(2)
Os(1)–O(2)	1.64(4)	Os(2)–O(6)	1.77(3)
Os(1)–O(3)	1.68(2)	Os(2)–O(7)	1.71(3)
Os(1)–O(4)	1.71(3)	Os(2)–O(8)	1.69(3)
Os(1)–O(5)	2.22(2)	Os(2)–O(9)	1.62(4)
O(1)–Os(1)–O(2)	120(2)	O(5)–Os(2)–O(6)	179(1)
O(1)–Os(1)–O(3)	118(1)	O(5)–Os(2)–O(7)	81(1)
O(1)–Os(1)–O(4)	101(1)	O(5)–Os(2)–O(8)	79(1)
O(1)–Os(1)–O(5)	82(1)	O(5)–Os(2)–O(9)	82(1)
O(2)–Os(1)–O(3)	114(2)	O(6)–Os(2)–O(7)	100(1)
O(2)–Os(1)–O(4)	100(2)	O(6)–Os(2)–O(8)	101(2)
O(2)–Os(1)–O(5)	80(1)	O(6)–Os(2)–O(9)	97(2)
O(3)–Os(1)–O(4)	99(1)	O(7)–Os(2)–O(8)	118(1)
O(3)–Os(1)–O(5)	78(1)	O(7)–Os(2)–O(9)	116(2)
O(4)–Os(1)–O(5)	177(1)	O(8)–Os(2)–O(9)	119(2)
Os(1)–O(5)–Os(2)	133(1)		

Shortest heavy-atom distances

Os(1) ··· Os(2)	4.060
Cs(1) ··· Os(1)	4.006
Cs(1) ··· Os($2^{\rm I}$)	4.133
Cs(1) ··· O	3.12—3.50 (3.32 mean of 14)

Symmetry label: I $-\frac{1}{2} + x, \frac{1}{2} + y, z$.

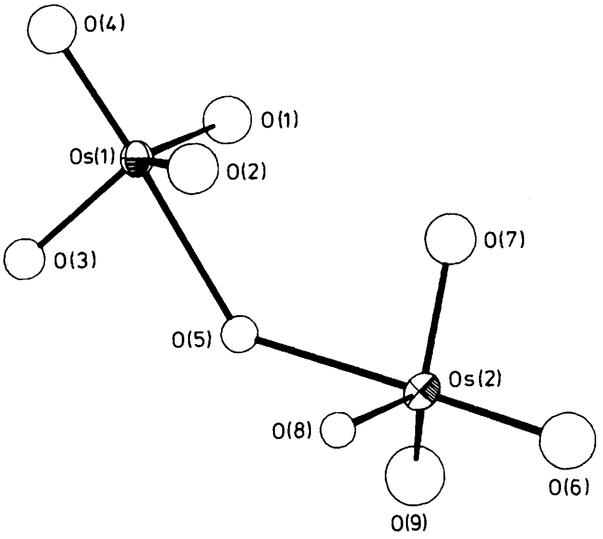


Figure 2. The anion in $Cs[Os_2O_8(OH)]$ showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level

in OsO_4·qncd (av. 1.706 Å),[18] and slightly shorter on average (~2σ) than those in the octahedral $[OsO_4(OH)_2]^{2-}$ (av. 1.76 Å).[11,12] The distorted t.b.p. geometry about the osmium is similar to that in OsO_4·amine adducts.[18] The Os–OH (bridge) bonds are longer by *ca.* 3σ [2.22(2) Å] than the terminal Os–OH in $[OsO_4(OH)_2]^{2-}$ (2.10—2.17 Å). The caesium ion lies in a 14-co-ordinate environment [Cs ··· O 3.12—3.50 (av. 3.32) Å] shown in Figure 3. Similar distances have been found in other compounds, for example the caesium alums.[19] There are no additional Cs ··· O contacts < 4.0 Å.

Barium and Strontium Osmates(VIII).—The reaction of saturated aqueous solutions of $Ba(OH)_2$ or $Sr(OH)_2$ with OsO_4 readily yielded red-brown crystals with compositions in agreement with the formulae $M[OsO_4(OH)_2]\cdot nH_2O$ [$n = 2$ (Ba) or 3 (Sr)]. The i.r. spectra of these compounds are very similar, but show considerable shifts from those of $M_2[OsO_4(OH)_2]$ (M = Na, K, Rb, or Cs) (Table 1). Preliminary *X*-ray data on the strontium compound established the crystal system and cell dimensions, but at this point the full structure (with similar cell dimensions) was published by Nevskii *et al.*,[13] and hence we did not proceed with the determination. Nevskii *et al.*[13] formulate their material as $Sr[OsO_5(H_2O)]\cdot 3H_2O$, with the dimensions of the anion as in (**I**) (standard deviations *ca.* 0.01—0.02 Å). The i.r. spectrum (Table 1) shows in addition to ν(Os=O) the characteristic vibrations of co-ordinated hydroxo-groups, δ(OH) = 1 060, 960, ν(Os–OH) = 545, 478 cm^{-1}, and of water, δ(OH_2) = 1 630 cm^{-1}, and several ν(OH) vibrations. The formulation of Nevskii *et al.*[13] is unsatisfactory from the bond length data (and inconsistent with the i.r. data), and alternatives consistent with the i.r. spectrum would be $Sr[OsO_4(OH)_2]\cdot 3H_2O$, $Sr[OsO_3(OH)_3]OH\cdot 2H_2O$ or $Sr[OsO_3(OH)_2(H_2O)][OH]_2\cdot H_2O$. The difference between Os–O(6) and Os–O(3) in (**I**) would appear to favour the last.

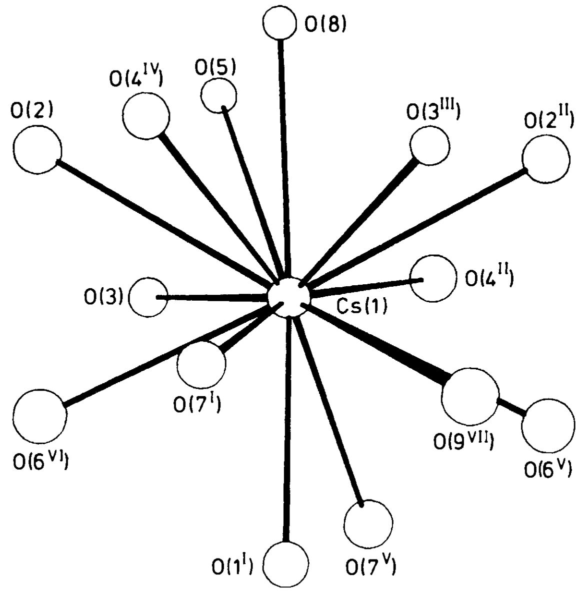
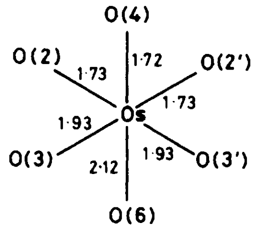


Figure 3. The co-ordination around Cs in $Cs[Os_2O_8(OH)]$. Symmetry labels: I $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; II $x, 1 + y, z$; III $x, 1 - y, -\frac{1}{2} + z$; IV $x, -y, -\frac{1}{2} + z$; V $-\frac{1}{2} + x, \frac{1}{2} + y, z$; VI $-\frac{1}{2} + x, -\frac{1}{2} + y, z$; VII $-\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z$



(**I**)

Experimental

Physical measurements were made as described previously.[20] Osmium tetraoxide (Johnson Matthey) and alkali- and alkaline-earth-metal hydroxides (BDH, Alfa, or Aldrich) were used as received. Osmium was determined spectrophotometrically as the thiourea complex,[21] and alkali metals by atomic absorption or emission. The tetrahydroxodioxo-osmate(VI) compounds $M_2[OsO_2(OH)_4]$ (M = Cs, Rb, or K) were prepared by reduction with ethanol[14] of aqueous solutions of MOH and OsO_4.

All preparations were conducted with exclusion of carbon dioxide, and isolated osmium(VIII) compounds were stored in sealed containers at −20 °C, in the dark.

Caesium Dihydroxotetraoxo-osmate(VIII), $Cs_2[OsO_4(OH)_2]$.—To a slight excess of cooled (*ca.* 0 °C) caesium hydroxide solution (0.75 g, 5 mmol CsOH in 3 cm³ H_2O), was added OsO_4 (0.5 g, 2 mmol). On standing, red-brown or dark red crystals separated which were filtered off, rinsed with a very small amount of cold water and vacuum dried (Found: Cs, 47.0; Os, 34.4. $H_2Cs_2O_6Os$ requires Cs, 47.9; Os, 34.3%).

$Rb_2[OsO_4(OH)_2]$ was obtained similarly (Found: Os, 42.2; Rb, 36.5. $H_2O_6OsRb_2$ requires Os, 41.4; Rb, 37.2%).

Potassium Dihydroxotetraoxo-osmate(VIII), $K_2[OsO_4(OH)_2]$.—The deep red aqueous solution obtained from KOH and OsO_4 (2:1 mol ratio) was evaporated slowly under vacuum at room temperature over P_4O_{10}, until almost dry. The product was recrystallised from a small quantity of water as small dark red crystals (Found: K, 22.1; Os, 51.5. $H_2K_2O_6Os$ requires K, 21.4; Os, 51.9%).

$Na_2[OsO_4(OH)_2]\cdot 2H_2O$ was made similarly (Found: Na, 12.3; Os, 51.5. $H_6Na_2O_8Os$ requires Na, 12.4; Os, 51.4%).

Caesium Hydroxotetraoxo-osmate(VIII), $Cs[OsO_4(OH)]$.—A solution of CsOH (0.3 g, 2 mmol) in water (5 cm³) was added to OsO_4 (0.5 g, 2 mmol) and the mixture warmed until all the OsO_4 had melted and dissolved. The yellow solution was cooled quickly in ice, and the orange-yellow solid filtered off, rinsed with cold water and dried (Found: Cs, 34.0; Os, 46.5. $HCsO_5Os$ requires Cs, 32.9; Os, 47.0%).

$Rb[OsO_4(OH)]$ was made similarly (Found: Os, 53.2; Rb, 23.4. HO_5OsRb requires Os, 53.3; Rb, 23.95%).

Caesium μ-*Hydroxo-bis*[*tetraoxo-osmate*(VIII)], $Cs[Os_2O_8(OH)]$.—To a solution of CsOH (0.15 g, 1 mmol) in water (5 cm³) was added OsO_4 (0.5 g, 2 mmol), and the mixture warmed to *ca.* 50 °C, then cooled rapidly to 0 °C, when a yellow solid was deposited. This was filtered off, rinsed with cold water, and vacuum dried (Found: Cs, 19.6; Os, 58.1. $HCsO_9Os_2$ requires Cs, 20.2; Os, 57.8%).

$Rb[Os_2O_8(OH)]$ was made similarly (Found: Os, 60.6; Rb, 14.5. HO_9Os_2Rb requires Os, 62.1; Rb, 14.0%)

Strontium and Barium Osmates(VIII).—These were prepared by a similar route to that used for $Cs_2[OsO_4(OH)_2]$. Both crystallise easily from water. (Rigorous exclusion of carbon dioxide is necessary in these preparations.) Sr salt (Found: Os, 44.5; Sr, 20.5. H_8O_9OsSr requires Os, 44.25; Sr, 20.4%). Ba salt (Found: Ba, 29.9; Os, 40.9. H_6BaO_8Os requires Ba, 29.75; Os, 41.2%).

X-*Ray Crystallography*.—Yellow crystals were obtained after several days from aqueous solution by cooling an equimolar mixture of CsOH and OsO_4 to *ca.* 0 °C. Crystals were mounted in Lindemann capillaries and examined by photographic *X*-ray methods. It proved impossible to measure the density.

Crystal data. $HCsO_9Os_2$, $M = 658.31$, monoclinic, $a = 14.304(4)$, $b = 5.798(1)$, $c = 10.527(4)$ Å, $\beta = 109.92(3)°$, $U = 820.8$ Å³, $Z = 4$, $D_c = 5.326$ g cm⁻³, $F(000) = 1\,120$, $\mu(\text{Mo-}K_\alpha) = 339$ cm⁻¹, $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å, space group *Cc* (no. 9).

Intensity data were recorded on an Enraf Nonius CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation. From a crystal (0.15 × 0.25 × 0.35 mm) at room temperature, 870 reflections were recorded ($1.5 < \theta < 25°$, $\pm h,k,l$) including three check reflections. The check reflections showed no change during the experiment, and after removing systematically absent reflections and averaging multiply measured reflections ($R_{int.} = 0.015$; R_{int} measures internal consistency of data in SHELX) there remained 758 unique reflections used in structure analysis. The normalised

Table 3. Atomic co-ordinates (× 10⁴), with estimated standard deviations in parentheses, for $Cs[Os_2O_8(OH)]$

Atom	*x*	*y*	*z*
Os(1)	0	295(3)	10 000
Os(2)	1 795(1)	4 416(2)	8 718(2)
Cs(1)	−1 506(2)	5 022(5)	7 301(3)
O(1)	1 092(20)	−57(50)	11 237(35)
O(2)	−84(22)	22(51)	8 411(38)
O(3)	−789(15)	2 260(40)	10 241(23)
O(4)	−606(16)	−2 153(47)	10 196(26)
O(5)	700(14)	3 574(36)	9 709(21)
O(6)	2 665(23)	5 162(56)	7 933(39)
O(7)	2 178(18)	1 668(53)	9 236(27)
O(8)	717(17)	4 743(38)	7 419(27)
O(9)	2 122(22)	6 385(64)	9 886(35)

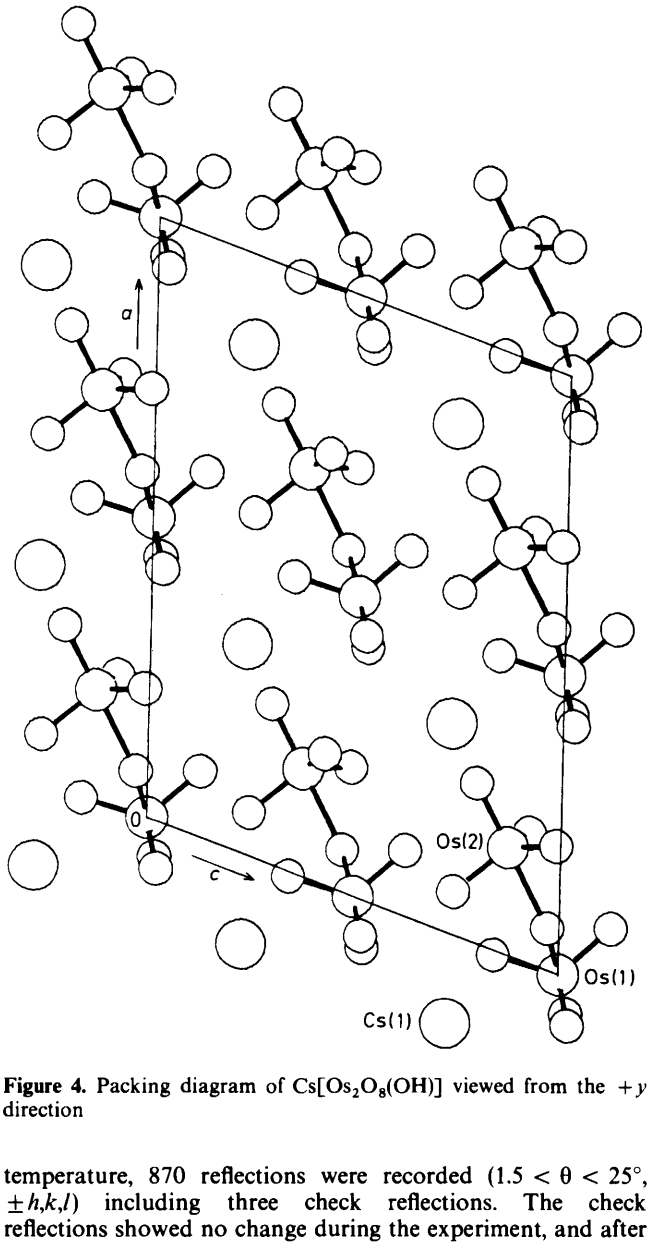


Figure 4. Packing diagram of $Cs[Os_2O_8(OH)]$ viewed from the $+y$ direction

structure factors favoured the non-centrosymmetric space group *Cc*. An empirical ψ scan was applied to the data [transmission: 99.0(max.)—28.5(min.)%].

Solution and refinement of the structure. The structure was solved by Patterson methods to locate the Cs and the two Os atoms, and the oxygen atoms located by a series of structure factor and electron density calculations. Location of the oxygen atoms and refinement of the structure proved troublesome in the early stages, a situation exacerbated by the large value of the absorption coefficient. With the help of a weighting scheme to down-weight strong reflections, refinement eventually converged at $R \sim 0.12$ with isotropic atoms and the absorption correction of Walker and Stuart[22] was applied. This dramatically improved the residual and the standard deviation of the atomic positions, and gave satisfactory thermal parameters. Refinement converged to $R = \Sigma\Delta/\Sigma F = 0.0593$ $\{R' = [\Sigma w\Delta^2/\Sigma F^2]^{\frac{1}{2}} = 0.0771\}$ {63 parameters, 710 reflections with $F > 3\sigma(F)$, anisotropic (Cs and Os) and isotropic (O) atoms, empirical weights, $w = 1/[\sigma^2(F) + 0.02F^2]$, and isotropic extinction parameter (0.000 88)}. Omitted from the refinement were 16 reflections with poor agreement between F_o and F_c (mainly $h0l$ and $h1l$). The ratio of reflections to parameters was 11.3 and a final difference electron-density synthesis showed no chemically significant features, with the largest peak being 4.14 e Å^{-3}, close to an Os atom. No attempt was made to locate the H atom. The absolute configuration was confirmed by inverting the structure whereupon R increased by 0.02.

The final atomic co-ordinates are presented in Table 3. Atomic scattering factors and anomalous dispersion corrections were taken from SHELX[23] (O) and ref. 24 (Os, Cs$^+$) and all calculations were performed using the programs SHELX,[23] DIFABS,[22] PLUTO,[25] XANADU,[26] and ORTEP.[27]

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