Synthesis and Properties of Alkali-metal Tetraoxo-osmate(VII) Compounds†

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The black compounds $M[OsO_4]$ (M = Na, K, Rb, or Cs) have been prepared from OsO_4 and MI in acetone. They are stable in dry air, but disproportionate immediately in aqueous acid solution to Os^{VIII} and Os^{IV}, and in basic solution to Os^{VIII} and Os^{VI}. The i.r. and electronic spectra are reported and discussed. *X*-Ray powder diffraction studies show that $M[OsO_4]$ (M = Na or K) have the scheelite structure.

Potassium tetraoxoruthenate(VII) ('perruthenate'), $K[RuO_4]$, was first reported in 1876,[1] and is a common ruthenium compound. The first example of the long sought osmium analogues, $[AsPh_4][OsO_4]$, was obtained very recently by reduction of OsO_4 with $[AsPh_4]I$ in dichloromethane.[2] Although a variety of alkali-metal osmate(VIII) compounds are known,[3] all attempts to isolate osmates(VII) by reduction in aqueous alkaline solution have failed. There is some evidence from polarographic[4] and e.s.r.[5] studies that Os^{VII} may be present in solutions of OsO_4 in dilute alkalis under some conditions. Several osmates(VII) $M_3[OsO_5]$ and $M_5[OsO_6]$ have been made by high-temperature fusion reactions of M_2O/Os in oxygen (M = Na or K).[6] Here we report the synthesis and characterisation of $M[OsO_4]$ (M = Na, K, Rb, or Cs).

Results and Discussion

In order to extend the method of Bilger *et al.*[2] to the preparation of $M[OsO_4]$ (M = alkali metal), we required an organic solvent in which the corresponding iodides MI were soluble, which was a poor donor, and which was not oxidised by OsO_4. Of the common solvents, acetone fulfils these requirements, and upon stirring OsO_4 with dry acetone solutions of MI at 0 °C, $M[OsO_4]$ precipitates in *ca.* 30—50% yield. The tetraoxo-osmates(VII) are black in bulk, but on grinding are seen to be dark greenish brown.

The sodium salt absorbs water on exposure to air, and slowly decomposes, but the compounds of the heavier alkali metals were unchanged after exposure to the laboratory atmosphere for 3 d. In water or dilute ($\sim$2 mol dm^{-3}) H_2SO_4, immediate disproportionation to OsO_4 and $OsO_2{\cdot}nH_2O$ occurs, whilst in alkali (*ca.* 1 mol dm^{-3} KOH) the products are Os^{VI} and Os^{VIII} $\{K_2[OsO_2(OH)_4]$ and $OsO_4\}$. Ethanolic KOH produces essentially quantitative conversion to $K_2[OsO_2(OH)_4]$.[3]

The i.r. spectra of $M[OsO_4]$ in Nujol mulls (Table 1) show a strong absorption at *ca.* 840—860 cm^{-1}, which is split when $M = K^+$ or PPh_4^+ but appears as a single broad band in the other examples. There are medium intensity absorptions at *ca.* 240—260 cm^{-1}. These bands are readily assigned as ν_3 and ν_4 respectively of pseudo-tetrahedral $[OsO_4]^-$, the splittings indicating that the site symmetry is lower than T_d (*cf.* $K[RuO_4]$, ν_3 = 846, 835, ν_4 = 316, 305 cm^{-1};[7] $[AsPh_4][OsO_4]$, ν_3 = 852, 834, ν_4 = 240 cm^{-1} [2]). The electronic spectrum of $K[OsO_4]$ in the solid state contains weak bands at *ca.* 14 500 and 17 200 cm^{-1}, and broad absorptions of ill defined maxima at $\geqslant$33 000 cm^{-1}. It is very slightly soluble in acetone, the solution has weak absorptions at 14 500, 15 200(sh), and 17 200 cm^{-1}, and an intense shoulder at *ca.* 28 000 cm^{-1} is evident below the solvent cut-off. Detailed assignments of the spectra of $[MO_4]^{n-}$ ions are difficult,[8] but the assignment of the bands at >33 000 cm^{-1} as $O \rightarrow Os$ charge-transfer (c.t.) bands is reasonable when compared with the lowest energy c.t. bands in $[RuO_4]^-$ ($\sim$25 900 cm^{-1})[9] and OsO_4 ($\sim$35 000 cm^{-1}).[10] The weak low-energy absorptions were present in all the spectra, suggesting they are not due to impurities, and hence are associated with the *d–d* transition $e \rightarrow t_2$, split by the large spin-orbit coupling expected[11] in Os^{VII}. The *d–d* transition of $[RuO_4]^-$ has been predicted[12] at *ca.* 11 000 cm^{-1}, but apparently has not been observed experimentally.

Table 1. Analytical[a] and i.r. spectroscopic data

Compound	M (%)	Os (%)	I.r./cm^{-1} [b] ν_3	ν_4
$Cs[OsO_4]$	34.4 (34.3)	50.0 (49.1)	845s	240m
$Rb[OsO_4]$	25.4 (25.2)	56.8 (56.0)	850s,br	250m
$K[OsO_4]$	13.2 (13.3)	64.2 (64.8)	860s, 840s	260m
$Na[OsO_4]$	8.1 (8.3)	70.0 (68.6)	840s,br	250m
$[PPh_4][OsO_4]$	*c*	32.5 (32.0)	855m, 838s	248m

[a] Calculated values in parentheses. [b] Nujol mulls, 4 000—180 cm^{-1} [c] C = 48.6 (48.55), H = 3.1 (3.4)%.

The magnetic moment of $K[OsO_4]$ at 298 K was found to be 1.40($\pm$0.1) B.M. which compares with 1.25 B.M. reported[2] for $[AsPh_4][OsO_4]$ and 1.47 B.M. for $OsOF_5$.[13] Comparison of the *X*-ray powder diffraction patterns of scheelite[14] ($Ca[WO_4]$) and $M[OsO_4]$ (M = Na or K) showed immediately that all three materials were isomorphous and hence belong to the tetragonal system, space group $I4_1/a$. Powder diffractometry on the potassium compound was used to obtain cell dimensions and confirmation of the correctness of the structure was provided by comparison of the calculated and observed intensities (see Table 2). The atom co-ordinates for $K[RuO_4]$[15] were used in this calculation with the atomic scattering factor for Os but no attempt was made to obtain the oxygen co-ordinates for $K[OsO_4]$ {Crystal data: $K[OsO_4]$, M = 293.3, tetragonal, a = 5.675, c = 12.713 Å, U = 409.4 Å^3, Z = 4, D_c = 4.757 g cm^{-3}, $F(000)$ = 508, space group $I4_1/a$, scheelite type}. Comparison of the powder patterns for $Rb[OsO_4]$ and $Rb[IO_4]$[14] (scheelite type) indicated isomorphism but no firm conclusions were drawn for $Cs[OsO_4]$ ($Cs[IO_4]$ is not of the scheelite type and is orthorhombic).

Experimental

Alkali-metal iodides were dried by heating *in vacuo* at *ca.* 200 °C for several hours. AnalaR acetone was dried over $CaSO_4$. Physical measurements were made as described previously.[3] For

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† *Supplementary data available* (No. SUP 56245, 3 pp.): *X*-Ray powder diffraction data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix.

Non-S.I. unit employed: B.M. = 0.927 × 10^{-23} A m^2.

Table 2. *X*-Ray powder diffraction data for $K[OsO_4]$

Line no.	$2\theta/^\circ$	d_{hkl}(obs.)[a]	d_{hkl}(calc.)[b]	*hkl*[c]	*I*(obs.)[d]	*I*(calc.)[e]
1	17.05	5.196	5.182	101	88	47
2	26.20	3.398	3.394	112, 103	100	100
3	28.05[f]	3.184	3.178	004	10	14
4	31.50	2.838	2.837	200	23	18
5	36.05	2.489	2.489	211	19	13
6	38.80	2.319	2.320	105	4	3
7	41.45	2.177	2.177	123	10	6
8	42.68[f]	2.116	2.117	204	15	22
9	45.15[f]	2.006	2.006	220	15	8
10	48.53[f]	1.874	1.874	116	13	16
11	50.77[f]	1.796	1.796	215	8	8
12	52.95	1.728	1.727	312, 132	28	25
13	54.00	1.697	1.697	224	8	11
14	59.10	1.562	1.562	321	4	4
15	61.00	1.518	1.518	305	2	2
16	62.90	1.476	1.476	127	6	7
17	65.75	1.419	1.419	400	2	3
18	67.50	1.386	1.387	208	6	6
19	68.45	1.369	1.369	136	9	14
20	70.30	1.338	1.338	325	2	1
21	72.10	1.309	1.309	332	8	8
22	73.00	1.295	1.296	404	2	4
23	74.75	1.269	1.269	420	6	5
24	76.40	1.246	1.246	228	3	4
25	78.95	1.212	1.212	11.10	3	4

[a] Calculated using Cu-$K_{\alpha 1}$ (λ = 1.5405 Å). [b] Calculated using $a = b = 5.675$, $c = 12.713$ Å. The cell dimensions were obtained from the 220 and 204 reflections. [c] Principal *hkl* values contributing to the intensity. [d] Peak heights scaled to maximum intensity = 100. [e] Intensity calculated using atomic co-ordinates from $K[RuO_4]$ (ref. 15). [f] Accurate 2θ value from Si calibration.

analysis, weighed samples of $M[OsO_4]$ were dissolved in dilute (1 mol dm^{-3}) HNO_3, and analysed for Os and M as described.[3]

$[PPh_4][OsO_4]$ was prepared by the method of Bilger *et al.*,[2] for purposes of comparison.

Potassium Tetraoxo-osmate(VII).—The preparation was carried out in Schlenk apparatus under dry nitrogen. To a cooled (0 °C) acetone solution of KI (0.5 g, 3 mmol in 40 cm^3) was added solid OsO_4 (0.5 g, 2 mmol). A green colour developed rapidly, which changed on stirring to blue, and then red-brown. The solution was stirred for 3 h at 0 °C and on standing for 1 h a black solid precipitated. This was filtered off, rinsed well with acetone, and dried *in vacuo*.

$Na[OsO_4]$ was prepared similarly. For $Rb[OsO_4]$ and $Cs[OsO_4]$, the rather lower solubility of the MI required larger volumes of acetone, and after reaction was complete the solutions were concentrated to about half volume before isolation of the products.

X-*Ray Powder Diffraction Patterns*.—These were recorded using a Unicam 19-cm diameter Debye-Scherrer camera and nickel-filtered Cu-K_α radiation. The $K[OsO_4]$ data were also recorded on a Phillips powder diffractometer and the calculation of the powder diffraction pattern performed using the program LAZY PULVERIX[16] available at the University of London Computer Centre.

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