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COORDINATION CHEMISTRY OF HIGHER OXIDATION STATES. 10 [1]. OXOFLUORO ANIONS OF OSMIUM(VIII) $[OsO_4F_2]^{2-}$ and $[OsO_3F_3]^-$

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SUMMARY

Trioxotrifluoroosmates(VIII) $M[OsO_3F_3]$ (M = Cs, Rb, K) have been prepared by direct combination of OsO_3F_2 and the appropriate alkali fluoride MF. The reaction of OsO_4 with M'F (M' = Cs, Rb) in aqueous solution produces the tetraoxodifluoroosmates(VIII) $M'_2[OsO_4F_2]$. On the basis of their vibrational spectra the assignment of a fac (C_{3v}) structure to $[OsO_3F_3]^-$ and a cis (C_{2v}) to $[OsO_4F_2]^{2-}$ is proposed. The electronic spectra of the anions have been recorded and are interpreted using the optical electronegativity concept.

INTRODUCTION

Few examples of osmium(VIII) compounds have been reported [2], simple compounds being limited to OsO_4, OsO_3F_2 and imido-oxo compounds $Os(NR)_nO_{4-n}$ (n = 1-3). Complexes include $[OsO_4(OH)_2]^{2-}$, $[OsO_3N]^-$, $[OsO_4L]$ (L = pyridine, quinuclidine, etc) and $OsO_4.2SbCl_5$. Two types of oxofluoro anion $[OsO_4F_2]^{2-}$ and $[OsO_3F_3]^-$ have been briefly reported. Krauss and Wilken [3] prepared $M^I_2[OsO_4F_2]$ (M = Cs, Rb) from OsO_4 and aqueous MF, and $M^I[OsO_3F_3]$ (M = Cs, K, Ag) were obtained by Hepworth and Robinson [4] from OsO_4, MBr and BrF_3, although only the silver salt was obtained in the pure state. Although both ions have been included in larger studies of the vibrational spectra of compounds with M=O multiple bonds [5,6], neither has been examined in detail. Here we report new preparations of $M[OsO_3F_3]$, and spectroscopic data on both series of complexes.

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EXPERIMENTAL

Infrared spectra were recorded on a Perkin Elmer 580B spectrometer in sodium-dried Nujol mulls. Raman spectra were obtained from the solid samples using a Cary 82 with a Spectrophysics He-Ne laser. Electronic spectra were recorded on a Perkin Elmer 554. Fluorine was determined by the lanthanum alizarin complexone method [7] and osmium spectrophotometrically as the thiourea complex [8].

Alkali-metal fluorides were obtained from Alfa Inorganics, and dried by prolonged heating *in vacuo*. Trioxodifluoroosmium(VIII) OsO_3F_2 was made from OsO_4 and fluorine in a Monel autoclave [9].

$Cs_2[OsO_4F_2]$

A warm (*ca* 50°C) concentrated solution of CsF (0.6 g, ∿4 mmol) in water was stirred with OsO_4 (0.25 g, 1 mmol), and the solution allowed to cool to room temperature. The yellow solid was filtered off, and dried briefly *in vacuo* over P_4O_{10}. Found Os = 34.25, F = 6.7. Calc Os = 34.1, F = 6.8%.

$Rb_2[OsO_4F_2]$

$Rb_2[OsO_4F_2]$ was obtained similarly using cold aqueous RbF. The yellow solid separated overnight. Found Os = 41.0, F = 8.3. Calc Os = 41.1, F = 8.2%

The reaction of CsF with OsO_4 in cold water gave a pale yellow solid.

Typical analyses.	Os = 47.8,	F = 6.0.	Calc for $CsF.OsO_4$	Os = 46.8%
	50.0	5.9		F = 4.8%

$M[OsO_3F_3]$ (M = Cs, Rb, K)

A silica ampoule fitted with a graded seal and connected to a vacuum line via a side arm closed with a Teflon tap (J T Young Ltd) was thoroughly flammed *in vacuo* ($<10^{-3}$ torr). It was then loaded in a dry box (≲10 ppm H_2O) with finely powdered alkali fluoride and OsO_3F_2 in a 1:∿1.2 mol ratio. The ampoule was evacuated, the tap closed and the mixture heated in an oil bath at *ca* 120-150°C for 2-3 hours. The product was an orange-yellow powder. The excess OsO_3F_2 was then sublimed away by warming under a dynamic vacuum. The free flowing powder was transferred to sealed containers in a dry box.

$Cs[OsO_3F_3]$ fd Os = 44.9, F = 13.3. Calc Os = 44.4, F = 13.9%
$Rb[OsO_3F_3]$ fd Os = 50.0, F = 14.35. Calc Os = 49.45, F = 14.9%
$K[OsO_3F_3]$ fd Os = 56.5, F = 17.6. Calc Os = 56.9, F = 17.1%.

RESULTS AND DISCUSSION

$M_2[OsO_4F_2]$ (M = Cs, Rb)

The reaction of OsO_4 with a concentrated aqueous solution of RbF produced a deep yellow solution, which on standing at room temperature slowly deposited yellow crystals of $Rb_2[OsO_4F_2]$. The corresponding reaction between OsO_4 and CsF at ambient temperature produced a pale yellow solid of rather variable composition approximating to "$CsF.OsO_4$", but when a warm (ca 50°C) concentrated CsF solution was used, yellow $Cs_2[OsO_4F_2]$ crystallised on cooling. Attempts to isolate potassium or tetramethylammonium salts were unsuccessful, although reaction occurred in solution.

Ruthenium tetroxide dissolves in aqueous CsF solution to give a deep yellow solution (cf Ref 10) but on standing brown-black $RuO_2.nH_2O$ deposits, and evaporation of the solution resulted in loss of the RuO_4. Thus there is no evidence that $[RuO_4F_2]^{2-}$ ions can be isolated. The result reflects both the greater instability of Ru(VIII) and the reluctance of the 4d element to increase its coordination number [11].

The $M_2[OsO_4F_2]$ slowly lose OsO_4 on standing, and the OsO_4 is completely lost on heating *in vacuo*. The two possible structures for the anion are *cis* (C_{2v}) or *trans* (D_{4h}), which can be distinguished by their vibrational spectra. For the stretching vibrations we have:

cis (C_{2v}) $\nu(OsO_4) = 2a_1 + b_1 + b_2$, $\nu(OsF_2) = a_1 + b_1$ (all IR + Raman active)
trans (D_{4h}) $\nu(OsO_4) = a_{1g}(R) + b_{1g}(R) + b_{1u}(IR)$, $\nu(OsF_2) = a_{1g}(R) + a_{2u}(IR)$.

From the coincidences between the IR and Raman spectra (Table), it is clear that the anion has a *cis* structure.

TABLE

Vibrational spectra of $[OsO_4F_2]^{2-}$ and $[OsO_3F_3]^-$

	$\nu(OsO_4)$	$\nu(OsF_2)$	$\delta(OsO_4)$	
$Cs_2[OsO_4F_2]$	948m,932s,916s,892s	478m,422m	325s,308s	IR
	946s,927s,919s,900m[a]			R
$Rb_2[OsO_4F_2]$	940sh,930s,916s,898s	480s,420s	322s,305s	IR
"$CsF.OsO_4$"	(953w[b]),935s,912s,895s	420w(?)	322s,308s	IR
	926s,917w,900m			R
	$\nu(OsO_3)$	$\nu(OsF_3)$	$\delta(OsO_3)$	
$Cs[OsO_3F_3]$	932sh,915s	565s,482s	330sh,310s	IR
$Rb[OsO_3F_3]$	928s,918s	568s,490s	340sh,310s	IR
$K[OsO_3F_3]$	932s,918s	570s,490s,478sh	340m,305s	IR
	932s,916s			R
"$Na[OsO_3F_3]$"[c]	935s,920s	580s,490s,460s	330m,303s	IR

[a] Compound decomposes slowly in laser beam.

[b] OsO_4 impurity.

[c] Also bands at 668m, 630s, 390s.

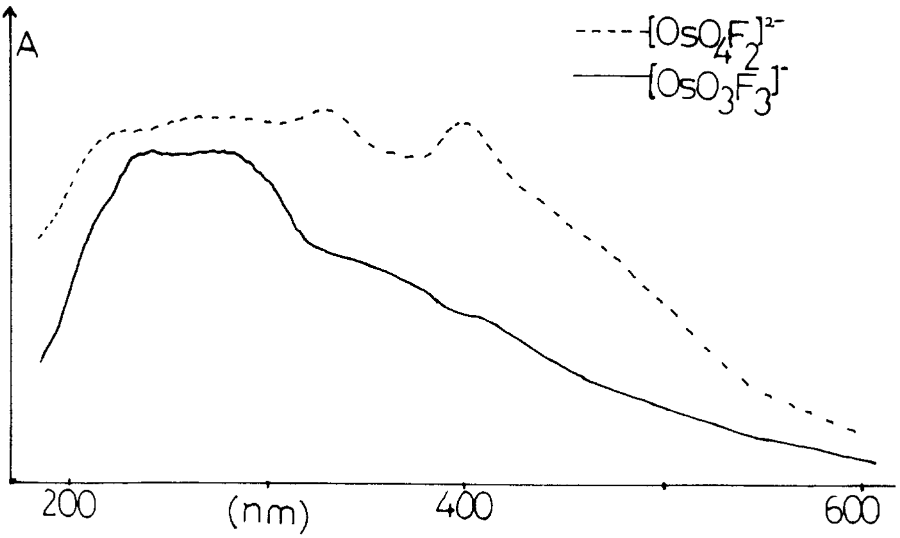

Fig. Diffuse reflectance spectra of the anions $[OsO_4F_2]^{2-}$ and $[OsO_3F_3]^-$.

The diffuse reflectance spectrum of $Cs_2[OsO_4F_2]$ is shown in the Figure. For a d^0 system the absorptions must arise from L → M charge transfer, and the energies of the lowest F → Os and O → Os transitions can be predicted approximately using the optical electronegativity formula [12].

$$E_{max} = 30[\chi_{opt}(L) - \chi_{opt}(M)] \times 10^3\ cm^{-1}$$

From the spectrum of OsO_4, χ_{opt} (Os^{VIII}) has been estimated [12] as ca 2.1, which allowing for the differences of 0.4-0.5 units observed between tetrahedral and octahedral environments of the same ion, would place χ_{opt} (Os^{VIII}) for a six-coordinate complex at ca 2.5-2.6. On this basis using χ_{opt} (F) = 3.9 and χ_{opt} (O) = 3.2, the formula predicts (±2000 cm^{-1}) the lowest energy F → Os transition at ca 39000 cm^{-1} and O → Os at ca 19000 cm^{-1}, in good agreement with the observed spectrum.

The $M_2[OsO_4F_2]$ salts are extensively hydrolysed in water, and in a saturated solution the ^{19}F NMR spectra consist of a single line at ca -118 ppm (relative external $CFCl_3$) which is not significantly different from the spectrum of the alkali-fluorides. Griffith [5] has reported the Raman spectrum of $Cs_2[OsO_4F_2]$ in solution in the presence of excess CsF, which is in good agreement with our data on the solid, showing that the dissociation is suppressed by excess F^-.

The nature of the product obtained from CsF and OsO_4 in cold water, approximating to "$CsF.OsO_4$" is less clear, and it has not been obtained with an accurately reproducible composition. It is not a mixture of OsO_4 and $Cs_2[OsO_4F_2]$ since its IR spectrum contains only a weak band at 953 cm^{-1} due to OsO_4 (a minor impurity) and it lacks the two OsF stretches of the $[OsO_4F_2]^{2-}$ anion. The presence of at least three ν(OsO) stretches in the IR and Raman spectra suggests relatively low symmetry, and it may contain five-coordinate $[OsO_4F]^-$ similar to the $[OsO_4L]$ (L = pyridine or quinuclidine) [13].

$M[OsO_3F_3]$ (M = Cs, Rb, K)

The literature preparation [4] of this anion using BrF_3 produces a material which cannot be freed completely from bromine. Pure samples of all these salts were easily obtained by heating the powdered alkali fluoride with a slight excess of OsO_3F_2 in an evacuated ampoule, and subsequently subliming away the excess OsO_3F_2, leaving the pure $M[OsO_3F_3]$

as deep orange-yellow powders. A similar reaction with NaF produced a material which from its analysis and IR spectrum was a mixture of $Na[OsO_3F_3]$ and another (uncharacterised) fluoroanion. Lithium fluoride failed to form an $[OsO_3F_3]^-$ salt, reflecting the usual decreasing stability of fluoro anions with decreasing cation size. Barium fluoride reacted only superficially with OsO_3F_2 under similar conditions. Yagodin et al. [14] have recently prepared $M_2[ReO_3F_3]$ (M = Cs, Rb, K) from ReO_3F with 2MF, but found NaF gave a mixture of $NaReO_4$ and $Na_2[ReO_3F_3]$.

For the $[OsO_3F_3]^-$ ion either a fac (C_{3v}) or mer (C_{2v}) geometry is possible. The predicted vibrations are:

fac (C_{3v}) $\nu(OsO_3) = a_1 + e$, $\nu(OsF_3) = a_1 + e$, all IR + Raman active
mer (C_{2v}) $\nu(OsO_3) = 2a_1 + b_1$, $\nu(OsF_3) = 2a_1 + b_1$, all IR + Raman active.

Previous studies by Griffith [5] and Jezowska-Trzebiatowska [6] have favoured a fac isomer, although a recent study [15] of the isoelectronic $[ReO_3F_3]^{2-}$ assigned a mer geometry to the latter. Our data (Table) is in reasonable agreement with the published data [5,6] and supports a C_{3v} structure, although we suspect the reported OsO_3 stretch at 952 cm^{-1} is due to OsO_4 produced by hydrolysis.

The electronic spectrum of the $[OsO_3F_3]^-$ ion (Figure) is generally similar to that of $[OsO_4F_2]^{2-}$ as expected, although the relative intensities of the bands differ.

The $M[OsO_3F_3]$ are much more stable thermally than the $M_2[OsO_4F_2]$, and are only partially decomposed on heating at ca 250°C in vacuo for several hours. On exposure to moist air hydrolysis occurs quite rapidly, the IR spectra of partially hydrolysed materials showing bands characteristic of OsO_4 and MHF_2, and new bands at 850 and 810 cm^{-1} suggesting formation of a new oxo-osmium species. The complexes dissolve in cold water to form a yellow solution which decomposes on standing.

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