Magnetic Resonance Studies on Osmium Pentafluoride Oxide†

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Well resolved electron spin resonance spectra of $OsOF_5$ were obtained in WF_6, Freon 133a (CF_3CH_2Cl) and SO_2 at 77 K. Hyperfine coupling to ^{189}Os and to four equivalent fluorine atoms was measured, but no coupling to the axial fluorine was observed. From analysis of the spin-Hamiltonian parameters it was concluded that ca. 11.5% of the unpaired electron was delocalised from the osmium d_{xy} orbital on to each equatorial fluorine atom. The results were compared with newly calculated data for $[MOF_5]^{2-}$ (M = Cr, Mo or W) and $[ReOF_5]^-$. The anisotropic parameter P for Os^{VII} was calculated to be 0.0326 cm^{-1}.

Osmium pentafluoride oxide ($OsOF_5$) is one of a limited number of stable neutral transition-metal(VII) species, and has been extensively studied. A single-crystal X-ray structure analysis [1] has confirmed that it adopts the expected distorted-octahedral structure, akin to that found in the platinum metal hexafluorides. IR and Raman data for the vapour [2,3] and for the solid isolated in inert-gas matrices [4] has allowed normal coordinate analysis,[2] force constant[5] and thermodynamic functions[6] to be calculated. The compound obeys the Curie–Weiss law with $\mu_{eff} = 1.47$ at 298 K and 1.49 at 78 K.[7] Its electronic spectrum as a cold solid and isolated in a nitrogen matrix[4] is satisfactorily assigned[8] using the optical electronegativity model for a C_{4v} molecule with the expected ground state $[Xe]5d_{xy}^1$. A single broad line in the ^{19}F NMR spectrum of $OsOF_5$ in a tungsten hexafluoride solution[9] has been assigned to the *trans*-fluoride, it having been argued, incorrectly, that since the unpaired electron is localised in the plane of the *cis*-fluoride it has no influence upon the spectrum of the *trans*-fluoride.

We have shown[10] that electron spin resonance spectroscopy is the technique of choice for characterising paramagnetic fluorides in solution, from which the bonding coefficients of the molecular orbitals of the isoelectronic and isostructural $[ReOF_5]^-$ have been calculated. In this paper, we report the ^{19}F NMR and ESR spectra for $OsOF_5$ in a variety of solvents at various temperatures allowing, for the first time, the molecular orbitals of this metal(VII) compound to be described.

Experimental

Osmium pentafluoride oxide was prepared by the literature route from OsF_6 and OsO_4 at 473 K in a Monel autoclave.[4] Chloro-2,2,2-trifluoroethane [Freon 133a, CF_3CH_2Cl (ICI)] was dried by distillation on to previously dried 4A molecular sieves. Tungsten hexafluoride (Fluorochem) was condensed and allowed to stand for 16 h on dry KF to remove all traces of HF.

Samples for ^{19}F NMR spectroscopy were prepared by condensing $OsOF_5$ and the solvent into prefluorinated FEP tubes (outside diameter 4 mm, inside diameter 3 mm), heat sealing the tubes under vacuum and placing them in precision glass NMR tubes (outside diameter 5 mm) with a small quantity of $[^2H_6]$acetone for locking. Samples for X-band ESR spectroscopy were prepared by vacuum transfer of $OsOF_5$ (0.15 mg, 0.5 μmol) and solvent (≈0.5 cm^3) into prefluorinated FEP tubes (outside diameter 4 mm) fitted with a poly(tetrafluoroethyl-

ene) valve (Production Techniques, Fleet, Hampshire; STD/VC-4P). Samples for Q-band ESR spectroscopy were loaded in a similar manner into drawn ESR-grade quartz capillaries, prepassivated with fluorine and ClF_3, and sealed using a microburner. All samples were then stored at 77 K before spectra were recorded.

The ^{19}F NMR spectra were recorded on a Bruker AM300 spectrometer at 282.13 MHz, Q- and X-band ESR spectra on Bruker ER 200D instruments with facilities for variable-temperature control. Spectra were standardised with a sample of diphenylpicrylhydrazyl (dpph).

Results and Discussion

We have shown that whilst $OsOF_5$ reacts with a number of standard solvents,[11] it dissolves, without reaction, in Freon 133a, WF_6, IF_5, SO_2 and HF. This range of solvents has allowed us to investigate the magnetic properties of this unique inorganic fluoride over a wide temperature range.

^{19}F *NMR Studies.*—Contrary to previous work[9] we could not observe any ^{19}F NMR signals assignable to $OsOF_5$ in HF or WF_6 solutions in the range δ +5000 to −2000. A re-examination of this earlier paper, taking into account current sign conventions with $CFCl_3$ as zero reference, places the peak assigned to the *trans*-fluoride of $OsOF_5$ at δ 55. The compound WOF_4 has been shown[12] to give a single ^{19}F NMR resonance at δ 65 in propylene carbonate solution, and we feel that the broad line observed for $OsOF_5$ in WF_6 may, alternatively, be assigned to a trace amount of WOF_4 in the sample of WF_6 used, presumably arising due to a small amount of hydrolysis.

ESR Studies.—Well resolved ESR spectra of $OsOF_5$ were obtained in WF_6, Freon 133a and SO_2 at 77 K. In fluid solution at higher temperatures only a broad single line with no hyperfine features was observed. The low-temperature spectra could be readily interpreted in terms of hyperfine coupling to ^{189}Os (16.1%, $I = \frac{3}{2}$) and to four equivalent ^{19}F atoms, each superimposed on three g features, g_z, g_x and g_y. The values of g_x and g_y were close and, to a first approximation, the spectrum could be described as having arisen from a molecule with axial symmetry with a slight rhombic distortion in the xy plane. As expected for a strongly axially symmetric molecule like $OsOF_5$ (C_{4v}), the unpaired electron was in the $d_{xy}(b_2)$ orbital. No hyperfine coupling to the axial fluoride could be detected. The values of g and analysis of the ^{189}Os hyperfine tensor (see below) confirmed this. Typical spectra are shown in Figs. 1–3. All spectra exhibited a signal at $g = 2$ arising from an organic

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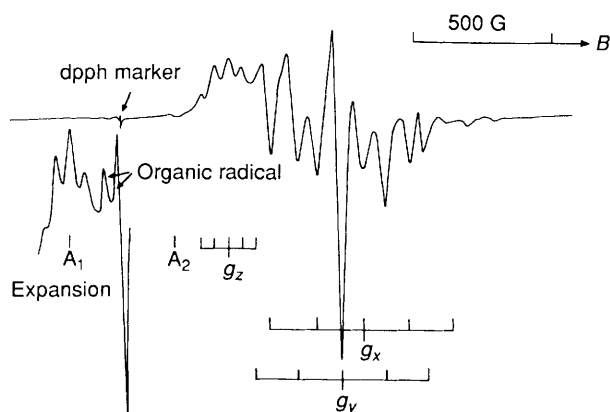† *Non-SI unit employed:* G = 10^{-4} T.

Fig. 1 X-Band ESR spectrum of $OsOF_5$ in WF_6 at 77 K. The stick diagram shows each g feature with a 1:4:6:4:1 quintet of lines due to four equivalent fluorides; A_1 and A_2 are the centres of quintets on the ^{189}Os $M_I = \frac{3}{2}$ and $\frac{1}{2}$ lines
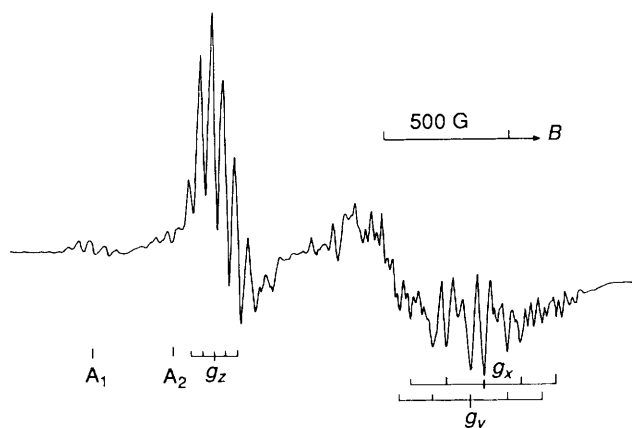

Fig. 2 Q-Band ESR spectrum of $OsOF_5$ in Freon 133a. Details as in Fig. 1
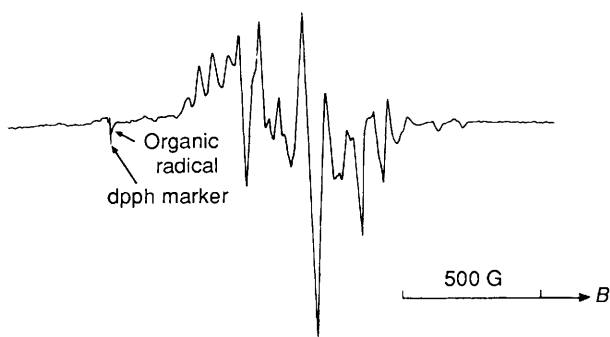

Fig. 3 X-Band ESR spectrum of $OsOF_5$ in Freon 133a at 77 K

radical generated during the preparation of the FEP sample tubes. In Figs. 1–3 stick diagrams are presented to show the analysis of the spectra. Computer simulations were carried out but, since quadrupole interactions to the ^{189}Os nucleus could not be readily accommodated, an exact simulation could not be accomplished. Despite this the computer simulation successfully reproduced line positions, so good values for the g and hyperfine tensors could be obtained. The resultant ESR parameters are given in Table 1 together with those for the related d^1 complexes $[CrOF_5]^{2-}$, $[MoOF_5]^{2-}$, $[WOF_5]^{2-}$ and $[ReOF_5]^-$.

Bonding Parameters.—Attempts were made to determine molecular orbital bonding parameters using the equations given by Manoharan and Rogers[14] as used by us for $[ReOF_5]^-$.[10] There is only one report in the literature of the electronic
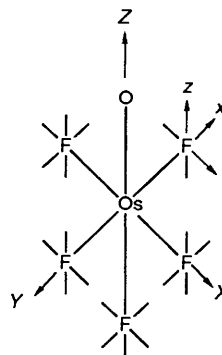

Fig. 4 Molecular axis notation (X,Y,Z) for $OsOF_5$ and local axes at fluorine (x,y,z)

spectrum of $OsOF_5$[4] by the matrix-isolation technique, in which only two d–d transitions (20 500 and 21 700 cm^{-1}) were observed. By comparison with data for the isoelectronic $[ReOF_5]^-$, it is likely that these bands are due to the second $(b_2 \longrightarrow b_1)$ and third $(b_2 \longrightarrow a_1)$ electronic transitions. Therefore, without values for the first d–d transition, there is insufficient information to deduce bonding parameters.

^{19}F *Superhyperfine Coupling.*—The well resolved superhyperfine coupling to four equivalent fluorine atoms showed that couplings on g_x and g_y were slightly different. This slight distortion in the xy plane is surprising for this type of molecule, but appears to occur in the single-crystal structure where two slightly different equatorial Os–F distances were measured.[1]

Analysis of the experimental couplings is complicated by not knowing their signs (+ or −). There are thus eight combinations of A_x, A_y and A_z each + or −. However, half can be eliminated since the average A_{iso} must be positive because real unpaired electron spin density reaches the fluorine directly. Table 2 summarises those combinations resulting in positive A_{iso}, and includes calculated values of the anisotropic hyperfine tensor A_{xx}, A_{yy}, A_{zz} and spin density in the p_y orbital on fluorine.

In order to deduce which set of values is correct we need to make a comparison with the predicted values of the tensor. Fig. 4 depicts the axis notation for the molecule, where X, Y and Z are the directions of the g and ^{189}Os hyperfine tensor and coincide with the molecular axes, and x, y and z are the local axes of each equatorial fluorine atom. In each case, the x axis is the Os–F σ-bond direction, the y axis the in-plane π-bond direction and the z axis is perpendicular to the xy plane of bonding. The form of the tensor has been described by Rogers and Whiffen[15] for the α-F tensor in the $O_2C\dot{C}FCF_2CO_2$ radical; the argument for $OsOF_5$ is the same. The in-plane π bonding would cause a direct dipolar hyperfine coupling and result in a positive hyperfine tensor component in the y direction. The unpaired electron in the d_{xy} orbital would polarise the Os–F σ bond and cause a negative hyperfine tensor component in the x direction. Coupling in the z direction would be very small (either + or −) because the p_z orbital would be in the nodal plane of the unpaired electron.

Only two combinations of signs (second and fourth rows in Table 2) satisfy the criteria of a large positive, large negative and a small hyperfine tensor, with values of either 150 or 144 G as the positive tensor component associated with in-plane π bonding. Since the expected value for an electron entirely in a p orbital on F is 1257 G,[16] then these represent spin densities of 11.9 and 11.5% respectively. Further support for choosing these two sets of tensors is that the calculated isotropic coupling is small, *viz.* 20 and 10 G respectively, rather than 123 and 93 G for the other pair of tensors. In the case of $[ReOF_5]^-$ the calculated value was only 19 G, while experimental values of A_{iso} (^{19}F) for other fluoride complexes do not exceed 11 G. The corresponding spin density for $OsOF_5$ in Freon 133a is 11.0%.

Table 1 ESR spin-Hamiltonian parameters for metal oxide pentafluorides

	[CrOF$_5$]$^{2-}$	[MoOF$_5$]$^{2-}$	[WOF$_5$]$^{2-}$	[ReOF$_5$]$^-$	OsOF$_5$ In WF$_6$	In Freon 133a
$g_\parallel$	1.959	1.894	1.555	1.72	1.805	1.817
$g_\perp$	1.969	1.913	1.685	1.74	1.597/1.633	1.681/1.688
$10^4 A_\parallel$(M)/cm^{-1}	40.7	90.1	161	960	132	277
$10^4 A_\perp$(M)/cm^{-1}	11.9	42.5	94	500	157/160	129/130
$10^4 A_{av}$(M)/cm^{-1}	21.5	58.4	116	653	209	179
$10^4 A_{an}$(M)/cm^{-1}	19	32	45	307	103	98
A_x(F$_{eq}$)/G	−17.9	−19.8	−30.5	}±45	170	155
A_y(F$_{eq}$)/G	37.5	57.6	54.6	}	154	150
A_z(F$_{eq}$)/G	−6.8	−4.4	−16.3	−33	45	45
$A_\parallel$(F$_{ax}$)/G	3.4	—	—	—	—	—
Ref.	13	13	13	10	This work	This work

Table 2 Possible combinations of signs for the observed hyperfine coupling (G) to ^{19}F which shows positive values of A_{av} for OsOF$_5$ in WF$_6$ and Freon 133a, and the deduced tensors and spin densities

Solvent	Observed hyperfine splitting A_x	A_y	A_z	Calculated A_{av}	Deduced hyperfine tensor A_{xx}	A_{yy}	A_{zz}	Spin density ρ_π (%)
WF$_6$	170	154	45	123	47	31	−78	—
	170	−154	45	20	150	−174	25	11.9
	170	154	−45	93	77	61	−138	—
	−170	154	45	10	−180	144	35	11.5
Freon 133a	155	150	45	117	38	33	−72	—
	155	−150	45	17	138	−167	28	11.0
	155	150	−45	87	68	63	−132	—
	−155	150	45	13	−168	137	32	11.0

Table 3 Observed hyperfine couplings (G) for other metal oxide pentafluorides, and deduced tensors and spin densities

Compound	Observed hyperfine splitting A_x	A_y	A_z	A_{av}	Deduced hyperfine tensor A_{xx}	A_{yy}	A_{zz}	Spin density ρ_π (%)	Ref.
[CrOF$_5$]$^{2-}$	−17.9	37.5	−6.8	4.3	−22.2	33.2	−11.2	2.6	13
[MoOF$_5$]$^{2-}$	−19.8	57.6	−4.4	11.1	−30.9	46.5	−15.5	3.7	13
[WOF$_5$]$^{2-}$	−30.5	54.6	−16.3	2.6	−33.1	52.0	−18.9	4.1	13
[ReOF$_5$]$^-$	average 45		33	—	—	—	—	8.5	10

Fluorine hyperfine couplings for [MOF$_5$]$^{2-}$ (M = Cr, Mo or W) have been measured by Van Kemenade.[13] They are analysed here for the first time, and the appropriate tensors and spin densities given in Table 3. The ^{19}F spin densities are 2.6, 3.7 and 4.1% for M = Cr, Mo and W respectively. This trend is as expected since both covalency and the overlap of progressively larger d orbitals with the fluorides increases as the group is descended. The other family [WOF$_5$]$^{2-}$, [ReOF$_5$]$^-$ and OsOF$_5$ have spin densities rapidly increasing in the order 4.1, 8.5 and 11–12%. Again, this trend is expected since the oxidation state changes from V to VII in the group and thus the fluorine atoms are held more tightly and closer, so that greater overlap of the 5d orbital with the fluorines causes progressively more delocalisation.

The axial fluorine. No interaction was observed with the axial fluorine atom. This is not surprising since there is neither mechanism for direct delocalisation of electron density nor much chance of the spin-polarisation mechanisms yielding hyperfine couplings large enough to be seen.

The osmium hyperfine tensor. The signs of the experimental hyperfine couplings to osmium are all taken to be negative since this is the only combination of signs which gives a negative isotropic hyperfine coupling, as almost always found for transition-metal ions, and a negative principal value of the anisotropic tensor, as expected for a b$_2$ ground state.[17] Calculated values for the anisotropic hyperfine tensor are given in Table 2 for OsOF$_5$ in WF$_6$ and Freon 133a.

For atoms where suitable wavefunctions are available values

can be calculated for the expected hyperfine coupling assuming 100% occupancy of a 5d orbital. Such values are available for the 3d and 4d ions in many electronic configurations,[18] but for osmium it is only known for the 5d^6 configuration (^{189}Os$^+$, 62 G). Since the value increases considerably as electrons are removed, then our value of 103 × 10^{-4} cm^{-1} for OsOF$_5$ in WF$_6$ is entirely reasonable. Unfortunately, without a reliable value for osmium in a d^1 configuration, we cannot estimate the electron population in the 5d$_{xy}$ orbital by this method.[19]

Since we know from the fluorine hyperfine tensor that there is ca. 11.5% delocalisation of the unpaired electron onto each of the four equatorial fluorides, this allows us to calculate an expectation value for the hyperfine coupling entirely in a 5d^1 orbital on osmium. Using 100.5 × 10^{-4} cm^{-1} as the average of principal values of the anisotropic hyperfine tensors (Table 1), then $P = 0.0326$ cm^{-1}.

The isotropic coupling to osmium is significantly larger in WF$_6$ solution (209 × 10^{-4} cm^{-1}) compared with Freon 133a (179 × 10^{-4} cm^{-1}), although the spin densities on osmium and fluorine are not significantly different. The larger value for OsOF$_5$ in WF$_6$ may be due to OsOF$_5$ isomorphously fitting snugly into the host lattice, whilst in the Freon the molecule fits loosely in a solvent cavity. The lattice pressure of WF$_6$ on OsOF$_5$ may cause the filled metal s orbitals to become slightly closer to the osmium nucleus with consequent larger polarisation of these electrons and larger coupling.

The g tensor. Although the slight rhombic distortion causes g_x and g_y to be slightly different, the gross symmetry of the OsOF$_5$
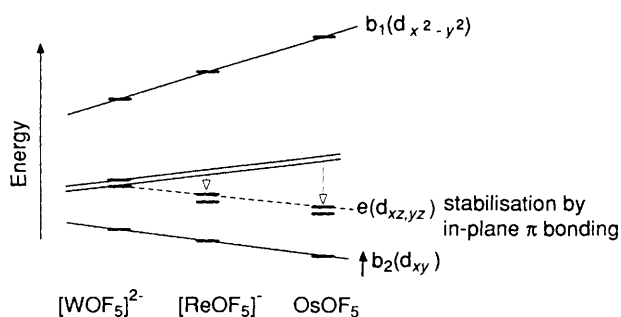
Fig. 5   Schematic representation of the relative energies of the b_2, e and b_1 orbitals in $[WOF_5]^{2-}$, $[ReOF_5]^-$ and $OsOF_5$

remains C_{4v}. The relative order of the molecular orbital energy levels is $b_2(d_{xy}) < e(d_{xz},d_{yz}) < b_1(d_{x^2-y^2}) < a_1(d_{z^2})$.

First-order perturbation theory predicts that $g_{\parallel} < g_{\perp} < 2$, and this is true for many d^1 pentahalide oxide ions. However, for some, notably those with chloride or bromide as the halide, $g_{\perp}$ and $g_{\parallel}$ are reversed. Manoharan and Rogers[14] have explained this in terms of a contribution to the g tensor by a spin–orbit interaction with ligands having a large spin–orbit parameter. In the case of $OsOF_5$, $g_{\parallel} > g_{\perp}$. It is unlikely that this reversal is the result of the spin–orbit interaction with fluoride ligands; more likely it is due to changes in the relative energies of the molecular orbitals. Within the series $[WOF_5]^{2-}$, $[ReOF_5]^-$ and $OsOF_5$, $g_{\parallel}$ increases, whilst $g_{\perp}$ increases from W to Re and then decreases. These relative values can be explained by the energy of each orbital as a function of (i) metal oxidation state and (ii) in-plane π bonding to equatorial fluorides.

As the charge increases, the molecular orbital energies diverge rapidly, as indicated in Fig. 5. First-order perturbation theory predicts expressions (1) and (2). The relative magnitude of $\Delta g_{\parallel}$

$$g_{\parallel} = g_0 - \frac{8\lambda}{\Delta E(b_2 - b_1)} \quad (1)$$

$$g_{\perp} = g_0 - \frac{2\lambda}{\Delta E(b_2 - e)} \quad (2)$$

and $\Delta g_{\perp}$ $(g - g_0)$ depends on the relative values of $8/\Delta E(b_2 - b_1)$ and $2/\Delta E(b_2 - e)$. As b_2 drops steadily, so e and b_1 rise rapidly. However, although e would rise steadily if there were no change in π bonding, in reality it is stabilised by the in-plane π bonding, as witnessed by the increase in electron delocalisation for M = W, Re, Os (ca. 16, 34, 46% respectively).

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