Electronic Wavefunctions and Solution Nuclear Magnetic Resonance Parameters of Some Mixed Fluorochloro-osmates(IV)

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The ^{19}F n.m.r. chemical shifts and spin–spin splitting parameters of some mixed fluorochloro-osmates(IV) have been measured in solution in various solvents and over a range of temperatures. The measured values have been analysed in terms of the electronic wavefunctions expected for the complexes. The analysis is facilitated by the preponderant effect of the first excited electronic state on their magnetic properties. Line broadening of ^{19}F n.m.r. resonances by *trans* but not by *cis* Cl atoms can thus be explained by electronic effects rather than interpositional exchange of the fluorine nuclei.

Late transition metals have interesting properties ranging from cluster formation[1] to unusual paramagnetism[2] to anti-cancer action.[3] It is therefore important to understand the chemical bonding in compounds of these metals. In principle, the nuclear shielding constant and thus the chemical shift, δ, and spin–spin coupling constants, J, of nuclear magnetic resonance give insights into chemical bonding; in practice they are often difficult to calculate, that is to relate to the electronic wavefunctions. That this is so can be readily seen by considering the theoretical expressions devised originally by Ramsey as discussed in, for example, Slichter's monograph on magnetic resonance.[4] This difficulty arises from the fact that both these effects are caused by the mixing of magnetic excited states into the ground electronic state, and so an infinite series of contributions occur. In general, approximations are necessary such as the average-energy assumption[5] but in special cases only a few low-lying excited states contribute significantly to the parameter in question. Such systems occur in co-ordination compounds, and the earlier study of paramagnetic transition-metal fluorides by Shulman and co-workers[6,7] demonstrated the power of the method. Other workers have occasionally used nuclear magnetic resonance[8–13] but more often electron paramagnetic resonance or electron nuclear double resonance (ENDOR) is used. The temperature-independent paramagnetic compounds are particular examples[14,15] of molecules whose chemical shift can be readily understood and calculated. Mixed-halogen complexes of osmium(IV) may be prepared[16] and give an opportunity for studying spin–spin splitting in such simple systems.[17] We report here such measurements with their theoretical analysis.

Experimental

Potassium hexafluoro-osmate(IV) was prepared by following Hepworth *et al.*,[18] and other materials were prepared as previously described[16] and solutions made up in deuterium oxide or deuteriated chloroform (Aldrich Chemical Co., used as supplied). N.m.r. spectra were measured at 188.5 MHz (National Institute for Medical Research Bruker WH200) or at 84.36 MHz (City of London Polytechnic, JEOL FX90). Concentrations of 10 mmol dm^{-3} were sufficient to give good signal intensity. A very wide (40 kHz) effective sweep width was necessary to encompass the large chemical shift range. Trifluoroacetic acid was used as an external standard.

Results and Discussion

The spectral parameters are summarised in the Table. Typical spectra are shown in Figure (*a*) and (*b*).

Although in simple terms these compounds have two unpaired electrons, the spectra are quite sharp, with well resolved $^{19}F-^{19}F$ couplings: this is as expected since the ground electronic state is non-magnetic[15] (the combined spin and orbital angular momentum is zero). The monochloro complex is notable for a broadened quintet in comparison to the doublet. On the other hand, the aqueous *cis*-$Cs_2[OsF_4Cl_2]$ shows a pair of sharp triplets. Since the chemical shift difference is much larger than the spin–spin coupling the spectra are all of AX_n, or first-order, type in contrast to spectra of analogous tin[19] and sulphur[20] compounds. The chemical shift is found to be temperature dependent and in the case of the caesium salt of *trans*-$[OsF_2Cl_4]^{2-}$ has a temperature coefficient of 250 Hz K^{-1}.

The magnitude of the spectral parameters can be explained in terms of a simple model. In cubic symmetry the spin and orbital motion of the electrons in the d^4 configuration of second- and third-row transition elements couple together (ζ_{4d}, ζ_{5d} are of the order of 10^3 cm^{-1}) to give a ground state which has A_1 symmetry (in Placzek's notation)[21] in spin-orbital product space, which corresponds to a total angular momentum vector, $J = 0$ in spherical symmetry. Such a state has no intrinsic magnetic properties, however in the presence of a magnetic field the first excited state (at energy of the order of 1 000 cm^{-1} above the ground state) will be admixed. Now the electronic orbitals contributing to these states are t_2 and contain some fluorine $2p_\pi$ character (with respect to the Os–F bond), *i.e.* they have electron density in the neighbourhood of fluorine nuclei and hence give rise to the large shifts of the ^{19}F resonance. Furthermore, a given t_2 orbital contains contributions from $2p_\pi$

Table. N.m.r. spectral parameters for complexes

Complex	^{19}F Chemical shift δ (p.p.m.)*	^{19}F Spin–spin coupling constant (Hz)	Linewidth $\Delta\nu_{\frac{1}{2}}$/Hz
$K_2[OsF_6]$	1 273.8	(245.7 for ^{187}Os–F)	1.5
$Cs_2[OsF_5Cl]$	F(a) 1 153	138	18.9
	F(e) 1 355		11.6
cis-$Cs_2[OsF_4Cl_2]$	F(t) 1 199.9	136.7	15
	F(c) 1 556.5		10
fac-$Cs_2[OsF_3Cl_3]$	1 308	—	15
trans-$Cs_2[OsF_2Cl_4]$	1 900	—	17
$[NBu_4]_2[OsF_5Cl]$	F(a) 1 245	160	13
	F(e) 1 424		6
fac-$[NBu_4]_2[OsF_3Cl_3]$	1 523	—	16

* a implies axial fluorine atom, e implies equatorial fluorine atom, t implies the fluorine atom which is *trans* with respect to the chlorine, and c implies the fluorine atom which is *cis* with respect to the chlorine.

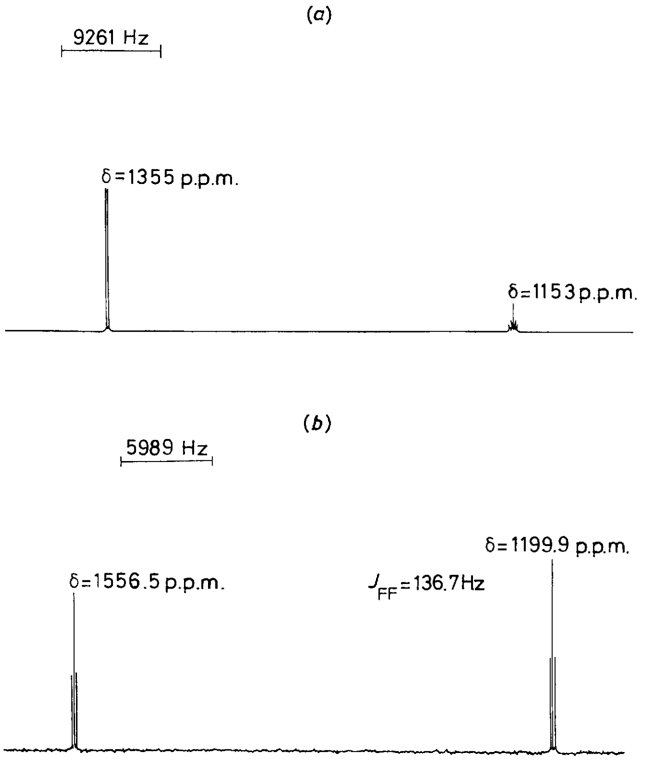

Figure. Fluorine-19 n.m.r. spectra for aqueous solutions at room temperature of (*a*) $Cs_2[OsF_5Cl]$ (188.5 MHz) and (*b*) *cis*-$Cs_2[OsF_4Cl_2]$ (84.36 MHz). Reference CF_3CO_2H

orbitals of more than one ligand, and this enables coupling of two inequivalent fluorine nuclei as seen in the spectra presented here.

A possible, although from the chemical considerations, unlikely explanation of the broadening of the axial ^{19}F multiplet is the occurrence of rapid intramolecular positional exchange of equatorial and axial fluorine atoms, as Muetterties *et al.*[22] concluded in explaining similar broadening seen in the ^{19}F n.m.r. spectra of PF_5 and SF_5Cl. The fluorine nucleus may exchange at a rate which is fast in comparison to the inverse of the linewidth associated with the n.m.r. measurements. This interpretation might be favoured in view of the fact that the broadening increases with temperature. This possibility was tested by doing a ^{19}F-{^{19}F} double-resonance experiment, where saturation of one of the two resonances would have produced a decrease in the intensity of the other resonance in the case of intramolecular exchange in the molecule, but no change in the intensity, as expected if the molecule is static, was found. The intramolecular exchange process is unlikely, then, to be the explanation of the broadening seen in the resonance line of the axial fluorine atom of $[OsF_5Cl]^{2-}$.

Should chlorine nuclei, which possess a quadrupole, be present then coupling of the fluorine to the chlorine can give rise to broadening. The details of the coupling depend on whether the chlorine is *cis* or *trans* to the fluorine since the $2p_\pi$ orbitals enter, differently, the integrals hidden in the coupling constant J. Detailed calculations,[17] outlined below, indicate that this is the origin of the broadening of the quintet in the $[OsF_5Cl]^{2-}$ spectrum: the chlorine is strongly coupled to the *trans* fluorine but not to the *cis* fluorine and its quadrupole relaxation gives rise to broadening.

The model explains why such broadening increases with temperature. The chlorine nucleus relaxes more slowly at higher temperatures and is moving from the fast relaxation (decoupled) limit to a slower regime. This effect can be seen by considering the effect of the chlorine relaxation or coupling as a scalar relaxation of the second kind[23] for the ^{19}F nucleus. Increasing the temperature will, then, lead to an increase in the longitudinal relaxation time of the chlorine nucleus and hence an increase in the correlation time governing scalar relaxation.

Calculation of nuclear spin–spin coupling may be carried out within the ligand-field model using second-order perturbation theory.[24] In principle the electron orbital–nuclear spin, dipolar electron–nuclear spin, and the Fermi interactions can give rise to the required couplings. The latter are not so important as in Ramsey's original calculation on HD; the unpaired spins in these complexes give a large effect *via* the dipolar coupling since they occupy t_{2g} orbitals which, within the linear combination of atomic orbitals (LCAO) picture, include p orbitals on the two coupled fluorine nuclei. The Fermi term would operate through core polarisation and the t_{2g} orbitals or *via* the s content of the e_g orbitals, which are fully occupied. Both effects will be small, and are difficult to calculate precisely.

The orbital and spin dipolar mediated couplings have been calculated by expansion of the operators into one-electron form, use of Slater determinant functions describing the T_1 (first excited) and A_1 (ground) states, and expansion of the t_{2g} elements of the determinants as LCAO involving fluorine $2p$ orbitals.

The bonding coefficients in the LCAO may be deduced from the nuclear shielding measurements[15] and indicate about 1% electron transfer between osmium and fluorine. Using the value so deduced, the value of J may be deduced, and after spherical averaging is found to be of the order of 130 Hz for the $[OsF_5Cl]^{2-}$ complexes, in good agreement with experiment. Further as pointed out above, *trans* coupling is found to be greater than *cis*. Although this is common in transition-metal complexes, it is not always so.[25] Furthermore, we know of no explicit calculation of this effect.

The temperature dependence of the shifts can be explained by considering the averaging implied in the spin-Hamiltonian parameters σ and J since the n.m.r. time-scale is long compared to electronic and vibrational states. At higher temperatures the higher vibrational sites are more populated and these have a different averaging effect. Since the electronic T_1 state and the vibrational states are coupled a change in temperature will lead to a change in δ. It has been suggested that this explanation [which other workers have also put forward for cobalt(III) complexes] is not in accordance with the Franck–Condon principle. We would point out that no vibrational energy change is implied during the n.m.r. observation. Since internuclear distance affects the energy separation of the A_1 and T_1 states, a given δ would be observed which would change as the nuclei moved during vibration, but not during the actual vibrational transition, assuming the Franck–Condon principle. Since vibration is rapid, a 'fast exchange' type of averaging of the n.m.r. spectrum occurs and only one resonance is observed. It would be interesting to irradiate the solution with a far-i.r. laser during the n.m.r. measurement since excitation of the vibrational levels should, according to our explanation, give rise to a change in chemical shift.

The solution spectrum of $K_2[OsF_6]$ at high amplification shows a doublet forming wings about the central peak which we ascribe to the species $[^{187}OsF_6]^{2-}$. Although ^{189}Os ($I = \frac{3}{2}$) is 16% abundant [*cf.* ^{187}Os ($I = \frac{1}{2}$), 1.6% abundant] it seems reasonable that no hint of the $[^{189}OsF_6]^{2-}$ is present as the quadrupole moment of the $I = \frac{3}{2}$ nucleus is extremely large and so that nucleus is probably relaxing so fast as not to give a spin–spin splitting. Some comment should be made on the solid-state spectra.[15,17,26] Although the shifts in solution are large and thus would not be masked by dipolar broadening in the solid, the shift anisotropies are also large and lead to complicated spectra even for the hexafluoro complex. Assuming an axial nuclear shielding tensor, σ, we obtain $\sigma = 1\ 500$ p.p.m. (± 10 p.p.m.) and $\sigma_\perp$ 700 p.p.m., the solid-state derivative spectrum being treated analogously to an electron paramagnetic resonance spectrum (with axial g tensors) of a powder. Thus $\sigma_{av.} = \frac{1}{3}(2\sigma_\perp + \sigma) = 1\ 000$ which is a little less than the solution value, but much less accurately determined.

Finally, we have prepared tris (oxalato) complexes of Os^{IV} and measured the ^{13}C n.m.r. spectra in solution. Quite small shifts are observed, so it seems that transmission of the osmium paramagnetism through two bonds is much less than through one, but this is complicated by the change in energy separation of the A_1 and T_1 states.

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