A ^{51}V and ^{19}F N.M.R. Study of Vanadium(V) Oxide Fluoride Complexes displaying Vanadium–Fluorine Coupling

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The complexes $VOCl_{(4-x)}F_x^-$ (x = 1,2,3,4), VO_2ClF^-, $VOF_3(NO_3)^-$, $VOF_2(NO_3)$, and $VOF(NO_3)_2$ have been characterised in organic solvents (MeCN, $MeNO_2$, $CDCl_3$) by their ^{51}V and ^{19}F n.m.r. chemical shifts and coupling constants.

Examples of vanadium(V) complexes displaying ^{51}V–^{19}F coupling (^{51}V, I = 7/2) are surprisingly rare. In addition the nature of the vanadium(V) species formed in aqueous[1,2] and anhydrous HF[2] has been the subject of some controversy. It was originally formulated as VOF_4^- but Gillespie and Rao[3] have argued that it is in fact $VO_2F_4^{3-}$. Gillespie and Rao have also suggested that hydrolysis of VOF_4^- to $VO_2F_4^{3-}$ occurs in aqueous environments and that VOF_4^- can only exist in an H_2O free system. In the present work the species VOF_4^- has been generated in organic solvents (MeCN, $MeNO_2$, and $CDCl_3$) by addition of Et_4NCl to solutions of VOF_3; the species $VOCl_{(4-x)}F_x^-$ (x = 1 to 3) are also generated (Table 1). The ^{51}V n.m.r. spectrum of VOF_4^- is a well resolved binomial quintet (δ_V −797 p.p.m., $^1J_{V-F}$ 86 Hz) which is unequivocal evidence for a species with four fluorine atoms. Unlike $VO_2F_4^{3-}$ the coupling in VOF_4^- is also observed in the ^{19}F n.m.r. spectrum, which is a well resolved octet. The n.m.r. parameters recorded in Table 1 were obtained for solutions in MeCN but the n.m.r. data were essentially independent of the medium used.

This observed solvent independence invalidates the conclusions of Buslaev and coworkers[4] who claimed to have produced the octahedral species $VOCl_{(4-x)}F_xMeCN^-$ (x = 1 to 4) by addition of KF or HF to solutions of $VOCl_3$ in MeCN. The ^{51}V n.m.r. shifts for the $VOCl_{(4-x)}F_x^-$ (x = 1 to 3) series reported here differ considerably from those reported by Buslaev and coworkers[4] who failed to observe vanadium–fluoride couplings and conducted no ^{19}F n.m.r. studies. The characterisation of VOF_4^-, with different n.m.r. parameters to the species present in HF,[1—3] lends support to the conclusions of Gillespie and Rao.[3]

The assignment of the resonance at δ_V + 43 p.p.m. (Table 1) to $VOCl_4^-$ was established in separate experiments in which Et_4NCl was progressively added to solutions of $VOCl_3$ in MeCN. When less than the stoicheiometric amount of Et_4NCl was added a broad ^{51}V n.m.r. resonance intermediate

Table 1. ^{51}V and ^{19}F n.m.r. parameters for $VOCl_{4-x}F_x^-$, $VOF_3(NO_3)^-$, $VOF_2(NO_3)$, and $VOF(NO_3)_2$ in MeCN.

	^{51}V[a]			^{19}F[b]		
Species	Multiplicity	δ/p.p.m.	$^1J_{V-F}$/Hz	Multiplicity	δ/p.p.m.	$^1J_{V-F}$/Hz
VOF_4^-	Quintet	−797	86	Octet	129.2	88
$VOClF_3^-$	Quintet[c]	−641	99,49		150.8,178.9[d]	[e]
$VOCl_2F_2^-$ [f]	[g]	−474		[g]	222.0	
$VOCl_2F_2^-$ [f]	Triplet	−424	60	Octet	191.3	62
$VOCl_3F^-$	Doublet	−209	24	[g]	227.5	
$VOCl_4^-$	Singlet	+43				
$VOF_3(NO_3)^-$	Quintet[c]	−778	140,71	[g]	172.5,163.8[d]	
$VOF_2(NO_3)$	Triplet	−759	125	[g]	276.3	
$VOF(NO_3)_2$	Doublet[h]	−826	80	[g]	250.1	

[a] ^{51}V Spectra referenced to external $VOCl_3$. [b] ^{19}F Spectra referenced to external $CFCl_3$. [c] 1:2:2:2:1 Quintet analysed as overlapping doublet of triplets. [d] Area ratio of 1:2. [e] Multiplets showing both vanadium–fluorine and fluorine–fluorine coupling. [f] Two isomers of $VOCl_2F_2^-$ observed. [g] Coupling not resolved. [h] Using resolution enhancement natural linewidth 195 Hz.

in shift between $VOCl_3{\cdot}2MeCN$ (δ_V −114 p.p.m.)[4] and $VOCl_4^-$ was observed; when the $Et_4NCl : VOCl_3$ ratio was increased to unity and beyond the shift remained constant at +43 p.p.m.

To avoid any assignment ambiguities due to the reaction of residual H_2O in the solvents used, H_2O was deliberately added to MeCN solutions containing the $VOCl_{(4-x)}F_x^-$ series. Three extra ^{51}V n.m.r. resonances were produced. The extra resonances were assigned to $VO_2Cl_2^-$, $VO_2ClF,^-$ and $VO_2F_2^-$ on the basis of n.m.r. measurements for $Ph_4AsVO_2Cl_2$ [5] (δ_V −364 p.p.m.), $Ph_4AsVO_2F_2$ [5] (triplet, δ_V −595 p.p.m., $^1J_{V-F}$ 272 Hz), and a mixture of the two in MeCN. The ^{51}V n.m.r. spectrum of the mixture of $VO_2Cl_2^-$ and $VO_2F_2^-$ contained an additional resonance, a doublet, (δ_V −485 p.p.m., $^1J_{V-F}$ 207 Hz) assignable to the previously unreported VO_2ClF^-.

$VOF_3(NO_3)^-$ is produced by the addition of MNO_3 ($M = Me_4N^+, Et_4N^+, PhCH_2Ph_3P^+$) to solutions of VOF_3 in MeCN or $MeNO_2$. The neutral mixed fluoride nitrates are formed by mixing MeCN solutions of VOF_3 and $VO(NO_3)_3$. These species are the first examples of neutral complexes displaying vanadium–fluorine coupling, although the doublet structure of $VOF(NO_3)_2$ is only observed using resolution enhancement techniques. $VOF_3(NO_3)^-$, $VOF_2(NO_3)$, and $VOF(NO_3)_2$ are also noteworthy as rare examples of complexes containing both fluoride and nitrate.

$VOF_3(NO_3)^-$ and $VOClF_3^-$ have temperature dependent ^{51}V n.m.r. spectra which are 1:2:2:2:1 quintets below 273 K and unsymmetrical quartets at room temperature, indicating intramolecular fluorine exchange. At 253 K the ^{19}F n.m.r. spectrum of $VOClF_3^-$ consists of two multiplets (δ_F 150.8 and 178.9 p.p.m.) each of which has more than eight components indicating fluorine–fluorine as well as vanadium–fluorine coupling. Analysis of the 150.8 p.p.m. multiplet as an overlapping octet of triplets gives a value for $^2J_{F-F}$ of *ca.* 100 Hz.

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