Vanadium(V) Fluoride Complexes in Organic Solvents. A Vanadium-51 and Fluorine-19 Nuclear Magnetic Resonance Study

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The complexes $[\mathrm{VOCl}_{(4-n)}\mathrm{F}_n]^-$ (n = 1—4), $[\mathrm{VO(CF_3CO_2)}_{(4-n)}\mathrm{F}_n]^-$ (n = 1—3), $[\mathrm{VOF_3(NO_3)}]^-$, $[\mathrm{VOF_3(MeSO_3)}]^-$, $[\mathrm{VO_2ClF}]^-$, $[\mathrm{VOF_3(bipy)}]$ (bipy = 2,2'-bipyridine), $[\mathrm{VOF_3(phen)}]$ (phen = 1,10-phenanthroline), $\mathrm{VOCl_2F}{\cdot}n\mathrm{MeCN}$, and $\mathrm{VOClF_2}{\cdot}n\mathrm{MeCN}$ have been characterised in organic solvents by ^{51}V and ^{19}F n.m.r. spectroscopy. Most of the fluoro complexes display vanadium–fluorine coupling, the magnitude of which depends upon the degree of covalency of the vanadium–fluorine bond. Two isomers of $[\mathrm{VOCl_2F_2}]^-$ and $[\mathrm{VO(CF_3CO_2)_2F_2}]^-$ were observed indicating a square-pyramidal geometry for these anions. $[\mathrm{VOF_3(NO_3)}]^-$, $[\mathrm{VOF_3(bipy)}]$, and $[\mathrm{VOF_3(phen)}]$ are probably pseudo-octahedral. All the $[\mathrm{VOF_3X}]^-$ (X = Cl, $\mathrm{CF_3CO_2}$, $\mathrm{NO_3}$, or $\mathrm{MeSO_3}$) anions show fluxional behaviour.

Vanadium-51 is a favourable nucleus ($I = \frac{7}{2}$) for n.m.r. observation because of its high sensitivity and modest quadrupole moment. Vanadium-51 n.m.r. spectroscopy has therefore been extensively applied to the study of the aqueous chemistry of vanadium(V).[1] More recently, the non-aqueous chemistry of some vanadium(V) oxo complexes[2,3] has been examined by ^{51}V n.m.r., including a preliminary account of some of the species reported in this paper.[2]

In aqueous systems, vanadium–fluorine coupling is difficult to observe probably due to rapid fluoride exchange with free HF in solution. The only complex which appears to show well resolved coupling in such media is $[\mathrm{VO_2F_4}]^{3-}$.[4] The present work demonstrates the advantages of using organic solvents, over aqueous media, in which a range of new complexes displaying vanadium–fluorine coupling have been prepared and characterised.

Experimental

N.m.r. spectra were obtained in the Fourier transform mode on either a Bruker WM 250 spectrometer operating at 65.79 (^{51}V) and 235.39 MHz (^{19}F) or a Bruker WH 400 spectrometer operating at 105.12 MHz (^{51}V). Vanadium shifts were referred to external $\mathrm{VOCl_3}$ and fluorine shifts to external $\mathrm{CFCl_3}$. Vanadium-51 and ^{19}F spectra, of 0.1—0.01 mol kg^{-1} solutions, required between 1 000 and 10 000 transients at *ca.* 5 per second. Resolution enhancement was carried out by applying a Gaussian function and a suitable negative line broadening to the free induction decay.

2,2'-Bipyridine (bipy), 1,10-phenanthroline (phen), $[\mathrm{NBu_4}]\mathrm{F}{\cdot}2\mathrm{H_2O}$, $\mathrm{VOF_3}$, $\mathrm{VOCl_3}$, and trifluoroacetic anhydride (Aldrich) were used without further purification. $[\mathrm{AsPh_4}][\mathrm{VO_2Cl_2}]$, $[\mathrm{NBu_4}][\mathrm{VO_2Cl_2}]$, and $[\mathrm{AsPh_4}][\mathrm{VO_2F_2}]$ were prepared by literature methods.[5] Vanadium-51 n.m.r. spectroscopy indicated that $[\mathrm{AsPh_4}][\mathrm{VO_2F_2}]$ always contained some $[\mathrm{VOF_4}]^-$ impurity. $[\mathrm{NEt_4}]\mathrm{Cl}$ and $[\mathrm{NEt_4}]\mathrm{NO_3}$ (Fluka) were rigorously dehydrated in vacuum before use. $[\mathrm{NEt_4}][\mathrm{CF_3CO_2}]$ and $[\mathrm{NEt_4}][\mathrm{MeSO_3}]$ were prepared by neutralisation of 20% $[\mathrm{NEt_4}]\mathrm{OH}$ with the parent acid and then removal of all volatiles in vacuum. Acetonitrile was dried over molecular sieve (type 4A), refluxed with $\mathrm{CaH_2}$ and fractionated before use. Nitromethane and dichloromethane were dried over molecular sieve (type 4A) and fractionated before use. All deuteriated solvents were dried over molecular sieve prior to use. The handling of all moisture-sensitive reagents was carried out inside a dry-box.

Results and Discussion

Reactions employed are outlined in the Scheme.

$$\mathrm{VOF_3} + [\mathrm{NEt_4}]\mathrm{Cl} \longrightarrow [\mathrm{VOCl}_{(4-n)}\mathrm{F}_n]^-\ (n = 1\text{—}4) \qquad \text{(i)}$$

$$\mathrm{VOCl_3} + [\mathrm{NEt_4}]\mathrm{Cl} \longrightarrow [\mathrm{VOCl_4}]^- \qquad \text{(ii)}$$

$$[\mathrm{VO_2F_2}]^- + [\mathrm{VO_2Cl_2}]^- \longrightarrow [\mathrm{VO_2ClF}]^- \qquad \text{(iii)}$$

$$[\mathrm{VO_2F_2}]^- + \mathrm{(CF_3CO)_2O} \longrightarrow [\mathrm{VO(CF_3CO_2)}_{(4-n)}\mathrm{F}_n]^-\ (n = 1\text{—}3) \qquad \text{(iv)}$$

$$\mathrm{VOF_3} + [\mathrm{NEt_4}][\mathrm{CF_3CO_2}] \longrightarrow [\mathrm{VO(CF_3CO_2)F_3}]^- \qquad \text{(v)}$$

$$\mathrm{VOF_3} + [\mathrm{NEt_4}]\mathrm{X} \longrightarrow [\mathrm{VOF_3X}]^-\ (\mathrm{X} = \mathrm{NO_3}\text{ or }\mathrm{MeSO_3}) \qquad \text{(vi)}$$

$$\mathrm{VOF_3} + \overset{\frown}{\mathrm{N\,N}} \longrightarrow \left(\begin{smallmatrix}\mathrm{N}\\ \mathrm{N}\end{smallmatrix}\right>\mathrm{VOF_3}\ (\overset{\frown}{\mathrm{N\,N}} = \text{bipy or phen}) \qquad \text{(vii)}$$

$$\mathrm{VOF_3} + \mathrm{VOCl_3} \longrightarrow \mathrm{VOCl}_{(3-n)}\mathrm{F}_n\ (n = 0\text{—}3) \qquad \text{(viii)}$$

Scheme.

$[\mathrm{VOCl}_{(4-n)}\mathrm{F}_n]^-$ (n = 1—4) *and* $[\mathrm{VO(CF_3CO_2)}_{(4-n)}\mathrm{F}_n]^-$ (n = 1—3).—N.m.r. data for the mixed chloride–fluoride and trifluoroacetate–fluoride anions are collected in Table 1. The n.m.r. parameters for these species are independent of the medium used, indicating that solvent molecules are not present in the first co-ordination sphere of vanadium.

The presence of two isomers of $[\mathrm{VOCl_2F_2}]^-$ is evidence for a square-pyramidal geometry. In a trigonal-bipyramidal (tbp) structure the fluorines would be expected to occupy the axial positions[6] giving rise to a single form for $[\mathrm{VOCl_2F_2}]^-$. Variable-temperature ^{51}V n.m.r. studies demonstrated the equivalence of the four fluorines in $[\mathrm{VOF_4}]^-$ down to temperatures of 223 K, also consistent with a square-pyramidal geometry. However, this observation may not be conclusive since in the related tbp molecule $\mathrm{SOF_4}$ rapid intramolecular fluorine exchange occurs.[7]

The replacement of $\mathrm{F^-}$ by $\mathrm{Cl^-}$ has a marked effect upon δ(V) (Table 1), increasing it in approximate proportion to the number of bound chlorines. The effect on δ(V) of substituting $\mathrm{F^-}$ by $\mathrm{CF_3CO_2^-}$ is much less marked than substitution by $\mathrm{Cl^-}$. Whereas chloride substitution effects both the formal charge on vanadium and its temperature-independent para-

Table 1. Vanadium-51 and ^{19}F n.m.r. parameters for some vanadium(v) fluoro complexes in MeCN

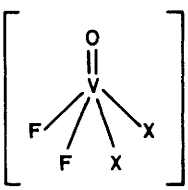
	^{51}V		^{19}F	
Species[a]	δ/p.p.m.[b]	^1J(V–F)	δ/p.p.m.[b]	^1J(V–F)
$[VOF_4]^-$	−797 (q)	86	129 (o)	88
$[VOClF_3]^-$	−641 (dt)[c]	99, 49	151, 179[d]	
cis-$[VOCl_2F_2]^-$	−474 (s)		222	
trans-$[VOCl_2F_2]^-$	−424 (t)	60	191 (o)	62
$[VOCl_3F]^-$	−209 (d)	24	228	
$[VOCl_4]^-$	+43 (s)			
$[VO(CF_3CO_2)F_3]^-$	−760 (dt)[c]	120, 72	170, 175[d]	
trans-$[VO(CF_3CO_2)_2F_2]^-$	−717 (t)	102	213 (o)	105
cis-$[VO(CF_3CO_2)_2F_2]^-$	−709 (t)	57	229	
$[VO(CF_3CO_2)_3F]^-$	−668 (d)	80	256	
$[VO_2F_2]^-$	−595 (t)	272	−33 (o)	275
$[VO_2ClF]^-$	−485 (d)	207	−5	
$[VO_2Cl_2]^-$	−364 (s)			
$[VOF_3(phen)]$	−738 (d)	144	168, 176[e]	
$[VOF_3(bipy)]$	−738 (dt)[f]	144, 53	168, 171[e]	
$[VOF_3(NO_3)]^-$	−778 (dt)[c]	140, 71	164, 173[e]	
$[VOF_3(MeSO_3)]^-$	−774 (dt)[c]	119, 80	174, 178[d]	

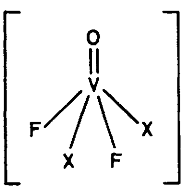
[a] Assignments of *cis* and *trans* isomers are very tentative. [b] Multiplicities given in parentheses: s = single, d = doublet, t = triplet, q = quintet, o = octet; where not indicated they are multiplets. [c] 1:2:2:2:1 quintets at 253 K analysed as overlapping doublets of triplets. [d] Area ratio 1:2. [f] Using resolution enhancement. [e] Area ratio 2:1.

magnetism, trifluoroacetate substitution probably only effects the formal charge.

In general, as the number of fluorines on vanadium is reduced ^1J(V–F) decreases. This is a consequence of the vanadium–fluorine bond becoming more ionic and therefore longer as the number of chlorines or trifluoroacetates increases. A smooth trend can be seen in the fluorine shifts δ(F) increasing as the number of fluorines decreases. This trend in δ(F) cannot however be explained by changes in the local paramagnetic term; increased ionic character in a V–F bond would result in greater shielding, *i.e.* a decrease in δ(F). However, δ(F) within a closely related series of compounds may be dominated by neighbouring dipoles; *e.g.* from chlorine, an increasing number of chlorines producing increased deshielding of fluorine, *i.e.* a more positive δ(F). Similar variations in fluorine shifts have been noted in the systems $[SnCl_{(6-n)}F_n]^{2-}$,[8] $[SbCl_{(6-n)}F_n]^-$,[9] and $[AsCl_{(6-n)}F_n]^-$ (n = 1—6).[9]

Both isomers of $[VO(CF_3CO_2)_2F_2]^-$ show resolvable vanadium–fluorine coupling; *cis* and *trans* configurations [structures (I) and (II)] cannot be assigned with absolute certainty on the basis of their ^1J(V–F) and δ(F) values alone. However, the *cis* isomer (I) might be expected to have the smaller ^1J(V–F) value since it should contain the more ionic vanadium–fluorine bond.


(I)


(II)

X = $CF_3CO_2^-$

The above structures are drawn assuming unidentate trifluoroacetates. Support for this assumption comes from the observation that $CF_3CO_2^-$ is unwilling to chelate[10] and also from the fact that in the compound $[NO_2][VO(CF_3CO_2)_4]$ i.r. spectroscopy indicates that the $CF_3CO_2^-$ groups are unidentate.[11]

Figure 1. Vanadium-51 n.m.r. spectra of $[VO(CF_3CO_2)F_3]^-$ at (*a*) 293, (*b*) 273, and (*c*) 253 K

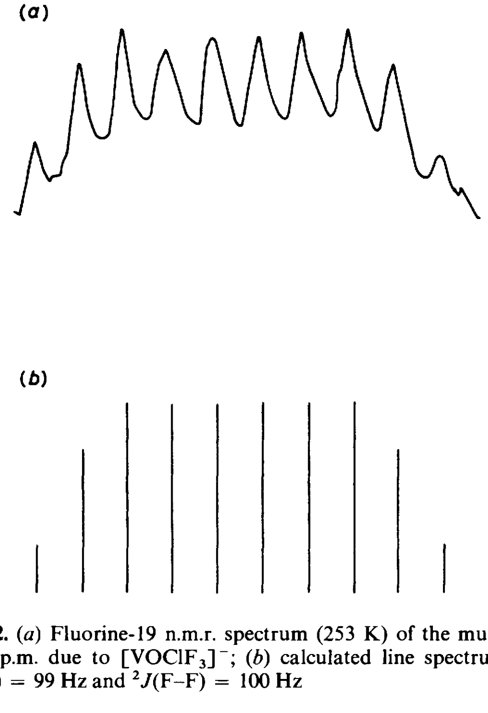


Figure 2. (*a*) Fluorine-19 n.m.r. spectrum (253 K) of the multiplet at 150.8 p.p.m. due to $[VOClF_3]^-$; (*b*) calculated line spectrum using ^1J(V–F) = 99 Hz and ^2J(F–F) = 100 Hz

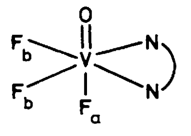
Both $[VOClF_3]^-$ and $[VO(CF_3CO_2)F_3]^-$ (Figure 1) have temperature-dependent ^{51}V n.m.r. spectra, indicating fluxional behaviour. Intramolecular fluorine exchange averages the two vanadium–fluorine couplings at room temperature. However, by cooling to 253 K the exchange is slowed and both couplings can be measured. The ^{19}F spectrum of $[VOClF_3]^-$ at 253 K consists of two multiplets each of which shows fluorine–fluorine as well as vanadium–fluorine coupling. Analysis of the multiplet at δ 151 as an overlapping octet of triplets (Figure 2) indicates a value for ^2J(F–F) of *ca.* 100 Hz.

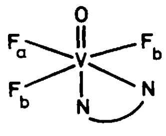
$[VO_2Cl_2]^-$, $[VO_2F_2]^-$, *and* $[VO_2ClF]^-$.—Trends in δ(V), δ(F), and ^1J(V–F) for $[VO_2Cl_2]^-$, $[VO_2F_2]^-$, and $[VO_2ClF]^-$ (Table 1) are analogous to those observed for the $[VOCl_{(4-n)}F_n]^-$ (n = 1—4) series; $[VO_2F_2]^-$ and $[VO_2ClF]^-$ both show large values for ^1J(V–F) and negative values for δ(F). These large ^1J(V–F) values are likely to be due in part to a greater *s* character of the V–F bond in the four-co-ordinate $[VO_2F_2]^-$ and $[VO_2ClF]^-$ compared to the other fluoro complexes.

Table 2. Vanadium-51 and ^{19}F n.m.r. parameters for $VOCl_{(3-n)}F_n$ (n = 0—3) in MeCN

	$\delta(^{51}V)$/p.p.m.*			$\delta(^{19}F)$/ p.p.m.
Species	294 K	253 K	223 K	(294 K)
$VOCl_3$	−118 (600)	−126 (370)	−131 (450)	
$VOCl_2F$	−379 (650)	−339 (1 700), −422 (490)	−341 (590), −418 (1 100)	268
$VOClF_2$	−588 (500)	−591 (490)	−582 (1 180), −606 (830)	241
VOF_3	−794 (400)	−794 (370)	−795 (490)	211

* Half-height linewidth ($w_{\frac{1}{2}}$ Hz) in parentheses.


(III)


(IV)

All other fluoro complexes reported here have co-ordination numbers of at least five.

[VOF_3(bipy)], [VOF_3(phen)], *and* $[VOF_3X]^-$ (X = NO_3 *or* $MeSO_3$).—The n.m.r. data for the VOF_3 adducts with 2,2′-bipyridine and 1,10-phenanthroline are reported in Table 1. Vibrational spectroscopy[12] has failed to distinguish between the isomeric possibilities, structures (**III**) and (**IV**), when $\widehat{NN}$ = phen.

A very tentative assignment to structure (**III**) can be made on the basis of ^1J(V–F) values. In structure (**IV**) $^1J(V\text{–}F_b)$ should be greater than $^1J(V\text{–}F_a)$ since F_a is *trans* to a fairly electropositive nitrogen whereas F_b is *trans* to fluorine, this is contrary to the experimental observation. In (**III**) $^1J(V\text{–}F_a)$ should be greater than $^1J(V\text{–}F_b)$, since F_a is *trans* to multiply bound oxygen and F_b to nitrogen.

The values of $^1J(V\text{–}F_a)$ and $\delta(F_a)$ for $[VOF_3(NO_3)]^-$ are similar to those for [VOF_3(bipy)] and [VOF_3(phen)] and indicate that $[VOF_3(NO_3)]^-$ may have a structure analogous to (**III**) with a bidentate nitrate. $[VOF_3(MeSO_3)]^-$ displays n.m.r. parameters very similar to those of $[VO(CF_3CO_2)F_3]^-$. Like $CF_3CO_2^-$, $MeSO_3^-$ is less willing to chelate than NO_3^-. Although all the $[VOF_3X]^-$ species are fluxional at room temperature, [VOF_3(bipy)] and [VOF_3(phen)] showed no signs of intramolecular fluorine exchange at temperatures up to 343 K.

Neutral Chloride–Fluorides.—An equimolar mixture of $VOCl_3$ and VOF_3 in MeCN gave rise to four ^{51}V and three ^{19}F resonances (Table 2). The ^{51}V peaks at −379 and −588 (Table 2) are assigned to the species $VOCl_2F$ and $VOClF_2$. These two species did not display vanadium–fluorine coupling, although it is possible using resolution enhancement to measure a ^1J(V–F) value of 112 Hz for VOF_3 in MeCN. Upon cooling to 253 K the $VOCl_2F$ peak splits into two broad resonances. Upon further cooling to 223 K, the $VOClF_2$ peak also splits into two resonances.

The low-temperature experiments provide evidence for the existence of at least two isomers of $VOCl_2F$ and $VOClF_2$ in MeCN. Isomers of $VOCl_2F$ and $VOClF_2$ can only exist if solvating MeCN is present in these species. $VOCl_3$ is known to form the complex $VOCl_3{\cdot}2MeCN$.[13]

Hydrolysis of $[VOCl_{(4-n)}F_n]^-$.—Studies into the hydrolysis of $[VOCl_4]^-$ and $VOCl_3$ have been reported elsewhere.[3] The primary hydrolysis product of $[VOCl_4]^-$ was shown to be $[VO_2Cl_2]^-$. The latter is also the primary hydrolysis product when H_2O is added to a solution containing the $[VOCl_{(4-n)}F_n]^-$ series. When more H_2O is added, $[VO_2ClF]^-$ and $[VO_2F_2]^-$ are also produced. Hydrolysis of VOF_3 in MeCN with $[NBu_4]F{\cdot}2H_2O$ gives predominantly $[VO_2F_2]^-$, indicating that $[VO_2F_2]^-$ is the primary hydrolysis product of $[VOF_4]^-$. Studies into the hydrolysis of VOF_3 with H_2O were hampered by ready precipitation of solid.

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