

## $^{51}\text{V}$ and $^{19}\text{F}$ N.M.R. Study of $\text{VO}_2\text{F}_4^{3-}$ in Solution

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N.m.r. evidence is presented for the existence of  $\text{VO}_2\text{F}_4^{3-}$  in aqueous solutions.

Hatton *et al.*<sup>1</sup> first reported the  $^{51}\text{V}$  n.m.r. spectrum of a  $\text{V}_2\text{O}_5$ -48% HF mixture to be a 1:4:6:4:1 quintet which they attributed to  $\text{VOF}_4^-$ . They assumed that this ion has a square pyramidal structure to explain the equivalence of the four fluorine atoms on the n.m.r. time scale. A recent e.s.r. study<sup>2</sup> of  $\gamma$ -irradiated polycrystalline  $(\text{NH}_4)_3\text{VO}_2\text{F}_4$  concluded that there are discrete  $\text{VO}_2\text{F}_4^{3-}$  ions in the solid. In this communication we present the results of a study of both the  $^{51}\text{V}$  and  $^{19}\text{F}$  n.m.r. spectra of acidified aqueous solutions of  $\text{Na}(\text{NH}_4)_2\text{VO}_2\text{F}_4$  as well as some other aqueous solutions such as  $\text{V}_2\text{O}_5$  in 48% HF.

Figure 1 shows the observed  $^{51}\text{V}$  and  $^{19}\text{F}$  n.m.r. spectra of  $\text{Na}(\text{NH}_4)_2\text{VO}_2\text{F}_4$  in water at *ca.* +7 °C. These spectra were analysed using the two dimensionless parameters  $y$  and  $x$  defined by the relations  $y = 2\pi J\tau$  and  $x = (\omega_0 - \omega)/2\pi J$  where  $J$  is the spin-spin coupling constant between the two nuclei,  $\tau$  is the relaxation time of the quadrupole nucleus  $^{51}\text{V}$ , and  $\omega_0$  and  $\omega$  are the angular frequencies at the centre and any other point, respectively, of the n.m.r. multiplet.<sup>3-6</sup> The theoretical  $^{51}\text{V}$  spectrum was simulated as a 1:4:6:4:1 multiplet with a separation of  $J$  between any two adjacent components and all components having a Lorentzian shape. The corresponding  $^{19}\text{F}$  spectrum was computed using an extension of Poples' treatment.<sup>3</sup> The computed n.m.r. line shapes of  $^{51}\text{V}$  and  $^{19}\text{F}$  that gave a good fit for the observed spectra of  $\text{Na}(\text{NH}_4)_2\text{VO}_2\text{F}_4$  are given in Figure 1. A solution of  $(\text{NH}_4)_3\text{VO}_2\text{F}_4$  gave essentially the same results. The relevant parameters are given in Table 1. The value of  $J$  deduced independently from an apparently featureless  $^{19}\text{F}$  n.m.r. spectrum agrees well with that obtained from the fit of the  $^{51}\text{V}$  multiplet. This agreement shows that it is possible to obtain a reasonably reliable value of the coupling constant from an unresolved spectrum of a

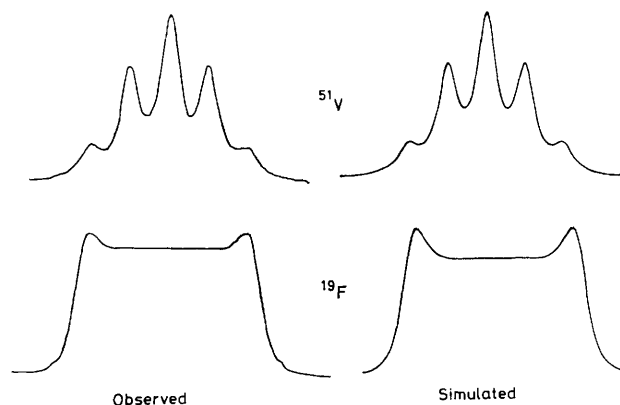


Figure 1. Observed and computer simulated  $^{51}\text{V}$  and  $^{19}\text{F}$  n.m.r. spectra at *ca.* +7 °C of  $\text{Na}(\text{NH}_4)_2\text{VO}_2\text{F}_4$  dissolved in water acidified with 48% HF.

spin- $\frac{1}{2}$  nucleus coupled to a high-spin nucleus. These results confirm that the species in solution contains four equivalent fluorine atoms coupled to a  $^{51}\text{V}$  nucleus. The n.m.r. parameters obtained from the  $^{51}\text{V}$  and  $^{19}\text{F}$  spectra of related solutions such as  $\text{V}_2\text{O}_5$ -48% HF are also included in Table 1 for comparison. The differences in the line widths of the  $^{19}\text{F}$  spectra in different solutions at room temperature arise from chemical exchange between free  $\text{F}^-$  and the species containing the four fluorines on vanadium. It is clear that the same species gives rise to all the observed spectra in aqueous HF solutions. It was assumed by Hatton *et al.*<sup>1</sup> that this species was the square pyramidal  $\text{VOF}_4^-$  ion in order to account for the equivalence of the four fluorine atoms indicated by the n.m.r. data. Although VSEPR (valence shell electron pair repulsion) theory<sup>7</sup> would predict  $\text{VOF}_4^-$  to have a trigonal bipyramidal structure, it has indeed been found to have a square pyramidal structure in crystalline  $\text{CsVOF}_4$ .<sup>8</sup>

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**Table 1.**  $^{51}\text{V}$  and  $^{19}\text{F}$  N.m.r. spectral parameters in solutions containing  $\text{VO}_2\text{F}_4^{3-}$  and in other related solutions.

Solution	$^{51}\text{V}$				$^{19}\text{F}$			
	Signal	$\delta$ , p.p.m. <sup>a</sup>	$J_{\text{V-F}}$ /Hz	Ref.	Line width /Hz	$\delta$ , p.p.m. <sup>b</sup>	$J_{\text{V-F}}$ /Hz	Ref.
Aq. $(\text{NH}_4)_3\text{VO}_2\text{F}_4$	q <sup>d</sup>	-775	117	This work	840	-246	117	This work
Aq. $\text{Na}(\text{NH}_4)_2\text{VO}_2\text{F}_4$	q <sup>d</sup>	-770	117	This work	830	-247	117	This work
$\text{V}_2\text{O}_5$ -48% HF	—	-777	116	1, 9, this work	1215	-250	—	9
$\text{NH}_4\text{VO}_3$ -48% HF	—	—	—	—	1190	-255	—	This work
$\text{CsVOF}_4$ -HF	q <sup>d</sup>	—	140 <sup>c</sup>	9	1106	-259	—	9
$\text{NH}_4\text{VO}_3$ -HF	q <sup>d</sup>	—	140 <sup>c</sup>	9	1125	-255	—	9
KF- $\text{V}_2\text{O}_5$ -HF	q <sup>d</sup>	—	140 <sup>c</sup>	9	1230	-250	—	9

<sup>a</sup> With reference to  $^{51}\text{V}$  in  $\text{VOCl}_3$ . <sup>b</sup> With reference to  $^{19}\text{F}$  in solvent HF. <sup>c</sup> No quantitative fit for the spectra presented in ref. 9. <sup>d</sup> Quin- tet structure observed.

However, this is a consequence of fluorine bridging between the  $\text{VOF}_4^-$  ions which leads to an approximately octahedral arrangement of five fluorine atoms and one oxygen atom around the vanadium atom. The fluorine bridge is presumably destroyed in solution and the  $\text{VOF}_4^-$  ion would not then be expected to retain a square pyramidal shape. Howell and Moss<sup>9</sup> assumed in fact that  $\text{VOF}_4^-$  in solution had the expected trigonal bipyramidal structure and they proposed that fast intramolecular fluorine exchange (pseudo-rotation)<sup>10</sup> was responsible for the apparent equivalence of the four fluorines on the n.m.r. time scale. The broad  $^{19}\text{F}$  spectrum of the trigonal bipyramidal  $\text{AsF}_5$  molecule at room temperature has been interpreted<sup>11</sup> as arising from five fluorines undergoing fast intramolecular exchange (pseudo-rotation) coupled to  $^{75}\text{As}$  ( $I = 3/2$ ) undergoing rapid quadrupole relaxation. In spite of the pseudo-rotation in  $\text{AsF}_5$ , the value of  $eq$ , the electric field gradient, at the  $^{75}\text{As}$  site is not small enough to give a large enough  $\tau$  (or  $\gamma$ -value) to give a well resolved multiplet. Thus even if pseudo-rotation were to lead to equivalence of the four fluorines, the  $^{51}\text{V}$  nucleus in  $\text{VOF}_4^-$  ( $I 7/2$  and  $J_{\text{V-F}}$  120 Hz) is not anticipated to have a large enough  $\tau$  to give such a well resolved multiplet as is observed in solutions of  $\text{V}_2\text{O}_5$  in 48% HF. This implies that the species in solution contains  $^{51}\text{V}$  in a site with symmetry higher than the  $C_{2v}$  symmetry of  $\text{VOF}_4^-$  undergoing pseudo-rotation.

One of the conclusions from a recent e.s.r. study of  $\gamma$ -irradiated solid  $(\text{NH}_4)_3\text{VO}_2\text{F}_4$  was that the  $\text{VO}_2\text{F}_4^{3-}$  ion has a *trans* structure with  $D_{4h}$  symmetry as expected from the VSEPR theory.<sup>7</sup> Since  $(\text{NH}_4)_3\text{VO}_2\text{F}_4$  can be recrystallised from its aqueous solutions it is reasonable to assume that  $\text{VO}_2\text{F}_4^{3-}$  retains its identity in solution and that the n.m.r. spectra in Figure 1 are due to this anion. With a  $D_{4h}$  symmetry, all four fluorines are equivalent and as the  $^{51}\text{V}$  has a pseudo-octahedral environment, it is not surprising that V-F coupling is observed. Thus on the basis that the species in aqueous solutions is  $\text{VO}_2\text{F}_4^{3-}$  with  $D_{4h}$  symmetry, all the n.m.r. observations are rationalised.

Although, on the basis of the n.m.r. evidence alone we cannot rule out the possibility that the species in solution is  $\text{VOF}_4^-$  with a square pyramidal structure it is very probable that it would be hydrated by a water molecule in aqueous solutions thus causing it to adopt a *trans* octahedral  $\text{VO}(\text{OH}_2)\text{F}_4^-$  structure. Depending on the acidity, this species might lose one or two protons to give finally  $\text{VO}_2\text{F}_4^{3-}$ . Non-hydrated  $\text{VOF}_4^-$  presumably only exists in solutions containing very little water, e.g., in solutions in anhydrous HF. It is noteworthy that the reported  $^{51}\text{V}$ - $^{19}\text{F}$  coupling constant for anhydrous HF solution is 140 Hz compared with the value of 120 Hz in aqueous solutions.

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