

Direct Nuclear Quadrupole Resonance Evidence for Vanadium-Halogen Bonding in Vanadium Trihalide Hexahydrates

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Summary The nuclear quadrupole resonance spectra of $\text{VCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{VBr}_3 \cdot 6\text{H}_2\text{O}$ show frequencies characteristic of metal-bonded halogen nuclei.

THERE is indirect evidence that the compounds $\text{VX}_3 \cdot 6\text{H}_2\text{O}$ ($\text{X} = \text{Br}, \text{Cl}$) contain the $[\text{V}(\text{H}_2\text{O})_4\text{X}_2]^+$ ion. Similar species have been established, by X-ray diffraction techniques, to be present in $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ¹ and green $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$.² Webb³ has commented on the large axial field splitting of the electronic ground state of the above vanadium complexes. The corresponding hexaurea vanadium complexes show similar splittings yet seem unlikely to contain co-ordinated halogens.⁴ Furthermore the electronic spectra of $\text{VCl}_3 \cdot 6\text{H}_2\text{O}$ ⁵ and more recently $\text{VBr}_3 \cdot 6\text{H}_2\text{O}$ ⁶ have been interpreted in favour of the existence of $[\text{V}(\text{H}_2\text{O})_4\text{X}_2]^+$. In confirmation of this evidence we have obtained the nuclear quadrupole resonance (n.q.r.) spectra of $\text{VCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{VBr}_3 \cdot 6\text{H}_2\text{O}$. These spectra show resonances at frequencies characteristic of halogen nuclei bonded to metals.

Green solutions of V^{III} halides were obtained by refluxing vanadium powder with concentrated hydrochloric and hydrobromic acids respectively.⁷ The green complexes were precipitated from these solutions by passing in the appropriate gaseous hydrogen halide. The stoichiometry was confirmed by vanadium and halogen analyses. Nuclear quadrupole resonance spectra were recorded on a Wilks NQR 1A super-regenerative spectrometer at 24°. Frequencies were measured with a BC221 frequency meter to an estimated precision of $\pm 0.02\%$. The centre line was distinguished from those due to the side bands by varying

the quench frequency. The observed frequencies are given in the Table.

Observed nuclear quadrupole resonance frequencies

	Frequency (MHz)	Signal : noise	Nucleus
$\text{VCl}_3 \cdot 6\text{H}_2\text{O}$	8.412	5	³⁵ Cl
$\text{VBr}_3 \cdot 6\text{H}_2\text{O}$	57.04 68.27	10 9	⁸¹ Br ⁷⁹ Br

The resonances observed for $\text{VBr}_3 \cdot 6\text{H}_2\text{O}$ have a frequency ratio of 1.197 confirming their assignment to ⁷⁹Br and ⁸¹Br nuclei.⁸ The ³⁷Cl resonance was not observed for $\text{VCl}_3 \cdot 6\text{H}_2\text{O}$.

The only previously reported n.q.r. spectrum of a vanadium halide is that for VCl_3 , the ³⁵Cl frequency found being 9.40 MHz at 24°. Although the resonance found in $\text{VCl}_3 \cdot 6\text{H}_2\text{O}$ is at lower frequency than this it is still well above that for a purely ionic chlorine in a crystal lattice. For example in $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl} \cdot \text{HCl} \cdot x\text{H}_2\text{O}$ the cobalt bonded chlorine resonance is at 16.058 MHz whereas the "free" chlorine resonance occurs at 2.858 MHz.¹⁰ Similarly CrBr_3 ⁹ gives a ⁸¹Br resonance at 85.73 MHz.

Clearly the n.q.r. data indicate halogen-vanadium bonds in $\text{VCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{VBr}_3 \cdot 6\text{H}_2\text{O}$. This is in agreement with the formulation $[\text{V}(\text{H}_2\text{O})_4\text{X}_2]\text{X} \cdot 2\text{H}_2\text{O}$.^{5,6}

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