The $^{51}$V NMR Spectra of Some Oxo-, Peroxo-, Nitrosyl- and Hydroxylamidovanadium Complexes

Dieter Rehder* and Karl Wieghardt

Institut für Anorganische Chemie der Universität Hamburg,
Martin-Luther-King-Platz 6, D-2000 Hamburg 13
Lehrstuhl für Anorganische Chemie I der Ruhr-Universität Bochum,
Universitätstraße 150, D-4630 Bochum

Z. Naturforsch. 36b, 1251-1254 (1981); received June 12, 1981

$^{51}$V NMR Spectra, Oxovanadium, Nitrosylvanadium, Hydroxylamidovanadium

The $^{51}$V NMR spectra are recorded for 3 dinuclear complexes (VO(ONR$_2$)$_2$)$_2$O and 13 mononuclear vanadium (+V) and (+III) chelate complexes of the general formula [VXYZ], where X = O$^2-$, NO$^-$; Y = O$^2-$, O$_2$NO$^-$; and Z = picolinate-(pic), dipicolinate$_2^-$ (dipic), nitrilo-tri(2-propanolate)$_2^-$, and o-phenanthroline (phen). Shielding of the $^{51}$V nucleus increases as O$^2-$ is replaced for NO$^-$, and in the series (O$_2^-$ + dipic) < (2 O$_2^-$ + pie) < (2 H$_2$NO$^-$ + dipic) < (2 H$_2$NO$^-$ + phen) < (2 H$_2$NO$^-$ + pie); H$_2$NO$^-$ < H(Me)NO$^-$ < H$_2$NO$^-$; and (dinuclear complexes) CsH$_2$NO$^-$ < Cs$_2$NO$^-$ < Et$_2$NO$^-$. These trends are explained on the basis of variations of molecular parameters correlated to electronic and steric factors associated with the ligands. Line widths of the $^{51}$V NMR signals are discussed in terms of influences originating from variations of the electric field and the molecular correlation time.

**Introduction and Theory**

The nucleus $^{51}$V (natural abundance: 99.76%, nuclear spin = 7/2, sensitivity at constant field $B_0$ relative to $^1$H: 0.328) is unique among the quadrupolar transition metal nuclei inasmuch as its electric nuclear quadrupole moment is very small (~0.05 $\cdot$ 10$^{-28}$ m$^2$ [1]). Interactions between the quadrupole moment $eQ$ and local electric field gradients, $eQ$, are thus restricted to a minimum, allowing the observation of comparably sharp signals even where the molecule actually has no symmetry. This amounts to a considerable advantage compared to more common nuclei such as $^{55}$Mn and $^{59}$Co, the $eQ$ of which is greater by an order of magnitude.

$^{51}$V chemical shift values $\delta$ have been shown to be extremely sensitive to variations in the coordination sphere of the vanadium nucleus, spanning an approximate range of 2500 ppm (surveyed in [2] to [4]). Variations in $\delta$ are dominated by the paramagnetic deshielding contribution $\sigma_p$ to the overall shielding $\sigma = \sigma_d + \sigma_p$ (where the diamagnetic term $\sigma_d$, which is governed by the core electrons, is practically constant for a given nucleus [5]). $\sigma_p$ is correlated to the bonding parameters $\langle T \rangle$ (mean energy separation between lowest occupied and highest unoccupied orbitals; all transitions are symmetry-allowed in our complexes of low point symmetry considered here), the distance of the metal-valence electrons from the nucleus, $r$, and the metal character of the molecular orbitals taking part in transitions, quantified, e.g., by the LCAO coefficients $c_m$. Thus

$$\sigma_p = -const \cdot \left\langle T \right\rangle \cdot \langle r^2 \rangle \cdot c_m^2$$

(1)

large $\sigma_p$ values give rise to low overall shielding $\sigma$, i.e. the signal will appear at relatively low $B_0$. Since all $^{51}$V signals are to high field of VOCl$_3$ (which is adopted as standard in $^{51}$V NMR spectroscopy), the $\delta$ values are negative. In order to avoid irritation with the terms “chemical shift $\delta$” and “shielding $\sigma$”, we will therefore not refer to $\delta$ itself, but to $|\delta|$. The statements “increasing $|\delta|$” and “increasing $\sigma$” are then compatible.

While there exists a large body of $^{51}$V shielding data [4], line widths $\Delta\nu_{1/2}$ have not yet been treated systematically. Investigations carried out on e.g. cobalt complexes [6-8] have shown, however, that half widths may be an equally sensitive parameter. For quadrupolar nuclei, where quadrupolar relaxation is by far the main relaxation mechanism, $\Delta\nu_{1/2}$ may be expressed in the form (extreme narrowing case, i.e. $2\pi\nu_0\tau_c \ll 1$, $\nu_0 =$ NMR frequency, $\tau_c =$ molecular correlation time)

$$\Delta\nu_{1/2} = \frac{3\pi^2}{10} f(I) \left( \frac{e^2qQ}{h} \right)^2 \left( 1 + \frac{\eta^2}{3} \right) \tau_c$$

(2)
f(I) for the $^{51}$V nucleus is 0.136, and $\eta$ is the asymmetry parameter. In many cases, the relaxation is dominated by $r_\eta$, and its influence can be understood on the basis of O'Reilly's quasi-lattice model [9, 10]: bulky molecules and high viscosity of the solution broaden the signals. On the other hand, when different molecules of approximately identical steric requirements and in identical surroundings are considered, the main influence is via $\delta$. The interaction between $\delta$ and eQ decreases with increasing local symmetry ($\delta$ vanishes for cubic symmetry), resulting in decreased half widths; but $\Delta r_{I/2}$ is also (via $\delta$) affected by bond characteristics rooting in the ligand system.

The coordination properties of the ligands, i.e. steric and electronic factors associated with the behaviour of the ligands on coordination, and structural features of the complex are hence reflected in the NMR parameters $\delta$ and $\Delta r_{I/2}$. $^{51}$V NMR measurements may thus be considered a practicable tool not only for the identification of distinct species, but also for the discussion of the bonding situation in the complexes and for the classification of ligands with respect to their steric and electronic nature. Synthesis and reactivity of the compounds under investigation in this work have been subject of previous reports [11–14]. We shall now discuss the $^{51}$V NMR spectra of representative examples.

**Results and Discussion**

The $^{51}$V NMR data are listed in the Table. The compounds are arranged in the order of increasing shielding (increasing $|\delta|$). In the Figure, a schematic presentation is given for the shift values of a variety of vanadium complexes, incorporating those discussed in this work.

The different $\delta$ values for I dissolved in H$_2$O and EtOH, or acetone, respectively, very likely reflect exchange of the H$_2$O ligand for the solvent molecule in the manner demonstrated previously for the substitution of H$_2$O by CO$_3^{2-}$ and CN$^-$. $\delta$ values for the cyano and carbonato complexes are $-557$ and $-568$ ppm, respectively, while the signal appearing at $-483$ (which is also observed in aqueous solutions of the CN$^-$ and CO$_3^{2-}$ complexes) should correspond to the aqua complex 1.14, when dissolved in water, exhibits six $^{51}$V NMR signals ($-537$, $-570$, $-755$, $-945$, $-1096$, $-1273$ ppm). Apparently, this complex degrades to yield a variety of different species. Addition of excess KCN reduces

<table>
<thead>
<tr>
<th>No.</th>
<th>Group</th>
<th>Complex</th>
<th>Solvent</th>
<th>$\delta$ of Main Resonance</th>
<th>Half-width</th>
<th>Other Resonances</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(Ia)</td>
<td>VOCl$_3$</td>
<td>EtOH</td>
<td>-711.4 (0.1)</td>
<td>477 (8)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>(Ib)</td>
<td>VOCl$_3$</td>
<td>EtOH</td>
<td>-707.7 (0.4)</td>
<td>191 (14)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>(II)</td>
<td>VOCl$_3$</td>
<td>EtOH</td>
<td>-720.0 (0.4)</td>
<td>1290 (46)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>(Ic)</td>
<td>VOCl$_3$</td>
<td>EtOH</td>
<td>-725.8 (0.1)</td>
<td>132 (14)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>(Ic)</td>
<td>VOCl$_3$</td>
<td>EtOH</td>
<td>-732.4 (0.1)</td>
<td>110 (4)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>(Ic)</td>
<td>VOCl$_3$</td>
<td>EtOH</td>
<td>-726.8 (0.2)</td>
<td>61 (2)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>(Ic)</td>
<td>VOCl$_3$</td>
<td>Me$_2$SO</td>
<td>-724.8 (0.3)</td>
<td>540 (13)</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>(Ic)</td>
<td>VOCl$_3$</td>
<td>Me$_2$SO</td>
<td>-696.4 (0.1)</td>
<td>343 (21)</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>(Ic)</td>
<td>VOCl$_3$</td>
<td>Me$_2$SO</td>
<td>-696.4 (0.1)</td>
<td>343 (21)</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>(Ic)</td>
<td>VOCl$_3$</td>
<td>Me$_2$SO</td>
<td>-711.4 (0.1)</td>
<td>477 (8)</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>(Ic)</td>
<td>VOCl$_3$</td>
<td>Me$_2$SO</td>
<td>-707.7 (0.4)</td>
<td>191 (14)</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>(Ic)</td>
<td>VOCl$_3$</td>
<td>Me$_2$SO</td>
<td>-720.0 (0.4)</td>
<td>1290 (46)</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>(Ic)</td>
<td>VOCl$_3$</td>
<td>Me$_2$SO</td>
<td>-725.8 (0.1)</td>
<td>132 (14)</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>(Ic)</td>
<td>VOCl$_3$</td>
<td>Me$_2$SO</td>
<td>-732.4 (0.1)</td>
<td>110 (4)</td>
<td></td>
</tr>
</tbody>
</table>

The coordination properties of the ligands, i.e. steric and electronic factors associated with the behaviour of the ligands on coordination, and structural features of the complex are hence reflected in the NMR parameters $\delta$ and $\Delta r_{I/2}$. $^{51}$V NMR measurements may thus be considered a practicable tool not only for the identification of distinct species, but also for the discussion of the bonding situation in the complexes and for the classification of ligands with respect to their steric and electronic nature. Synthesis and reactivity of the compounds under investigation in this work have been subject of previous reports [11–14]. We shall now discuss the $^{51}$V NMR spectra of representative examples.

The different $\delta$ values for I dissolved in H$_2$O and EtOH, or acetone, respectively, very likely reflect exchange of the H$_2$O ligand for the solvent molecule in the manner demonstrated previously for the substitution of H$_2$O by CO$_3^{2-}$ and CN$^-$. $\delta$ values for the cyano and carbonato complexes are $-557$ and $-568$ ppm, respectively, while the signal appearing at $-483$ (which is also observed in aqueous solutions of the CN$^-$ and CO$_3^{2-}$ complexes) should correspond to the aqua complex 1.14, when dissolved in water, exhibits six $^{51}$V NMR signals ($-537$, $-570$, $-755$, $-945$, $-1096$, $-1273$ ppm). Apparently, this complex degrades to yield a variety of different species. Addition of excess KCN reduces
the number of resonances to one main signal \((-942\, \text{ppm})\), which we tentatively assign the \([(\text{CN})_4\text{V(NO)}(\text{ONH}_2)]^{3-}\) anion, and a signal of medium intensity at \((-533\, \text{ppm}).\)

As to the complexes 2 to 13, four groups may be distinguished, namely (i) vanadium \((+V)\) complexes containing (in addition to dipic, pic, phen, and \(\text{H}_2\text{O}\)) oxo-ligands \(\text{O}^{2-}\) only (group Ia), one or two peroxo ligands \(\text{O}_2^{2-}\) (Ib) and one or two hydroxylamido ligands \(\text{R}_2\text{NO}^-\) (Ic), and (ii) vanadium complexes with \(\text{NO}\) ligands (group II). Ic includes the three dinuclear, oxo-bridged complexes 8, 9 and 10.

In group II \((\text{V(NO)}_4)^2\), the vanadium is formally \(V(+III)\) \((\text{NO})^-\) or \(V(+I)\) \((\text{NO}^+)\). The \(\sigma\) values fall into the same range as those observed for other \(V(+III)\) and \(V(+I)\) complexes, with a tendency to an additional deshielding.

In contrast, there is a clear tendency for the ligand systems of the group I complexes (pronounced for Ie) to increase the shielding of the \(\text{V}^{51}\) nucleus beyond that known from other \(V(+V)\) complexes. The largest \(|\sigma|\) values reported thus far for \(V(+V)\) are those of peroxovanadates [16] and fluoro-vanadates [17].

Quite interestingly, replacement of one oxo for one peroxo ligand \((2 \rightarrow 4)\) results in an increase of \(|\sigma|\) by 66 ppm, which compares to the findings of Howarth and Hunt [16] in the series \([\text{HVO}_4]^{2-} \rightarrow [\text{HVO}_5(\text{O}_2)]^{2-} \rightarrow [\text{HVO}_5(\text{O}_2)_2]^{2-} \rightarrow [\text{HVO}](\text{O}_2)_3]^{2-}\) and was explained by an increase of \(\Delta E\) as going from \(\text{O}^{2-}\) to \(\text{O}_2^{2-}\), where \(\Delta E\) should represent the ligand-to-metal charge transfer transition. This explanation implies, however, that the ligand orbitals involved in this transition are partly bonding (since otherwise \(c_\text{M} = 0\), and the transition does not contribute to \(\sigma_p\); cf. Eq. (1)). A more substantial shielding contribution may well arise from effects originating in the parameters \(<r^3>\) in Eq. (1): the greater nephelauxetic effect of the ligand \(\text{O}_2^{2-}\) should lead to a reduction of \(<r^3>\) and hence of \(\sigma_p\). The larger average \(V-(\text{O}_2)\) distance \((190\, \text{pm})\) as compared to \(160\, \text{pm}\) for the \(V-\text{O}\) bond length [16]) supports this view. \(|\sigma|\) increases further, when \(\text{O}_2^{2-}\) is replaced for \(\text{R}_2\text{NO}^-\) (see 4 and 5, 6, 7, or 3 and 13). Shielding hence increases in the series

\[\text{O}^{2-} < \text{O}_2^{2-} < \text{Et}_2\text{NO}^- < \text{H(Me)NO}^- < \text{H}_2\text{NO}^- < \text{C}_5\text{H}_{10}\text{NO}^- < \text{Bz}_2\text{NO}^- < \ldots\]
Et$_2$NO$^-$ (complexes 5, 6, 7; 8, 9, 10) parallels an increase of the basicity of the N-function in the same order and hence suggests a dominance of electronic influences upon $\delta$. However, these trends can also be interpreted in terms of factors primarily steric in nature. We have shown that increasing ligand bulkiness may drastically decrease the shielding [18] due to hindered overlap between vanadium and ligand orbitals (which, in this case, are donor orbitals located on the nitrogen). The resulting decrease of V-N interaction diminishes $\Delta E$ and increases $\delta_M$, which gives rise to increasing $\sigma_p$ or an overall deshielding. Both, the increase of basicity and the decrease of steric requirement in the above series, should also be reflected in the line widths of the NMR signals. But the two effects are supposed to counteract each other: increasing basicity was shown to increase the field gradient at the nucleus and thus $\Delta v_{1/2}$ [8, 19] (see Eq. (2)), while decreasing ligand bulkiness will decrease $\Delta v_{1/2}$ (via a decrease of $\tau_c$). Accordingly, although the signals for the spacious dinuclear complexes are significantly broader than those of the mononuclear complexes, there is no uniform trend for the line widths of the compounds 8 (448 Hz), 9 (540), 10 (477), 5 (192), 6 (61) and 7 (110). One may derive, however, from this series that steric influences upon $\Delta v_{1/2}$ override those originating from electronic provenience. As shown for 1, 5 and 10, a solvent influence has also to be taken into account.

**Experimental**

The complexes were prepared as described in Refs. [11–14]. Ca. 0.02 M or – for compounds only slightly soluble (2, 3, 10) – saturated solutions were employed for the measurements. The spectra were scanned on a Bruker WH 90 PFT spectrometer equipped with a multi-nuclear accessory at 23.66 MHz ($^1$H) and 300 ± 1 K. The samples were filled into 7.5 mm diameter vials, fitted into 10 mm vials containing acetone-d$_6$ as external lock. External standard was VOCl$_3$ neat. Pulse width was 5 $\mu$s (no repetition time), spectral width 25 kHz, and 2000 scans (depending on the sample concentration and line width) were usually necessary in order to obtain sufficiently intense resonances. The signals were digitalized and fitted by a least squares method, employing the program system NMRFIT [20]. The absolute error for the chemical shifts thus obtained generally is less than 0.1 ppm (greater errors and the errors of the line widths are indicated in the Table).

This work was supported by the Deutsche Forschungsgemeinschaft.