Structure of Monovanadates in Aqueous Solution

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Harnung, S. E., Larsen, E. and Pedersen, E. J., 1993. Structure of Monovanadates in Aqueous Solution. – Acta Chem. Scand. 47: 674–682.

Using the ammonium salt of the dimeric coordination compound of 2-ethyl-2-hydroxybutanoic acid and vanadate(V) with known crystal structure as a reference, the structures of analogous compounds in aqueous solutions have been deduced by means of ^1H, ^{13}C and ^{51}V NMR. In these cases vanadate(V) is five-coordinate. Through an analysis of literature equilibrium data for the system dihydrogen vanadate(V) plus 1,2-ethanediol, giving a dimeric vanadate of presumed six-coordinate structure, the precise reaction scheme was established. This scheme is only consistent with a five-coordinate dihydrogen vanadate(V) ion having the composition $H_4VO_5^-$. The UV–VIS and MCD spectra of this ion are almost identical to those of the five-coordinate reference structure mentioned above.

The recent interest in the interactions of vanadate(V) with biologically important molecules leads to a need for a precise knowledge of the solution stereochemistry of the vanadate species. There are a few 'reference' structures, i.e. molecular structure determinations in the solid phase that may be considered or even proved to prevail in solution. Thus, for example, VO_4^{3-} has been shown to be of tetrahedral structure,[1] and we have shown that aqueous solutions of the salt at pH > 12 have a magnetic circular dichroism that is only compatible with a vanadate ion of T_d symmetry.[2,3] Likewise a crystal structure determination of the dimeric species $(NH_4)_2[VO_2(ehba)]_2$ (for abbreviations, see Table 1) shows the existence of a five-coordinate vanadate(V) species.[4] We show here that the solution ^1H, ^{13}C and ^{51}V NMR spectra of this coordination compound and of some analogous ones prove that the dinuclear, five-coordinate vanadate structure also exists in solution. In the literature there are many claims on specific structures for vanadates without evidence other than the chemical shift value of a ^{51}V NMR peak. We hope that the present paper will elucidate some basic vanadate systems which then may serve as references with regard to the structure of vanadate(V) derivatives.

Part of the interest in vanadates in biochemistry comes from the fact that vanadate(V) sometimes acts as an inhibitor for enzymes catalyzing reactions with phosphates. It is quite possible that vanadate(V) has a ground state of a low-lying excited state with a structure resembling that of a high-energy transition state for phosphate undergoing enzymatic catalysis. The geometry

of the phosphate transition state has been considered to be five-coordinate, whether the transformation was for ribonucleases, phosphatases or ATP-ases. Krauss and Basch[5] found that the electronic structures for $H_4VO_5^-$ and $H_4PO_5^-$ had both similarities and differences. The assumed geometry was $VO(OH)_4^-$ (1) and the two species were energy-gradient optimized to give the geometry of lowest energy. However, when the assumption 1 is made without a comparison with $VO_2(OH)_2(OH_2)^-$ (2) for vanadium, an uncertainty is introduced for the validity of the conclusion concerning the vanadate(V) ion. In many cases the VO_2^+ unit seems to be recognizable, and it is conceivable that $H_4PO_5^-$ has structure 1 while $H_4VO_5^-$ takes structure 2.

1   2
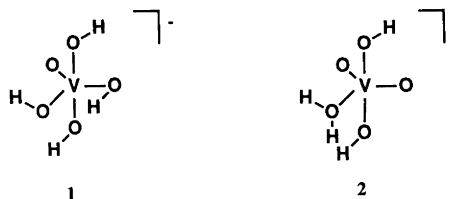
In the present paper spectral properties (UV–VIS, MCD, ^{51}V NMR) of the trigonal bipyramidal VO_5 moiety have been determined, and it is pointed out that the dihydrogenvanadate ion is almost identical in these respects. In fact, the differences between the spectra of vanadate(V) and those of monohydrogenvanadate(V) are small, but rather dramatic changes take place when further acid is added under equilibrium conditions to a solution of monohydrogenvanadate(V). We suggest that these changes reflect a simultaneous uptake of a proton and of water to form an ion of the composition $H_4VO_5^-$.

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Table 1. Abbreviations for α-hydroxy acids.

H$_2$alac	$(C_6H_5)(CH_3)C(OH)COOH$	atrolactic acid, 2-hydroxy-2-phenylpropanoic acid
H$_2$ehba	$(C_2H_5)_2C(OH)COOH$	2-ethyl-2-hydroxybutanoic acid
H$_2$hiba	$(CH_3)_2C(OH)COOH$	2-hydroxy-2-methylpropanoic acid
H$_2$hmba	$(C_2H_5)(CH_3)C(OH)COOH$	2-hydroxy-2-methylbutanoic acid

Experimental

The abbreviations used for α-hydroxy acids are listed in Table 1.

NMR. Spectra were obtained at 300 K, or at the temperatures mentioned, with a Bruker AM250 spectrometer at the magnetic induction 5.9 T. The ^{1}H and ^{13}C spectra were recorded with the sample in 5 mm o.d. NMR tubes, while 10 mm o.d. NMR tubes were used for the ^{51}V spectra. In all cases D$_2$O was used as a lock.

^{1}H NMR. The spectra were measured at 250 MHz using a spectral width of 5 kHz, a pulse width corresponding to 90° and a repetition time equal to 3.3 s (32k data table). A line broadening of 0.1 Hz was used, and frequencies are given relative to TMS.

^{13}C NMR. The spectra were measured at 62.9 MHz using a spectral width of 18 kHz, a pulse width corresponding to ca. 50° and a repetition time equal to 0.9 s (32k data table). The number of accumulations was approximately 500, and a line-broadening of 3 Hz was applied. Frequencies are given relative to TMS.

^{51}V NMR. The spectra were measured at 65.8 MHz using a spectral width of 62.5 kHz, a pulse width corresponding to 90° and a repetition time equal to 0.07 s (8k data table). The number of accumulations varied from 100 to 30000 depending on the concentration. A line broadening of 5 Hz was applied. The frequencies were measured relative to VOCl$_3$ which was placed in a capillary tube inside the NMR tube during the last 10 accumulations. Negative chemical shifts correspond to lower frequencies.

Powder diagrams. X-Ray powder photographs were recorded with a Guinier–Hägg camera using Cu Kα radiation and Si as reference.

CD and MCD. Natural circular dichroism and magnetically induced circular dichroism spectra were recorded on a spectrometer as described previously.[6]

UV-VIS. Absorption spectra were measured on Perkin-Elmer λ-17 and λ-3 VIS–UV spectrometers.

Materials

Divanadiumpentaoxide, V_2O_5. NH$_4$VO$_3$ (Merck) was heated 48 h at 200°C (hood) and then 3 h at 400°C (oven). Anal. V$_2$O$_5$: V.

(NH$_4$)$_2$[V(O)$_2${OC(CH$_2$CH$_3$)$_2$COO}]$_2$ or *(NH$_4$)$_2$ [VO$_2$(ehba)]$_2$.* 5.28 g (40 mmol) of H$_2$ehba (Aldrich) were treated with 2 M ammonia to give (NH$_4$)Hehba. The solution was evaporated to dryness and the (hygroscopic) salt was boiled with 20 ml of water and 3.50 g (19.2 mmol) of V$_2$O$_5$. The volume was reduced to 8 ml (rotatory evaporator, 30°C external bath), cooled on ice and filtered. The light yellow crystals were dried *in vacuo* over Sicapent (Merck) for 10 h.

Anal. C$_{12}$H$_{28}$O$_{10}$N$_2$V$_2$: C, H, N, V. UV–VIS: ε/m^2 mol^{-1}, ℏω/μm^{-1}, c/mol l^{-1}: 359(sh), 4.00, 2.56 × 10^{-3}. MCD: c = 2.56 × 10^{-3} mol l^{-1}, B = 1.2 T; Δε/m^2 mol^{-1} T^{-1}, ℏω/μm^{-1}: +0.034 (peak), 3.72; 0, 4.25; negative at higher energies. ^{51}V NMR: Only one line was observed, δ = −551.8 ppm, Δν$_{1/2}$ = 420 Hz. ^{13}C NMR: Only one isomer was observed, δ(CH$_3$) = 7.41 ppm, δ(CH$_2$) = 30.71 ppm, δ(C–O) = 92.81 ppm, δ(C=O) = 183.82 ppm. ^{1}H NMR: The prochiral center in the ligand causes the two protons in the methylene group to be non-equivalent. Only one isomer was observed. δ(CH$_3$) = 0.872 ppm, J = 7.2 Hz; δ$_a$(CH$_2$) = 1.67 ppm, δ$_b$(CH$_2$) = 1.83 ppm, J$_{ab}$ = 14.6 Hz. X-Ray powder photographs were indexed to give unit cell parameters that coincide with the published crystal data[4] to within the experimental uncertainty.

We were unable to prepare the compound in the manner described in the literature;[4] however, our data show that we have indeed synthezised the compound, but in a different way.

(NH$_4$)$_2$[V(O)$_2${OC(CH$_3$)$_2$COO}]$_2$ or *(NH$_4$)$_2$- [VO$_2$(hiba)]$_2$.* Basic hydrolysis (NaOH) of the methyl ester (Fluka) gave the sodium salt, which was converted into the ammonium salt (not hygroscopic) by ion exchange and evaporation of the eluate. The title compound was prepared as described above for the ehba complex.

Anal. C$_8$H$_{20}$O$_{10}$N$_2$V$_2$: C, H, N, V. UV–VIS: ε/m^2 mol^{-1}, ℏω/μm^{-1}, c/mol l^{-1}: 380(sh), 4.00, 1.24 × 10^{-4}. MCD: c = 2.40 × 10^{-3} mol l^{-1}, B = 1.2 T;

$\Delta\varepsilon/\text{m}^2\,\text{mol}^{-1}\,\text{T}^{-1}$, $\hbar\omega/\mu\text{m}^{-1}$: +0.030(peak), 3.7; 0, 4.0; −0.03, 4.4(peak). ^{51}V NMR: Only one line was observed, $\delta = -547.9$ ppm, $\Delta v_{1/2} = 240$ Hz. ^{13}C NMR: Only one isomer was observed, $\delta(\text{CH}_3) = 24.55$ ppm, $\delta(\text{C-O}) = 85.37$ ppm, $\delta(\text{C}=\text{O}) = 185.11$ ppm. ^1H NMR: $\delta(\text{CH}_3) = 1.425$ ppm.

(NH$_4$)$_2$[V(O)$_2${(±)-OC(CH$_2$CH$_3$)(CH$_3$)COO}]$_2$ or *(NH$_4$)$_2$[VO$_2$((±)-hmba)]$_2$*. The racemic ammonium salt NH$_4$Hhmba was prepared from the acid (Aldrich). An aqueous solution was reacted with V$_2$O$_5$ as described above for the ehba complex to give the title compound.

Anal. $\text{C}_{10}\text{H}_{24}\text{O}_{10}\text{N}_2\text{V}_2$: C, H, N, V. MCD: $c = 2.96 \times 10^{-3}$ mol l^{-1}, $B = 1.2$ T; $\Delta\varepsilon/\text{m}^2\,\text{mol}^{-1}\,\text{T}^{-1}$, $\hbar\omega/\mu\text{m}^{-1}$: +0.030(peak), 3.67; 0, 4.2. ^{51}V NMR: Only one line was observed, $\delta = -550.7$ ppm, $\Delta v_{1/2} = 315$ Hz. ^{13}C NMR: Two isomers were observed with the amount of substance ratio $n_a : n_b = 1 : 1$.

	isomer a	isomer b
$\delta(\underline{\text{C}}\text{H}_3\text{-CH}_2\text{-})$/ppm	7.59	7.52
$\delta(\underline{\text{C}}\text{H}_3\text{-C})$/ppm	24.49	24.19
$\delta(\text{CH}_3\text{-}\underline{\text{C}}\text{H}_2\text{-})$/ppm	30.80	31.12
$\delta(\underline{\text{C}}\text{-O})$/ppm	88.95	88.95
$\delta(\underline{\text{C}}=\text{O})$/ppm	184.42	184.42

^1H NMR: Two isomers were observed with the ratio $n_a : n_b = 1 : 1$; the asymmetric C atom causes the two protons in the CH$_2$ group to be non-equivalent.

	isomer a	isomer b	
$\delta(\text{C}\underline{\text{H}}_3\text{-CH}_2\text{-})$/ppm	0.862	0.833	$J = 7.3$ Hz
$\delta(\text{C}\underline{\text{H}}_3\text{-C})$/ppm	1.42	1.41	
$\sigma_a(\text{C}\underline{\text{H}}_2)$/ppm	1.70	1.72	
$\delta_b(\text{C}\underline{\text{H}}_2)$/ppm	1.83	1.85	$J_{ab} \approx 14.9$ Hz

(NH$_4$)$_2$[V(O)$_2${(−)$_D$-OC(CH$_2$CH$_3$)(CH$_3$)COO}]$_2$ · 3H$_2$O or (NH$_4$)$_2$[VO$_2$((−)-hmba)]$_2$·3aq. (±)-H$_2$hmba was resolved with brucine (Fluka) to give the less soluble brucinium salt.[8] This was converted first into the acid* (−)$_D$-H$_2$hmba by ion exchange (Dowex 50) and then to the ammonium salt. This salt was reacted with V$_2$O$_5$ in water as described for the ehba-vanadate compound.

Anal. $\text{C}_{10}\text{H}_{30}\text{O}_{13}\text{N}_2\text{V}_2$: N, V. UV–VIS: $\varepsilon/\text{m}^2\,\text{mol}^{-1}$, $\hbar\omega/\mu\text{m}^{-1}$, $c/\text{mol}\,\text{l}^{-1}$: ca. 280(sh), 4.00, 1.78×10^{-3}. CD: $c = 1.78 \times 10^{-3}$ mol l^{-1}; $\Delta\varepsilon/\text{m}^2\,\text{mol}^{-1}$, $\hbar\omega/\mu\text{m}^{-1}$: −0.09(peak), 3.53; 0, 3.70; +0.18, 3.90(peak); 0, 4.2; +0.24, 4.52(peak); 0, 4.6; negative at higher energies. ^{51}V NMR: Only one line was observed, $\delta = -550.8$ ppm, $\Delta v_{1/2} = 315$ Hz. ^{13}C NMR and ^1H NMR. Only signals belonging to the isomer a were observed.

(NH$_4$)$_2$[V(O)$_2${(±)$_D$-OC(C$_6$H$_5$)(CH$_3$)COO}]$_2$·2H$_2$O or (NH$_4$)$_2$[VO$_2$((±)alac)]$_2$·2aq. Racemic atrolactic acid, (±)-H$_2$alac, was prepared from acetophenone and

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* As far as we know, the absolute configuration of (−)$_D$-H$_2$ hmba has not been determined.

hydrogen cyanide.[8] The alac complex was prepared from the ammonium salt and V$_2$O$_5$ in the same way as the ehba complex. After some months at room temperature the compound was partially destroyed (the colour was darkened and the sample smelled of acetophenone).

Anal. $\text{C}_{18}\text{H}_{28}\text{O}_{12}\text{N}_2\text{V}_2$: N, V. UV–VIS: $\varepsilon/\text{m}^2\,\text{mol}^{-1}$, $\hbar\omega/\mu\text{m}^{-1}$, $c/\text{mol}\,\text{l}^{-1}$: 523(sh), 4.00, 1.86×10^{-3}. MCD: $c = 1.86 \times 10^{-3}$ mol l^{-1}, $B = 1.2$ T; $\Delta\varepsilon/\text{m}^2\,\text{mol}^{-1}\,\text{T}^{-1}$, $\hbar\omega/\mu\text{m}^{-1}$: +0.02(peak), 3.67; 0, 3.94; negative at higher energies. ^{51}V NMR: Only one line was observed, $\delta = -545.7$ ppm, $\Delta v_{1/2} = 755$ Hz. ^{13}C NMR: Two sets of lines belonging to two isomers were observed with the amount of substance ratio $n_a : n_b = 1 : 1$.

	isomer a	isomer b
$\delta(\underline{\text{C}}\text{H}_3\text{-C})$/ppm	21.61	21.80
$\delta(\underline{\text{C}}\text{-O})$/ppm	88.08	88.08
$\delta(\underline{\text{C}}=\text{O})$/ppm	183.6	183.6
$\delta(\underline{\text{C}}_1)$/ppm	139.84	139.84
$\delta(\underline{\text{C}}_4)$/ppm	125.71	125.78
$\delta(\underline{\text{C}}_3), \delta(\underline{\text{C}}_5)$/ppm	128.12	128.12
$\delta(\underline{\text{C}}_2), \delta(\underline{\text{C}}_6)$/ppm	128.44	128.44

Here, the carbon atoms of the phenyl group are numbered from the substituent, and the assignments of the pairs (3,5) and (2,6) are ambiguous. ^1H NMR. Two isomers were observed with the ratio $n_a : n_b = 1 : 1$.

	isomer a	isomer b	
$\delta(\text{C}\underline{\text{H}}_3\text{-C})$/ppm	1.80	1.82	
$\delta(\text{C}\underline{\text{H}}_o)$/ppm	7.45	7.48	
$\delta(\text{C}\underline{\text{H}}_m)$/ppm	7.33	7.33	$J_{om} \approx 7.4$ Hz
$\delta(\text{C}\underline{\text{H}}_p)$/ppm	7.27	7.27	$J_{mp} \approx 7.4$ Hz

Here, indices o, m and p refer to the position in the phenyl group.

(NH$_4$)$_2$[V(O)$_2${(+)$_D$-OC(C$_6$H$_5$)(CH$_3$)COO}]$_2$ or *(NH$_4$)$_2$[VO$_2$((+)-alac)]$_2$*. (±)-H$_2$alac was resolved[9] as the less soluble salt with (−)$_D$-1-phenylethane amine[10,11] from which the acid (S)-(+)$_D$-H$_2$alac was obtained by ion exchange.† The vanadium(V) complex was formed from the ammonium salt of (+)$_D$-H$_2$alac and V$_2$O$_5$ in aqueous solution at room temperature (^{51}V NMR), but any attempt to isolate a crystalline compound failed, because the ligand was decarboxylated and oxidized to acetophenone.

^{51}V NMR: $\delta = -546$ ppm, but small intensity, broad absorptions were seen at −500 and −461 ppm. ^{13}C NMR and ^1H NMR: Only signals assigned to the isomer a were observed.

Na$_3$VO$_4$·9.1H$_2$O. NH$_4$VO$_3$ (Merck) was boiled with the equivalent amount of 6 M NaOH. Recrystallization from water.

Anal. V, Na.

† The absolute configuration is (S)-(+)$_D$-H$_2$ alac.[12]

1,2-ethanediol. This product (Merck) was used without further purification.

Aqueous solutions of 1,2-ethanediol and vanadate. The solutions were prepared by adding sodium orthovanadate to the diol solution and then adjusting the pH with hydrochloric acid.

Results

The spectral characteristics of dimer vanadate complexes with α-hydroxy carboxylic acids include absorption spectra (UV–VIS), natural circular dichroism (CD), magnetically induced circular dichroism (MCD) and NMR of the nuclei ^{51}V, ^{13}C and ^1H.

Two isomers of the complex ion $[VO_2(ehba)]_2^{2-}$ are possible, *viz.* **3a** (=**3b**) and **4a** (=**4b**), with $R_1 = R_2 = Et$. Recently, the crystal structure of $(NH_4)_2[VO_2(ehba)]_2 \cdot aq$ was published,[4] and our data confirm the result which was found previously, that only the isomer **3** is present in aqueous solution as well as in the solid state.

3 a

3 b
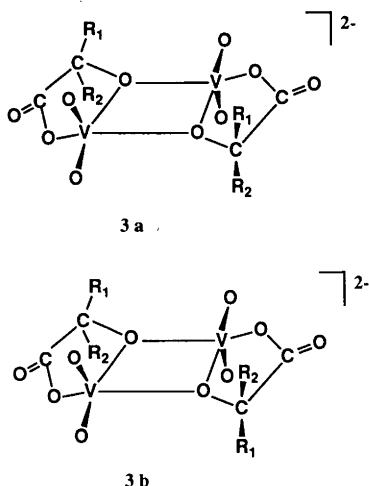
Similarly, two isomers of the ion $[VO_2(hiba)]_2^{2-}$ are possible, namely **3a** (=**3b**) and **4a** (=**4b**) with $R_1 = R_2 = Me$, but only the isomer **3** with one ^{51}V NMR signal is found.

4 a

4 b
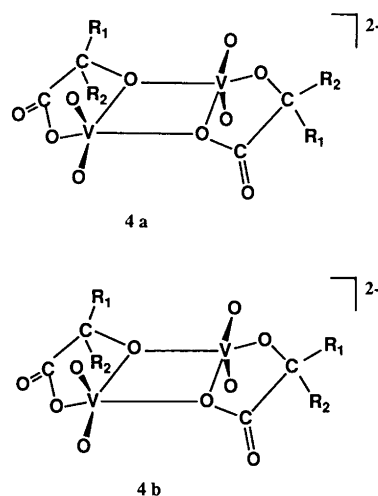
Two isomers of $[VO_2((\pm)\text{-hmba})]_2^{2-}$ and one of $[VO_2((-)_D\text{-hmba})]_2^{2-}$ have been observed and our data show that they are of type **3**. With $R_1 = Me$ and $R_2 = Et$, **3a** is $[VO_2((S)\text{-hmba})]_2^{2-}$, which is optically active; its mirror image has $R_1 = Et$ and $R_2 = Me$.[8] Compound **3b** is $[V_2O_4((S)\text{-hmba})((R)\text{-hmba})]^{2-}$, which has a center of inversion and is optically inactive. The fact that the two isomers of $[VO_2((\pm)\text{-hmba})]_2^{2-}$ are found in almost equal amounts shows that no preferential geometry obtains, i.e. the intramolecular interaction between the ethyl groups in **3a** is weak.

Two isomers of $[VO_2((\pm)\text{-alac})]_2^{2-}$ and one of $[VO_2((+)_D\text{-alac})]_2^{2-}$ have been observed, and our data show that they are of type **3**. With $R_1 = Me$ and $R_2 = Ph$, **3a** is $[VO_2((S)\text{-}(+)_D\text{-alac})]_2^{2-}$, which is optically active;

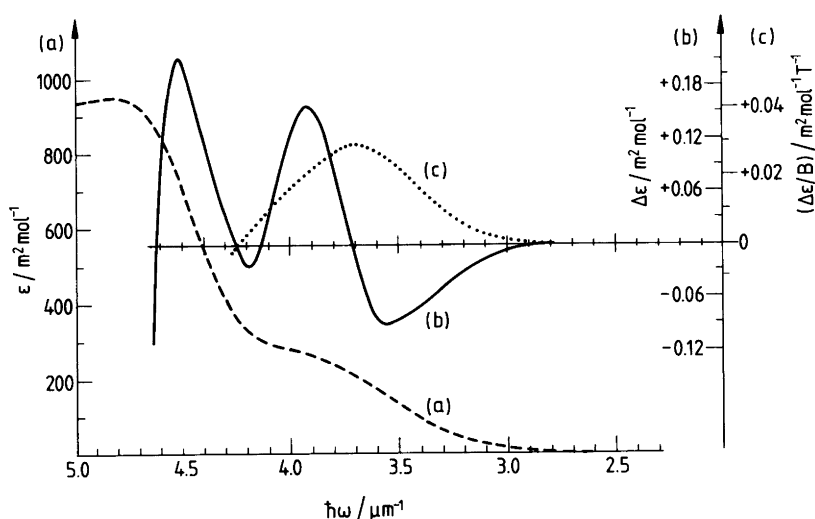*Fig. 1.* VIS–UV spectra of $(NH_4)_2[VO_2((-)_D\text{-hmba})]_2$ in aqueous solution. (a) UV–VIS, (b) CD and (c) MCD. For technical reasons the MCD was measured on the racemic compound.

Table 2. Equilibrium concentrations of complexes in the vanadate(V)–1,2-ethanediol–water system as a function of the temperature.[a]

T/K	[V]/M	[VL]/M	[VL$_2$]/M	[V$_2$L$_2$]/M
273	3.9×10^{-6}	2.63×10^{-5}	8.88×10^{-5}	1.91×10^{-4}
283	2.92×10^{-5}	7.32×10^{-5}	1.24×10^{-4}	1.37×10^{-4}
297	6.32×10^{-5}	1.86×10^{-4}	7.32×10^{-5}	8.90×10^{-5}
313	1.42×10^{-4}	2.83×10^{-4}	≈ 0	3.77×10^{-5}
333	1.50×10^{-4}	3.21×10^{-4}	≈ 0	1.43×10^{-5}

[a] $c(\text{Na}_3\text{VO}_4) = 5.0 \times 10^{-4}$ M, $c(\text{C}_2\text{H}_6\text{O}_2) = 5.64$ M, pH 7.64 (25°C). V = vanadate, L = ligand.

its mirror image has $R_1 = \text{Et}$ and $R_2 = \text{Ph}$.[13] Compound **3b** is $[\text{V}_2\text{O}_4((S)\text{-}(+)_D\text{-alac})((R)\text{-}(-)_D\text{-alac})]^{2-}$, which has a center of inversion and is optically inactive. The fact that **3a** could not be isolated indicates a strong intramolecular interaction between the phenyl groups in this compound.

As an example of the UV–VIS data of dimer vanadate complexes with α-hydroxycarboxylic acids, the experimental results for $[\text{VO}_2((\pm)\text{-hmba})]_2^{2-}$ and $[\text{VO}_2((-)_D\text{-hmba})]_2^{2-}$ are given in Fig. 1. Common to all coordination compounds of this series, one finds the first ligand-to-metal charge transfer transition (LMCT) as a broad shoulder around 4 μm^{-1} with the absorption coefficient ε in the range 140–190 m^2 mol^{-1} per V. Associated with this absorption the $[\text{VO}_2((-)_D\text{-hmba})]_2^{2-}$ ion shows *two* CD signals, which proves that the absorption is due to at least two electronic transitions. These transitions may be a result of a coupling of two charge-transfer transitions to each vanadium. For all the complexes the MCD spectra in this region are very similar, and in the light of the CD result, they must be interpreted as due to one or more positive *B*-terms.

Equilibrium in the system vanadate(V)-1,2-ethanediol–water was measured as a function of temperature using ^{51}V NMR. The results are given in Table 2.

Discussion

The objective of the discussion is to present experimental evidence showing that the dihydrogen vanadate ion is five-coordinate with respect to the oxygen ligands. Although this is yet to be proved, we shall use the generic formula H_4VO_5^- for the monomeric vanadate species which is found in aqueous solutions at ca. pH 7–8.

It will be shown that not only do the spectroscopic results point to this interpretation, but also previously published equilibrium data give this result if, for concentrated solutions, activities are used instead of concentrations in the calculation of equilibrium constants.

^{51}V NMR. The orthovanadate ion VO_4^{3-}, as it is found in 1 M NaOH, has tetrahedral coordination,[13] a chemical shift $\delta = -538$ ppm and a linewidth at half height $\Delta v_{1/2} = 9$ Hz (Ref. 14 and this work). The uptake of one proton to form HVO_4^{2-} (ca. pH 11) changes the symmetry group of the ion from T_d to C_{3v}, and it is accom-
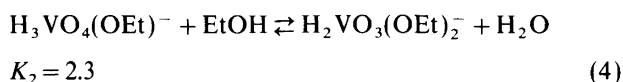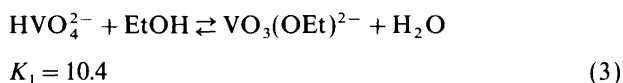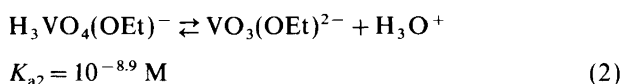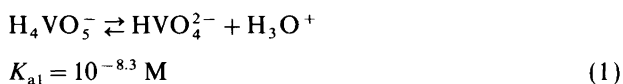
panied by a small change of chemical shift to -534 ppm and an increase in the half-width to 40–85 Hz, depending on the concentration. Further uptake of a proton by lowering pH to ca. 7 changes the chemical shift to a value around -558 ppm and the half width to 110 Hz (Ref. 14 and this work).

In the present work a series of five-coordinate vanadium(V) species with almost trigonal-bipyramidal structure has been prepared, and the solution chemical shift was found to be in the range -546 to -552 ppm. The increase of the half-widths from 240 to 755 Hz follows roughly the increasing 'bulkiness' of the ligand. We note that the chemical shifts of six-coordinate vanadium(V) $(\text{VO}_2^+, \text{H}_3\text{V}_{10}\text{O}_{28}^{3-})$ are found at less negative values than -545 ppm and that four-coordinate vanadium(V) $(\text{V}_4\text{O}_{12}^{4-}, \text{V}_4\text{O}_{13}^{6-}, \text{V}_5\text{O}_{15}^{5-})$ with low symmetry (i.e. not T_d or C_{3v}) has shift values more negative than -565 ppm.[13]

It is concluded that the chemical shift of dihydrogen vanadate is within the limits observed for five-coordinate vanadium(V) species.

^{1}H and ^{13}C NMR. In principle six isomers of types **3** and **4** with the general formula $[\text{VO}_2(\pm)\text{-hmba}]_2^{2+}$ are possible, but the NMR study proves that only the three isomers of type **3** are formed. Structure **3a** (two isomers) is optically active and structure **3b** is the inactive meso-isomer.
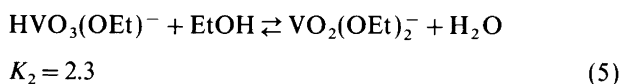
Equilibrium in vanadate–ethanol–water. This complex equilibrium system was studied by Gresser and Tracey,[15] who used the peak areas in the ^{51}V NMR spectra of various solutions to determine the four equilibrium constants of reactions (1)–(4).

$$\text{H}_4\text{VO}_5^- \rightleftarrows \text{HVO}_4^{2-} + \text{H}_3\text{O}^+$$

$$K_{a1} = 10^{-8.3} \text{ M} \tag{1}$$

$$\text{H}_3\text{VO}_4(\text{OEt})^- \rightleftarrows \text{VO}_3(\text{OEt})^{2-} + \text{H}_3\text{O}^+$$

$$K_{a2} = 10^{-8.9} \text{ M} \tag{2}$$

$$\text{HVO}_4^{2-} + \text{EtOH} \rightleftarrows \text{VO}_3(\text{OEt})^{2-} + \text{H}_2\text{O}$$

$$K_1 = 10.4 \tag{3}$$

$$\text{H}_3\text{VO}_4(\text{OEt})^- + \text{EtOH} \rightleftarrows \text{H}_2\text{VO}_3(\text{OEt})_2^- + \text{H}_2\text{O}$$

$$K_2 = 2.3 \tag{4}$$

The acidity constants were determined for solutions with composition $C_V = 0.50$ mM, $C_{\text{EtOH}} = 5.10$ M and pH varying from 7.2 to 11.0, and the consecutive stability constants were similarly determined using the conditions $C_V = 0.39$ mM, pH 7.5 and C_{EtOH} varying from 2.55 to 7.65 M. All constants were evaluated using concentrations, and it was stressed that the water concentration is a necessary part of the constants K_1 and K_2, so they are in effect equilibrium constants for water displacement reactions.

The four constants account for the concentration dependence of the observed ^{51}V NMR spectra, and this

interpretation implies that five vanadium species exist: The two vanadate species show one peak whose chemical shift varies from -534 ppm at pH 11.0 to -559 ppm at pH 7.2, the two monoesters show one peak whose position varies similarly from -532 ppm to -554 ppm, and finally, one diester is observed between pH 7.2 and 10, with the chemical shift at -551 ppm independent of pH. It was believed by Gresser and Tracey,[15] but not proved, that all species have a four-coordinate geometry around the vanadium center; in fact, they used reaction (5) in place of reaction (4).

$$HVO_3(OEt)^- + EtOH \rightleftarrows VO_2(OEt)_2^- + H_2O$$

$$K_2 = 2.3 \tag{5}$$

Equilibrium in vanadate-1,2-ethanediol–water. This system was studied by Gresser and Tracey[16] by methods similar to those used in their work on ethanol. Part of the chemistry was described by means of equations such as eqns. (1)–(4) with the ligand being monodentate, i.e. with 2-hydroxyethyl replacing ethyl [eqns. (6)–(9)].

$$K'_{a1} = 10^{-8.8} \text{ M} \tag{6}$$

$$K'_{a2} = 10^{-8.9} \text{ M} \tag{7}$$

$$K'_1 = 18.6 \pm 1.0 \tag{8}$$

$$K'_2 = 4.9 \pm 0.3 \tag{9}$$

The acidity constants were determined for aqueous solutions with the composition $C_V = 0.50$ mM, $C_{diol} = 5.64$ M and pH varying from 7 to 10, and the consecutive stability constants were determined using similar conditions except that the pH was kept at 7.5, whereas the concentration of 1,2-ethanediol varied from 0.805 to 13.7 M.* In all experiments[16] 20 mM tris(hydroxymethyl)methaneammonium chloride was used as buffer, but this is without significance for the results (this work). Again it was pointed out that the inclusion of the water concentrations in the stability constants is essential for the results. The ^{51}V NMR chemical shifts of the vanadates varies from -537 ppm at pH 10.1 to -559 at pH 7.6, and for the two monoesters the corresponding values are -535 and -555 ppm. The chemical shift of the diester varies only slightly with pH: -550 ppm at pH 10.1 and -552 ppm at pH 7.6.[16]

The species discussed until now are analogous to those found in the ethanol study, and it was claimed but not proved that they all posessed a four-coordinate geometry. In addition, a species with a chemical shift around -521 ppm was found,[16] and it was shown that its stoichiometric composition is $n_{vanadate} : n_{1,2-ethanediol} = 2:2$. At pH 7.6 one may write eqn. (10), with the overall

(concentration) stability constant $\beta_{22} = 2.58 \times 10^9$ M (this work).

$$2H_4VO_5^- + 2Et(OH)_2$$
$$\rightleftarrows V_2O_2(EtO_2)_2(OH)_4^{2-} + 4H_2O \tag{10}$$
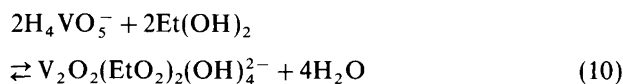
An equilibrium study of the formation of the 2 : 2 complex based on the concentration mass action law of Guldberg and Waage must be unreliable because the vapor pressure of water and ethylene glycol (and thereby their activities) vary nonlinearly with their concentration.[17] Using the 12 sets of data, lines 2–13 of Table II in Ref. 16, and tables of vapor pressure,[17] we obtained at 294 K the values shown in eqn. (11).

$$K'_1 = 18.5, \quad K'_2 = 4.6, \quad \beta_{22} = 3.79 \times 10^9 \text{ M} \tag{11}$$

Here the vanadium-containing species are considered as ideal solutes, and the standard state for the activity is the infinitely diluted solution with the concentration unit $1 \text{ mol } l^{-1} = 1$ M. As the standard state for the activity of the solvent a mixture with $c°(H_2O) = 37.625$ M, $p°(H_2O) = 24.3$ mbar and $c°(Et(OH)_2) = 5.880$ M, $p°(Et(OH)_2) = 223$ μbar was chosen. Thus, the activity of the components in the solvent mixture is given by eqn. (12) to the first order of approximation, with

$$c(x) = [c°(x)/p°(x)]p(x) \tag{12}$$

$x = H_2O$ or $Et(OH)_2$. Since data for the vapor pressure of ethylene glycol as a function of temperature are sparse, we used instead eqn. (13), with the equilibrium constant

$$2H_3VO_4(OEtOH)^-(aq)$$
$$\rightleftarrows V_2O_2(EtO_2)_2(OH)_4^{2-}(aq) + 2H_2O(g) \tag{13}$$
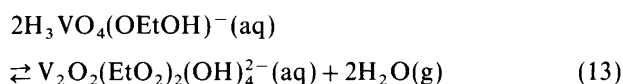
given by $K_{22} = \beta_{22}K'_1{}^{-2}$. Using the values of Table 2 one obtains $\Delta H° \approx -7 kJ \text{ mol}^{-1}$ for this reaction, but this is only correct to the order of magnitude, since $\ln K_{22}$ is not quite linear in T^{-1}.

The amount of water in eqn. (13) deserves some comment, because the corresponding reaction in Ref. 16 was given with one mole of water, and therefore the reaction which in Ref. 16 would correspond to eqn. (10) should give three moles of water, *vide infra*, eqn. (18). The discussion to follow is based upon the twelve sets of data,[16] together with the activity data for water at 294 K as referred to above.[20] For reaction (14) the number n is to

$$2VL \rightleftarrows V_2L_2 + n \text{ aq}$$

$$K(n) = [V_2L_2]\{aq\}^n/[VL]^2 \tag{14}$$

be determined as the value that gives the best fit of K to the data. Here VL is the monoester and V_2L_2 the 2 : 2 complex, [ ] denotes concentrations, and { } either

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* The figures and accuracy are quoted after Ref. 16; we have obtained similar but not identical figures.

concentration or activity (corrected concentration) of water. Using concentrations one obtains eqn. (15), and

$$K(0) = (7.0 \pm 2.5) \times 10^3 \, \text{M}^{+1} \quad f \approx 2.4$$
$$K(1) = (2.4 \pm 0.3) \times 10^5 \quad\quad f \approx 1.1 \quad\quad (15)$$
$$K(2) = (8.6 \pm 1.7) \times 10^6 \, \text{M} \quad f \approx 1/1.8$$

with activities one has eqn. (16)

$$K(1) = (2.6 \pm 0.6) \times 10^5 \quad f \approx 1.7$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad (16)$$
$$K(2) = (1.0 \pm 0.1) \times 10^7 \, \text{M} \quad f \approx 1.1$$

If the 12 sets of data are arranged according to decreasing concentration of water, then the variation of the 12 calculated equilibrium constants may show a trend, i.e. being correlated with the concentration or activity. f denotes the ratio between the last and the first constants in a set, meaning that K increases through a set to an extent indicated by the factor f. It is obvious now that $K(1)$ fits best to the concentration data, whereas $K(2)$ fits best to the activity data, because data with f near 1 are randomly distributed.

The similarity of the ^{51}V NMR chemical shifts of the monoesters formed with ethanol and with 1,2-ethanediol clearly indicates that the vicinal diol is non-chelate. Further, the NMR spectrum of the 2 : 2 compound shows the equivalence of the two vanadium atoms and indicates a change in the coordination number of vanadium when this compound is formed. These facts and the preferred concentration constant $K(1)$ from eqn. (15) led to the conclusion[18] that four-coordinate reactants form a five-coordinate product according to eqn. (17). However, when activities are used, eqn. (19) below is obtained.

$$\quad (17)$$
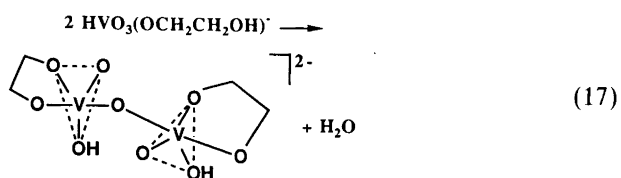
NMR and CD of vanadate–nucleoside–water. This complex system has recently been investigated by several authors.[6,18,19] Vanadate(V), in short V, reacts with each of the common nucleosides, L (L = adenosine, cytidine, guanosine, uridine and inosine) in aqueous solution at pH 7–8 to form essentially two products. The major one has the stoichiometry V_2L_2 and a ^{51}V NMR chemical shift at -523 ppm. For all the nucleosides the overall stability constants for reaction (18) are of the same order of magnitude as $\beta_{22}/[\text{H}_2\text{O}]$ from eqn. (10). The minor product, of the stoichiometry VL, is a monoester. Its chemical shift coincides with the dihydrogenvanadate resonance at -560 ppm.[18] The V_2L_2 complexes are not formed with the deoxynucleosides,[6,18] and ^{13}C NMR

$$2V + 2L \rightleftarrows V_2L_2 + 3H_2O \quad\quad\quad (18)$$

leaves no doubt that the binding is through the $2',3'$-diols of the ribose ring.[6,20]

Circular dichroism showed that neither the monoesters nor the 2 : 2 complexes contain the bidentate diols bound as chelate ligands. The interpretation of this fact and of the NMR results is that the 2 : 2 complex has a molecular structure composed by two edge-shared VO_6 octahedra that form a $O_4V(\mu\text{-}O)_2VO_4$ skeleton, with the vicinal diols bridging the two vanadium centers.[6]

Combination of the known structure of the 2 : 2 complex with the activity constant $K(2)$ of eqn. (16) leads to eqn. (19) rather than that eqn. (17). As is explicitely written in eqn. (19), all experiments are consistent with the notion that the dihydrogenvanadate(V) ion is five-coordinate at pH 7–8.

$$\quad (19)$$
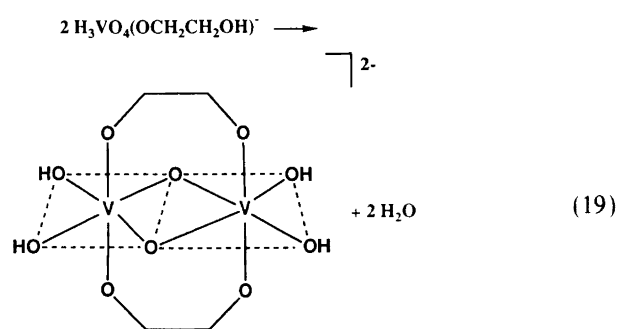
The ^{51}V NMR results of the nucleoside complexes were obtained in self-buffered solutions[6] or in solutions with the buffer N-(2-hydroxyethyl)piperazine-N'-2-ethanesulfonic acid (HEPES) added.[18] This buffer seems to be inactive in the sense that no additional NMR resonance appears when it is added to the solutions. Solutions that are buffered with imidazole show a resonance with a chemical shift -480 ppm.[6] This is due to a 1 : 1 complex whose optical activity indicates that the nucleoside here binds as a chelate ligand; most likely the complex contains the buffer and is six-coordinate. This is in agreement with a recent result that vanadate forms no complex with imidazole but does indeed form a ternary complex of the type vanadate–nucleoside–imidazole.[21] Addition of the buffer tris(hydroxymethyl)methaneamine (Tris) to solutions of vanadate and the nucleosides gives rise to two resonances at -510 and -542 ppm,[18] but the corresponding species have not been further studied.

Absorption spectra and MCD of vanadates. The near-UV absorption of vanadate(V) varies characteristically with pH.[2,3,22] Thus in 1 M NaOH one finds a distinct peak at $3.67 \, \mu\text{m}^{-1}$ with the absorption coefficient $\varepsilon \approx 700 \, \text{m}^2 \, \text{mol}^{-1}$, but at pH 10–11 this peak is moved towards higher energies and ε decreases to ca. $400 \, \text{m}^2 \, \text{mol}^{-1}$. During this lowering of pH the MCD remains of the A-type but with small changes that have been fully explained[3] as a weak perturbation of the VO_4 skeleton due to the uptake of the proton, which changes the symmetry group from T_d to C_{3v}.

However, when a proton is added to HVO_4^{2-}, i.e. when the pH is lowered to 7–8 and dihydrogenvanadate is formed, more profound changes in the spectral properties take place. The distinct absorption peak disappears, ε is decreased to less than $200\,m^2\,mol^{-1}$ in this spectral range, and the MCD spectrum is changed from an A-type into a B-type one.[2,3] In fact, the spectra are very similar to those of five-coordinate vanadium(V) (Fig. 1); note that here $\varepsilon = 140\,m^2\,mol^{-1}$ per V atom.

Obviously, the spectral properties of the dihydrogen-vanadate ion indicate that the coordination number is increased relative to the vanadate ion, i.e. that the formula is $H_4VO_5^-$ rather than $H_2VO_4^-$.

Five coordination of dihydrogenvanadate. Recently, the possibility of an increase in the coordination number of monomeric vanadium(V) when the pH is lowered from 12–13 (CN 4) to 7–8 (CN 5–6) has been mentioned in a discussion on the ^{51}V NMR of vanadates, but the subject was not further pursued.[23] Now, given the five coordination of the dihydrogen vanadate ion, it remains to decide which of the structures 1 or 2 the ion may take. We shall give some arguments that point to the structure 2, which posesses the characteristic cis-VO_2 unit.

Note first the difference in the pH dependence of the ^{51}V NMR of the ethanol esters of vanadates(V) as reported by Gresser and Tracey.[15] The NMR of the monoesters, eqn. (2), follows very closely the behaviour of the vanadates themselves, whereas the NMR of the diester, eqn. (4), is independent of pH, and this ion exists only in the same pH range as the $H_4VO_5^-$ ion.

Secondly, the Pauling–Ricci rules[24] for the pK of monomer oxoacids gives ca. 12 for structure 1 and ca. 7 for structure 2. The observed acidity constant of $VO_2(OH)_2(OH_2)^-$ is some 10 times weaker than expected for $VO_2(OH)_2^-$; it has been observed previously that an additional coordinated molecule of water weakens the strength of the oxoacids of transition metals.[25]

A recent paper[26] on the interaction between vanadate(V) and proteins concludes that the formation of vanadate complexes at physiological pH takes place through a dissociative mechanism. The rate-limiting step is the loss of a hydroxy or an aqua ligand from dihydrogenvanadate. This was not easy to understand, because the assumption of this ion being four-coordinate requires a tricoordinate intermediate. With the present findings those experiments are well accounted for.

The growing interest in vanadium chemistry is partly a result of surprising bioinorganic discoveries. Among the first examples of this chemistry was the ability of certain marine ascidians to accumulate vanadium in blood cells. Recently[27] it has been reported that a 18-crown-6 ether with an amino group is presumably responsible for the vanadium uptake and transport. Actually complexes between transition metals and crown ethers are scant, but in this case it is quite conceivable that the five-coordinate

dihydrogenvanadate coordinates through hydrogen bonding which includes bonding to the protonated amino group.

Conclusions

A series of dinuclear vanadium(V) complexes with α-hydroxy acids without H atoms on the α-carbon atom has been prepared. It has been shown that among several possible isomers only the structures 3 are found. The vanadium nuclei are five-coordinate with respect to oxygen ligands, and the spectral properties (^{51}V NMR, UV–VIS, MCD) of the VO_5 moiety have been characterized.

The similarity between the spectral properties of dihydrogenvanadate and those of the VO_5 moiety suggests that the former ion is five-coordinate.

The very reliable literature data[16] for the equilibrium between vanadate and vicinal diols have been reinterpreted using activities instead of concentrations in the calculation of the equilibrium constants. In this way it has been shown that the equilibrium data are also in accord with an assumption of dihydrogenvanadate being five-coordinate. This means that we have arrived at a consistent picture embracing all published experiments, and we conclude that the dihydrogenvanadate ion is five-coordinate.

Note added in proof. After the submission of this paper, further ^1H and ^{13}C NMR results have been published in order to decide on the structure of the vanadate–nucleoside dimer.[28] Although the experiments did not point to the five-coordinate structure shown in eqn. (17), no final conclusions were obtained because the water stoichiometry using concentrations excludes the cis-coordinate structure, eqn. (19) above.

Given the structure, eqn. (19), two different vanadate–nucleoside dimers are expected. They give rise to three ^{51}V NMR signals, of which two are of equal intensity. Recently, the vanadate–uridine–water system was studied, and a ^{51}V NMR spectrum was obtained with improved resolution on a 500 MHz instrument.[29] The experiments showed two lines (-521.7 and -523.4 ppm) of almost equal intensity and one line (-527.2 ppm) of lower intensity.

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