Multicomponent Polyanions. 45. A Multinuclear NMR Study of Vanadate(V)–Oxalate Complexes in Aqueous Solution

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Ehde, P. M., Pettersson, L. and Glaser, J., 1991. Multicomponent Polyanions. 45. A Multinuclear NMR Study of Vanadate(V)–Oxalate Complexes in Aqueous Solution. – Acta Chem. Scand. 45: 998–1005.

The two complexes formed in the aqueous vanadooxalate system, $V(Ox)^-$ and $V(Ox)_2^{3-}$, have been characterized using ^{51}V, ^{13}C and ^{17}O NMR.

For the $V(Ox)_2^{3-}$ complex, two peaks are observed in ^{13}C NMR and four in ^{17}O NMR. This leads to the conclusion that each oxalate ligand has two different distances to the VO_2 group. This fact, together with the peak integrals and the chemical shifts, indicates strongly that the hexacoordinate complex $[VO_2(C_2O_4)_2]^{3-}$ found in single-crystal X-ray structure determinations persists in aqueous solution. The dependence of the ^{13}C NMR linewidths upon temperature reveals two types of dynamic processes: (1) a rearrangement in which the two different $V-O_{ox}$ switch places and (2) an exchange of the oxalate ligands in the $[VO_2(C_2O_4)_2]^{3-}$ complex with free oxalate, probably through a dissociative process. Rate constants and activation parameters for the two dynamic processes involving $[VO_2(C_2O_4)_2]^{3-}$ have been calculated from the shape of the ^{13}C NMR signals.

For the $V(Ox)^-$ complex, only one relatively narrow peak is obtained in ^{13}C NMR and three peaks in ^{17}O. This fact, as well as the relative positions of these peaks, is in accordance with a pentacoordinate complex $[VO_2(C_2O_4)H_2O]^-$, where the two V–O distances to the oxalate ligand are equal. We also show that, in the pH range 0.8–6.6, there is no protonation of the studied complexes, in agreement with previous potentiometric results.

The impact of vanadium(V) on biological systems has reached increased attention in recent years and numerous studies have been made on interactions with and effects on various metabolites and enzymes.[1] Oxalic acid is abundant both in natural waters and in living cells.[2] The interaction between vanadate and oxalate has been determined previously in 0.6 M Na(Cl) at 25 °C.[3] Two strong complexes were established, $V(Ox)^-$ and $V(Ox)_2^{3-}$, the first being formed in more acidic solutions.

The ^{51}V[4,5] and ^{17}O NMR[5] characteristics for the binary vanadates are known from earlier studies. However, the VO_2^+ cation has never been observed in ^{17}O NMR, probably owing to fast exchange with water.[6]

Several structural determinations have been performed on vanado-organic complexes in the solid state. The structure of $V(Ox)_2^{3-}$ (Fig. 1) has been determined from single-crystal X-ray studies.[7,8] The vanadium atom has six-coordination consisting of two terminal oxygens (O_1 and O_2) mutually cis ($\angle OVO \approx 104°$) and four oxalate oxygens (O_3-O_6). The short distance between the vanadium atom and the terminal oxygens, 1.6 Å, indicates strong multiple-bond character. The oxygens trans to the terminal oxygens (O_5-O_6) have long bonds to V, 2.2 Å. Each oxalate has one oxygen with a long and one with a medium V–O bond length, 2.0 Å.

To our knowledge, no structure determination of the $V(Ox)^-$ complex has been published, but the structure of a related $VO_2F(C_2O_4)^{2-}$ complex has been determined and is shown in Fig. 2.[9] Here vanadium is pentacoordinate with two terminal oxygens at the same short distance as in $[VO_2(C_2O_4)_2]^{3-}$ (1.6 Å), equal V–O_{ox} distances (2.0 Å) and a fluorine atom in the fifth coordination site.

Little is known about the structure of vanado-organic complexes in aqueous solution. It is of great importance to know the structure in solution in order to understand how vanadate affects natural and biological systems.[10] A knowl-
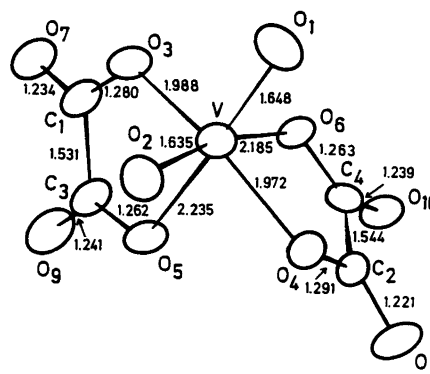

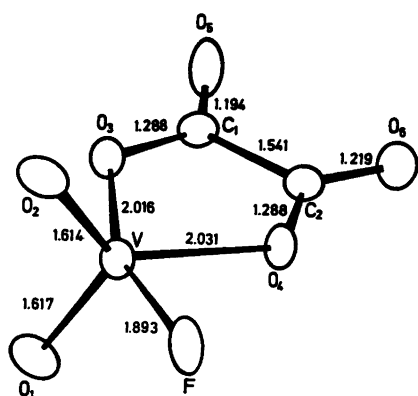Fig. 1. Structure of $[VO_2(C_2O_4)_2]^{3-}$ redrawn from Ref. 7.

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Fig. 2. Structure of $[VO_2F(C_2O_4)]^{2-}$ redrawn from Ref. 9.

edge of the structure is also vital when discussing reaction mechanisms.

To elucidate if the structure of $V(Ox)_2^{3-}$ in the solid phase persists in solution and to explore the structure of $V(Ox)^-$, multinuclear (^{51}V, ^{13}C and ^{17}O) NMR measurements on aqueous solutions containing these species have been performed in the present study. We have also obtained kinetic results which will briefly be described. EXAFS measurements on VO_2^+, $V(Ox)^-$ and $V(Ox)_2^{3-}$, and a single-crystal X-ray structure determination of a ($V(Ox))_n^{n-}$ complex[‡] are in progress and will be reported in forthcoming papers.

Experimental

Chemicals. $H_2C_2O_4 \cdot 2H_2O$, $Na_2C_2O_4$ and NaCl (all Merck *p.a.*) and $NaVO_3 \cdot 2H_2O$ (Fluka > 97 %) were used without any pretreatment. Distilled and boiled water was used when preparing the solutions. Concentrated HCl (Merck *p.a.*) was diluted and standardized against dried Trizma-base (Sigma Reagent Grade). For enrichment 18 at. %

[‡] *Note added in proof:* The solid phase has been found to contain discrete $[V_4O_8(C_2O_4)_4(H_2O)_2]^{4-}$ anions. All four vanadiums are hexacoordinated, forming a ring of edge- and cornershared octahedra. The two water molecules, however, are weakly bonded ($V-O_{aq} \approx 2.4$ Å), and therefore five-coordination may be an alternative description.

^{17}O-enriched water (ISO-YEDA, Rehovot, Israel) was used. The pH was measured with calibrated pH meters.

Preparation of solutions. In order to facilitate the interpretation of NMR spectra it was necessary to prepare solutions containing as few species as possible. For this purpose, the computer programs SOLGASWATER[11] and IGNASI[12] were used to calculate at which pH and total concentrations optimal fractions of vanadium and oxalate are bound in the two complexes. In the calculations the equilibrium constants from Ref. 3 were used. When possible, solutions were 0.6 M in Na(Cl), *i.e.* the medium in which the equilibrium constants were determined.[3] As the temperature and medium were not always the same as in Ref. 3, the concentrations obtained from the calculations could be expected to differ from the true concentrations. However, the calculated concentrations were found to agree rather well with values obtained from the NMR integrals, implying that the different conditions have only minor effects on the equilibria.

For the $V(Ox)_2^{3-}$ complex, a solution containing nearly 100 % of the complex could be prepared (Fig. 3). However, this was not possible for $V(Ox)^-$, since at the high concentrations needed for ^{17}O NMR at most 70 % of the vanadium is bound in this complex. We found it advantageous to have a mixture of binary vanadates and $V(Ox)^-$ rather than a mixture of $V(Ox)_2^{3-}$ and $V(Ox)^-$, since $V(Ox)_2^{3-}$ and $V(Ox)^-$ have overlapping NMR peaks for all the three nuclei studied. It is extremely difficult to prepare a suitable solution of $V(Ox)^-$ owing to reduction, precipitation of amorphous V_2O_5 and fast exchange in the acid pH region where this complex predominates. The reduction and exchange accelerate when the pH is lowered. To minimize all these problems, less acid solutions with a small excess of vanadate were prepared when studying $V(Ox)^-$.

As ^{17}O has a low natural abundance (0.04 %), spectra have to be recorded from relatively concentrated solutions to achieve acceptable signal/noise ratios.[*] Initially,

[*] Addition of ^{17}O-enriched water to the investigated solutions leads to selective enrichment of some oxygen sites. Heating the solutions or storing them for a time sufficient for complete enrichment led to decomposition of the species under study.
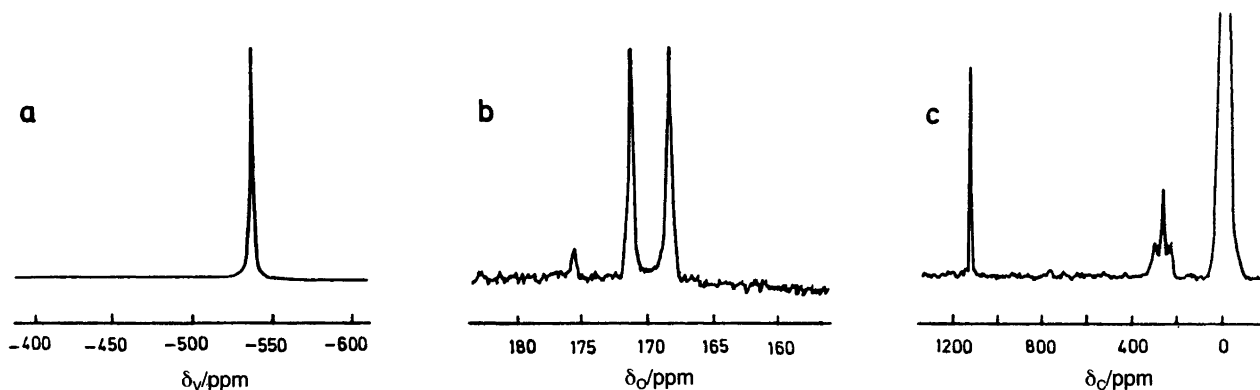

Fig. 3. Spectra for a Ox/V= 2 solution at pH 4.8 containing mainly $V(Ox)_2^{3-}$: (a) ^{51}V NMR at 25 °C, (b) ^{13}C NMR at −5 °C and (c) ^{17}O NMR at 12 °C.

0.5–1 M solutions were prepared. At such high concentrations the ^{17}O NMR peaks are broad for the two complexes. As this could be due to fast chemical exchange, measurements were attempted at lower concentrations. (Factors affecting the linewidths in ^{17}O NMR are further discussed in the Results and Discussion section.)

Vanadium(V) has low solubility at pH 2–3, which is in the range where the $V(Ox)^-$ complex is formed, but the precipitation is slow. Solutions that contained small amounts of precipitated amorphous V_2O_5 were filtered. The acid solutions, pH < 3, were stored in a refrigerator as the cold and darkness decreased the precipitation rate as well as the reduction of V(V) to V(IV). The solutions of $Na_2C_2O_4(s)$ and of $NaHC_2O_4(s)$ were heated to 50 °C and allowed to cool to room temperature. Undissolved substances were removed by filtration.

NMR measurements. The measurements were performed on Bruker AM 400 or AM 500 spectrometers. Multinuclear broadband probes (10 mm) were used. Some typical NMR parameters for the 400 MHz spectrometer are given below.

Oxygen-17 NMR: Spectrometer frequency (SF) 54.24 MHz, time domain (TD) 16 K, spectral width (SW) 100 kHz, pulse width (PW) 8.0 μs, acquisition time (AQ) 0.08 s. Under these conditions, peak integrals were quantitative within 10 %. Before integration of the peaks, baseline correction was performed. The chemical shifts are reported in ppm toward higher frequency with respect to external tap-water at 25 °C (0 ppm).

Carbon-13 NMR: SF 100.61 MHz, TD 4 K, SW 5 kHz, PW 10.0 μs (≈ 70° pulse) and AQ 0.4 s. Tetramethylsilane (TMS) at 25 °C was used as external standard. A pulse repetition time of 20 s was sufficient to obtain reliable integrals.

Vanadium-51 NMR: SF 105.24 MHz, TD 4 K, SW 33 kHz, PW 10.0 μs and AQ 0.03 s. The chemical shifts are referred to external $V_4O_{12}^{4-}$, set to $\delta_V = -576.4$ ppm at 25 °C and in 0.6 M Na(Cl) medium, corresponding to $\delta_V(VOCl_3) = 0$ ppm.

Results and discussion

A large number of ^{13}C, ^{17}O and ^{51}V NMR spectra were recorded for solutions containing varying amounts of the species at different pH values and temperatures. Some representative results are shown in Tables 1–3 and Figs. 3 and 4.

The oxalate system. The results from the $H^+-C_2O_4^{2-}$ system are shown in Table 1. The ^{13}C chemical shift increases when oxalic acid is deprotonated. The value $\delta(HC_2O_4^-) - \delta(H_2C_2O_4) = 4.5$ ppm is in accordance with previous measurements on monocarboxylic acids for which the difference between base and acid was found to be 4.7 ± 0.2 ppm.[13] There is also a considerable increase in the linewidth, by a factor of about ten, when going from $H_2C_2O_4$ to $C_2O_4^{2-}$ (Table 1).

The ^{17}O chemical shift also becomes higher when the pH is increased, but here a slight decrease in linewidth is observed. The linewidth decreases when the temperature is raised, probably because quadrupolar relaxation becomes less efficient. In a recent multinuclear NMR investigation of Al^{3+}-carboxylic acid complexes similar values of the chemical shift were obtained, $\delta_O = 253$ ppm for $H_2C_2O_4$ and $\delta_O = 267$ ppm for $C_2O_4^{2-}$ (D_2O, 75 °C).[14]

The $V(Ox)_2^{3-}$ complex. A ^{51}V NMR spectrum for a solution at pH 4.8 which, according to the equilibrium model, contains 0.098 M $V(Ox)_2^{3-}$, 0.007 M $C_2O_4^{2-}$ and negligible amounts of binary vanadates shows only one peak at -536.3 ppm [Fig. 3(a)]. The ^{13}C NMR spectrum for the same solution (recorded at -5 °C because of fast exchange at room temperature, see under Kinetics below) contains one peak for free oxalate at 175 ppm and two peaks of equal intensity for the complex at 171 and 168 ppm. The free oxalate peak is small, in accordance with a SOLGASWATER calculation, although the calculation is valid for 25 °C and the spectrum is measured at -5 °C.

The simplest interpretation of the presence of two ^{13}C

Table 1. ^{13}C and ^{17}O NMR parameters for the $H^+-C_2O_4^{2-}$ system in water.

Aqueous solution of	Concentration /mol l^{-1}	^{13}C NMR			^{17}O NMR		
		$T/°C$	δ^a/ppm	$\Delta v_{\frac{1}{2}}^b$/Hz	$T/°C$	δ^c/ppm	$\Delta v_{\frac{1}{2}}^b$/Hz
$H_2C_2O_4(s)^d$	0.8	-8	164.8 (163.5)^g	0.7	25	252 (250)^g	320
$NaHC_2O_4(s)^e$	0.2	-5	168.3 (168.0)^h	2	25	256 (256)^h	220
$Na_2C_2O_4(s)^f$	0.25	-8	175.6 (175.6)^i	8	-5	262 (262)^i	350
					25	262	200
					40	262	165

^{a}In ppm toward higher frequency from external TMS. ^{b}Signal width at half height. ^{c}In ppm toward higher frequency from external H_2O at 25°C. ^{d}Contains 70 % $H_2C_2O_4$ and 30 % $HC_2O_4^-$. ^{e}Contains 91 % $HC_2O_4^-$, 3 % $H_2C_2O_4$ and 6 % $C_2O_4^{2-}$. ^{f}Contains 99 % $C_2O_4^{2-}$ and 1 % $HC_2O_4^-$. ^{g}Recalculated to the individual chemical shift for the species $H_2C_2O_4$. ^{h}Recalculated to the individual chemical shift for the species $HC_2O_4^-$. ^{i}Recalculated to the individual chemical shift for the species $C_2O_4^{2-}$.

Table 2. ^{13}C NMR parameters for the H^+–$H_2VO_4^-$–$C_2O_4^{2-}$ system in aqueous 0.6 M NaCl solution.

Species	Concentration of vanadium/mol l^{-1}	Ox/V^a	pH	T/°C	δ^b/ppm (Δv$_{\frac{1}{2}}^c$/Hz)	Remarks
(I)						
VO$_2$(C$_2$O$_4$)$^-$	0.2	0.8	1	−5	170.1(23)	75 % of the total vanadium in VO$_2$(C$_2$O$_4$)$^-$.
VO$_2$(C$_2$O$_4$)$^-$	0.05	0.8	1	−5	169.7(12)	75 % of the total vanadium in VO$_2$(C$_2$O$_4$)$^-$.
VO$_2$(C$_2$O$_4$)$^-$	0.2	0.8	2.1	−5	170.0(18); 169.1, 171.6	VO$_2$(C$_2$O$_4$)$^-$ in equilibrium with VO$_2$(C$_2$O$_4$)$_2^{3-}$. [58 % of vanadium in VO$_2$(C$_2$O$_4$)$^-$, 11 % in VO$_2$(C$_2$O$_4$)$_2^{3-}$].
VO$_2$(C$_2$O$_4$)$^-$	0.2	0.8	2.1	25	169.6(35)	Only one peak; fast exchange between VO$_2$(C$_2$O$_4$)$^-$ and VO$_2$(C$_2$O$_4$)$_2^{3-}$?
(II)						
VO$_2$(C$_2$O$_4$)$_2^{3-}$	0.2	1.95	3.8	−5	168.5(30), 171.5(30)	95 % of the total vanadium in VO$_2$(C$_2$O$_4$)$_2^{3-}$.
VO$_2$(C$_2$O$_4$)$_2^{3-}$	0.2	1.95	3.8	20	170.1(240)	95 % of the total vanadium in VO$_2$(C$_2$O$_4$)$_2^{3-}$.

^{a}(Total concentration of oxalate)/(total concentration of vanadate). ^{b}In ppm toward higher frequency from external TMS at 25°C. ^{c}Signal width at half height when available.

Table 3. ^{17}O and [51]V NMR parameters for the H^+–$H_2VO_4^-$–$C_2O_4^{2-}$ system in aqueous 0.6 M NaCl solution.

	Species	Concentration of vanadium/mol l^{-1}	Ox/V^a	pH	T/°C	δ$_O^b$/ppm (Δv$_{\frac{1}{2}}^c$/Hz)	δ$_V^d$/ppm (Δv$_{\frac{1}{2}}^c$/Hz)
(I)	VO$_2$(C$_2$O$_4$)$^-$	0.2	0.8	2.1	5	255,290,1127(700)	−532.6(490)
(II)	VO$_2$(C$_2$O$_4$)$_2^{3-}$	0.2	1.95	3.8	12	230, 261, 301, 1122(315)	−536.2(305)

^{a}(Total concentration of oxalate)/(total concentration of vanadate). ^{b}In ppm toward higher frequency from external H$_2$O. ^{c}Signal width at half height when available. ^{d}In ppm toward higher frequency from external VOCl$_3$.

peaks being observed for this complex would be that there are two magnetically inequivalent oxalate ligands in the complex. However, this is not to be expected owing to the following: (i) Oxalate is a bidentate ligand in all cases for which the structure of a discrete complex has been determined.[7-9,15] (ii) It is well established that the VO$_2$ unit is bent, with short V–O distances of ca. 1.6 Å, and that the mean angle is 106 ± 1° (from twelve vanado-organic oxo ligand crystal structures, see for instance Refs. 7–9 and 16). Moreover, a Raman study of the VO$_2^+$ ion in aqueous solution[17] has shown that this configuration persists in solution.

It seems most likely that the aqueous V(Ox)$_2^{3-}$ complex should have these two structural features. If so, coordination with two oxygens from the same oxalate *cis* to the VO$_2$ oxygens is impossible for steric reasons. It would demand the oxygen–oxygen distance in the oxalate ion, which is normally ca. 3.3 Å,[18] to be stretched out to ca. 4 Å (O$_3$–O$_4$

in Fig. 1). Thus, two magnetically different oxalate ligands can be ruled out.

Therefore, the only reasonable interpretation of the ^{13}C NMR spectrum is that the structure is the same as in the solid state.

^{17}O NMR for the same solution at 12 °C [Fig. 3(c)] shows one peak at 1122 ppm originating from the VO$_2$ oxygens[6] and three overlapping peaks at 230, 261 and 301 ppm. This is also in accordance with the structure in the solid state. In order to assign the peaks to certain oxygens it is of value to obtain peak integrals. This is a difficult task in ^{17}O NMR spectra mainly because of the 'rolling baseline' problem[19] and relatively broad peaks, especially if the studied species are present in low concentration. Nevertheless, we have estimated the integrals in order to obtain more information about the complexes. To facilitate this estimation, we have tried to obtain peaks as narrow as possible. Three factors can influence their linewidth:[20] (i) quadrupolar relaxation

of ^{17}O, (ii) quadrupolar relaxation of oxygen through its spin–spin coupling to ^{51}V and (iii) chemical exchange. Therefore, ^{17}O NMR spectra have been recorded at different temperatures for solutions of varying concentrations of the complexes and with varying pH.

A ratio of 3.5–4 between the area of the three peaks at 230–300 ppm and the area of the VO$_2$ peak could best be estimated from an ^{17}O spectrum for a more concentrated solution ($V_{tot} \approx 0.4$ M), containing practically all vanadium in the form of V(Ox)$_2{}^{3-}$. This ratio and, especially, the chemical shift values, show that the peaks at 230–300 ppm originate from the oxalate oxygens in the complex, as well as from the small amount of the free oxalate present in the solution (cf. Tables 1 and 3). The best resolution of the three peaks at 230, 261 and 301 ppm was obtained in the spectrum shown n Fig. 3(c), and the integral ratios were evaluated as ca. 1:2:1. The peak at 230 ppm approximately retains the same intensity and linewidth as the peak at 301 ppm when temperature and concentrations are varied. The middle peak, at 261 ppm, has a chemical shift close to that of the free C$_2$O$_4{}^{2-}$ ion (cf. Table 1).

It has been shown previously by means of potentiometry and ^{51}V NMR that the V(Ox)$_2{}^{3-}$ complex is not protonated.[3] This is also evident from this study, where both ^{13}C and ^{17}O NMR chemical shifts for the complex are independent of pH, in contrast to the free oxalate ion (cf. Table 1).

Therefore, taking into account the above considerations concerning the ^{13}C spectra, we propose that the ^{17}O peak at 261 ppm originates from the uncoordinated oxygens in the oxalate ligands (O$_7$–O$_{10}$ in Fig. 1) and that the peaks at 230 and 301 ppm correspond to the coordinated oxygens (O$_3$–O$_6$). It is not easy to decide which of the two latter peaks belongs to which oxygens in the complex. When the double-bond character of the C–O or V–O bonds increases, the ^{17}O chemical shift increases.[14,21] This can also be seen from the higher chemical shift of the oxalic acid upon deprotonation (Table 1). In the solid state the average bond length between the carbons and the oxygens bound to vanadium (O$_3$–O$_6$) is longer by ca. 0.04 Å than that between the carbons and the terminal oxygens (O$_7$–O$_{10}$)

(Fig. 1). Thus, if the bond length C–O was the major factor influencing the chemical shift of the oxygens, the uncoordinated oxygens would have the highest shift. Since this is not the case, the bond length V–O can instead be expected to determine the chemical shift of the oxygens. There is also a larger difference in bond length between V–O$_{short}$ and V–O$_{long}$, ≈ 0.23 Å.

Taking all these factors into account, it is most likely that the oxalate oxygens with a longer V–O distance appear at 230 ppm and those with shorter V–O distance at 301 ppm. The outer oxygens (O$_7$–O$_{10}$) give rise to the peak in the middle. This assignment is supported by the 1:2:1 integral ratio of the bound oxalate ligands and the marked influence that vanadium(V) has on the ^{17}O shift.[5] Venema *et al.*[14] arrived at a different assignment for the ^{17}O NMR oxalate peaks in the species Al(Ox)$_3{}^{3-}$. They proposed that their peak at 295 ppm belongs to the outer oxygens and that at 219 ppm to the inner. Since the oxygen shifts for aluminium are quite unlike those for transition metals, both assignments can be correct. Although the Me–O$_{ox}$ bonds in the solid state vary considerably, the oxalate ligands in the complexes are very similar. For instance, the mean distances C–O$_{outer}$/C–O$_{inner}$ are 1.22/1.28 Å for Al(Ox)$_3{}^{3-}$ (Ref. 15) and 1.23/1.28 Å for VO$_2$(Ox)$_2{}^{3-}$ (Ref. 7).

To conclude, both the number of peaks and the ratio between their integrals in ^{17}O NMR support the conclusions from ^{13}C NMR that the V(Ox)$_2{}^{3-}$ structure in solution is the same as that shown in Fig. 1. Therefore, the complex should be designated as [VO$_2$(C$_2$O$_4$)$_2$]$^{3-}$.

The V(Ox)$^-$ complex. A ^{51}V NMR spectrum for a solution at pH 2.1, which according to the equilibrium model (25 °C) contains 0.12 M V(Ox)$^-$, 0.006 M H$_n$V$_{10}$O$_{28}{}^{(6-n)-}$, 0.02 M V(Ox)$_2{}^{3-}$ and 0.005 M VO$_2{}^+$, shows one predominant peak at −532.6 ppm [Fig. 4(a)]. This peak originates from the complex V(Ox)$^-$ and the other three peaks from the decavanadate species, as has been shown in previous investigations.[3,4] The V(Ox)$_2{}^{3-}$ peak is hidden under the V(Ox)$^-$ peak. No separate VO$_2{}^+$ peak can be observed, as the cation is in fast exchange with V(Ox)$^-$ on the ^{51}V NMR timescale. The −532.6 ppm value for V(Ox)$^-$

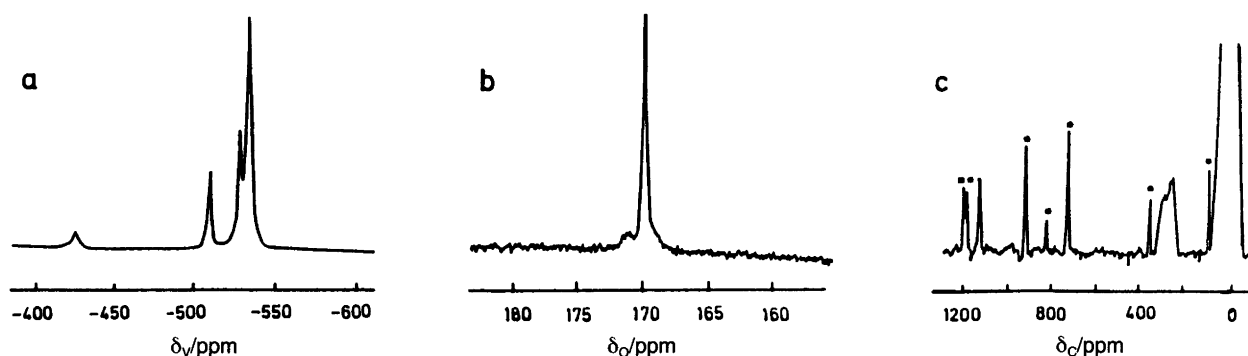*Fig. 4.* Spectra of an Ox/V= 0.8 solution at pH 2.1 containing 0.12 M V(Ox)$^-$, 0.006 M H$_n$V$_{10}$O$_{28}{}^{(6-n)-}$, 0.02 M V(Ox)$_2{}^{3-}$ and 0.005 M VO$_2{}^+$ (25 °C): (a) ^{51}V NMR at 25 °C, (b) ^{13}C NMR at −5 °C and (c) ^{17}O NMR at 5 °C. The peaks marked by an asterisk in the ^{17}O spectrum (c) belong to the decavanadates.

is between that of the octahedrally coordinated vanadium in decavanadates (-422 to -534 ppm) and tetrahedrally coordinated vanadium in the vanadates formed in the neutral and alkaline region (-537 to -585 ppm).[4] Thus, in the present study the δ_V value cannot be used for prediction of the coordination number in the complex.

A ^{13}C NMR spectrum of the same solution at $-5\,^{\circ}$C [Fig. 4(b)] shows one peak at 170.0 ppm belonging to $V(Ox)^-$ and, barely visible, the two peaks from $V(Ox)_2^{3-}$. The simplest explanation for the fact that only one peak is obtained is that both the carbons in $V(Ox)^-$ are magnetically equivalent. Another possibility is fast intramolecular exchange between two nonequivalent carbon sites. The concentration of free oxalate species is probably too small in our solutions to influence the spectra.

An ^{17}O NMR spectrum for the same solution at $5\,^{\circ}$C [Fig. 4(c)] shows one peak at 1127 ppm originating from the VO_2 group[6] and two broad overlapping peaks at about 255 and 290 ppm belonging mainly to the oxalate in $V(Ox)^-$. The other peaks, marked by an asterisk, belong to the decavanadates.[5] The decavanadate peak at 353 ppm (just to the left of the $V-O_{ox}$ peaks) arises from a three-coordinate oxygen with a mean $V-O$ distance of 1.98 Å in the solid state (cf. Fig. 2).

The average ^{17}O chemical shift for $V(Ox)^-$ is $\delta_O = 273$ ppm [$= (255 + 290)/2$] ($5\,^{\circ}$C) and for $V(Ox)_2^{3-}$ 263 ppm [$= (230 + 2\,261 + 301)/4$] ($12\,^{\circ}$C). Since δ_O for the oxalate oxygens in $V(Ox)^-$ is higher than in $V(Ox)_2^{3-}$, the average $V-O_{ox}$ distance in $V(Ox)^-$ should be shorter than the corresponding distance in $V(Ox)_2^{3-}$ (cf. the discussion in the previous section). As can be seen from Table 1, a small temperature difference does not alter the chemical shift noticeably.

We have recorded ^{17}O NMR spectra at different temperatures in an attempt to enhance the spectral resolution for a solution containing approximately equal amounts of complex $V(Ox)^-$ and $V(Ox)_2^{3-}$. At $70\,^{\circ}$C the oxalate oxygen peaks are averaged to one peak ≈ 600 Hz wide owing to chemical exchange. At lower temperatures the peak is broadened (1200 Hz) owing to intermediate chemical exchange (and possibly also owing to quadrupolar relaxation of ^{17}O, see above). Below room temperature, at $10\,^{\circ}$C, the oxygen peaks are partially resolved, and peaks corresponding to the complex $V(Ox)^-$ can be discerned. The resolution is unfortunately not increased further when lowering the temperature to $0\,^{\circ}$C. We have chosen to show the spectra for $V(Ox)^-$ recorded at $5\,^{\circ}$C, since this is the only temperature where the oxalate ligand peaks are at least partially resolved [Fig. 4(c)].

One also notes that the complex $V(Ox)^-$ shows almost no change in the ^{13}C chemical shift when the pH is varied between 0.8 and 3.6, thus confirming the previous EMF and ^{51}V NMR results that this complex is not protonated.[3] (We were not able to determine whether the ^{17}O shifts for this complex are also independent of pH, since the bound oxalate peaks were normally not resolved).

When discussing the solution structure of $V(Ox)^-$ we

assume that oxalate is a bidentate ligand and that the VO_2 unit retains its configuration [as discussed in the $V(Ox)_2^{3-}$ section above]. The vanadium atom is either hexacoordinate as in Fig. 1 or pentacoordinate as in Fig. 2, with water molecules filling up the empty coordination sites. Tetracoordinate vanadium seems unlikely, as discussed below.

Hexacoordination. If the vanadium atom is hexacoordinate as in Fig. 1, but with only one oxalate ligand and two water molecules, there are two possibilities.

(1) The oxalate ligand is *trans* to the terminal vanadium oxygens (i.e. O_5 and O_6 in Fig. 1). This is in accordance with one peak in ^{13}C NMR, but not with a medium $V-O_{ox}$ distance as indicated in ^{17}O NMR. The O_5-O_6 distance does not need to be longer than 2.8 Å [as in the complex $V(Ox)_2^{3-}$], since the angle O_5-V-O_6 in the complex $V(Ox)^-$ can be smaller. However, a smaller $O-V-O$ angle and *trans* $V-O_{ox}$ coordination seem energetically unfavourable, and the long bonding distances should lead to a weak complex. Thus a *trans* oxalate is less probable.

(2) One oxalate oxygen is *axial* and the other *equatorial* to the O_1-V-O_2 plane. Two different $V-O_{ox}$ distances should result in two peaks in ^{13}C NMR and three or four in ^{17}O. The fact that there are only one and three peaks, respectively, might be due to fast exchange, probably intramolecular and between the *cis/trans* oxalate oxygens. This should lead to a broadening of the peak when the temperature/concentration is varied, which has not been observed. (Nevertheless, very fast intramolecular exchange on the actual NMR timescales would be in agreement with this type of coordination.) An oxalate ligand *cis* to the vanadyl oxygens (i.e. O_3 and O_4 in Fig. 1) is impossible for reasons discussed under the section on $V(Ox)_2^{3-}$ above.

Since the two alternatives seem less probable, hexacoordination is not likely.

Pentacoordination. The distances $V-O_3$ and $V-O_4$ in $V(Ox)_2^{3-}$ (Fig. 1) are somewhat shorter than $V-O_3$ and $V-O_4$ in $V(Ox)^-$ (Fig. 2). This would be in accordance with $\delta_O = 301$ ppm for the former and $\delta_O = 290$ ppm for the latter. The $V-O_3$ and $V-O_4$ distances in Fig. 2 are approximately equal and thus in accordance with one peak in ^{13}C NMR and three in ^{17}O. Therefore, it is most likely that $V(Ox)^-$ is pentacoordinate as in Fig. 2, with a water molecule replacing the fluorine atom and in fast exchange with solvent. Moreover, pentacoordinate $V(Ox)^-$ and hexacoordinate $V(Ox)_2^{3-}$ may explain why the two complexes are in slow exchange on the ^{51}V NMR timescale.

Tetracoordination. To our knowledge no monomeric tetrahedral vanadium(V) species containing oxo organic ligands has been observed in aqueous solution. Such a complex may be obtainable if one mimics the conditions under which tetracoordinate hydrolysis species are formed, i.e. high pH. As $V(Ox)^-$ is formed in the acidic range, tetracoordination is not likely. Moreover, tetracoordination should lead to significantly shorter $V-O_{ox}$ bonds and thus to much higher chemical-shift values in ^{17}O NMR spectra.

To conclude, pentacoordination seems to be the most

probable for the $V(Ox)^-$ complex, and accordingly this complex can be designated $[VO_2(C_2O_4)(H_2O)]^-$.

Kinetics

The present study was undertaken primarily to establish the structures of the vanadate–oxalate complexes in aqueous solution. However, we also obtained some limited kinetic information, which is summarized below.

It has already been shown in our previous paper,[3] and is confirmed in the present study, that the oxalate exchange between $[VO_2(C_2O_4)(H_2O)]^-$ and $[VO_2(C_2O_4)_2]^{3-}$ is slow on the actual ^{51}V NMR timescale. The chemical shift difference between the signals of these complexes is about 400 Hz, corresponding to a minimum lifetime of the complexes with respect to mutual exchange of about 1 ms.

The ^{13}C NMR signal for $V(Ox)^-$ in solutions not containing $V(Ox)_2^{3-}$ is only slightly broadened (≈ 5 Hz) when the temperature is increased from -5 to $25\,°C$. In solutions containing both complexes at $25\,°C$, only one ^{13}C resonance is observed (Table 2). At $-5\,°C$, this signal is partially resolved into a narrow signal for $V(Ox)^-$ and two strongly and equally broadened signals for $V(Ox)_2^{3-}$. At this temperature $\delta_C[V(Ox)^-]$ is 170.0 ppm and the mean $\delta_C[V(Ox)_2^{3-}]$ is $(169.1 + 171.6)/2 = 170.3$ ppm; thus the difference is only 0.3 ppm. At $25\,°C$ the signals from $V(Ox)_2^{3-}$ coalesce because of internal exchange. That only one signal is obtained at $25\,°C$ may be due to the small shift difference between this signal and the $V(Ox)^-$ signal, rather than fast chemical exchange between $V(Ox)^-$ and $V(Ox)_2^{3-}$.

A different situation occurs in solutions containing $V(Ox)_2^{3-}$ and a small amount of free oxalate (Fig. 5). At $25\,°C$, the free oxalate signal is broadened and the two signals for the complex $V(Ox)_2^{3-}$ have coalesced but are still broadened by chemical exchange. When the temperature is lowered to $10\,°C$, the free oxalate signal is sharpened, and the two signals from the complex are resolved. Finally, at $-5\,°C$ the free oxalate signal reaches its non-exchange limit, and the two other signals are only slightly but equally broadened. The non-exchange limit for the $V(Ox)_2^{3-}$ signals cannot be reached, as the solution freezes if the temperature is lowered further. The exchange within $V(Ox)_2^{3-}$ is thus faster than the exchange reaction between $V(Ox)_2^{3-}$ and the free ligand and also faster than the reaction between $V(Ox)_2^{3-}$ and $V(Ox)^-$.

Assuming that the non-exchange linewidth for the ^{13}C-peaks in $V(Ox)_2^{3-}$ is the same as for $V(Ox)^-$, i.e. ≈ 12 Hz, rate constants can be calculated using the complete line-shape analysis approach.[22] The rate constant for the internal exchange within $V(Ox)_2^{3-}$ is $k_{obs}^{internal} = 60, 320$ and 640 s^{-1} at -5, 10 and $25\,°C$, respectively. From these values, the following activation parameters were calculated: $\Delta H^{\#} = 22$ kJ mol^{-1} and $\Delta S^{\#} = 40$ J K^{-1} mol^{-1}. The rearrangement within the $V(Ox)_2^{3-}$ ion is such that two $V-O_{ox}$ bonds within the same oxalate moiety, e.g. O_4 and O_6 in Fig. 1, switch places. It seems reasonable that the
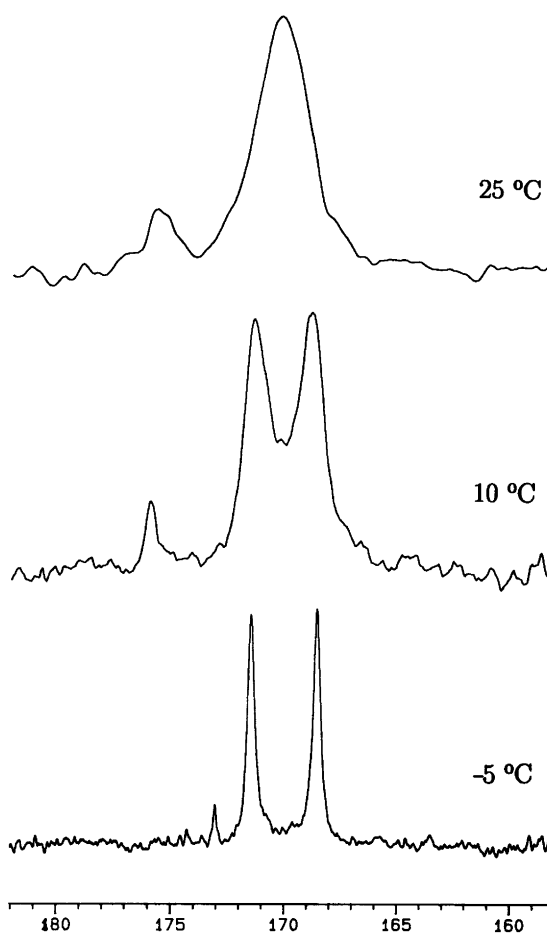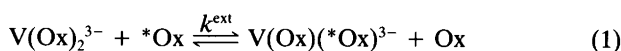
Fig. 5. ^{13}C NMR spectra for a solution containing 0.19 M $V(OX)_2^{3-}$, 0.009 M $V(Ox)^-$ and 0.002 M free $C_2O_4^{2-}$ at three temperatures. The tallest peak is adjusted to the same height in all spectra.

transition state for this rearrangement has a higher entropy than the equilibrium state.

For reaction (1) between $V(Ox)_2^{3-}$ and the unbound

$$V(Ox)_2^{3-} + {}^*Ox \xrightleftharpoons{k^{ext}} V(Ox)({}^*Ox)^{3-} + Ox \qquad (1)$$

oxalate a systematic study would probably shed more light on the kinetics and mechanism(s). However, this is outside the scope of the present study. Nevertheless, assuming that the reaction $C_2O_4^{2-} + H^+ \rightleftharpoons HC_2O_4^-$ is very fast, rate constants for reaction (1) could be calculated: $k_{obs}^{ext} = 44$ and 130 s^{-1} at 10 and $25\,°C$, respectively. The activation parameters are $\Delta H^{\#} = 21$ kJ mol^{-1} and $\Delta S^{\#} = 30$ J K^{-1} mol^{-1}. Considering that in the $V(Ox)_2^{3-}$ complex the vanadium atom is coordinatively saturated, it seems less probable that the relatively large oxalate ion would be able to add to the complex without previous dissociation of the latter. Accordingly, a dissociative mechanism for reaction (1) is to be preferred, in agreement with the positive entropy of activation.

A rearrangement of a different type in the $V(Ox)_2^{3-}$

complex has been proposed by Scheidt *et al.*[7] They claim that the two oxalate oxygens with long distances to vanadium (O_5 and O_6 in Fig. 1) should switch places owing to the *trans* effect. Such a rearrangement cannot be observed in ^{13}C NMR, as it does not lead to any broadening of the signals.

In the vanadium(IV)–oxalate system the predominant species formed have the same stoichiometry as in the pentavalent system, and a similar intramolecular rearrangement as in $V(Ox)_2^{3-}$ is proposed for $VO(Ox)_2^{2-}$.[23] The formation constants in the two systems are of the same magnitude, $\log K_1 = 6.45$ (6.11) and $\log K_2 = 5.33$ (4.04), with the values for the pentavalent species in parentheses.

When ^{17}O-enriched water is added to solutions containing either $V(Ox)_2^{3-}$ or $V(Ox)^-$, the VO_2 oxygens are enriched within a few minutes at room temperature, despite the short V–O distance. This is in contrast to VO^{2+}, where the terminal oxygen exchanges exceedingly slowly ($k_{ex} = 3 \times 10^{-5}$ s^{-1}).[24] The oxalate oxygens in $V(Ox)_2^{3-}$ and $V(Ox)^-$ exchange slowly at room temperature: it takes several hours before any noticeable enrichment occurs.

Conclusions

Vanadium seems to have different coordination numbers in the two vanadooxalate species, $V(Ox)^-$ and $V(Ox)_2^{3-}$, although they exist in nearly the same pH range. The monooxalate species, $V(Ox)^-$, is probably pentacoordinate, with equal V–O_{ox} distances, whereas $V(Ox)_2^{3-}$ appears to have a hexacoordinate $[VO_2(C_2O_4)_2]^{3-}$ structural arrangement similar to that found in the solid phase,[7,8] with the two V–O_{ox} distances from each oxalate ligand being different. The formula for the two complexes should thus be written as $[VO_2(C_2O_4)(H_2O)]^-$ and $[VO_2(C_2O_4)_2]^{3-}$, respectively. In $[VO_2(C_2O_4)_2]^{3-}$ the exchange within the complex is faster than the exchange between the unbound oxalate anion and the complex. This exchange, in turn, is faster than that between the two vanadooxalate complexes.

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