for chelating butanedithiolato or butanediolato ligands. We have synthesized a series of oxomolybdenum(V) complexes with similar chemical environments but varying chelate ligand backbones. This series has provided an opportunity to investigate the effect of systematic ligand variations on the spectroscopic properties and reduction potentials of mononuclear oxomolybdenum(V) centers.

The effects of the chelate ring size and flexibility on the stability of metal complexes are well-known.[53] In this research, we have observed that the size of the chelate ring and of the alkyl substituents on the chelate ring backbone have substantial effects on the spectroscopic properties of LMoO[S–$(CH_2)_n$–S] and LMoO[O–$(CH_2)_n$–O] complexes and can lead to changes in the reduction potential of up to 0.2 V/CH_2 unit. In the absence of crystal structures for these complexes the geometrical effects from the changes in the ligand skeleton are unknown. However, the changes in the torsional angles of the donor heteroatom that result from changes in chelate ring size and ring substituents provide a promising mechanism for transmitting seemingly remote ligand effects to the properties of the metal center. This rationale has been used previously to account for the unusually low reactivity of CpMo(NO)$(SPh)_2$ and related compounds.[54]

Finally, it has not escaped our attention that the significant changes in metal properties which we have observed with changes in the ligand skeleton may be important for understanding the properties of the molybdenum cofactor (I), which is thought to possess a five-membered chelate ring with two side chains.

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Supplementary Material Available: Listings of elemental analyses, mass spectral data, and infrared absorption data for compounds **1–13** (Tables S1–S3, respectively) (3 pages). Ordering information is given on any current masthead page.

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Interactions of Vanadate with Mono- and Dicarboxylic Acids

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The condensation reactions between vanadate and a variety of mono- and dicarboxylic acids in aqueous solution have been investigated by ^{51}V NMR spectroscopy. Equilibration with acetate occurred rapidly, about 10^4 s^{-1}, to form predominantly a bis(acetato)vanadate (−541 ppm) although formation of a mono derivative could be detected. With pentanoic acid and the dicarboxylic acids, a product (−536 ppm) in slow equilibration with vanadate was formed. This product occurred in addition to a rapidly exchanging product and contained only one ligand (except possibly for the pentanoic acid derivative, which was not well characterized). In addition to the above products, succinic acid gave a product with a ^{51}V chemical shift at −548 ppm. This derivative also contained one ligand. Variation of the pH showed that product formation occurred from the acid form of the ligands and that no protons were required for generation of any of the products.

Introduction

Over the past few years the aqueous chemistry of vanadium(IV) and vanadium(V) oxoanions has been receiving increasing attention because of the relevance of these materials to the investigation of various biochemical processes. It may be that some of the function of vanadium derives from its role as a phosphate analogue. In addition to this, vanadium occurs at the active site of some seaweed bromoperoxidases[1] and is found in a secondary enzymic system for nitrogen fixation in some nitrogen fixing bacteria.[2,3]

In aqueous solution the vanadium(V) anion, vanadate, rapidly and spontaneously condenses with alcohols and phenols to form vanadate esters.[4,5] Beyond this it is well-known that vanadate undergoes self-condensation to form divanadate and other oligomers[6] and that it also condenses with other weak acids such as phosphate and arsenate.[7,8] Despite this evidence that aqueous vanadate readily forms products with a wide variety of hydroxyl-bearing ligands, it has often been stated or implied that it does not react with acetic acid (frequently used as a buffer) and, by extension, other monofunctional carboxylic acids. Of course, it is well-known that vanadium(V) in aqueous solution readily forms cyclic derivatives with a variety of multifunctional carboxylate-containing ligands such as the α-hydroxy carboxylates, the pyridine-2-carboxylates, and others.[9-16] The aspect of vanadate chemistry of primary interest here is the interaction of the vanadate ion, $VO_4H_2^-$, with carboxylate functionalities and is not concerned with peroxo and other derivatives of this anion. In a non-aqueous medium $VOCl_3$ reacts with alkane- and arenecarboxylic acids to form tris(carboxylato) derivatives.[17,18] Crystal structure analysis has shown that there is a bidentate coordination for each car-

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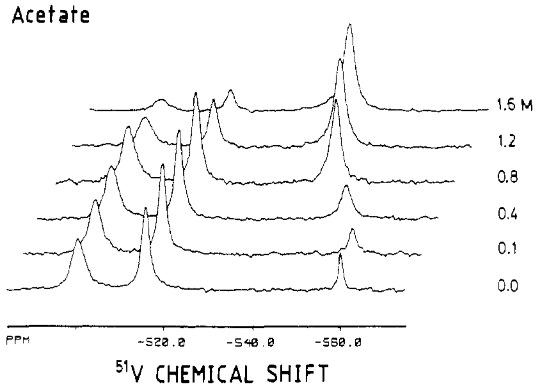

Figure 1. ^{51}V NMR spectra showing the effects of added acetate. The signal at −560 ppm derives from $VO_4H_2^-$ and the position of this signal varies with acetate concentration as a new product in rapid equilibration is formed. The signals at −515 and −500 ppm arise from decavanadate, for which a third signal at −426 ppm was also observed. Conditions of the experiments: 1.0 mM total vanadate; 1.0 M ionic strength maintained with KCl; pH 4.67; the indicated total acetate concentrations.

boxylate group, but IR spectra from CH_2Cl_2 solutions indicated the presence of both mono- and bidentate coordination.[17] Furthermore, these complexes were found to be unstable in the presence of even stoichiometric amounts of alcohol or water.[17] This instability indicates there is a major reorganization of the coordination shell. However, the aqueous vanadate ion does readily react with acetic acid, and in this report, the condensation of vanadate with acetic acid and a selection of other mono- and dicarboxylic acids is described.

Experimental Section

Materials. Where applicable, reagent grade materials were checked for purity by either ^{1}H or ^{13}C NMR spectroscopy. All were used without further purification. The preparation of aqueous solutions of vanadate has been previously described, and the procedures utilized here are not significantly different.[8] All solutions were prepared at an ionic strength of 1.0 M by addition of appropriate amounts of KCl. Caution must be exercised when the solutions are prepared at a desired pH to minimize formation of decavanadate. Appropriate amounts of ligand and KCl were first diluted by distilled water to 0.5 mL less than the final volume (normally 10 mL). The pH of the solution was adjusted to about 0.2 pH units below the desired pH value and then the appropriate amount of vanadate as $H_2VO_4^-$ in a stock solution was added. The final volume was reached by adding more water, and the pH was adjusted to its final value. At no time was acid added to the vanadate solutions.

Spectroscopy. All NMR spectra were obtained in the unlocked mode of operation at 105 MHz and at ambient temperature on a Bruker WM-400 NMR spectrometer. Spectrum widths were 40 KHz, pulse widths were 50°, and acquisition times were 0.025 s. Spectra were acquired into a 2K data set and zero-filled to an 8K set before transforming them to the frequency domain. Chemical shifts are reported to the external standard, $VOCl_3$, which has been assigned as 0 ppm. Signal intensities were measured by using the integration routine provided by the instrument manufacturer.

Methods. The results were analyzed by putting the equations describing the various equilibria into the appropriate form as outlined in the text and then analyzing the data by using the least-squares program of a microcomputer in order to obtain the best estimation of the slope and the *y* intercept of the line. Errors in the slope and intercept were obtained by assuming 10% measurement errors in integrals.

Results

The reaction between vanadate and acetate has been studied at various pH values ranging from pH 5.42 to pH 3.83. In this pH range under the 1.0 M ionic strength conditions of this study, the predominant form of vanadate at the vanadate concentrations utilized in this study is generally decavanadate. Both divanadate and tetravanadate as well as the monomer may also be observable. The effect of incorporating increasing amounts of acetate into the vanadate solutions is to cause a change in chemical shift in the signal of the vanadate monomer from −560 to −541 ppm and to increase its concentration relative to the amount of decavanadate in solution. This behavior is clearly evident in Figure 1 where the spectra were obtained for a pH 5.0 solution.

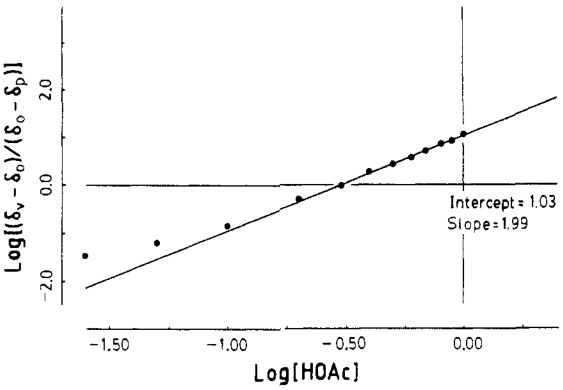

Figure 2. Graph showing that a bis(acetato)vanadate derivative is formed at the higher ligand concentrations but that a mono product is formed at the lower ligand concentrations. The intercept (log K_1) gives the formation constant, and the slope gives the number of ligands incorporated into the product. Conditions of the experiments are as for Figure 1.

This behavior is consistent with the formation of a vanadate/acetate derivative that is in rapid equilibrium with vanadate itself. A similar rapid equilibration has been observed in studies of vanadate/phosphate interactions.[7,8] Because of the buffering action of the decavanate, which keeps the monomeric vanadate concentration nearly constant while allowing for large changes in decavanadate concentration, it is not possible to tell from the information contained in Figure 1 whether one or two vanadate ions are required in order to form the product. It is possible to obtain some information concerning this problem by maintaining the ligand concentration constant and varying the total vanadate in solution, although here also decavanadate buffering is a problem. Results were obtained for the case when the acetate concentration was held at 1.0 M while the total vanadate in solution was varied from 0.25 to 4.0 mM. Throughout this range of concentrations, the averaged signal position from vanadate and its product acetate (at −548.4 ppm) did not vary to within 0.1 ppm. This strongly indicates that the product formed contains in it only one vanadate moiety since otherwise the peak position would depend on vanadate concentration. A rough estimate, using the chemical shift limits from the acetate concentration study, shows that the vanadate signal should have shifted about 1 ppm if the product contained even two vanadium nuclei. Since only one vanadate was found in the product, the equilibria involved can be written as in eq 1

$$V_i + n\text{AcOH} \overset{K_1}{\rightleftharpoons} V(\text{OAc})_n \qquad (1)$$

where V_i refers to vanadate ($VO_4H_2^-$ throughout the pH range in this study), AcOH to acetic acid, and OAc to acetate, $CH_3CO_2^-$. In this equation, water stoichiometry, which cannot be determined, is ignored. If the chemical shift for vanadate is δ_V and the shift for $V(OAc)_n$ is δ_P then the formation constant, K_1, for the product can be written in terms of the observed chemical shift, δ_o, as in eq 2. δ_V is known, so that a plot of $1/[HOAc]^n$ vs $1/(\delta_V - \delta_o)$

$$\frac{1}{[\text{HOAc}]^n} = \frac{K_1(\delta_V - \delta_P)}{\delta_V - \delta_o} - K_1 \qquad (2)$$

provides the intercept $-K_1$ and slope $K_1(\delta_V - \delta_P)$, which provide the formation constant and the chemical shift of the product. Alternatively, if δ_P is known, e.g. from measurements of the limiting chemical shift at high ligand concentration, then K_1 can be obtained from eq 3. Both eqs 2 and 3 are general; however,

$$\log \frac{\delta_V - \delta_o}{\delta_o - \delta_P} = n \log [\text{HOAc}] + \log K_1 \qquad (3)$$

the more useful application of eq 2 requires a knowledge of ligand stoichiometry while application of eq 3 requires the chemical shift of the product. The concentration of HOAc is given from the pK_a of acetic acid, measured under the conditions of these experiments, i.e., 1.0 M ionic strength with KCl. When the ex-

Table I. Formation Constants for Bis(acetato)vanadate Complexes Determined at Various pH Values[a]

pH	n[b]	K, M^{-2}	pH	n	K, M^{-2}
3.38	1.94	10.7 ± 0.5	4.28	1.98	11.5 ± 0.3
4.67	1.99	10.7 ± 0.5	5.00	2.03	10.3 ± 0.9
5.44	2.03	8.0 ± 1.0			

[a] Equilibrium constants were determined under conditions of 1.0 M ionic strength maintained with KCl, 1.0 mM total vanadate, the indicated pH, and varying concentrations of acetate. The values are for formation of products from acetic acid, pK_a = 4.67, not total acetate. [b] Experimental value for the number of acetates in the product complex.

perimental results were plotted according to eq 3, it was found that at concentrations above about 0.3 M acid the graph was linear with a slope of 2, but below this concentration, the graph showed curvature toward a slope of 1. This behavior is evident in Figure 2, which depicts the results for pH 4.67 solutions. At the higher concentrations it was therefore possible to obtain a formation constant of the bis ligand product from V_i and HOAc. This was not possible for the mono product, and the results are consistent with a pronounced positive cooperativity in that the mono ligand derivative is not favored relative to free vanadate whereas the bis compound is highly favored relative to the mono precursor.

Equilibrium constants were obtained by application of eq 3 for a variety of solutions of different pH by utilizing the following parameters; $pK_a(HOAc) = 4.67$, $\delta_V = -560.1$ ppm, and $\delta_P = -540.6$ ppm. The pH values, the slopes (which give n) and the formation constants, K_1, are given in Table I. It is evident from this table that no protons are required for formation of the product. From the separation in chemical shifts between vanadate and its derivative and also from the observation of a significant line broadening in the intermediate acetate concentration range, it can be estimated that the rate of chemical exchange is on the order of 10^4 s^{-1} at room temperature.

Even at the highest acetate concentrations of this study, no vanadate signals other than those already discussed were observed in the NMR spectrum. However, if *n*-pentanoic (valeric) acid was utilized in place of acetic acid a signal, which occurs at −536 ppm, was observable. This signal was in addition to the signal with a concentration dependent chemical shift. Because of problems with solubility, it was not possible to use this shift dependence to obtain an accurate value of the limiting chemical shift and thus an accurate formation constant of the bis compound, which was analogous to that formed with acetate. The value obtained was 30 ± 6 M^{-2} for formation from the free acid at pH 5 and 1.0 M ionic strength. It was also not possible to unambiguously obtain a formation constant for the product giving rise to the −536 ppm signal since it was broad and under the experimental conditions of this study never of very high intensity. The results obtained were consistent with the incorporation of two ligands with a formation constant of 0.7 ± 0.2 M^{-2}. A product giving rise to a similar chemical shift was also found to form in solutions containing a variety of dicarboxylic acids including the succinic, adipic, and glutaric acids. A broad signal near this chemical shift was also observed for malonic acid but only at low temperature (269 K). No such signal was observed for the acetic acid system at low temperature, but the corresponding product probably is formed. If so, and if the product is of nonnegligible concentration, this introduces some additional uncertainty into the determination of the formation constant of the bis(acetato) complex.

The condensation of vanadate with the diacids is particularly interesting. There is a variety of products formed with succinic acid as can be seen in Figure 3. This figure depicts the effects of adding increasing amounts of succinate to a 2.0 mM vanadate solution at pH 5.00 and 1.0 M ionic strength maintained with KCl. With increasing proportions of succinate in solution the NMR signals at −535.7 and −547.6 ppm became increasingly intense. In addition to this, the signal at −560.1 ppm was broadened and shifted to low field, a process similar to that observed for acetate. At pH 6.0, the formation constant of this latter product can, in principle, be obtained most directly from the concentration of tetravanadate, V_4, by application of eq 4, where ℓ refers to the

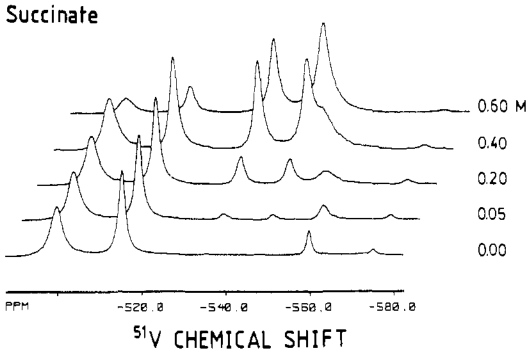

Figure 3. ^{51}V NMR spectra showing the effects of added succinate. The signals at −500 and −515 ppm are from decavanadate as is a third signal at −426 ppm (not shown). Vanadate ($VO_4H_2^-$) gives rise to the signal at −560 ppm. The position of this signal varies with added succinate as a new, rapidly equilibrating product is formed. The remaining signal at −575 ppm arises from tetravanadate; other vanadate oligomers are of low concentrations. New products give rise to signals at −536 and −548 ppm. Conditions of the experiments: 2.0 mM total vanadate; 1.0 M ionic strength maintained with KCl; pH 5.00; indicated succinate concentrations.

$$\frac{[V_i] + [V\ell] + [V\ell_2]}{[V_4]^{1/4}} = K_o^{-1/4} + K_o^{-1/4}K_1[\ell] + K_o^{-1/4}K_1K_2[\ell]^2 \quad (4)$$

ligand and $V\ell$ and $V\ell_2$ represent the mono- and bis(ligand) products, respectively. The y intercept obtained from plotting tthe ratio on the left of eq 4 vs $[\ell]$ gave the value $K_o^{-1/4} = (2.5 \pm 0.2) \times 10^{-3}$ $M^{3/4}$, from which $[V_i]$ can be determined for any concentration if $[V_4]$ is known. Unfortunately, since only a small amount of product was formed, a meaningful determination of K_1 or K_1K_2 was not possible. However, from the observed change in chemical shift, the limiting chemical shift obtained at lower pH, and the assumed incorporation of two ligands, the value of 0.7 ± 0.3 M^{-2} was estimated by using eq 3 with HOAc replaced by ℓ. Note that for all the diacids of this study, the formation constants are determined from total ligand concentrations and not from the diacid or its monoionic form.

Of some interest in Figure 3 was the observation that the ^{51}V signals at −536 and −547 ppm are of essentially identical intensity. This observation indicated that the two signals might derive from the same product. In an effort to verify this at pH 6.0, both ligand and vanadate concentration studies were done. Ligand concentrations were varied from 0.0 to 0.6 M at a fixed 2.0 mM vanadate concentration while vanadate concentrations were varied from 0.25 mM to 3.0 mM at a fixed 0.6 M ligand concentration. In contrast to the expected result, the observed concentration dependencies were consistent only with the occurrence of two products each containing one vanadate and one ligand. Thus formation of either product occurs as described in eq 5, where the ^{51}V chemical shift

$$V_i + suc \overset{K_2}{\rightleftharpoons} -536 \qquad [V_i][suc]K_2 = [-536] \quad (5)$$

identifies the particular product. At a fixed ligand concentration, eq 5 predicts that a plot of [−536]/[suc] vs $[V_i]$, where $[V_i]$ can be obtained from $[V_4]$ and K_o in eq 4, will give a straight line. If the product contained more than one vanadium, the above plot would show upward curvature. As seen from Figure 4 an excellent linear relationship is obtained. The equilibrium constant measured was 1.2 ± 0.1 M^{-1}. The corresponding value from the ligand concentration study was 1.4 ± 0.1 M^{-1}. Both the −536 and −548 ppm products contain one vanadium and one ligand and at pH 6.00 and under conditions of 1.0 M ionic strength maintained with KCl are formed equally well with the formation constant K_2 = 1.3 ± 0.1 M^{-1}.

The formation of these two products is more highly favored at lower pH, as can be seen from Table II. The results are

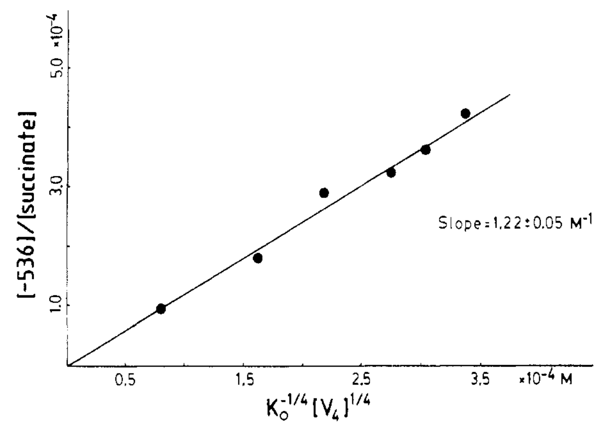

Figure 4. Plot of [-536]/[succinate] vs $K_o^{-1/4}[V_4]^{1/4}$. That this graph is linear shows that the -536 ppm succinate product contains only one vanadium atom. Conditions of the experiments: 0.6 M succinate; 1.0 M ionic strength maintained with KCl; pH 5.00; varying total vanadate concentrations.

Table II. pH Dependence of the Formation Constants of the Succinato Vanadate Complexes[a]

pH	equilibrium eq	equilibrium const
6.0	$VO_4H_2^- + suc \rightleftharpoons -536$	$1.3 \pm 0.1\ M^{-1}$
5.0		$7.3 \pm 0.2\ M^{-1}$
4.3		$28.5 \pm 2.2\ M^{-1}$
6.0	$VO_4H_2^- + suc \rightleftharpoons -548$	$1.3 \pm 0.1\ M^{-1}$
5.0		$7.3 \pm 0.2\ M^{-1}$
4.3		$28.5 \pm 2.2\ M^{-1}$
6.0	$VO_4H_2^- + 2suc \rightleftharpoons -541$[b]	$0.7 \pm 0.3\ M^{-2}$
5.0		$5.8 \pm 0.8\ M^{-2}$
4.3		$38 \pm 6\ M^{-2}$
5.0	$10VO_4H_2^- \rightleftharpoons V_{10}$	$(8.9 \pm 0.2) \times 10^{34}\ M^{-9}$
4.3		$(1.2 \pm 0.2) \times 10^{38}\ M^{-9}$

[a] Formation constants were determined under conditions of 1.0 M ionic strength maintained with KCl, varying total amounts of succinate or vanadate, and the indicated pH. The values are for formation of the products from total succinate in solution not from the diacid form. [b] This product is in rapid equilibrium (on the NMR time scale) with the free vanadate.

consistent with a condensation reaction between $VO_4H_2^-$ and succinate in the diacid form. The two NMR signals that are observed must then derive from products of different coordination geometry. The third product that is formed apparently is analogous to the product formed from acetate. The results in Table II suggest that this latter product can be formed from either the succinate diacid or the monoanion as would be expected for an acyclic product. Unlike in the acetate case discussed previously, sufficiently high ligand concentrations to give almost completely bis ligand products were not obtained so that analysis of the chemical shift dependence in terms of product formation was difficult and imprecise.

In an attempt to obtain more information concerning the -536 and -548 ppm products, the condensation of vanadate with the chloro- and methylsuccinic acids were studied at pH 5.0. As for succinic acid itself, the products giving rise to the -536 and -548 ppm signals were formed equally well from each ligand. However, the ease of formation of these products varied greatly from ligand to ligand but in a systematic manner. The formation constants for the -536 ppm (and -548 ppm) products were 1.4 ± 0.1 M^{-1}, 7.3 ± 0.2, and 16.7 ± 1.0 M^{-1} for the methylsuccinic, succinic, and chlorosuccinic acids, respectively.

Products similar to those that are formed with succinic acid might also be formed with glutaric acid (pentanedioic acid) or adipic acid (hexanedioic acid). However, only a product giving rise to a signal at -536 ppm was observed for these two diacids. In addition, of course, the -560 ppm vanadate signal showed a change in chemical shifts with incremental amounts of either acid. No product giving rise to an NMR signal near -548 ppm was observed either as a function of pH or of ligand concentration. It appears that if this product is formed, it either has a relatively broad NMR signal or is in rapid exchange with the free vanadate. Cooling a 0.6 M glutarate solution to 269 K at pH 5.0 did not provide evidence for a rapid equilibration process.

The formation constants for the -536 ppm products from glutaric and adipic acids at pH 5.0 were determined as 1.8 ± 0.1 M^{-1} and 1.9 ± 0.1 M^{-1}, respectively. No evidence for incorporation of more than one ligand to form a secondary product was obtained. From the change in chemical shift of the -560 ppm vanadate signal as the ligand concentration was increased, the bis(ligand) products in rapid equilibrium with the free vanadate had formation constants of 9 ± 1 M^{-2} and 11 ± 1 M^{-2} for the glutarate and adipate products, respectively, at pH 5.0 and 1.0 M ionic strength, which compare with a value of 7.3 ± 0.2 M^{-2} for the succinate ligand also at pH 5.0. The upward trend in the value of the formation constants with increasing chain length possibly may reflect the differences in pK_a's of these acids.

The ^{51}V chemical shifts for the exchanging bis(ligand) products were determined to be -541 ppm for the three succinate ligands and the glutarate and adipate ligands. This compares with -540.6 ppm for the acetate and -541 ppm for the valerate products. Thus all of these products gave rise to similar ^{51}V chemical shifts, indicating a close structural correspondence.

The reaction of malonic acid at pH 5.0 with vanadate is very favorable compared to the other diacids. In this case 100 mM malonate is sufficient to convert most of the vanadate (2.0 mM total) to products. The product was in rapid equilibration with free vanadate and from high malonate concentrations was found to have a chemical shift of -538.0 ppm. This product contained two malonate ligands and had a formation constant of (1.13 ± 0.05) × 10^3 M^{-2}. This value is about half the value that has been determined for the formation of the octahedral bis(oxalato)vanadate product, albeit determined at pH 7.0.[12] Some evidence that at least two malonate products were formed was obtained by cooling the aqueous sample in an attempt to slow the chemical exchange process. However, the results were not conclusive. Analysis of the results of the malonate concentration study according to eq 6, where decavanadate, V_{10}, provides a reference

$$\frac{[VO_4H_2^-] + [V(mal)] + [V(mal)_2]}{[V_{10}]^{1/10}} = K_{10}^{-1/10} + K_{10}^{-1/10}K_1[mal] + K_{10}^{-1/10}K_1K_2[mal]^2 \quad (6)$$

point also was not conclusive but did give the values $K_{10} = (4.2 \pm 1.2) \times 10^{34}\ M^{-9}$, $K_1 = 5 \pm 3\ M^{-1}$, and $K_1K_2 = (1.13 \pm 0.05) \times 10^3\ M^{-2}$ where K_{10} is the formation constant of decavanadate from $VO_4H_2^-$, K_1 is the formation constant for V(mal) from vanadate and malonate, K_2 is the formation constant of $V(mal)_2$ from V(mal) and malonate and K_1K_2 is the overall formation constant of $V(mal)_2$ from $VO_4H_2^-$ and two malonates.

Discussion

Condensation of the vanadate monoanion, $VO_4H_2^-$, with the acids and diacids of this study consistently provided labile mono- and bis(ligand) products with ^{51}V chemical shifts near -541 ppm. Formation of these products does not require incorporation of a proton for their formation from the acid, and formation might occur as depicted in the top line of Scheme I.

The rationale for the change in coordination geometry indicated in Scheme I is based, to an extent, on the observation that the formation of the bis(ligand) product is favored over that of the precursor mono(ligand) product. This phenomenon of positive cooperativity seems to be common to many oxometalates. It has been suggested that the effect arises because there are more hydroxyl groups in the mono than in the bis complex and that it is the hydroxyl groups which promote ligand dissociation.[20] Such cooperativity would not be expected for simple anhydride formation and is not observed when either tetrahedral vanadate esters[4,5] or phosphovanadate anhydrides[7] are formed. The ^{51}V chemical shift of -540.6 ppm is close to those of the mono- and

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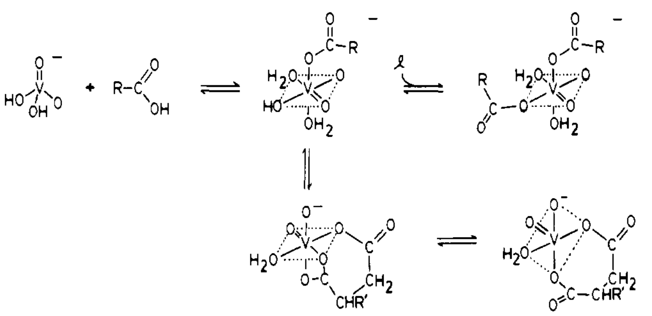
(20) Ehde, P. M.; Anderson, I.; Petterson, L. *Acta Chem. Scand.* **1986**, *A40*, 489-499.

Scheme I



bis(oxalato)vanadates, which occur at −541 and −536 ppm, respectively. The oxalato system also shows positive cooperativity and both products are thought to have octahedral coordination in aqueous solution.[12,20] The bis(oxalato) derivative certainly does in the solid.[21]

In addition to this, the chemical shifts of the anhydrides, divanadate (−570 ppm),[7,22] arsenovanadate (−575 ppm),[7] and phosphovanadate (−583 ppm),[7] are upfield from vanadate and about 40 ppm from the above-mentioned products. These three derivatives are thought to have tetrahedral coordination about vanadium. Also, studies of ligands of differing oxidation state have suggested that more highly electron-withdrawing ligands favor higher coordination.[12]

In addition to the above products, vanadate derivatives with a chemical shift near −536 ppm were observed for all ligands except acetate, but including valeric (pentanoic) acid. Although it is evident that a second type of vanadate derivative might be formed from the diacids by a simple cyclization to give the −536 ppm product, there is some evidence that this is not a straightforward reaction. Valeric acid provides a −536 ppm product, and here there is no possibility of cyclization. This suggests, if the −541 and −536 ppm products are both octahedral, that the mode of coordination is different. Bidentate coordination of carboxylate groups is frequently observed as for the tris(arene- or alkanecarboxylato)vanadium(V) derivatives.[17,18] Although these materials are not stable under aqueous conditions, it is possible that a bidentate coordination to at least one valerate does occur in aqueous solution. A possible alternative, albeit an unlikely one, is that the −536 ppm signal derives from an impurity in the valeric acid. The acid, however, was recrystallized, and also a ^{13}C NMR spectrum of valeric acid with a high signal to noise ratio was obtained and no impurities were detected. That the exchange rates are fast for all of the −541 ppm products but slow for all the −536 ppm products also suggests a different mode of coordination. Other evidence for a different mode of coordination of the carboxylate group is obtained from the study of the succinic acid products. Study of Table III shows that the −541 ppm products in rapid equilibration with vanadate have formation constants of 9.1, 5.8, and <0.2 M^{-2} for the methylsuccinate, succinate, and chlorosuccinate ligands, respectively, at pH 5.0. This trend is the reverse of that observed for the slowly exchanging products (−536 ppm products) where the formation constants are 1.4, 7.3, and 16.7 M^{-1} for the above ligands, respectively. The trend observed for the acyclic products can be rationalized in terms of the decrease in pK_a values on going form the methyl- to the chlorosuccinate. The acyclic product is formed by condensation with the acid form of the ligand (see Table I), and the proportion of this material drops with the decrease in pK_a. It is difficult to account for the increase in formation constants for the −536 ppm products that also form from the acid (see Table II). Formation of the products might be enhanced by the presence of the more highly electron-withdrawing substituent if all of the ligands of the complex, taken together, have a tendency to saturate the electron-accepting capability of the vanadate center. That this might happen has been suggested by other work.[4,12]

Table III. Formation Constants for Vanadium(V) Complexes Formed from Various Ligands at pH 5.00[a]

$2\ell + V_i \rightleftharpoons -541$	K, M^{-2}
acetate	1.6 ± 0.2
valerate	3.9 ± 0.5
chlorosuccinate	<0.2
succinate	5.8 ± 0.8
methylsuccinate	9.1 ± 0.9
glutarate	9.0 ± 1.0
adipate	11.0 ± 1.0
$2\ell + V_i \rightleftharpoons -536$	K, M^{-2}
valerate[b]	0.7 ± 0.2
$\ell + V_i \rightleftharpoons -536$	K, M^{-1}
chlorosuccinate	16.7 ± 1.0
succinate	7.3 ± 0.2
methylsuccinate	1.4 ± 0.1
glutarate	1.8 ± 0.1
adipate	1.9 ± 0.1
malonate	5 ± 3
$\ell + V_i \rightleftharpoons -548$	K, M^{-1}
chlorosuccinate	16.7 ± 1.0
succinate	7.3 ± 0.2
methylsuccinate	1.4 ± 0.1
$2\ell + V_i \rightleftharpoons -538$	K, M^{-2}
malonate	(1.13 ± 0.05) × 10^3

[a] Conditions of the measurements: 1.0/ M ionic strength maintained with KCl; pH 5.0; varying vanadate or ligand concentrations. [b] Ligand stoichiometry was not unequivocally established.

Changing the mode of coordination so that the metal forms a chelate with the carboxylate group[23] would be expected to slow the exchange rate of the product with free vanadate and might also change the dependence of product formation on the properties of substituents. There seems little reason to suspect the presence of a seven-coordinate product; since oxovanadium(V) tricarboxylates are unstable in the presence of water and even in solution in dichloromethane, the evidence suggests that one or more of the three chelate rings are easily opened.[17,18] A change in coordination from six- to five-coordinate, as depicted in the bottom line of Scheme I, could account for the remaining vanadate derivative with a ^{51}V chemical shift of −548 ppm. A product with a chemical shift at −550 ppm has been observed in the pyridine-2-carboxylate system[13] and this latter product may have a similar coordination. A point to be made is that the methyl- and chlorosuccinate ligands are both asymmetrical. Since there is no reason to expect a high degree of orientational selectivity in forming the product, this implies that if the −548 ppm product is pentacoordinate, then it is most likely square pyramidal with the oxygen of the V=O moiety occupying the apical position. If this were not so then the −548 ppm signal of the succinate product might be replaced by two signals for either of the chloro- or the methylsuccinate derivatives and one signal for each of the two possible isomers as has been observed for other ligands.[8,24] It is not obvious why the −536 and −548 ppm products should be formed in the same one to one proportion from the various succinate ligands of this study, and this aspect of vanadate chemistry is of continuing interest.

In addition to the condensation of these acids with monomeric vanadate, it is interesting to note from Figures 1 and 3 that there is no indication of formation of products with decavanadate. In contrast to this, alcohols readily condense with decavanadate to form mono, bis, and perhaps tris products.[25]

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