Inorg. Chem. **2007**, *46*, 1575−1585

Inorganic Chemistry
Article

Structural and Spectroscopic Evidence for the Formation of Trinuclear and Tetranuclear Vanadium(III)/Carboxylate Complexes of Acetate and Related Derivatives in Aqueous Solution

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Received July 17, 2006

The formation of vanadium(III) complexes with nuclearity greater than two is believed to occur in aqueous solution on the basis of potentiometric, electrochemical, and/or UV–vis spectroscopy titration measurements, although structural evidence for this is limited. Upon the addition of 1–2 equiv of acetate, propionate, chloroacetate, trifluoroacetate, or bromoacetate to an aqueous, acidic solution of vanadium(III), trinuclear and tetranuclear complexes are formed. The structures of $[V_4(\mu\text{-OH})_4(\mu\text{-OOCCF}_3)_4(OH_2)_8]Cl_4\cdot 7.5H_2O$ (**1**), $[V_4(\mu\text{-OH})_4(\mu\text{-OOCCH}_3)_4(OH_2)_8]Cl_4\cdot CH_3COOH\cdot 12H_2O$ (**2**), $[V_4(\mu\text{-OH})_4(\mu\text{-OOCCH}_3)_4(OH_2)_8]Cl_4\cdot 3H_2O$ (**3**), $[V_3(\mu_3\text{-O})(\mu\text{-OOCCH}_2Br)_6(OH_2)_3]CF_3SO_3\cdot H_2O$ (**4**), $[V_3(\mu_3\text{-O})(\mu\text{-OOCCH}_2CH_3)_6(OH_2)_3]Cl\cdot 2H_2O$ (**5**), $[V_3(\mu_3\text{-O})(\mu\text{-OOCCH}_3)_6(OH_2)_3]Cl\cdot 3.5H_2O$ (**6**), and $[V_3(\mu_3\text{-O})(\mu\text{-OOCCH}_2Cl)_6(OH_2)_3]CF_3SO_3\cdot H_2O$ (**7**) have been determined by X-ray diffraction. Importantly, electrospray mass spectrometry and ^1H NMR measurements suggest that these complexes are not purely solid-state phenomena but are also present in solution. For the vanadium(III)/acetate and vanadium(III)/propionate systems, two paramagnetic ^1H NMR signals corresponding to two distinct complexes (species A and B) are observed in the 40–55 ppm region for 0.20 mol equiv of acetate or propionate, at pD 3.44. No corresponding signals are observed for the vanadium(III)/bromoacetate and vanadium(III)/chloroacetate systems under the same conditions or for the vanadium(III)/trifluoroacetate system using ^{19}F NMR spectroscopy. UV–vis spectra suggest that species B are structurally analogous for the vanadium(III)/acetate and vanadium(III)/propionate systems, whereas structurally different complexes are the major species for the other systems. Diffusion coefficients of species B for the vanadium(III)/acetate and vanadium(III)/propionate systems determined by pulsed-field-gradient spin–echo NMR spectroscopy measurements are $(3.0 \pm 0.1) \times 10^{-6}$ and $(3.23 \pm 0.01) \times 10^{-6}$ $cm^2\ s^{-1}$, respectively, and are most consistent with species B being trimeric, rather than tetranuclear, complexes.

Introduction

The importance of vanadium in biology is well established,[1−4] although whether vanadium is an essential element for humans is still debated.[5] In nature, vanadium occurs in a variety of oxidation states ranging from V^{II} to V^{V}, including the vanadium-dependent nitrogenases in azotobacteria ($V^{II/III}$), vanadium-dependent haloperoxidases in marine algae (V^{V}), amavadin in the mushroom *Amanita muscaria* (V^{IV}), V^{III} in the marine fanworm *Pseudopotamilla occelata*, and V^{III}/V^{IV} in some ascidian species.[1−4] Utilization of vanadium complexes (V^{III}, V^{IV}, and V^{V}) in the treatment of diabetes and cancer are also active areas of research.[6−9]

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10.1021/ic0613210 CCC: $37.00

Much less is known about the aqueous chemistry of V^{III} compared with vanadium's higher oxidation states, V^{IV} and V^{V}. V^{III} (d^2) is paramagnetic, frequently making its complexes unsuitable for NMR studies. Electron paramagnetic resonance (EPR) spectroscopy signals are typically also not observed for V^{III} complexes with lower than cubic symmetry using conventional EPR spectrometers[10] because spin−orbit coupling results in a large zero-field splitting and short spin−lattice (T_1) relaxation times.[11] Undoubtedly, the unsuitability of both NMR and EPR spectroscopies for elucidating the structures of V^{III} complexes has hindered progress in understanding their solution chemistry compared with V^{IV} and V^{V}. In addition, the coordination chemistry of aqueous V^{III} species is complex, even in the absence of coordinating ligands.[12−16] Aqueous V^{III} complexes are air-sensitive and insoluble at pH > 4.5.[2] Upon deprotonation of the first aqua group of $[V(OH_2)_6]^{3+}$ (pK_a 2.3[16]), dimerization and subsequent deprotonation occurs to form μ-oxo-bridged V^{III} dimers.[12−17] Further aggregation in aqueous solution to form trinuclear and tetranuclear V^{III} complexes is suggested from detailed potentiometric, electrochemical, and/or UV−vis spectroscopic titration measurements.[13,14,17] It is also speculated that oxo/hydroxo-bridged multinuclear V^{III} complexes may be important in vanadium-accumulating ascidians because a number of metalloproteins exist with active sites involving oxo/hydroxo-bridged Fe or Mn units.[18] However, there is extremely limited structural evidence for the existence of V^{III} complexes of nuclearity greater than two in aqueous solution; to our knowledge, there is only one report of a trinuclear vanadium(III)/chloroacetate complex crystallized over 2 decades ago by two independent groups.[19,20] Importantly, it is also unclear whether this trinuclear species actually exists in aqueous solution itself or is purely a solid-state phenomenon.

A further reason for our interest in aqueous vanadium(III)/carboxylate chemistry concerns recent reports of polynuclear V^{III} complexes isolated from organic solvents or neat carboxylic acid solutions with interesting structures, spectroscopic properties, and magnetic properties.[21−29] Dimeric, trimeric, tetranuclear, octanuclear, and decanuclear vanadium(III)/carboxylate complexes have been isolated. V^{III} complexes have potentially interesting magnetic properties,[23−27,30−36] including switching between strong ferromagnetic coupling and antiferromagnetic coupling upon protonation of the μ-oxo ligand of dimeric V^{III} complexes,[25−27,31] exhibiting spin-frustration effects[37] and/or single-molecule magnetic behavior.[24,30] Vanadium(III)/carboxylate chemistry is also of interest in the development of new microporous materials.[38] Finally, we note that, because NMR and EPR spectroscopies are generally unhelpful in studying V^{III} speciation, an increasing number of potentiometric and UV−vis spectroscopic titration studies are being performed to elucidate the species formed between V^{III}(aq) and biogenic ligands and to determine the associated acid dissociation and stability constants.[17,39−41] However, to obtain useful acid dissociation and stability constant data for these complex systems from potentiometric and UV−vis spectroscopic data, there is an urgent need for reliable structural models for multinuclear oxo- and hydroxovanadium(III) complexes formed in aqueous solution.[17]

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We report the structural and spectroscopic characterization of a series of trinuclear and tetranuclear vanadium(III)/carboxylate complexes of acetate and related derivatives. To our knowledge, we present the first examples of tetranuclear V^{III} complexes from aqueous solution. Importantly, mass spectrometry (MS) and ^1H NMR spectroscopy measurements suggest that the integrity of these complexes is retained in the aqueous solution itself. The structures of the trinuclear and tetranuclear vanadium(III)/acetate complexes reported herein have been previously communicated.[42]

Experimental Section

General Methods. All reactions were carried out using standard Schlenk techniques under an atmosphere of argon or nitrogen and/or in an MBRAUN Labmaster 130 (1250/78) glovebox. Anhydrous VCl_3 (98%), $NaOOCCH_3$ (99%), and $CFCl_3$ (≥99%) were purchased from Aldrich, and $NaOOCCH_2CH_3$ (99%) was obtained from Alfa Aesar. $Pb(OOCCH_3)_2{\cdot}3H_2O$ (99%), $NaOOCCH_2Cl$ (98%), $BrCH_2COOH$ (99%), CF_3COOH (99%), CF_3SO_3H (99%), and 2-(*N*-morpholino)ethanesulfonic acid (MES; 99%) were purchased from Acros. *N*-(2-Hydroxyethyl)piperazine-*N′*-2-ethanesulfonic acid (HEPES; 99.5%) was purchased from Sigma. All chemicals were used without further purification. Water was purified using a Barnstead Nanopure Diamond water purification system. $V(CF_3SO_3)_3$ was prepared according to a published procedure.[43]

pH measurements were made in an argon atmosphere at room temperature with an Orion model 710A pH meter equipped with a Wilmad 6030-02 pH electrode. Alternatively, a Corning model 445 pH meter equipped with a Mettler-Toledo Inlab 423 electrode was used. Both electrodes were filled with a 3 M KCl/saturated AgCl solution, pH 7.0, and standardized with standard BDH buffer solutions at pH 4.01 and 6.98. The solution pH was adjusted using concentrated CF_3SO_3H or concentrated NaOH solutions as necessary.

IR spectra were recorded on a Bruker Tensor 27 as KBr pellets from 4000 to 400 cm^{-1}. UV−vis spectra were recorded using a Cary 5000 spectrophotometer operating with WinUV Bio software (version 3.00) and equipped with a thermostated (25.0 ± 0.1 °C) cuvette holder. Electrospray MS (ES-MS; positive mode) spectra were recorded using a Bruker Esquire∼LC mass spectrometer.

Preparation of Vanadium(III)/Carboxylate Solutions for NMR and UV−Vis Spectroscopy Measurements. A series of solutions of VCl_3 (0.0100 M) and $CH_3COO(H)$ (0.20−2.0 mol equiv of free CH_3COO^-) in buffer, pD 3.44 ± 0.02, were prepared in a glovebox from anaerobic stock solutions of VCl_3 (0.0200 M) in 0.0500 M HEPES (the pH was adjusted to pD 3.50 using 0.10 M MES buffer, pD ∼6.3[44]), $CH_3COO(H)$ in D_2O (the pD was adjusted to 3.50 using 5.0 M NaOH and CF_3SO_3H; $[CH_3COOH]_T = 2.00$ M and $[CH_3COO^-] = 0.118$ M using $pK_a(CH_3COOH) = 4.7$) and a 0.0500 M HEPES buffer solution (pD 3.50). Note that the pH dropped 0.06 units upon mixing of the solutions. The solutions were left to equilibrate overnight. The purity of commercially available VCl_3 can vary; hence, the concentration of the stock solutions of VCl_3 (calculated concentration = 0.0200 M based on the mass of VCl_3 weighed) was checked by measuring the UV−vis spectrum of an aliquot of the solutions in 1.00 M $HClO_4$ and was found to be 0.0200 M within experimental error (0.198 and 0.0212 M, respectively, for two separate solutions; $\epsilon(396\ \text{nm}) = 8.3\ M^{-1}\ cm^{-1}$ and $\epsilon(588\ \text{nm}) = 5.8\ M^{-1}\ cm^{-1}$ for $[V(OH_2)_6]^{3+}$ in 1.0 M $HClO_4$).[13]

Similar procedures were used to prepare the other vanadium(III)/carboxylate solutions for NMR and UV−vis spectroscopy measurements. The pH changed up to 0.07 units upon mixing of the solutions.

^1H NMR Spectroscopy Measurements. All NMR spectra were recorded at 22 ± 1 °C using a Varian Unity/Inova 500-MHz spectrometer equipped with a 5 mm probe. ^1H NMR spectra were recorded with a delay time of 4 s, and a 2 mm diameter capillary of 3-(trimethylsilyl)propionic-*2,2,3,3-d*$_4$ acid sodium salt in D_2O was used as an external standard. ^{19}F NMR spectra were recorded using a delay time of 1 s, and a 2 mm diameter capillary of $CFCl_3$ in $CHCl_3$ was used as an external standard. NMR samples were prepared in a glovebox and the tubes fitted with a septum cap.

Pulsed-Field-Gradient (PFG) NMR Diffusion Coefficient Measurements. The following parameters were used for the gradient-echo pulse sequence: maximum field gradient amplitude $G = 20$ G cm^{-1} (water diffusion coefficient experiment) or 40 G cm^{-1} [vanadium(III)/carboxylate diffusion coefficient experiments], echo time = 10 ms, and duration of the gradient pulses $\delta = 1 - 5$ ms.

X-ray Crystallography Experiments. Experimental details concerning the X-ray structures of compounds **2**, **3**, and **6** are reported in a preliminary communication.[42] X-ray diffraction data for compound **1** were measured at 100 K (Bruker KRYO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å) operating at 2000 W. Crystals were mounted on a cryoloop using Paratone N−Exxon oil and placed under a stream of nitrogen. The detector was placed at a distance of 5.009 cm from the crystals. Frames were collected with a scan width of 0.3° in ω. Analyses of the data sets showed negligible decay during data collection. The data were corrected for absorption with the *SADABS* program. The structures were refined using the Bruker *SHELXTL Software Package* (version 6.1) and were solved using direct methods until the final anisotropic full-matrix, least-squares refinement of F^2 converged. H−O bond lengths were restricted to ideal lengths (0.95 Å for water and 0.85 Å for hydroxide), and the H atoms were refined isotropically.[45]

X-ray diffraction data for compounds **4**, **5**, and **7** were measured at 100 K (Oxford 700 series cryostream) on a Bruker AXS platform single-crystal X-ray diffractometer upgraded with an APEX II CCD detector. Graphite-monochromatized Mo Kα radiation was used ($\lambda = 0.71073$ Å). Crystals were mounted on a thin glass fiber from a pool of Fluorolube and placed under a stream of nitrogen. The data were corrected for absorption with the *SCALE* program within the *APEX2 Software Package*. The structures were refined using the *APEX2 Software Package* (version 1.27) and were solved using direct methods. This procedure yielded the heavy atoms, along with a number of C and O atoms. Subsequent Fourier synthesis yielded the remaining atom positions. The H atoms are fixed in positions of ideal geometry and refined within the *XSHELL* software. These idealized H atoms had their isotropic temperature factors fixed at 1.2 or 1.5 times the equivalent isotropic *U* of the C

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Table 1. Crystal Data and Structure Refinement Parameters for $[V_4(\mu\text{-OH})_4(\mu\text{-OOCR})_4(OH_2)_8]Cl_4{\cdot}m CH_3COOH{\cdot}n H_2O$ [R = CF_3, $m = 0$, $n = 7.5$ (**1**); R = CH_3, $m = 1$, $n = 12$ (**2**); R = CH_3, $m = 0$, $n = 3$ (**3**)]

parameter	**1**	**2**[42]	**3**[42]
fw	1144.8	1110.20	848.95
a/Å	11.8284(10)	13.6330(8)	17.7698(11)
b/Å	26.167(2)	13.6330(8)	17.7698(11)
c/Å	18.9800(12)	12.7744(14)	11.3900(14)
α/deg			
β/deg	127.331(4)		
γ/deg			
V/Å^3	4671.1(6)	2374.2(3)	3596.6(5)
cryst syst	monoclinic	tetragonal	tetragonal
space group	$P2_1/c$	$I\bar{4}2m$	$P4_2/mnm$
cryst size/mm^3	0.10 × 0.10 × 0.01	0.20 × 0.20 × 0.10	0.30 × 0.05 × 0.03
Z	4	2	4
T/K	100(2)	100(2)	100(2)
calcd density/(Mg/m^3)	1.615	1.553	1.568
R1, wR2 [$I > 2\sigma(I)$]	R1 = 0.0654	R1 = 0.0255	R1 = 0.0843
	wR2 = 0.1349	wR2 = 0.0610	wR2 = 0.2104
R1, wR2 (all data)	R1 = 0.0865	R1 = 0.0261	R1 = 0.0888
	wR2 = 0.1425	wR2 = 0.0613	wR2 = 0.2126

Table 2. Selected Bond Lengths and Bond Angles for $[V_4(\mu\text{-OH})_4(\mu\text{-OOCR})_4(OH_2)_8]Cl_4{\cdot}m CH_3COOH{\cdot}n H_2O$ [R = CF_3, $m = 0$, $n = 7.5$ (**1**); R = CH_3, $m = 1$, $n = 12$ (**2**); R = CH_3, $m = 0$, $n = 3$ (**3**)]

parameters	**1**	**2**	**3**
V−O[a] (Å)	1.929(3)−1.949(3)	1.9393(10)	1.933(3)−1.947(4)
V−O[b] (Å)	2.017(3)−2.042(3)	2.0246(14)	2.004(5)−2.012(5)
V−O[c] (Å)	1.974(3)−2.046(3)	2.0376(17)	2.046(6)−2.057(5)
V−V (Å)	3.512−3.558	3.527	
cis-O−V−O[d] (deg)	87.11(12)−95.89(12)	93.58(13)	95.1(3)
cis-O−V−O[e] (deg)	88.29(12)−96.77(12)	91.57(8)−94.73(7)	90.9(3)−94.7(3)
cis-O−V−O[f] (deg)	86.94(12)−91.93(13)	89.64(8)	89.8(3)- 90.8(3)
trans-O−V−O[f] (deg)	172.33(13)−178.46(13)	176.77(9)	173.7(3)−175.1(3)
trans-O−V−O[g] (deg)	169.70(12)−171.96(12)	170.80(9)	171.0(2)

[a] *V*−(μ-*O*H). [b] *V*−*O*C(R)O. [c] *V*−*O*H$_2$. [d] (μ-*O*H)−*V*−(μ-*O*H). [e] O(R)C*O*−*V*−(μ-*O*H). [f] (μ-*O*H)−*V*−*O*H$_2$. [g] O(R)C*O*−*V*−*O*C(R)O.

Table 3. Crystal Data and Structure Refinement Parameters for $[V_3(\mu_3\text{-O})(\mu\text{-OOCR})_3(OH_2)_6]X{\cdot}n H_2O$ [R = CH_2Br, X = CF_3SO_3, $n = 1$ (**4**); R = C_2H_5, X = Cl, $n = 2$ (**5**); R = CH_3, X = Cl, $n = 3.5$ (**6**); R = CH_2Cl, X = CF_3SO_3, $n = 1$ (**7**)]

parameters	**4**	**5**	**6**[42]	**7**
fw	1217.63	732.77	675.64	950.87
a/Å	13.699(4)	11.0342(18)	13.6094(14)	13.4904(12)
b/Å	14.218(4)	11.3901(19)	23.118(2)	14.0237(12)
c/Å	18.674(6)	14.607(2)	9.1340(10)	18.0199(16)
α/deg		67.527(3)		
β/deg	107.652(7)	70.775(3)		107.065(2)
γ/deg		66.979(3)		
V/Å^3	3466.0(18)	1526.0(4)	2873(5)	3259.0(5)
cryst syst	monoclinic	triclinic	orthorhombic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_12_12$	$P2_1$
cryst size/mm^3	0.20 × 0.15 × 0.10	0.10 × 0.10 × 0.05	0.40 × 0.40 × 0.40	0.25 × 0.18 × 0.11
Z	4	2	4	4
T/K	100(2)	100(2)	100(2)	100(2)
calcd density/(Mg/m^3)	2.333	1.595	1.562	1.938
R1, wR2 [$I > 2\sigma(I)$]	R1 = 0.0798	R1 = 0.0386	R1 = 0. 0.0431	R1 = 0. 0.0751
	wR2 = 0.2252	wR2 = 0.0981	wR2 = 0.1083	wR2 = 0.1582
R1, wR2 (all data)	R1 = 0.1081	R1 = 0.0491	R1 = 0.0453	R1 = 0. 0.1512
	wR2 = 0.2400	wR2 = 0.1084	wR2 = 0.1094	wR2 = 0.1946

atoms to which they were bound. The final refinement of each compound included anisotropic thermal parameters on all non-H atoms.

Further experimental details for the structures of **1**, **4**, **5**, and **7** are provided in Tables 1 and 3.

Syntheses. $[V_4(\mu\text{-OH})_4(\mu\text{-OOCCF}_3)_4(OH_2)_8]Cl_4{\cdot}7.5H_2O$ (1). Trifluoroacetic acid (7.8 mL, 2.7 M, 21 mmol) was added dropwise to a solution of VCl_3 (3.28 g, 20.9 mmol) in water (6.0 mL) with stirring, causing the solution to change from green to blue-green. The solution was reduced in vacuo (~4 mL) until solid appeared. The product was heated gently until the solid redissolved, and then the flask was placed in a Dewar of hot (~70 °C) water. Upon slow cooling of the solution to room temperature, green crystals formed. Some of the crystals were removed for X-ray diffraction studies, and the remaining crystals were filtered, washed with distilled water, and dried in vacuo. The bulk crystallized product (1.2 g) was found to be a mixture of complexes, as determined by elemental analysis. ES-MS of the product solution (degassed H_2O, *m/z*): 181 [V_4(μ-

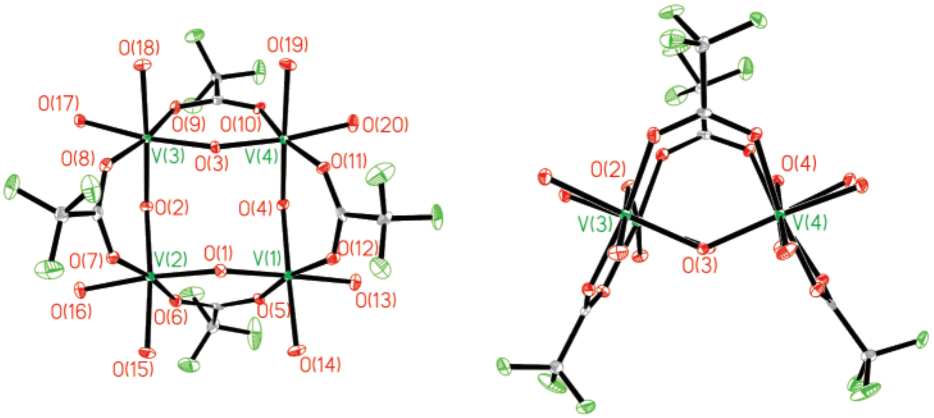

Figure 1. Thermal ellipsoid plots (50%) of the $[V_4(\mu\text{-OH})_4(\mu\text{-OOCCF}_3)_4(OH_2)_8]^{4+}$ core (**1**). The four V^{III} atoms are bridged by one μ-hydroxo ligand and one μ-trifluoroacetato ligand. The remaining coordination sites are occupied by water ligands.

$OH)_4(\mu\text{-OOCCF}_3)_4]^{4+}$, 195 $[V_4(\mu\text{-OH})_4(\mu\text{-OOCCF}_3)_4(OH_2)_3]^{4+}$, 221 $[[V_4(\mu\text{-OH})_4(\mu\text{-OOCCF}_3)_4(OH_2)_8] + H_2O]^{4+}$, 235 $[[V_4(\mu\text{-OH})_4(\mu\text{-OOCCF}_3)_4(OH_2)_8] + 4H_2O]^{4+}$, 276 $[[V_4(\mu\text{-OH})_4(\mu\text{-OOCCF}_3)_4(OH_2)_8] + 13H_2O]^{4+}$, 315 $[[V_4(\mu\text{-OH})_4(\mu\text{-OOCCF}_3)_4(OH_2)_6] + OOCCF_3]^{3+}$, 339 $[[V_4(\mu\text{-OH})_4(\mu\text{-OOCCF}_3)_4(OH_2)_8] + 2H_2O + OOCCF_3]^{3+}$.

$[V_4(\mu\text{-OH})_4(\mu\text{-OOCCH}_3)_4(OH_2)_8]Cl_4\cdot CH_3COOH\cdot 12H_2O$ (2) and $[V_4(\mu\text{-OH})_4(\mu\text{-OOCCH}_3)_4(OH_2)_8]Cl_4\cdot 3H_2O$ (3). The synthesis and characterization of these compounds were reported in a preliminary communication.[42]

$[V_3(\mu_3\text{-O})(\mu\text{-OOCCH}_2Br)_6(OH_2)_3]CF_3SO_3\cdot H_2O$ (4). Solid bromoacetic acid (0.28 g, 2.0 mmol) was added to a solution of $V(CF_3SO_3)_3$ (0.82 g, 1.7 mmol) in water (~8 mL), upon which the brown solution became green. The volume was reduced in vacuo until a few dark-green crystals appeared, suitable for X-ray diffraction studies. Several attempts were made in subsequent identical syntheses to crystallize out more product for elemental analysis measurements, without success.

$[V_3(\mu_3\text{-O})(\mu\text{-OOCCH}_2CH_3)_6(OH_2)_3]Cl\cdot 2H_2O$ (5). VCl_3 (1.22 g, 7.76 mmol) was dissolved in water (8.0 mL), and solid sodium propionate (0.79 g, 8.1 mmol) was added with stirring. The brown solution immediately became green and was stirred for an additional 10 min, until all of the solid dissolved. The solution was reduced in vacuo (~2 mL) until solid appeared. The reaction flask was placed in a Dewar of hot (~70 °C) water. Upon slow cooling of the solution to room temperature, a few dark-green crystals appeared, suitable for X-ray diffraction studies. The bulk crystallized product (1.2 g) was found to be a mixture of complexes, as determined by elemental analysis. ES-MS of the product solution (degassed H_2O, *m/z*): 662 $[V_3(\mu_3\text{-O})(\mu\text{-OOCCH}_2CH_3)_6(OH_2)_3]^+$, 696 $[V_3(\mu_3\text{-O})(\mu\text{-OOCCH}_2CH_3)_6(OH_2)_3] + H + Cl]^+$.

$[V_3(\mu_3\text{-O})(\mu\text{-OOCCH}_3)_6(OH_2)_3]Cl\cdot 3.5H_2O$ (6). The synthesis and characterization of **6** was reported in a preliminary communication.[42]

$[V_3(\mu_3\text{-O})(\mu\text{-OOCCH}_2Cl)_6(OH_2)_3]CF_3SO_3\cdot H_2O$ (7). Sodium chloroacetate (5.3 mL, 0.27 M, 1.4 mmol) was added dropwise to a solution of $V(SO_3CF_3)_3$ (0.71 g, 1.4 mmol) in water (4.0 mL), causing the solution to change from brown-red to green. The solution was reduced in vacuo (~1 mL), causing the solution to change from green to blue, until solid appeared. The product was heated gently until all of the solid had redissolved, and then the flask was placed in a Dewar of hot (~70 °C) water. Upon slow cooling of the solution to room temperature, dark-green crystals suitable for X-ray diffraction studies and elemental analysis formed. Yield: 90 mg, 6.7%. Elem anal. Calcd for $[V_3(\mu_3\text{-O})(\mu\text{-OOCCH}_2Cl)_6(OH_2)_3](SO_3CF_3)(CF_3SO_3H)\cdot 3H_2O$, $C_{14}H_{25}O_{25}Cl_6S_2F_6V_3$: C, 14.80; H, 2.12; Cl, 18.72; V, 13.44; S, 5.64; F, 10.03. Found: C, 14.16; H, 1.99; Cl, 17.84; V, 13.84; S, 5.91; F, 10.26. Selected IR data (cm^{-1}, KBr): 3422 (br), 1606 (s), 1560 (m), 1455 (s), 1350 (m), 1230 (w), 1033 (m), 902 (w), 666 (m), 617 (m).

Results and Discussion

Crystal Structures. Upon the addition of ~1 mol equiv of CF_3COOH or $Pb(OOCCH_3)_2$ to VCl_3, deep-green/blue crystals of tetranuclear **1**−**3** were obtained. Crystal data and structural refinement parameters and important bond length and bond angle data for **1**−**3** are given in Tables 1 and 2. The asymmetric unit of **1** contains the entire V_4 cation, four chloride anions, and seven and a half lattice waters. Thermal ellipsoid plots of the V_4 cation of **1** are shown in Figure 1. The novel cationic structure comprises four coplanar V^{III} centers, with a μ-hydroxo ligand and a μ-trifluoroacetato ligand bridging the V centers above and below the plane in an alternate arrangement around the ring. The H atoms of the μ-hydroxo groups were observed crystallographically. The distorted octahedral coordination environment of each V^{III} center is completed by two water ligands, and the cation has virtual S_4 symmetry. There are four V_4 cations in the unit cell. The V_4 cationic complex of **1** is isostructural with the two tetranuclear vanadium(III)/acetate complexes **2** and **3**. The structure of **2** is described in detail in a preliminary communication.[42] The asymmetric unit of **3** comprises the entire V_4 cation, four chloride anions, and three lattice water molecules. The unit cell contains four such units.

Important bond length and bond angle data for **1**−**3** are given in Table 2. Sufficient amounts of **3** were obtained for elemental analysis measurements and are reported in the preliminary communication on this work.[42] Room-temperature magnetic moment measurements of **3** confirmed the 3+ oxidation states of the V centers [$\mu_{eff} = 2.92\ \mu_B$ (300 K) per V center[42]]. Repeated attempts to obtain a crystalline product with an elemental analysis consistent with **1** failed, with the % Cl and % C typically being much closer to values expected for *trans*-$[V(OH_2)_4Cl_2]Cl$. In line with this, X-ray diffraction quality crystals of light-green *trans*-$[V(OH_2)_4Cl_2]Cl\cdot 2H_2O$ were obtained from some of the vanadium(III)/carboxylate solutions (the structure of *trans*-$[V(OH_2)_4Cl_2]$-

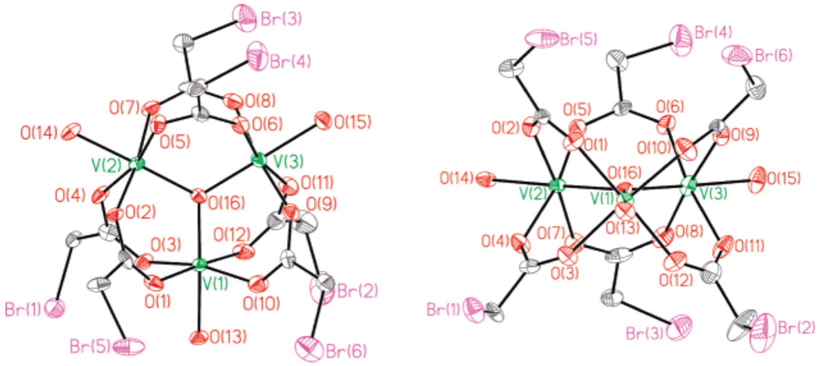

Figure 2. Thermal ellipsoid plots (50%) of the $[V_3(\mu_3\text{-O})(\mu\text{-OOCCH}_2Br)_6(OH_2)_3]^+$ core (**4**), showing two different views. **4** has a triangular V(μ_3-O) core, with two μ-bromoacetato ligands bridging the V centers on opposite sides of the V_3 plane.

Table 4. Selected Bond Lengths and Bond Angles for $[V_3(\mu_3\text{-O})(\mu\text{-OOCR})_3(OH_2)_6]X\cdot nH_2O$ [R = CH_2Br, X = CF_3SO_3, n = 1 (**4**); R = C_2H_5, X = Cl, n = 2 (**5**); R = CH_3, X = Cl, n = 3.5 (**6**); R = CH_2Cl, X = CF_3SO_3, n = 1 (**7**); R = CH_2Cl, X = CF_3SO_3, n = 10.5 (**8**); R = CH_2Cl, X = ClO_4, n = 3 (**9**)]

parameters	**4**	**5**	**6**	**7**	**8**[19]	**9**[20]
V−O[a] (Å)	1.910(7)−1.948(7)	1.908(2)−1.921(2)	1.920(2)−1.928(2)	1.904(6)−1.933(6)	1.909(4)−1.943(3)	1.90(1)−1.95(1)
V−O[b] (Å)	1.991(8)−2.043(8)	1.992(2)−2.048(2)	2.002(2)−2.051(2)	1.968(6)−2.052(6)	2.000(5)−2.025(4)	1.99(1)−2.03(1)
V−O[c] (Å)	2.016(8)−2.052(9)	2.021(2)−2.041(2)	1.997(2)−2.018(2)	2.035(6)−2.037(6)	2.023(3)−2.054(3)	2.04(1)−2.10(1)
trans-V−O−V[d] (deg)	119.3(4)−120.7(4)	119.74(11)−120.37(11)	119.57(11)−120.20(11)	119.4(3)−120.6(3)	119.6(2)−120.3(2)	119.5(5)−120.8(5)
trans-O−V−O[e] (deg)			176.36(10)−178.64(10)			
cis-O−V−O[f] (deg)	85.0(3)−94.7(3)	86.14(10)−92.89(10)	82.44(10)−93.20(12)	85.5(3)−94.3(3)	87.04−91.80	86.5(5)−92.4(5)
trans-O−V−O[f] (deg)	166.7(3)−175.7(3)	170.16(10)−172.48(10)	167.62(11)−175.54(10)	166.6(2)−174.9(2)	167.54−173.07	167.8(5)−173.3(5)
trans-O−V−O[g] (deg)	178.3(3)−179.0(3)	176.86(10)−178.33(10)	176.36(10)−178.64(10)	176.8(3)−177.4(3)	176.7(1)−179.7(2)	177.0(5)−177.5(5)

[a] *V−(μ_3-O)*. [b] *V−O*C(R)O. [c] *V−OH*$_2$. [d] *V−(μ_3-O)−V*. [e] *(μ_3-O)−V−O*C(R)O. [f] O(R)C*O−V−O*C(R)O. [g] *(μ_3-O)−V−OH*$_2$.

$Cl\cdot 2H_2O$ is reported elsewhere).[46] Note, however, that despite having no elemental analyses for crystals of **1**, we are confident about the V^{III} assignment for all of the V centers, given the similarities in both the procedures used to synthesize **1**−**3** and the excellent agreement between the bond lengths and angles (Table 2).

The $V^{III}-OH_2$ bond lengths in **1**−**3** (1.97−2.06 Å, Table 2) are within the range expected for V^{III} centers.[47,48] The V−O bond lengths for the μ-OH (1.93−1.95 Å) and μ-OOCCH$_3$/μ-OOCCF$_3$ ligands (2.00−2.04 Å) also occur within the ranges observed in other V^{III} complexes with μ-OH (1.93−1.96 Å[25,26,28,31,49]) and μ-carboxylates (2.00−2.05 Å[19,21,24,28,50]). The O−V−O bond angles involving all three O ligands (H_2O, μ-OH, and μ-OOCCH$_3$/μ-OOCCF$_3$) are consistent with those of distorted octahedral V^{III} centers (86.94−96.77° for *cis*-O−V−O and 169.70−178.46° for *trans*-O−V−O). V···V distances range from 3.51 to 3.56 Å; hence, there is no metal−metal bonding.[30]

Seven types of vanadium(III)/carboxylate complexes isolated from organic solvents or neat carboxylic acid solutions have been structurally characterized in the literature: (i) monomeric carboxylate complexes,[51−54] (ii) dimeric species, bridged by one oxo (or hydroxo) group and two carboxylates[25−27,31−34] or bridged by four carboxylates,[35,36] (iii) complexes with a triangular (μ_3-O)V_3 core with two μ-carboxylates bridging the V centers (COO^- can be replaced by RS^- or phosphate groups),[19,20,23,28,50,55−58] (iv) tetranuclear, butterfly-type V^{III} complexes, in which two of the V^{III} centers are bound to a μ_3-oxo ligand, three μ-carboxylate ligands, and a bidentate ligand (2,2′-bipyridine), while the other two are bound to two μ_3-oxo ligands and four μ-carboxylate ligands,[23,24,30] (v) cyclic V_8 complexes bridged by μ-hydroxo, μ-carboxylate, and μ-ethoxy ligands,[28] (vi) a cyclic V_{10} complex bridged by μ-methoxide and μ-acetate ligands,[21] and (vii) an unusual capped cube structure with a $Zn_4V_4O_4$ core.[29] Hence, the tetranuclear vanadium(III)/carboxylate complexes **1**−**3** belong to a new structural type. They are

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(47) Cotton, F. A.; Fair, C. K.; Lewis, G. E.; Mott, G. E.; Ross, F. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 5319−5323.

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(49) A bond length of 1.83 Å was reported in ref 21.

(50) Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* **1982**, *21*, 3316−3321.

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(56) Cannon, R. D.; White, R. P. *Prog. Inorg. Chem.* **1988**, *36*, 195−298.

(57) Jezowska-Trzebiatowska, B.; Pajdowski, L. *Rocz. Chem.* **1958**, *32*, 1061−1072.

(58) Allin, B. J.; Thornton, P. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 449−452.

also significantly different from reported structures of tetranuclear vanadium(V)/carboxylate complexes with V_4-(μ-oxo)(μ-carboxylate)$_4$ cores.[59]

Upon the addition of ~1.2 mol equiv of bromoacetic acid to an aqueous solution of VCl_3, deep-green crystals of trinuclear **4** were obtained. Crystal data and structural refinement parameters and important bond length and bond angle data for **4** are given in Tables 3 and 4. Thermal ellipsoid plots of the V_3 cation are shown in Figure 2. The cation of **4** consists of an essentially planar-triangular V_3 core of three equivalent V^{III} centers bridged to a central μ_3-oxo ligand, residing ~0.017 Å above the V_3 plane. Each V^{III} is also bridged via two μ-bromoacetato ligands to an adjacent V^{III} center, with these ligands lying on opposite sides of the $V^{III}{}_3$(μ_3-O) plane. The distorted octahedral coordination is completed at each V center by a water ligand. The cation has virtual D_{3h} symmetry, and the asymmetric unit consists of one cation, a triflate anion, and one lattice water molecule. Complexes with structures of the type $[V_3(\mu_3\text{-O})(\mu\text{-OOCR})_6L_3]^{n+}$ have previously been crystallized from neat carboxylic acid and/or organic solvents.[19,20,50] This structural type is also found for carboxylate complexes of other transition metals.[56]

Crystals of **5**, with a V_3 cation structure analogous to that of **4**, were obtained from a solution of VCl_3 and ~1 mol equiv of $NaOOCC_2H_5$. Crystal data and structural refinement parameters and important bond length and bond angle data for **5** are given in Tables 3 and 4. The asymmetric unit has one cation, one chloride, and two water molecules.

6 was obtained from a solution of VCl_3 and 2 equiv of $NaOOCCH_3$, as described in a preliminary communication.[42] It crystallized in space group $P2_12_12$. The cation $[V_3(\mu_3\text{-O})(\mu\text{-OOCCH}_3)_6(OH_2)_3]^+$ is isostructural to **4** and **5**, and the asymmetric unit is completed by a chloride anion and three and a half water molecules.

Finally, dissolving equimolar amounts of $V(SO_3CF_3)_3$ and $NaOOCCH_2Cl$ resulted in crystallization of **7**. This complex was crystallized previously as a triflate salt $[V_3(\mu_3\text{-O})(\mu\text{-OOCCH}_2\text{Cl})_6(OH_2)_3]SO_3CF_3{\cdot}10.5H_2O$ [**8**, $P\bar{1}$, $a = 12.91$ Å, $b = 15.89$ Å, $c = 11.25$ Å, $\alpha = 93.41°$, $\beta = 1\ 15.2°$, $\gamma = 85.32°$[19]] and as a perchlorate salt $[V_3(\mu_3\text{-O})(\mu\text{-OOCCH}_2\text{Cl})_6(OH_2)_3]ClO_4{\cdot}3H_2O$ [**9**; $P2_1/c$, $a = 12.7444(7)$ Å, $b = 15.067(7)$ Å, $c = 17.963(7)$ Å, $\alpha = 90.00°$, $\beta = 95.55(8)°$, $\gamma = 90.00°$[20]].

Important bond lengths and angles for **4**−**7** are given in Table 4, along with comparable data for the two previously crystallized V^{III} trimers of chloroacetate. The $V^{III}-OH_2$ bond lengths in **4**−**7** (2.00−2.05 Å; Table 4) are within the range expected for V^{III} centers.[47,48] The V−O bond lengths for the μ_3-oxo (1.90−1.95 Å) are similar to other $V^{III}{}_3$(μ_3-O) complexes crystallized from nonaqueous solvents.[19,50] The V−O bond lengths for the μ-carboxylate ligands (1.97−2.05 Å) also occur within the expected range.[19,21,24,28,50] The O−V−O bond angles involving the O ligands of OH_2 and μ-carboxylate or μ_3-oxo are consistent with distorted octahedral V^{III} centers (82.4−94.7° for *cis*-O−V−O and 166.6−179.7° for *trans*-O−V−O). Note that elemental analyses are only reported for **6** and **7**;[42] however, we are confident of the V^{III} assignment for the V centers of **4** and **5** given the similarities in the procedures used to synthesize **7** and the similarities in the bond lengths and angles of these species. Insufficient amounts of **4** were obtained for an elemental analysis (~10 mg is required for a V analysis and ~5 mg for a halide analysis). Importantly, repeated attempts to obtain a crystalline product with an elemental analysis consistent with **5** failed, with the % Cl typically being twice that expected for **5**, again suggesting that the bulk crystallized product contained *trans*-$[V(OH_2)_4Cl_2]Cl$ in addition to **5**.

Further Characterization of Complexes 1−7. To investigate whether complexes **1**−**7** retain their integrity in solution, ES-MS (positive mode) spectra were obtained for solutions of VCl_3 and the various carboxylate ligands. Peaks corresponding to solvated or unsolvated species of the parent cations $[V_4(\mu\text{-OH})_4(\mu\text{-OOCCH}_3)_4(OH_2)_8]^{4+}$, $[V_4(\mu\text{-OH})_4(\mu\text{-OOCCF}_3)_4(OH_2)_8]^{4+}$, $[V_3(\mu_3\text{-O})(\mu\text{-OOCCH}_3)_6(OH_2)_3]^+$, and $[V_3(\mu_3\text{-O})(\mu\text{-OOCCH}_2\text{CH}_3)_6(OH_2)_3]^+$ were observed. No interpretable *m*/*z* data corresponding to the trinuclear or tetranuclear complexes were observed for the vanadium(III)/chloroacetate and vanadium(III)/bromoacetate systems, suggesting that appreciable amounts of these complexes do not form under dilute conditions (approximately micromolar) required for ES-MS measurements. This agrees with UV−vis and ^{1}H NMR spectroscopic data for these systems, which also suggest that significant amounts of trinuclear and tetranuclear vanadium(III)/carboxylate complexes are not formed even at higher concentrations (~0.010 M, see below). Note that all of the crystals used for X-ray diffraction measurements were obtained from solutions that were orders of magnitude more concentrated than those prepared for UV−vis, ^{1}H NMR, and ES-MS measurements.

The formation of polynuclear vanadium(III)/carboxylate complexes can be monitored by NMR spectroscopy. Isotropic NMR shifts in these complexes arise mainly as a result of Fermi hyperfine contact interactions in which α spin is transferred from the ligands to the metal via π-orbital delocalization pathways rather than through space, electron−nuclear interactions.[60] The net effect is that relaxation of the unpaired electrons is extremely rapid, such that NMR spectroscopy signals are observed. Figure 3 gives paramagnetic ^{1}H NMR spectra of the ~40−55 ppm region for equilibrated solutions of VCl_3 and 0.20 mol equiv of free CH_3COO^- or $CH_3CH_2COO^-$ at pD 3.44. In each case, two peaks are observed (species A and B), corresponding to two separate vanadium(III)/carboxylate complexes. The signals in the 40−55 ppm region can be assigned to the methyl protons of V^{III}-bound CH_3COO^- and the methylene protons of V^{III}-bound $CH_3CH_2COO^-$. The methyl protons of V^{III}-bound $CH_3CH_2COO^-$ are expected to resonate at chemical shift values <3 ppm[24] because the paramagnetic shift of nuclei bound to a paramagnetic metal center is proportional to r^{-3}, where r is the distance between the ^{1}H and V^{III} nuclei. These peaks were not observed experimentally, almost

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(59) See ref 30 in ref 42.

(60) Horn, R. R.; Everett, G. W., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 7173−7178.

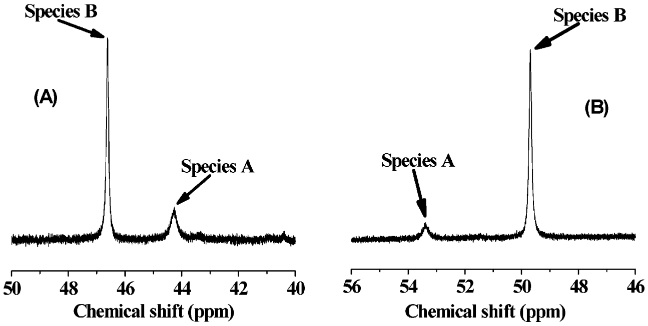

Figure 3. Paramagnetic ^{1}H NMR spectra for equilibrated solutions of VCl_3 (0.0100 M) and 0.20 mol equiv of free (corrected for % RCOOH and $RCOO^-$) CH_3COO^- (A) or $CH_3CH_2COO^-$ (B), in an aqueous buffer (D_2O, HEPES, and MES), pD 3.44 ± 0.02, at 22 ± 1 °C. The solutions were equilibrated overnight prior to measurements. Two peaks are observed in each case (species A and B), corresponding to two separate vanadium(III)/carboxylate complexes. Chemical shifts and relative peak areas are given in Tables 5 and 6, respectively.

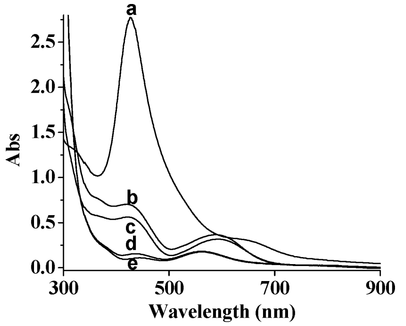

Figure 4. UV−vis spectra for equilibrated solutions of VCl_3 (0.0100 M) and 2.0 mol equiv of free CF_3COO^- (a, λ_{max} = 428 ± 2 nm, pD 3.52), CH_3COO^- (b, λ_{max} = 419 ± 2 and 593 ± 3 nm, pD 3.44), $CH_3CH_2COO^-$ (c, λ_{max} = 418 ± 2 and 590 ± 4 nm, pD 3.44), $ClCH_2COO^-$ (d, λ_{max} = 436 ± 4 and 562 ± 5 nm, pD 3.57), or $BrCH_2COO^-$ (e, λ_{max} = 445 ± 5 and 561 ± 3 nm, pD 3.52) in an aqueous buffer (D_2O, HEPES, and MES), at 25.0 °C. The solutions were equilibrated overnight prior to measurements.

Table 5. ^{1}H NMR Spectroscopy Chemical Shifts and Relative Intensities for Equilibrated Solutions of VCl_3 (0.0100 M) and CH_3COO^-/CH_3COOH ($[CH_3COO^-] = 2.00 \times 10^{-3}-0.0200$ M) in Aqueous Buffers (HEPES and MES), pD 3.44 ± 0.02 at 22 ± 1 °C

CH_3COO^- added (mol equiv)	species A (±0.2 ppm)	species B (±0.2 ppm)	peak area of species B/ peak area of species A
0.20	44.3	46.6	4.1
0.50	44.1	46.5	13
1.0		46.6	
2.0		46.6	

Table 6. ^{1}H NMR Spectroscopy Chemical Shifts and Relative Intensities for Equilibrated Solutions of VCl_3 (0.0100 M) and $CH_3CH_2COO^-/CH_3CH_2COOH$ ($[CH_3CH_2COO^-] = 2.00 \times 10^{-3}-0.0200$ M) in Aqueous Buffers (HEPES and MES), pD 3.44 ± 0.02 at 22 ± 1 °C

$CH_3CH_2COO^-$ added (mol equiv)	species A (±0.3 ppm)	species B (±0.3 ppm)	peak area of species B/ peak area of species A
0.20	53.4	49.7	9.1
0.50	53.4	49.7	41
1.0		49.8	
2.0		50.0	

certainly because of overlap with the intense buffer signals in this region.

Upon the addition of further carboxylate to these solutions (0.50−2.0 mol equiv of carboxylate), the intensity of species B increases at the expense of the intensity of species A. Significant amounts of other species are not observed by ^{1}H NMR spectroscopy. The results are summarized in Tables 5 and 6. At 1.0 and 2.0 mol equiv of carboxylate, only species B is observed for both the vanadium(III)/acetate and vanadium(III)/propionate systems. Species B remains the major complex in solution at 20 equiv of acetate or propionate (Figures S3 and S4 in the Supporting Information), and an additional two species are also observed for both systems. Further details are available in the Supporting Information. No attempt was made to identify these new species.

In our earlier communication on the vanadium(III)/acetate system, we speculated that species B is the trinuclear $[V_3(\mu_3\text{-}O)(\mu\text{-}OOCCH_3)_6(OH_2)_3]^+$ complex whereas species A is the tetranuclear $[V_4(\mu\text{-}OH)_4(\mu\text{-}OOCCH_3)_4(OH_2)_8]^{4+}$ species, on the basis of MS evidence for the existence of both species in solution and the requirement for 1 and 2 equiv of acetate for the respective formation of species A and B. We are unable to unequivocally assign the structures of species A and B observed by NMR spectroscopy, although UV−vis spectroscopy and diffusion coefficient data do suggest that species B is structurally similar for the vanadium(III)/acetate and vanadium(III)/propionate systems (see below). Diffusion coefficient data are also consistent with species B being a trinuclear rather than a tetranuclear complex (see below). If correct, it is unusual that the order of the chemical shifts for species A and B is reversed for the vanadium(III) propionate system, suggesting that species A are not necessarily isostructural for the two systems.

^{1}H NMR spectra were also recorded for the vanadium(III)/chloroacetate (0.0100 M VCl_3, pD 3.57 ± 0.02) and vanadium(III)/bromoacetate (0.0100 M VCl_3, pD 3.52 ± 0.02) systems. No peaks were observed at chemical shift values >5 ppm for 0.50, 1.0, 2.0, and 20 equiv of carboxylate for the vanadium(III)/bromoacetate system. For the vanadium(III)/chloroacetate system, a single, low-intensity peak is observed at δ 54.4 ppm for 20 equiv of chloroacetate; no peaks were observed at 0.50, 1.0, or 2.0 equiv of chloroacetate. Peaks were not observed by ^{19}F NMR spectroscopy for the vanadium(III)/trifluoroacetate system at 0.50, 1.0, 2.0, and 20 equiv of CF_3COO^- either (0.0100 M VCl_3, pD 3.52 ± 0.02), apart from peaks corresponding to free CF_3COO^- and $CF_3SO_3^-$ (triflic acid was used to adjust the pD of the solutions), suggesting that insignificant amounts of polynuclear complexes form under these conditions.

Figure 4 gives UV−vis spectra for solutions of VCl_3 (0.0100 M) with 2.0 equiv of carboxylate, obtained under the same conditions as the ^{1}H NMR spectroscopy spectra (pD 3.5 ± 0.1). The corresponding UV−vis spectrum of 0.0100 M VCl_3 under these conditions is given in Figure S1 in the Supporting Information and is dominated by a peak at 421 ± 2 nm, corresponding to the μ-O-to-V^{III} charge-transfer transition for the oxo-bridged V^{III} dimer. The spectrum of VCl_3 with 2.0 mol equiv of CF_3COO^- (Figure 4a) is very similar to that for Figure S1 in the Supporting Information, in agreement with the ^{19}F NMR spectroscopy results, which suggest that insignificant amounts of polynuclear complexes form under these conditions. For the remaining spectra in Figure 4b−e, the bands in the ∼550−600 nm region and the 410−450 nm region can be assigned to $^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ and $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ d−d transitions, respectively.[61] The shoulder at ∼375 nm can be tentatively assigned to a $^3T_{1g}(F) \rightarrow 3A_2(F)$ transition, which is weaker and of higher energy compared with the $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ transition, as expected.[61] The similarity in the UV−vis spectra in Figure 4 for vanadium(III)/acetate (b) and vanadium(III) propionate (c) systems, obtained under conditions where only one polynuclear complex (species B) is observed in the ^{1}H NMR spectrum, suggests that species B are structurally analogous for the two systems. UV−vis spectra for VCl_3 with 2.0 mol equiv of $ClCH_2COO^-$ (d) and $BrCH_2COO^-$ (e) are also shown in Figure 4. As expected on the basis of the absence of ^{1}H NMR spectroscopy signals at $\delta > 5$ ppm for the latter two systems under these conditions, these spectra (d and e) differ significantly from those observed for VCl_3 and 2.0 mol equiv of acetate and propionate under the same conditions. Furthermore, the band intensities in spectra d and e are significantly weaker than those observed for the species giving rise to spectra b and c, suggesting that the V^{III} center is more centrosymmetric in the former systems. Given that oxo ligands are strongly electronegative compared with other ligands, binding of one or more oxo ligands to a V^{III} center in an asymmetric geometry could explain the higher intensities of the d−d transitions in spectra b and c.

Because either only a very weak signal or no signals are observed at chemical shift values of >5 ppm for the vanadium(III)/chloroacetate and vanadium(III)/bromoacetate systems and no additional peaks were observed for the vanadium(III)/trifluoroacetate system by ^{19}F NMR spectroscopy, it is tempting to speculate that polynuclear vanadium(III)/carboxylate complexes are not formed in significant amounts under these conditions. However, we cannot rationalize why this may be so. Because halogenated carboxylates are poorer electron donors compared with acetate and propionate, the V^{III} centers of complexes of these ligands are better Lewis acids. Aqua ligands coordinated to the metal center would therefore have a lower acid dissociation constant and therefore deprotonate more easily, promoting the formation of oxo-bridged polynuclear complexes.

UV−vis spectra were also recorded for all systems at 20 equiv of carboxylate, pD 3.50. The shape and wavelength maxima for the vanadium(III)/acetate ($\lambda_{max} = 419 \pm 2$ and 593 ± 2 nm) and vanadium(III)/propionate systems ($\lambda_{max} = 419 \pm 2$ and 596 ± 3 nm) at 20 equiv of carboxylate (spectra f and g, respectively, in Figure S4 in the Supporting Information) are very similar to the spectra observed for 2.0 equiv of carboxylate (spectra b and c, respectively, in Figure 4). This agrees with the ^{1}H NMR spectroscopy results indicating that species B remains the predominant species in solution at 20 equiv of carboxylate for both systems (Figure S3 in the Supporting Information). Upon increasing the carboxylate from 2.0 to 20 equiv, wavelength maxima and intensities of the UV−vis spectra for the vanadium(III)/chloroacetate [$\lambda_{max} = 429 \pm 5$ (s) and 589 ± 2 nm, spectrum h in Figure S4 in the Supporting Information] and vanadium(III)/bromoacetate [$\lambda_{max} = 440 \pm 5$ (s) and 570 ± 5 (s) nm, spectrum i in Figure S4 in the Supporting Information] systems significantly change toward parameters expected if species B or a structurally similar complex (or complexes) was now formed for these systems. The largest changes are observed for the vanadium(III)/chloroacetate system, in line with the observation of a small signal at δ 54.4 ppm under these conditions by ^{1}H NMR spectroscopy. For the vanadium(III)/trifluoroacetate system, increasing the carboxylate from 2.0 to 20 equiv resulted in a similar spectrum of higher intensity (spectrum j in Figure S5 in the Supporting Information).

Determination of the Diffusion Coefficient for Species B by Gradient-Echo NMR Spectroscopy Measurements. Determination of diffusion coefficients for complexes in solution can provide estimates of the molecular masses of these species because diffusion coefficients primarily depend upon the molecular mass and geometry of the complex. The PFG spin−echo NMR technique is a useful method to directly determine diffusion coefficients.[62−65] This technique is mainly used for liquids, where the anisotropic spin interactions are averaged by molecular motions and the NMR peaks are sharp. The decay of the echo intensity in the Stejskal−Tanner experiment[62−65] is described by

$$I = I_0 \exp[-(\gamma G)^2 \delta^2 (\Delta - \delta/3) D] \tag{1}$$

where I is the echo intensity for the spectral peak of interest, I_0 is the echo intensity at $\delta = 0$, γ is the gyromagnetic ratio of the nuclei, G is the amplitude of the two gradient pulses, δ is their duration, Δ is the interval between the gradient pulses, and D is the diffusion coefficient. The experiment is performed at constant echo time $\Delta + \delta$ by varying the duration and the time interval between the gradient pulses δ. From eq 1, it can be shown that the plot of $\ln_e(I/I_0)$ vs $\gamma^2 G^2 \delta^2 (\Delta - \delta/3)$ produces a straight line with slope $-D$. Hence, by simultaneously varying Δ and δ and keeping the echo time constant, the diffusion coefficient for the molecule with a specific NMR resonance peak can be directly determined.

To validate our experimental design, we initially measured the diffusion coefficient for water. These results are given in the Supporting Information. We obtained a value of $(2.55 \pm 0.01) \times 10^{-5}$ cm^2 s^{-1}, which is in excellent agreement with a literature value of 2.6×10^{-5} cm^2 s^{-1} for free water.[65] Accurate measurement of diffusion coefficients requires either sharp NMR peaks or strong pulsed gradients. The line widths of species A for the vanadium(III)/acetate and vanadium(III)/propionate systems were ∼165 and ∼113 Hz, respectively, and attempts to determine reliable diffusion coefficients for these species failed. However, the line widths

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(65) Hong, Y. S.; Lee, C. H. *J. Agric. Food Chem.* **2006**, *54*, 219−223.

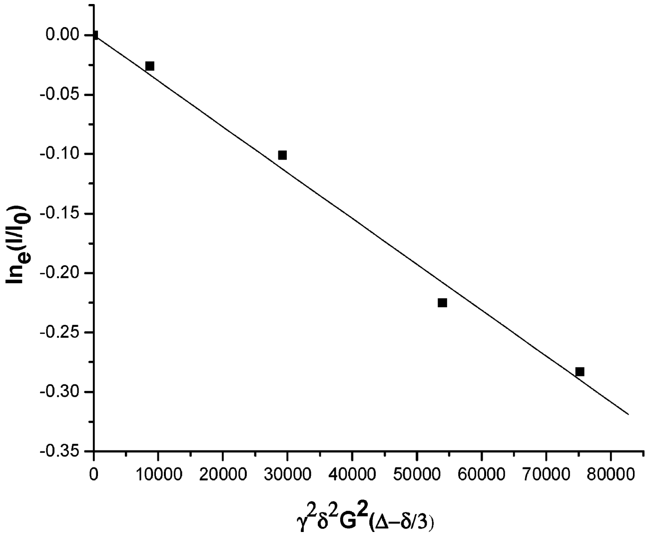

Figure 5. Plot of $\ln_e(I/I_0)$ vs $\gamma^2G^2\delta^2(\Delta - \delta/3)$ for the signal at δ 46.6 ppm (species B) for an equilibrated solution of VCl_3 (0.0100 M) and 2.0 mol equiv of free CH_3COO^-, in an aqueous buffer (D_2O, MES, and HEPES), pD 3.44 ± 0.02, at 22 ± 1 °C. The best fit of the data gives a straight line with slope (=−diffusion coefficient) = $(-3.9 \pm 0.1) \times 10^{-6}$ $cm^2\ s^{-1}$.

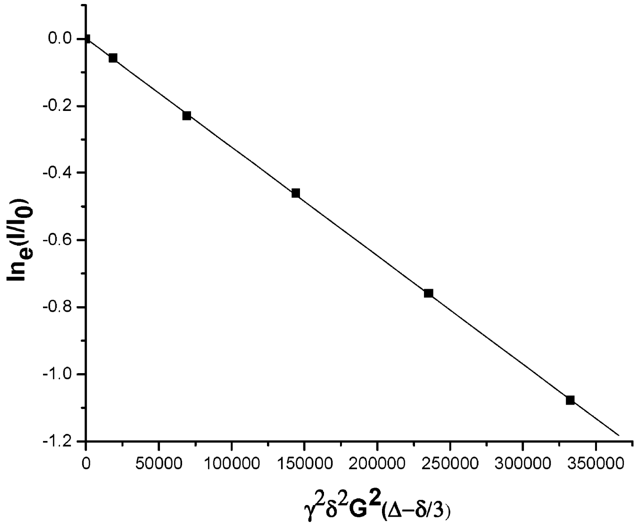

Figure 6. Plot of $\ln_e(I/I_0)$ vs $\gamma^2G^2\delta^2(\Delta - \delta/3)$ for the signal at δ 49.7 ppm (species B) for an equilibrated solution of VCl_3 (0.0100 M) and 2.0 mol equiv of free $CH_3CH_2COO^-$, in an aqueous buffer (D_2O, MES, and HEPES), pD 3.44 ± 0.02, at 22 ± 1 °C. The best fit of the data gives a straight line with slope (=−diffusion coefficient) = $(-3.23 \pm 0.01) \times 10^{-6}$ $cm^2\ s^{-1}$.

for species B for the vanadium(III)/acetate and vanadium(III)/propionate systems were ~71 and ~58 Hz, respectively, and the diffusion coefficients for these species have been determined.

Plots of $\ln_e(I/I_0)$ vs $\gamma^2G^2\delta^2(\Delta - \delta/3)$ are presented in Figures 5 and 6. From the slope, the diffusion coefficients of species B were $(3.9 \pm 0.1) \times 10^{-6}$ and $(3.23 \pm 0.01) \times 10^{-6}$ $cm^2\ s^{-1}$ for the vanadium(III)/acetate and vanadium(III)/propionate systems, respectively. Duplicate experiments gave identical values within experimental error (data not shown). The higher scattering in the data for the vanadium(III)/acetate system can be accounted for by the faster relaxation rate of this system.

Because the diffusion coefficients of molecules decrease with increasing size or molecular weight, assuming that species B are structurally similar for the two systems, one can approximate that

$$M_P/M_A = D_A/D_P \qquad (2)$$

where M_A and M_P are the molecular weights of species B for the vanadium(III)/acetate and vanadium(III)/propionate systems, respectively, and D_A and D_P are the corresponding diffusion coefficients.[62] The similarity of the UV−vis spectra of species B (Figure 4b,c) for both systems indicates that this is most likely the case. Assuming that species B are the trimers for both systems ($[V_3(\mu_3\text{-O})(\mu\text{-OOCR})_6(OH_2)_3]^+$, R = CH_3 and CH_2CH_3; M_A = 577.1 and M_P = 661.3, respectively), then M_P/M_A = 1.15, which is close to the experimental ratio D_A/D_P = 1.19 ± 0.03. Alternatively, if species B are both the tetrameric species ($[V_4(\mu\text{-OH})_4(\mu\text{-OOCR})_4(OH_2)_8]^{4+}$, R = CH_3 and CH_2CH_3; M_A = 652.1 and M_P = 708.2, respectively), M_P/M_A = 1.09, which deviates significantly from the experimental observations. Hence, the results of the diffusion cofficient experiments are most consistent with species B being the trimeric, rather than the tetranuclear, complexes.[66]

The diffusion coefficient is also related to the hydrodynamic radius of the diffusing object, which can be calculated using the Stokes−Einstein equation[64]

$$D = k_BT/6\pi\eta R_H \qquad (3)$$

where k_B is the Boltzmann constant, T is the temperature, η is the dynamic viscosity of the solvent (=0.89×10^{-2} g cm^{-1} s^{-1} for water),[67] and R_H is the hydrodynamic radius. The hydrodynamic radii of species B were calculated for the vanadium(III)/acetate ($R_{H(A)}$) and vanadium(III)/propionate ($R_{H(P)}$) systems using eq 3 and found to be 6.4 and 7.5 Å, respectively. As expected, the hydrodynamic radius of species B is larger for the vanadium(III)/propionate system. For comparison purposes, the radii of gyration (R_G) for the $[V_3(\mu_3\text{-O})(\mu\text{-OOCCH}_3)_6(OH_2)_3]^+$ and $[V_3(\mu_3\text{-O})(\mu\text{-OOCCH}_2\text{CH}_3)_6(OH_2)_3]^+$ cores were calculated from the crystal structures of **6** and **5** using eq 4[68] assuming a spherical motion and were found to be 3.14 ($R_{G(A)}$) and 3.50 ($R_{G(P)}$) Å, respectively.

$$R_G = \left(\frac{\sum_i m_i r_i^2}{\sum m_i}\right)^{1/2} \qquad (4)$$

For these calculations, the center of mass was taken as the μ_3-O atom, and the H atom contributions to the radius of gyration were assumed to be negligible. The hydrodynamic radius is twice the radius of gyration. This can be attributed

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(66) If species B is the trimer for the vanadium(III)/acetate system and the tetramer for the vanadium(III)/propionate system, then M_P/M_A = 1.23. If species B is the tetramer for the vanadium(III)/acetate system and the trimer for the vanadium(III)/propionate system, M_P/M_A = 1.01.

(67) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 73rd ed.; CRC Press: Boca Raton, FL, 1992−1993; Chapter 6, p 164.

to the inclusion of solvent molecules (water) in the hydrodynamic radii, whereas the radii of gyration are calculated for the cationic core of the complexes only. There is, however, good agreement between the ratio of the hydrodynamic radii for the two systems, $R_{H(P)}/R_{H(A)}$ (=1.2) with the ratio of the radii of gyration, $R_{G(P)}/R_{G(A)}$ (=1.12), consistent with species B being the trimeric vanadium(III)/carboxylate complexes. It was not possible to calculate $R_{G(P)}/R_{G(A)}$ assuming species B were both tetramers for the two systems because the diffusion coefficients of the V_4 tetramers could not be measured.[69]

Summary

The structures of trinuclear $[V_3(\mu_3\text{-O})(\mu\text{-OOCR})_6(OH_2)_3]^+$ and tetranuclear $[V_4(\mu\text{-OH})_4(\mu\text{-OOCR})_4(OH_2)_8]^{4+}$ complexes have been determined by X-ray diffractometry for acetate and the closely related derivatives bromoacetate, chloroacetate, trifluoroacetate, and propionate. ES-MS and ^{1}H NMR spectroscopy results suggest that these complexes are not purely solid-state phenomena but are also present in solution. Crystals of both the trinuclear and tetranuclear complexes were obtained from some of the vanadium(III)/carboxylate solutions, and cocrystallization of *trans*-$[V(OH_2)_4Cl_2]Cl$ also occurred when VCl_3 was used as a reactant, suggesting complex equilibria exist between the various species in solution. Substituting VCl_3 for $V(trif)_3$ led to the cocrystallization of sodium triflate in some instances because of the very soluble nature of the vanadium(III)/carboxylate complexes. Peaks in the 40−55 ppm region corresponding to two separate complexes (species A and B) are observed by ^{1}H NMR spectroscopy for solutions of VCl_3 (0.010 M) and 0.20 mol equiv of acetate or propionate (p*D* 3.44). At 1.0 and 2.0 mol equiv of acetate or propionate, only one complex, species B, is observed. The similarity of the UV−vis spectra for solutions of VCl_3 and 2.0 mol equiv of acetate or propionate under the same concentration and pH conditions suggests that species B are structurally analogous for these two systems. The diffusion coefficients and hydrodynamic radii of species B are consistent with species B being the trinuclear complex.

Acknowledgment. We thank Dr. Anatoly Khitrin, Kent State University, for assisting us with the gradient-echo NMR spectroscopy measurements and Dr. Michael Baldwin, University of Cincinnati, for helpful discussions. Acknowledgment is made to the donors of the American Chemical Society Petroleum Research Fund for support of this research (PRF 42123-G3 to N.E.B). C.J.Z. acknowledges the NSF Grant CHE-0116041 used to purchase a Bruker-Nonius diffractometer.

Supporting Information Available: UV−vis spectrum of 0.0100 M VCl_3 in buffer, pD 3.44 (Figure S1), plot of $\ln_e(I/I_0)$ vs $\gamma^2 G^2 \delta^2(\Delta - \delta/3)$ for water (Figure S2), ^{1}H NMR spectra for 0.0100 M VCl_3 and 20 equiv of CH_3COO^- or $CH_3CH_2COO^-$ (Figure S3), UV−vis spectra of 0.0100 M VCl_3 and 20 equiv of carboxylate at pD 3.50 (Figures S4 and S5), and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. The CCDC deposition numbers for **1**−**7** are 634342 (**1**), 251499 (**2**), 251501 (**3**), 634343 (**4**), 634344 (**5**), 251500 (**6**), and 634345 (**7**). These can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or 12 Union Road, Cambridge CB2 1EZ, U.K. (tel +44 1223 336408, fax +44 1223 336033).

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(68) McNaught, A. D.; Wilkinson, A. *Compendium of Chemical Terminology*, 2nd ed.; Blackwell Science: Oxford, U.K., 1997; p 338.

(69) The ratio of $R_{G(P)}/R_{G(A)}$ was also calculated assuming that species B is a tetramer for the vanadium(III)/acetate system and a trimer for the vanadium(III)/propionate system. The distances from the centroid of the tetramer were used to calculate $R_{G(A)}$. In this case, $R_{G(P)}/R_{G(A)}$ = 0.97, which is significantly different from the $R_{H(P)}/R_{H(A)}$ ratio obtained from measurement of the diffusion coefficients of species B (1.2).