Stepwise Cluster Assembly Using VO$_2$(acac) as a Precursor: *cis*-[VO(OCH(CH$_3$)$_2$)(acac)$_2$], [V$_2$O$_2$(μ-OCH$_3$)$_2$(acac)$_2$(OCH$_3$)$_2$], [V$_3$O$_3${μ,μ-(OCH$_2$)$_3$CCH$_3$}$_2$(acac)$_2$(OC$_2$H$_5$)], and [V$_4$O$_4$(μ-O)$_2$(μ-OCH$_3$)$_2$(μ_3-OCH$_3$)$_2$(acac)$_2$(OCH$_3$)$_2$]·2CH$_3$CN[1]

Feilong Jiang,[2] Oren P. Anderson, Susie M. Miller, John Chen, Mohammad Mahroof-Tahir, and Debbie C. Crans*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872

The studies of an underexplored synthetic reagent, VO$_2$(acac) (Hacac = acetylacetone) and semirational strategies for the formation of a complete series of simple vanadium(V) alkoxide clusters in alcohol-containing solvents. The neutral mono-, di-, tri-, and tetranuclear oxovanadium(V) complexes [V$_2$O$_2$(μ-OCH$_3$)$_2$(acac)$_2$(OCH$_3$)$_2$] (**1**), [V$_4$O$_4$(μ-O)$_2$(μ-OCH$_3$)$_2$(μ_3-OCH$_3$)$_2$(acac)$_2$(OCH$_3$)$_2$]·2CH$_3$CN (**2**), [V$_4$O$_4$(μ-O)$_2$(μ-OCH$_3$)$_2$(μ_3-OCH$_3$)$_2$(acac)$_2$-(OCH$_3$)$_2$] (**3**), [V$_3$O$_3${μ,μ-(OCH$_2$)$_3$CCH$_3$}$_2$(acac)$_2$(OR)] (R = CH$_3$ (**4**), C$_2$H$_5$ (**5**)), and *cis*-[VO(OCH(CH$_3$)$_2$)(acac)$_2$] (**6**) with alkoxide and acac$^-$ ligands were obtained by reaction of VO$_2$(acac) with a monoalcohol and/or a tridentate alcohol. The structures of complexes **1**–**3**, **5**, and **6** were determined by X-ray diffraction methods. Complex **1** crystallized in the monoclinic system, *P*2$_1$/*n*, with *a* = 7.8668(5) Å, *b* = 15.1037(9) Å, *c* = 8.5879(5) Å, β = 106.150(1)°, *V* = 980.1(1) Å^3, *Z* = 2, and *R* (w*R*2) = 0.040 (0.121). Complex **2** crystallized in the monoclinic system, *P*2$_1$/*n*, with *a* = 8.531(2) Å, *b* = 14.703(3) Å, *c* = 12.574(2) Å, β = 95.95(2)°, *V* = 1568.7(5) Å^3, *Z* = 2, and *R* (w*R*2) = 0.052 (0.127). Complex **3** crystallized in the triclinic system, *P*$\bar{1}$, with *a* = 8.5100(8) Å, *b* = 8.9714(8) Å, *c* = 10.3708(10) Å, α = 110.761(1)°, β = 103.104(1)°, γ = 100.155(1)°, *V* = 691.85(11) Å^3, *Z* = 1, and *R* (w*R*2) = 0.040 (0.105). Complex **5** crystallized in the monoclinic system, *P*2$_1$/*n*, with *a* = 14.019(2) Å, *b* = 11.171(2) Å, *c* = 19.447(3) Å, β = 109.18(1)°, *V* = 2876.5(8) Å^3, *Z* = 4, and *R* (w*R*2) = 0.062 (0.157). Complex **6** crystallized in the monoclinic system, *P*2$_1$/*n*, with *a* = 15.0023(8) Å, *b* = 8.1368(1) Å, *c* = 26.5598-(2) Å, β = 95.744(1)°, *V* = 3225.89(8) Å^3, *Z* = 8, and *R* (w*R*2) = 0.060 (0.154). Complex **1** is a discrete, centrosymmetric dimer in which two vanadium atoms are bridged by two methoxide ligands. Compound **2** contains a V$_4$O$_4$ eight-membered ring with both μ-oxo and μ-alkoxo bridging ligands; the ring is capped above and below by two triply bridging methoxo ligands. Compound **3** has the same structure as **2**. The three vanadium atoms in complex **5** are linked by four bridging oxygen atoms from two tridentate thme^{3-} ligands to form a V$_3$O$_4$ chain in which V−O bonds alternate in length. The V−O(isopropoxo) bond in **6** is cis to V=O, and the V−O(acac) bond trans to the oxo group is relatively long. The V$_2$O$_2$ rings of complex **1** and the mononuclear 1:2 complex can be considered to be the basic building block of the trinuclear complexes **4** and **5** and the tetranuclear complex **2**, acting to extend the vanadium−oxide framework. ^{51}V and ^{1}H NMR spectroscopic studies of the solution state of complexes **1**–**6** revealed dramatic differences in structural and hydrolytic stability of these complexes. Compounds **1** and **3** only remained intact at low temperature in CDCl$_3$ solution, whereas the mononuclear compound **6** could remain at ambient temperature for ∼10 h. Compound **4** only maintained its solid-state structure at low temperature in CDCl$_3$ solution, whereas compound **5** was significantly more stable. The structural integrity of oligomeric vanadium−oxygen frameworks increased significantly when the coordinating alkoxide group showed more resistance to exchange reactions than the methoxide group. The solid state and solution properties of this new group of complexes not only testify to the versatility of VO$_2$(acac) as a vanadium(V) precursor but also raise questions relating to solution structure and properties of related vanadium complexes with insulin-mimetic properties and catalytic properties.

Introduction

Oxovanadium alkoxide complexes are attracting interest due to their biological relevance[3] as well as their application as catalysts.[4,5] We have been interested in these types of compounds in order to explore the coordination geometry about the vanadium atom(s) in complexes containing both simple and complex alcohols. In addition to determining the overall limitations in the vanadium−phosphorus analogy, specific examination of the structural and chemical selectivity of complexes with di- or polyfunctional ligands is important to understanding the modes by which vanadium acts in biological systems.[3,4,6,7] Complexation of vanadium by a variety of alkoxy groups has produced a number of compounds with a wide range of structural and/or solution properties.[8–15] Although vanadium alkoxides can be formed both in organic solvents and in water

(1) Abbreviations: acac$^-$, acetylacetone anion; bipy, bipyridine; c-HOC$_5$H$_9$, cyclopentanol; Hacac, acetylacetone; H$_3$thme, 1,1,1-tris(hydroxymethyl)ethane; OiPr, isopropoxide; OtBu, *tert*-butoxide; Phpy, 4-phenylpyridine; thme^{3-}, 1,1,1-tris (hydroxymethyl)ethane trianion.
(2) Permanent address: Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou Fujian, 350002, China.
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and the reactions of vanadate with alcohols in aqueous solution have been investigated extensively,[7,16-21] studies of oxovanadium alkoxides in organic solvents typically have relied on a few synthetic precursors in a limited number of solvents. Since simple oxovanadium(V) alkoxides are labile and hydrolytically sensitive, these reactions are often accompanied by metal reduction. Even though oxovanadium trialkoxides are often generated in a large excess of alcohol, the reagent alcohol is rarely used as a solvent for formation of other oxovanadium-(V) alkoxides from starting material other than $VO(OR)_3$.[22-29] The synthetic strategy of using a polydentate oxygen donor ligand (acac) allows us to show in this work that monofunctional alcoholic solvents can act in the same capacity as polyfunctional alcoholic ligands.

Oxobis(2,4-pentanedionato-O,O')vanadium(IV) ($VO(acac)_2$) is a well-known reagent used in many oxidation reactions.[26,30-32] $VO(acac)_2$ reacting with amines and other organic compounds with nucleophilic groups has been well characterized.[33-39] In reactions with amines, the stability of the resulting complexes depends on the nucleophilicity (as reflected in the pK_a value of the protonated amine) and the steric demands of the amine. The reactivity of the corresponding vanadium(V) acetylacetonate complex ($VO_2(acac)$) is much less well developed.[40] Thus, it may have desirable properties as a ligand for vanadium(V) in generating a species sufficiently stabilized against undesirable reduction but sufficiently reactive to remain an effective molecule building unit. Vanadium(V) precursors such as $VOCl_3$, oxovanadium trialkoxides, vanadate salts, and V_2O_5 all form $VO(OR)_3$ upon dissolution in an alcohol. $VO_2(acac)$ does not completely convert to $VO(OR)_3$, reflecting the stability of various vanadium(V) complexes containing the acac functionality. Thus, even though some $VO(OR)_3$ complexes do form in the acac-containing mixture, there is much less tendency to reduction of the vanadium(V) center and this gives the VO-(acac) unit the necessary lifetime to be an effective unit in building of new vanadium complexes.

Monodentate, bidentate, and tridentate ligands with oxygen donors generate oxovanadium(V) alkoxide derivatives in which the oxygen donor can coordinate in terminal, μ, or μ_3 coordination modes. The vanadium in these complexes will have four, five, six, or seven substituents in a coordination geometry determined by the nature of the specific oxygen donor ligand and the reaction conditions for complex preparation. Most of the reported oxovanadium(V) alkoxide complexes contain a six-coordinated vanadium in a distorted octahedral geometry[41-44] and are neutral complexes.[15,26,41,47,51] The fact that most complexes known are neutral may reflect the isolation procedures employed. It is also possible that it is a very favorable situation when the coordinated oxygen donors provide the exact countercharge for the positive oxovanadium unit and at the same time surround the metal center sterically in a stable octahedral coordination environment.[15,46-49] Several neutral oxovanadium-(V) alkoxide complexes have already been characterized both in the solid state and in solution state, but only one of these contains an acac$^-$ functionality.[51b]

Mononuclear oxovanadium(V) alkoxides of simple alcohols, such as methanol, ethanol, and isopropyl alcohol, and those analogues in which one or two of the alkoxide groups have been substituted by chloride ligands are well-known.[4,52] These

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compounds are very labile when dissolved in solution.[53-57] The lability of these complexes was dramatically decreased by replacing the R group in the RO⁻ ligand with more bulky alkyl groups.[58] In addition, we recently showed that the lability could be decreased by the use of a tridentate oxygen donor ligand (thme³⁻), even though such complexes still contained the methoxy or ethoxy group.[15] In this paper we report the preparation, structural characterization, and solution behavior of a series of neutral mono-, di-, tri-, and tetranuclear oxovanadium(V) complexes containing both alkoxide and acac⁻ ligands.

Experimental Section

Materials. All manipulations were carried out under nitrogen atmosphere using standard Schlenk techniques to avoid hydrolysis. Monoalcohols and organic solvents were dried over molecular sieves (3 Å) and then purified by standard methods and stored under N₂ before use.[59] Tris(hydroxymethyl)ethane (H₃thme) and acetylacetone (Hacac) were purchased from Aldrich and used without further purification. Literature procedures were used for the preparation of VO₂(acac), VO-(OCH₃)₃, and VO(OC₂H₅)₃.[55,57,60]

Methods. ^{51}V NMR spectra were recorded at 79 MHz on a Bruker ACP-300 NMR spectrometer, and chemical shifts were reported relative to a neat VOCl₃ reference at 0 ppm. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 76 MHz, respectively, on a Bruker ACP-300 NMR instrument, employing routine parameters. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer. Elemental analyses were performed by the Desert Analytics Laboratory, Tucson, AZ.

[V₂O₂(μ-OCH₃)₂(acac)₂(OCH₃)₂], 1. VO₂(acac) (0.36 g, 2.0 mmol) was dissolved in 40 mL of methanol. The solution was heated to reflux and stirred for 4 h, during which the color of reaction solution changed from red-brown to red. After filtration, the filtrate gave red crystalline **1** on standing at −20 °C for 7 days. The crystals were filtered off, washed with hexane (2 × 10 mL), and dried in vacuo, affording 0.32 g (71%) of **1**. Yield of the material could be improved (to more than 77% overall) if the filtrate was further concentrated and stored at −20 °C. ^{51}V NMR: (78.94 MHz, 233 K, CHCl₃) δ −478 ppm; (298 K, CHCl₃) δ −478, −502, −573 ppm. ^{1}H NMR: (300.1 MHz, 298 K, CDCl₃) δ 5.84 (3H s), 5.67 (H, s), 5.58 (H, s), 4.84 (9H, br), 2.19 (3H, s), 2.14 (3H, s), 2.08 (3H, s), 1.97 (3H, s) ppm. ^{13}C NMR: (75.6 MHz, 298 K, CDCl₃) 194.6, 194.1, 183.2, 181.2, 103.70, 102.63 (2C), 79.42, 71.38, 71.08, 27.80, 27.05, 26.23, 25.40 ppm. IR (KBr pellet cm⁻¹): 2920 (m), 2805 (m), 1575 (vs), 1525 (vs), 1419 (m), 1360 (s), 1285 (m), 1024 (m), ν(V=O) 984 (vs), ν(V−O−V) 772 (s), ν(V−O−V) 670 (m), 612 (m), 572 (m), 450 (m). Anal. Calcd for C₁₄H₂₆O₁₀V₂: C, 36.86; H, 5.74; V, 22.34. Found: C, 36.69; H, 5.59; V, 22.78.

[V₄O₄(μ-O)₂(μ-OCH₃)₂(μ₃-OCH₃)₂(acac)₂(OCH₃)₂]·2CH₃CN, 2. VO₂(acac) (0.36 g, 2.0 mmol) was dissolved in 100 mL of methanol/acetonitrile (1:1). The solution was stirred for 72 h at room temperature, and the resulting dark red solution was filtered to remove undissolved solid. The filtrate was concentrated to 30 mL under reduced pressure. A red-orange crystalline product was obtained after the solution had been stored at −20 °C for 15 days. Additional crystalline material could be obtained if the filtrate was collected and most of the solvent

removed by reduced pressure, followed by storing the solution at −20 °C for several days. The red precipitate (0.26 g, 68%) was isolated and collected by filtration, washed with hexane (2 × 15 mL), and dried in vacuo.

[V₄O₄(μ-O)₂(μ-OCH₃)₂(μ₃-OCH₃)₂(acac)₂(OCH₃)₂], 3. Recrystallization of **2** in pure methanol gave red-orange single crystals of **3**. Compound **3** is identical to **2** except for the lack of CH₃CN in the crystal. Compounds **2** and **3** showed the same spectroscopic properties as described below, and X-ray diffraction analysis confirmed that both contain the same [V₄O₄(μ-O)₂(μ-OCH₃)₂(μ₃-OCH₃)₂(acac)₂(OCH₃)₂] core and structure. ^{51}V NMR: (78.94 MHz, 298K, CDCl₃) δ − 478, −496, −558 ppm. ^{1}H NMR: (300.1 MHz, 298 K, CDCl₃) δ 5.76 (3H, s), 5.69 (3H, s), 5.67 (H, s), 5.58 (H, s), 4.83 (12H, br), 2.19 (3H, s), 2.17 (3H, s), 2.08 (3H, s), 1.97 (3H, s) ppm. ^{13}C NMR: (75.6 MHz, 298 K, CDCl₃) δ 194.6, 192.1, 188.6, 183.2, 103.90, 103.21, 102.90 (2C), 79.40 (2C), 76.45, 73.85, 27.89, 26.56, 26.25, 25.63 ppm. IR (KBr pellet, cm⁻¹): 2960 (m), 2925 (m), 2800 (m), 1575 (vs), 1525 (vs), 1415 (m), 1355 (s), 1280 (m), 1057 (m), 1022 (s), ν(V=O) 988 (s), ν(V=O) 966 (s), ν(V−O−V) 785 (m), 665 (m), 605 (m), 570 (m), 450 (m). Anal. Calcd for C₁₆H₃₂O₁₆V₄: C, 28.09; H, 4.71; V, 29.78. Found: C, 28.01; H, 4.87; V, 29.04.

[V₃O₃{μ,μ-(OCH₂)₃CCH₃}₂(acac)₂(OCH₃)], 4. To a clear and colorless solution of H₃thme (0.12 g, 1.0 mmol) in methanol (30 mL) were added VO(OCH₃)₃ (0.16 g, 1.0 mmol) and Hacac (0.20 g, 2.0 mmol) with stirring, which resulted in an orange solution. The reaction mixture was stirred for 72 h at room temperature and then allowed to stand at −20 °C for 5 days. The orange crystals which deposited during this period were collected and dried in vacuo, affording 0.128 g of **4** (55% yield). ^{51}V NMR: (78.94 MHz, 298 K, CDCl₃) δ −514 (1V), −459 (2V) ppm. ^{1}H NMR: (300.1 MHz, 298 K, CDCl₃) δ 5.94 (3H, s), 5.65 (1H, s), 5.64 (1H, s), 5.47 (2H, m), 5.27 (2H, m), 5.10 (2H, m), 4.94 (1H, t), 4.34 (1H, t), 4.05 (2H, m), 3.48 (2H, m) 2.12 (3H, s), 2.11 (3H, s), 2.08 (3H, s), 2.07 (3H, s), 0.89 (3H, s), 0.85 (3H, s) ppm. ^{13}C NMR: (75.6 MHz, 298 K, CDCl₃) δ 193.2, 192.3, 188.0, 186.2, 103.4, 102.7, 91.9, 90.10, 87.17, 86.71, 84.97, 79.30, 75.06, 44.30, 36.60, 27.13, 26.60, 25.20, 24.60, 16.32, 15.19 ppm. IR (KBr pellet, cm⁻¹): 2959 (m), 2925 (m), 2897 (m), 2853 (m), 1585 (s), 1525 (s), 1455 (m), 1421 (w), 1390 (m), 1377 (m), 1360 (s), 1290 (w), 1276 (w), 1200 (w), 1185 (w), 1137 (w), 1116 (w), 1074 (s), 1030 (s), 1007 (m), ν(V=O) 962 (s), ν(V=O) 951 (s), ν(V−O−V) 792 (w), ν(V−O−V) 776 (w), 666 (s), 630 (m), 620 (m), 607 (m), 578 (w), 569 (w), 540 (m), 462 (m). Anal. Calcd for C₂₁H₃₅O₁₄V₃: C, 37.97; H, 5.31; V, 23.00. Found: C, 37.94; H, 5.69; V, 22.50.

[V₃O₃{μ,μ-(OCH₂)₃CCH₃}₂(acac)₂(OC₂H₅)], 5. To a rapidly stirring clear and colorless solution of H₃thme (0.12 g, 1.0 mmol) in ethanol (30 mL) were added VO(OC₂H₅)₃ (0.20 g, 1.0 mmol) and then Hacac (0.20 g, 2.0 mmol) to give an orange solution. After 72 h of stirring at room temperature, the solution was stored at −20 °C for several days. The orange crystals of **5** formed during this period were collected and dried in vacuo (0.113 g, 50%).

In an alternative preparation, H₃thme (0.12 g, 1.0 mmol) was dissolved in 100 mL of ethanol and solid VO₂(acac) (0.18 g, 1.0 mmol) was added. The mixture was stirred for 72 h at ambient temperature, during which the solution turned orange. After filtration and concentration, storage at −20 °C gave orange crystalline **5**, which was filtered off, washed with hexane, and dried in vacuo (0.106 g, 47%). ^{51}V NMR: (78.94 MHz, 298 K, CDCl₃) δ −511, −465, −458 ppm. ^{1}H NMR: (300.1 MHz, 298 K, CDCl₃) δ 6.17 (2H, m), 5.65 (1H, s), 5.61 (1H, s), 5.54 (1H, d), 5.37 (2H, d), 5.27 (1H, d), 5.17 (2H, d), 5.01 (1H, d), 4.84 (1H, d), 4.32 (1H, d), 4.10 (2H, t), 3.47 (1H, d), 2.11 (3H, s), 2.10 (3H, s), 2.06 (3H, s), 2.03 (3H, s), 1.77 (3H, t), 0.88 (3H, s), 0.85 (3H, s) ppm. ^{13}C NMR: (75.6 MHz, 298 K, CDCl₃) δ 193.90, 192.40, 188.30, 185.90, 103.10, 102.90, 91.59, 90.26, 88.16, 87.42, 86.77, 85.12, 75.34, 49.66, 37.21, 27.21, 26.79, 26.47, 25.63, 19.00, 16.50, 15.40 ppm. IR (KBr pellet, cm⁻¹): 2965 (m), 2926 (m), 2897 (m), 2849 (m), 1585 (s), 1525 (s), 1455 (m), 1428 (w), 1390 (m), 1360 (s), 1288 (w), 1274 (w), 1198 (w), 1122 (w), 1049 (s), 1030 (s), ν(V=O) 1005 (m), ν(V=O) 953, ν(V=O) 968 (s), ν(V−O−V) 781 (w), ν(V−O−V) 669 (s), 620 (m), 540 (m), 467 (m). Anal. Calcd for C₂₂H₃₇O₁₄V₃: C, 38.95; H, 5.50; V, 22.53. Found: C, 38.90; H, 5.75; V, 23.10.

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Table 1. Crystallographic Data for Complexes **1**, **2**, **3**, **5**, and **6**

	1	2	3	5	6
chem formula	$C_{14}H_{26}O_{10}V_2$	$C_{20}H_{38}N_2O_{16}V_4$	$C_{16}H_{32}O_{16}V_4$	$C_{22}H_{37}O_{14}V_3$	$C_{13}H_{21}O_6V$
fw	456.23	766.28	684.18	678.34	324.24
crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a (Å)	7.8668(5)	8.531(2)	8.5100(8)	14.019(2)	15.0023(3)
b (Å)	15.1037(9)	14.703(3)	8.9714(8)	11.171(2)	8.1368(1)
c (Å)	8.5879(5)	12.574(2)	10.3708(10)	19.447(3)	26.5598(2)
α (deg)	90	90	110.761(1)	90	90
β (deg)	106.150(1)	95.95(2)	103.104(1)	109.18(1)	95.744(1)
γ (deg)	90	90	100.155(1)	90	90
V (Å^3)	980.1(1)	1568.7(5)	691.85(11)	2876.5(8)	3225.89(8)
Z	2	2	1	4	8
T (K)	159	173	298	173	165
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
D_{calc} (g cm^{-3})	1.55	1.62	1.64	1.57	1.34
$F(000)$	472	784	348	1400	1360
no. of reflns collected	4331	2170	3143	3908	20 621
no. of indep reflns	1413	2065	1991	3780	7721
R^a	0.040	0.052	0.040	0.062	0.060
w$R2^a$	0.121	0.127	0.105	0.157	0.154
largest diff peak and hole (e Å^{-3})	0.53, −0.44	0.41, −0.39	0.36, −0.38	0.49, −0.39	0.51, −0.44

^{a} $R = \sum ||F_o| - |F_c||/\sum |F_o|$. w$R2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

cis-**[VO(OCH(CH₃)₂)₂(acac)₂], 6.** VO₂(acac) (0.36 g 2.0 mmol) was added to 80 mL of 2-propanol. The resulting brown-red suspension was refluxed with stirring for 2 h and then condensed under reduced pressure and filtered. Storage at −20 °C provided red crystalline **6**, which was collected by filtration, washed with hexane (2 × 15 mL), and dried in vacuo (0.28 g, 43%). ⁵¹V NMR: (78.94 MHz, 298 K, CDCl₃) δ −495 ppm. ¹H NMR: (300.1 MHz, 298 K, CDCl₃) δ 6.72 (H, m), 5.66 (H s), 5.51 (H, s), 4.05 (2H, m), 2.14 (3H, s), 2.10 (3H, s), 2.04 (3H, s), 1.97 (3H, s), 1.51 (3H, d), 1.44 (3H, d), 1.26 (6H, d), 1.25 (6H, d) ppm. ¹³C NMR: (75.6 MHz, 298 K, CDCl₃) δ 194.1, 192.1, 187.6, 183.1, 103.1, 102.6, 94.38, 77.41 (2C), 27.91 (2C), 26.83 (2C), 25.68 (2C), 25.54 (2C), 25.40 (2C) ppm. IR (KBr pellet, cm⁻¹): 2975 (m), 2925 (m), 1610 (m), 1580 (vs), 1525 (vs), 1420 (m), 1360 (vs), 1265 (m), 1105 (m), 1023 (m), ν(V=O) 953 (s), 798 (m), 670 (m). Anal. Calcd for C₁₃H₂₁O₆V: C, 43.44; H, 6.71; V, 19.39. Found: C, 44.47; H, 5.35; V, 18.63.

X-ray Crystallography of [V₂O₂(acac)₂(OCH₃)₄] (1), [V₄O₆(acac)₂-(OCH₃)₆]·2CH₃CN (2), [V₄O₆(acac)₂(OCH₃)₆] (3), [V₃O₃{(OCH₂)₃-CCH₃}₂(acac)₂(OC₂H₅)] (5), and *cis*-[VO(OCH(CH₃)₂)₂(acac)₂] (6). Diffraction data were collected at 159 K (**1**), 298 K (**3**), and 165 K (**6**) on a Siemens SMART CCD diffractometer and at 173 K (**2**, **5**) on a Siemens P4 diffractometer. For **2** and **5**, the intensities of three standard reflections were examined every 97 reflections; no significant changes in intensity were noted. Lorentz and polarization corrections were applied in all cases, along with empirical absorption corrections (SADABS[61] for **1**, **3**, and **6**; XEMP[62] for **2** and **5**). Each structure was solved by direct methods and refined by using the Siemens SHELXTL program library.[62] Refinement employed full-matrix (119 parameters total, data/parameters = 11.9 for **1**; 190 parameters total, data/parameters = 10.9 for **2**; 163 parameters total, data/parameters = 12.2 for **3**; 352 parameters total, data/parameters = 10.7 for **5**; and 361 parameters total, data/parameters = 21.4 for **6**) weighted least-squares refinement on F^2 for all reflections. Selected details of data collection and refinement are given in Table 1. All non-hydrogen atoms were refined with anisotropic displacement parameters in all cases, with the exception of the atoms of the occluded acetonitrile solvent molecules for **2**. Hydrogen atoms were included in the structure factor calculations at idealized positions. Further crystallographic information pertaining to the five structures is provided in the Supporting Information.

Results and Discussion

Synthesis of Complexes 1−6. VO₂(acac), which is relatively unexplored as a vanadium(V) complex precursor, is readily

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accessible from Na₃VO₄ and Hacac.[60] As part of our studies exploring new vanadium(V) alkoxides and their properties, we have investigated the reaction of VO₂(acac) with simple alcohols and polydentate alkoxides. As in the past, we are continuing to explore the synthesis of neutral complexes. However, in contrast to the previous work where the VO(OR)₃ type of compounds were the targets, we have now attempted to prepare neutral vanadium(V) alkoxides by using the oxygen ligands RO⁻ and/or triolate to link oxovanadium(V) fragments containing six-coordinate vanadium atoms. We have employed a synthetic strategy that takes advantage of prior coordination of an acac⁻ ligand, which stabilizes the vanadium atom in a VO₂(acac) unit and may allow subsequent construction of larger VO(acac)²⁺-capped oxometalates.[29,36,37] The stability of the VO₂(acac) unit allows building the oxometalate manifold, which is capped by the VO(acac)²⁺ unit. This way one generates successive complexes with increasing numbers of coordinatively saturated {VO₆} units, and may be bridged by doubly or triply bridging oxygen atoms of either μ-OR or μ_3-OR functionality.

Complex **1** is obtained by mixing VO₂(acac) with excess methanol. This product forms at both ambient and elevated temperatures, although it is best prepared at elevated temperature due to solubility limitations at ambient temperatures. Similar yields of **1** are obtained under inert atmosphere and in the presence of oxygen. The red reaction mixtures are stable for extended periods under inert atmosphere, whereas reaction solutions open to air slowly change to a green color after 3−4 days. We have employed three strategies to generate complexes with variable sizes by modification of the reaction conditions: changing reaction temperatures, changing solvents, and adding a polydentate alcohol. Increasing the reaction temperature from ambient to reflux resulted in the same products. However, reacting the starting material, VO₂(acac), with methanol in a methanol/aprotic solvent (CH₃CN) mixture afforded an orange crystalline product **2**. The difference between compounds **1** and **2** was not apparent from the reaction mixtures, which were both deep red. However, crystals of **2** were different in color and shape from crystals of **1**. X-ray crystallography (see below) showed complex **1** to be dinuclear and compound **2** to be tetranuclear. The VO(acac)²⁺ unit is seen to be able to cap the V₂O₂(μ-OR)₂ core of the oxometalate unit, thus extending the metal−oxide framework with two more vanadium atoms by the minor modification of reaction conditions.
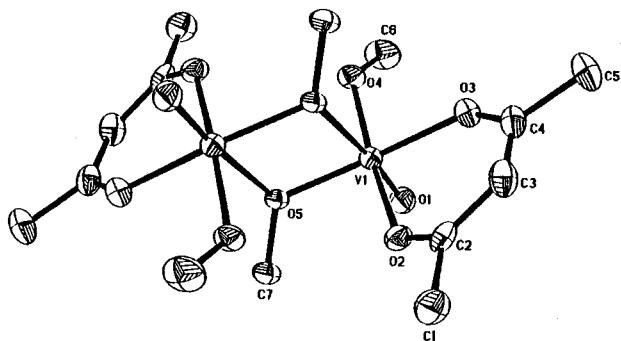
Figure 1. Molecular geometry and atomic labeling scheme for complex **1**, with ellipsoids drawn at the 50% probability level and hydrogen atoms omitted for clarity.

Modifying the oxometalate units further by the addition of a polydentate alcohol, H$_3$thme, to the methanolic and ethanolic reaction mixtures was also successful. Two trinuclear oxovanadium(V) compounds **4** and **5** (see below) were produced, either by dissolution of VO$_2$(acac) in ROH ((R = Me, Et) + H$_3$thme) or by using VO(OR)$_3$ in the presence of H$_3$thme and approximately 2 equiv of Hacac. Reaction of VO$_2$(acac) with H$_3$thme in methanol produced not only the major product, trinuclear [V$_3$O$_3${(OCH$_2$)$_3$CCH$_3$}$_2$(acac)$_2$(OCH$_3$)], **4**, but also a minor product, tetranuclear [V$_4$O$_4${(OCH$_2$)$_3$CCH$_3$}$_2$(OCH$_3$)$_6$].[15] In the latter tetranuclear complex, all acac$^-$ ligands were replaced by methoxide and thme^{3-} ligands. In contrast, the ethoxide-containing trinuclear **5** was prepared in pure ethanol by using VO$_2$(acac), with no evidence seen for the corresponding tetranuclear byproduct. In a mixture of ethanol and acetonitrile, a related tetranuclear compound, [V$_4$O$_4${(OCH$_2$)$_3$CCH$_3$}$_3$-(OC$_2$H$_5$)$_3$], was isolated.[15] Compounds **4** and **5** were stable for a few days in the alcoholic reaction solutions in both the presence and the absence of air and were also stable when redissolved in organic solvents such as chloroform and CH$_2$-Cl$_2$.

Additional studies were carried out using 2-propanol ((CH$_3$)$_2$-CHOH) as solvent. In this case, VO$_2$(acac) formed compound **6** containing the isopropoxide ligand. Unlike the reaction mixtures containing **1**, which were stable in the presence of air for 1−2 days, the reaction mixture of **6** was sensitive to air and rapidly produced a green crystalline precipitate which by IR spectroscopy appeared to contain both vanadium(IV) and the acac ligand. Since one might anticipate that the substitution of a methoxide ligand by an isopropoxide ligand would generate a more stable complex, we interpreted the greater instability of complex **6** to indicate that this complex was not the analogous dinuclear complex of **1**. Indeed, the structure of **6** reveals the less stable mononuclear complex.

Crystallographic Results for 1, 2, 3, 5, and 6. The structures and numbering schemes for **1, 2, 3, 5**, and **6** are shown in Figures 1, 2, 3, and 6, respectively. The selected bond distances and angles are summarized in Tables 2−5. Other results have been supplied as Supporting Information. Since the structure of tetranuclear **3** was very similar to that of the tetranuclear unit in **2**, we have only included details of this structure of **3** in the Supporting Information.

Description of the Structure of 1. In the discrete neutral dinuclear complex **1**, the two six-coordinate vanadium atoms are each coordinated to one acac$^-$ ligand, three CH$_3$O$^-$ ligands, and an oxo group (see Figure 1 and Table 2). The resulting dinuclear molecule possesses crystallographic inversion symmetry. The vanadium atoms are linked by two bridging methoxide groups to form a V$_2$O$_2$ ring, which is asymmetric

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**

Bond Lengths			
V1−O1	1.598(3)	V1−O5a	2.254(2)
V1−O2	2.025(2)	O2−C2	1.273(4)
V1−O3	2.001(3)	O3−C4	1.277(5)
V1−O4	1.783(2)	O4−C6	1.409(5)
V1−O5	1.870(2)	O5−C7	1.433(4)

Bond Angles			
O1−V1−O2	96.03(12)	O3−V1−O4	87.16(11)
O1−V1−O4	99.63(13)	O3−V1−O5	158.45(11)
O1−V1−O5	100.24(12)	O4−V1−O5	101.23(11)
O1−V1−O5a	174.78(11)	O5−V1−O5a	75.03(10)
O2−V1−O3	82.35(10)	V1−O5−V1a	104.97(10)
O2−V1−O4	162.20(11)	V1−O2−C2	131.4(2)
O2−V1−O5	84.15(10)	V1−O3−C4	132.3(2)

due to the fact that one of the V−O(bridging) bonds in the ring is trans to the V=O(terminal) bond. Each metal atom in **1** is coordinated by one terminal CH$_3$O$^-$ group to complete a distorted octahedron with O−V−O bond angles varying from 75.0(1)° (O5−V1−O5a) to 101.2(1)° (O4−V1−O5). The V$_2$O$_2$ core in **1** has been observed in other dinuclear oxovanadium-(V) complexes, one of which contained four-coordinate vanadium atoms ([V$_2$O$_2$Cl$_2$(OCH$_2$CH$_2$O)$_2$][63]), many of which contained five-coordinate vanadium atoms (for example, [V$_2$O$_2$-Cl$_2${OC(CH$_3$)$_2$C(CH$_3$)$_2$O}$_2$][64] and [V$_2$O$_2$(c-OC$_5$H$_9$)$_6$][65]) and two of which contained six-coordinate vanadium atoms ([V$_2$O$_2$Cl$_2$-(thme)$_2$][8] and [V$_2$O$_2$(OiPr)$_7$]$^{-9}$).

The V−O$_b$ (b = bridge) bond lengths in **1** are 1.870(2) and 2.254(2) Å. The long V−O$_b$ bond trans to the V−O(oxo) bond is much longer than V−O$_b$ bonds in [V$_6$O$_{12}$(OCH$_3$)$_7$]$^-$ (1.974-(7) Å),[42] [V$_8$O$_8$(OCH$_3$)$_{16}$(C$_2$O$_4$)]$^{2-}$ (1.99(2) Å),[66] [V$_4$O$_2$(OCH$_3$)$_6$-(acac)$_4$] (2.00(2) Å),[36] [V$_6$O$_{13}$(OCH$_3$)$_3${(OCH$_2$)$_3$CCH$_2$OH}]$^{2-}$ (2.01(1) Å),[43] and VO(OCH$_3$)$_3$ (2.02(4) Å).[56] The bond between the vanadium atom and the nonbridging methoxide oxygen atom is much shorter (V1−O4 = 1.783(2) Å) than the V−O$_b$ bonds and compares favorably to the V−O(methoxide) bond in **2** (1.760(4) Å). These V−O(methoxide) bond distances also compare favorably to those reported previously for [V$_4$O$_4$-(thme)$_2$(OCH$_3$)$_6$] (average 1.772(12) Å)[15] and VO(OCH$_3$)$_3$ (average 1.81(5) Å).[56] The V−O(acac) bond distances are 2.001(3) and 2.025(2) Å, the former being trans to the shorter V−O$_b$ bond and the latter being trans to the nonbridging methoxide ligand. The V−O(acac) bond lengths trans to alkoxide ligands in **1, 2**, and **5** range from 1.952(6) to 2.038(6) Å, which is similar to the range seen in other vanadium−acac complexes in which oxo groups are not trans to the acac$^-$ ligand atoms (see Table 6).[33,36,37,67]

Description of the Structure of 2. The discrete neutral complex **2** contains four vanadium atoms arranged about a crystallographic inversion center (see Figure 2 and Table 3). The tetranuclear complex contains five V$_2$O$_2$ units within the overall V$_4$O$_6$ framework. Two of the V$_2$O$_2$ units are linked by two slightly bent oxo bridges (O6, O6a) and two triply bridging methoxide oxygen atoms (O4, O4a). Two other V$_2$O$_2$ units are linked by two bridging methoxide oxygen atoms (O5, O5a) and the two triply bridging methoxide oxygen atoms. The fifth V$_2$O$_2$ unit is formed when the V$_4$O$_4$ ring is capped by the triply

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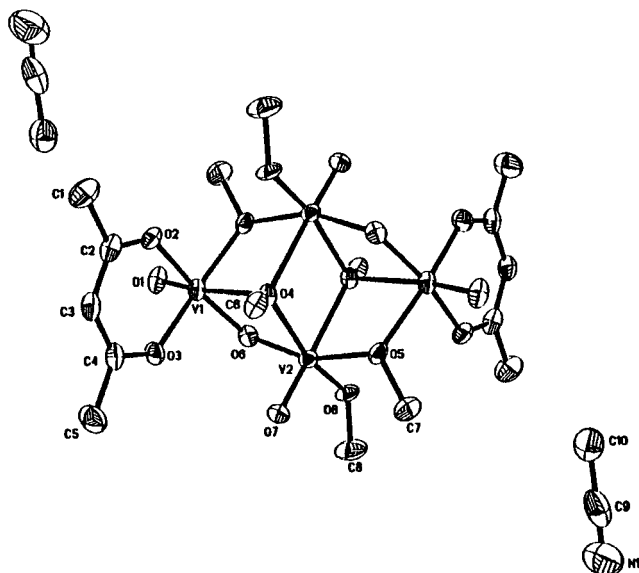
Figure 2. Structure of **2** (similar to the structure of **3**). Thermal ellipsoids have been drawn at the 50% probability level, and hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **2**

		Bond Lengths	
V1−O1	1.599(4)	V2−O6	1.911(4)
V1−O2	2.015(4)	V2−O7	1.597(4)
V1−O3	1.964(5)	V2−O8	1.760(4)
V1−O4	2.317(4)	O2−C2	1.287(8)
V1−O5a	1.950(4)	O3−C4	1.276(8)
V1−O6	1.747(4)	O4−C6	1.425(7)
V2−O4	2.059(4)	O5−C7	1.450(7)
V2−O5	2.004(4)	O8−C8	1.431(8)

		Bond Angles	
O1−V1−O4	171.2(2)	O4−V2−O7	96.5(2)
O1−V1−O5a	97.1(2)	O4−V2−O8	162.8(2)
O1−V1−O6	102.8(2)	O5−V2−O6	159.4(2)
O2−V1−O3	83.8(2)	O5−V2−O7	94.7(2)
O2−V1−O4	84.2(2)	O5−V2−O8	95.2(2)
O2−V1−O5a	83.2(2)	O6−V2−O7	101.0(2)
O2−V1−O6	159.7(2)	O6−V2−O8	94.8(2)
O4−V1−O5a	74.5(2)	O7−V2−O8	100.4(2)
O4−V1−O6	75.8(2)	V1−O4−V2	89.3(2)
O5a−V1−O6	94.7(2)	V1a−O5−V2	114.3(2)
O4−V2−O5	85.9(2)	V1−O6−V2	114.7(2)
O4−V2−O6	79.3(2)		

bridging methoxide oxygen atoms, one lying above and one lying below the best plane through the V_4O_4 ring. All of the vanadium atoms exhibit distorted octahedral coordination. For V1, two coordination sites are occupied by the oxygen atoms of the bidentate acac$^-$ ligand, while, for V2, one coordination site is occupied by a nonbridging methoxide oxygen atom (O8, O8a).

The differences in the core structure between the tetranuclear **2** and dinuclear **1** can be attributed to the triple bridging by two of the CH_3O^- groups in **2**. The trifunctional coordination mode in **2** generates an additional V_2O_2 unit that is not present in **1**, where methoxide bonds only in a bifunctional coordination mode. The V_4O_6 framework in **2** made up of several V_2O_2 units has been observed in other tetravanadium complexes, such as $[V_4O_2(\mu\text{-}OCH_3)_6(acac)_4]$[36] and $[V_4O_4\{(OCH_2)_3CCH_3\}_2\text{-}(OCH_3)_6]$.[15] The former mixed-valence vanadium(III,IV) complex was isolated from a reaction of $VO(acac)_2$ with 2-(3-(aminopropyl)amino)ethanethiol in methanol, although the resulting vanadium product did not contain any thiolate.[36] The latter complex formed in methanol in the presence of the
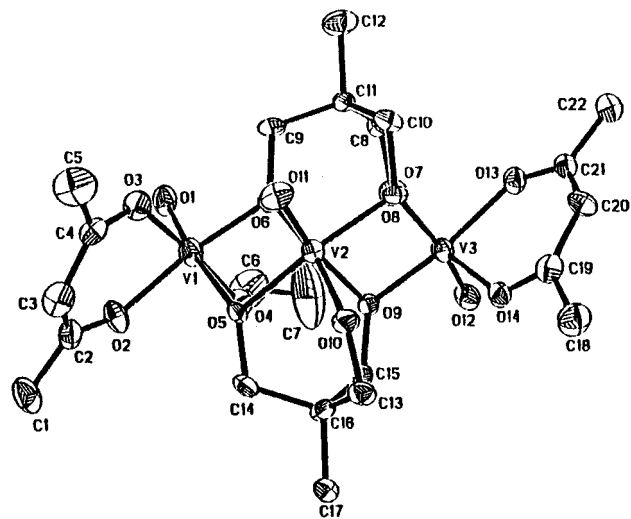

Figure 3. Molecular structure and atomic numbering scheme for complex **5**, with ellipsoids drawn at the 50% probability level and hydrogen atoms omitted for clarity.

tridentate H_3thme ligand. In $[V_4O_4\{(OCH_2)_3CCH_3\}_2(OCH_3)_6]$, the two bridging triol ligands fulfill the role collectively carried out by the two doubly bridging methoxide groups, two triply bridging methoxide groups, and two bridging oxo groups in **2**.[15] It is interesting that the simple methoxide ligands in **2** and the more complex trialkoxide thme^{3-} ligands can produce tetranuclear compounds with similar $V_4(\mu\text{-}O)_4(\mu_3\text{-}O)_2$ frameworks. This points to the stability of this oxometalate core.

As expected, the doubly bridging methoxide ligands (O5, O5a) in the V_4O_4 framework exhibit V−O bond distances (1.950(4), 2.004(4) Å) longer than the V−O distances for the bridging oxo ligands (O6, O6a) (1.747(4), 1.911(4) Å). The average V−O(oxo) bond lengths (average 1.83(4) Å) are similar to those in other tetramers with V_4O_4 frameworks, including $[V_4O_8(OCH_3)_4(bipy)_2]$ (1.84(11) Å),[46] $[V_4O_8(O_2CH_2tBu)]$ (average 1.85(9) Å),[68] and $[V_4O_8(C_2O_4)_4(H_2O)_2]^{4-}$ (average 1.81(3) Å).[69] The two types of V−O−V bond angles in the V_4O_4 framework involving singly bridging oxygen atoms are very similar (V1−O6−V2 = 114.7(2)°, V1−O5−V2 = 114.3(2)°), despite the differences in bond lengths noted. The distances between the vanadium atoms and the triply bridging methoxide oxygen atoms are quite different. The V1−O4 (2.317(4) Å) and V2a−O4 (2.193(4) Å) bonds, both of which are trans to V=O(terminal) bonds, are both longer than the V2−O4 (2.059-(4) Å) bond, and the average of these three bond distances (2.19-(13) Å) is similar to the average of the corresponding V−O bonds in $[V_4O_8(OCH_3)_4(bipy)_2]$ (2.20(14) Å)[46] and slightly longer than that in $[V_4O_2(OCH_3)_6(acac)_4]$ (2.14(18) Å).[36]

Description of the Structure of 5. Complex **5** is a discrete trinuclear oxovanadium(V) complex containing two thme^{3-}, two acac$^-$, and one ethoxide ligands (Figure 3 and Table 4). All three vanadium atoms in **5** exhibit distorted octahedral geometry, and the V_3O_4 framework can be viewed as being composed of two V_2O_2 four-membered rings that share a vanadium atom (V2). Several possible geometric arrangements are possible for trinuclear complexes: cyclic, linear, and triangular. The roughly linear arrangement of the three vanadium atoms in **5** sets this complex apart from cyclic trinuclear trioxovanadium complexes such as $[V_3O_3(C_6H_5CO_2)_6(THF)]$[70] and $[V_3O_3(salicylhydrox-

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Table 4. Selected Bond Distances (Å) and Angles (deg) for **5**

Bond Lengths			
V1–O1	1.589(6)	V3–O8	2.253(6)
V1–O2	1.952(6)	V3–O9	1.870(6)
V1–O3	2.038(6)	V3–O12	1.590(6)
V1–O4	1.821(6)	V3–O13	1.984(6)
V1–O5	2.157(6)	V3–O14	1.995(6)
V1–O6	1.933(6)	O2–C2	1.311(11)
V2–O5	1.937(5)	O3–C4	1.253(11)
V2–O6	2.052(5)	O5–C14	1.435(9)
V2–O8	1.898(6)	O6–C9	1.454(9)
V2–O9	2.184(6)	O7–C8	1.444(10)
V2–O10	1.781(5)	O8–C10	1.437(10)
V2–O11	1.600(6)	O9–C15	1.427(9)
V3–O7	1.808(6)	O10–C13	1.423(10)

Bond Angles			
O1–V1–O2	102.1(3)	O7–V3–O8	84.2(2)
O1–V1–O4	97.6(3)	O7–V3–O9	98.3(3)
O1–V1–O5	170.3(3)	O7–V3–O13	86.4(3)
O2–V1–O3	84.5(3)	O8–V3–O9	73.1(2)
O5–V1–O6	73.0(2)	O8–V3–O12	170.8(3)
O5–V2–O6	75.4(2)	O8–V3–O13	86.3(2)
O5–V2–O10	90.5(2)	O12–V3–O13	101.7(3)
O5–V2–O11	107.2(3)	O13–V3–O14	84.1(2)
O8–V2–O9	74.2(2)	V1–O5–V2	103.5(2)
O9–V2–O10	86.7(2)	V1–O6–V2	107.7(3)
O9–V2–O11	169.7(3)	V2–O8–V3	104.4(2)

imate)$_3$(CH$_3$OH)$_3$].[48] However, one mixed-valence linear trinuclear trioxovanadium complex has been reported, [V$_3$O$_3$-(quinato)$_2$]$^{2-}$, in which the quinato (trianion of quinic acid) ligand is a tridentate ligand, which (as does thme^{3-}) has limited steric flexibility.[10] Although the complex [V$_3$O$_3$(quinato)$_2$]$^{2-}$ has a framework similar to that of complex **5**, the vanadium atoms in **5** are six-coordinate whereas in [V$_3$O$_3$(quinato)$_2$]$^{2-}$ they are five-coordinate.[10] In addition, the coordination modes of the ligands in these two complexes are different.

The three vanadium atoms in **5** are bridged by two tridentate thme^{3-} ligands via four oxygen atoms (O5, O6, O8, O9) to form two V$_2$O$_2$ rings. The remaining oxygen atom in each thme^{3-} ligand is coordinated in a nonbridging mode. Both ends of the V$_3$O$_4$ framework, V1 and V3, are capped by acac$^-$ ligands. Since V1 is the only vanadium atom with a free sixth coordination site, the C$_2$H$_5$O$^-$ group is bound to this atom. In both of the V$_2$O$_2$ rings, particularly the V2–O8–V3–O9 ring, one V–O bond is much shorter (average 1.88(2) Å) than the other (average 2.22(5) Å), as was found in **1**. This pattern can be attributed to the trans influence, since the long V–O bonds in both **1** and **5** are trans to the V–O(oxo) bond. The pattern of long and short V–O bonds found in the V$_2$O$_2$ units in **1** and **5** is significantly different from the more similar V–O bond lengths (average 1.95(1) Å, 2.01(3) Å) in the V$_2$O$_2$ rings in [V$_3$O$_3$(quinato)$_2$]$^{2-}$.[10] The pattern of long and short V–O bonds found in the V$_2$O$_2$ units in **1** and **5** is observed in many compounds, including those containing five-coordinate vanadium atoms. Observation of the corresponding pattern in "linear" trinuclear complexes apparently depends on factors associated with the bridging ligand, as in the thme^{3-} and quinato^{3-} ligands. The thme^{3-} ligand imposes a smaller dihedral angle (97.1°) between the two V$_2$O$_2$ rings in **5** than the corresponding angle (119.5°) in [V$_3$O$_3$(quinato)$_2$]$^{2-}$, presumably because the "bite angle" in the thme^{3-} ligand is smaller. The V–O bond lengths involving the acac$^-$ ligand on V1 are 1.952(6) and 2.038(6) Å, while those involving the acac$^-$ ligand on V3 are 1.984(6) and 1.995(6) Å. The difference in the two

bonds coordinated to V1 is attributed to the trans influence of the nonbridging ethoxide ligand.

The three oxygen donor atoms of the thme^{3-} ligand often coordinate to vanadium atoms in bridging modes.[11–14] In **5**, the thme^{3-} ligands each use all three oxygen donor atoms to bind to the vanadium atoms in the O$_t$O$_b$O$_b$ coordination mode (t = terminal, b = bridging). This is the first time this coordination mode has been observed for the thme^{3-} ligand. There are two other examples of a thme^{3-} ligand coordinated in a terminally chelating manner, one in a dinuclear[8] and the other in a tetranuclear complex.[15] In each of these complexes the coordination mode of the thme^{3-} ligand was O$_t$O$_t$O$_b$. The average distance (2.04(15) Å) between vanadium and the bridging oxygen atoms of the thme^{3-} ligands in **5** is comparable to corresponding V–O bonds in [V$_4$O$_4$(thme)$_3$(OC$_2$H$_5$)$_3$] (average 2.01(8) Å).[15] The nonbridging V–O(7, 10) bond lengths in **5** (average 1.79(2) Å) are similar to corresponding bond lengths in [V$_4$O$_4$(thme)$_3$(OC$_2$H$_5$)$_3$][15] (average 1.786(8) Å). In addition, the bond length (1.821(6) Å) for the V1–O4 bond to the coordinated ethoxide ligand is only slightly longer than the corresponding V–O bond lengths (average 1.786(8) Å) in [V$_4$O$_4$(thme)$_3$(OC$_2$H$_5$)$_3$]. We expect that triply bridging oxygen atoms will continue to show interesting deviations from the patterns already documented.[15]

Among the increasing number of simple vanadium alkoxides with vanadium in oxidation states IV and/or V that are structurally characterized, most contain an even number of metal ions. This includes a large number of dinuclear vanadium alkoxides,[8,9,63–65,71] seven tetranuclear complexes,[15,36,46,47,68,72] a number of hexanuclear complexes,[11,14,41–43,73a] one octanuclear complex,[66] and many decanuclear complexes.[12,13] In contrast, only a few complexes with odd numbers of vanadium atoms have been structurally characterized, including the three trinuclear complexes described above and one pentanuclear complex.[73b] Trinuclear complexes may be common building blocks, considering the fact that two trinuclear complexes can, in principle, combine to form a stable hexanuclear complex. It seems likely that the small number of reports of trinuclear complexes indicates that these systems, particularly the linear varieties, are inherently less stable than alternative geometric arrangements unless coordinating ligands stabilize the linear trinuclear structure. In line with these considerations, among the more than 20 thme^{3-}-containing oxovanadium complexes that have been reported, none had previously contained an odd number of vanadium atoms. This includes one dinuclear complex,[8] two tetranuclear complexes,[15] 10 hexanuclear complexes,[11,14,41] and one decanuclear complex characterized by X-ray diffraction analysis[12] as well as analogues of these complexes.[12–14,41,43,73a] Complex **5** is the first vanadium alkoxide complex to contain an odd number of vanadium atoms, but in order to generate this complex, we clearly needed the stabilization that the capping acac$^-$ ligand provided.

IR Spectroscopy. The IR spectroscopic properties of complexes **1**–**6** were examined in KBr pellets. All complexes showed the characteristic V=O band in the frequency range 995–953 cm^{-1}. Compounds **2**–**5** exhibit more than one V=O stretch, supportive of a nuclearity higher than 1. Compounds **1** and **6** only exhibit one band, reflecting the symmetry or mononuclearity of these complexes. The characteristic three

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intense absorption bands for the O-coordinated acac⁻ ligands were at 1585–1575, 1525, and 1360–1355 cm⁻¹. The first and the last two bands shifted somewhat depending on specific complex, whereas the 1525 cm⁻¹ band varied very little. The absorption bands at 1060–1005 cm⁻¹ were attributable to C−O stretching frequencies arising from coordinated methoxy, ethoxy, and isopropoxy groups. The bands attributed to the coordinated thme³⁻ ligands in **4** and **5** were at 1455, 1390, 620, and 540 cm⁻¹, as would be expected, since these compounds are very similar. In addition, the V−O−V stretching modes for all five complexes were observed at about 780–670 cm⁻¹ in accord with those reported in the literature.[74] There is no doubt that IR spectroscopy provide valuable information on the ligands chelated to the vanadium atoms; however, less information on the nuclearity of these complexes can be deduced using this method.

Solution Studies. Dissolved Crystalline Compounds 1, 2, and 3. In our efforts to examine the solution properties of compounds **1**, **2**, and **3** for comparison with the solid-state material, we have examined spectroscopically solutions obtained from crystalline compounds as well as reaction mixtures. A solution of 20 mM of complex **1** in CHCl₃ at ambient temperature generates three ⁵¹V NMR signals (Table 7). Immediately after dissolution in CHCl₃, the three chemical shifts at −478, −502, and −573 ppm have the ratio of approximately 2:1:1; however, after 2 days, the ratio has changed to 11:1:1.5. Eventually only the signal at −478 ppm remains (ratio approximately 1:0:0). The chemical shifts for VO(OCH₃)₃ range from −542 to −583 ppm as a function of concentration and nature of solvent (Table 7). These changes are due to molecular association as previously described.[53,54,58] The chemical shifts for the signals at −478 and −502 ppm vary depending on the amount of CH₃OH in solution (Figure 4); however, the difference is much smaller than observed for the signal assigned to VO(OCH₃)₃.

A freshly prepared solution of 20 mM of **3** in CHCl₃ generates a ⁵¹V NMR spectrum with three ⁵¹V NMR signals at −478, −496, and −558 ppm with the ratio 2:1:1.5 (Figure 5). After 5 days, the signal ratio changes to 10:1:1. While the second and third resonances decrease, the chemical shifts for these signals move to −502 and −573 ppm. This solution now gives NMR signals with chemical shifts reminiscent of solutions of **1**. Only the signal at −478 ppm remains upon longer equilibration times (see Figure 5).[65] Since compounds **1** and **3** both give rise to solutions with three signals, one of which has the same chemical shift (−478 ppm) and a second that is assigned to V(OCH₃)₃ in both solutions (−573 and −558 ppm),[58,75] we examined the properties of the species at −478 and −502 ppm.

Nature of Solution Species at −478 and −502 ppm. Assigning the signal at highest field to VO(OCH₃)₃ conveniently allowed us to determine the nuclearity of the signals at −502 and −478 ppm by recording the ⁵¹V NMR spectra of a series of solutions (ranging from 0 to 40 mM) of VO₂(acac) in both CHCl₃ and CH₃OH (data not shown; see also Table 7). Plotting the concentration of the compound with the chemical shift at −502 ppm as a function of the concentration of VO(OCH₃)₃ generated a straight line, whereas plotting the concentration of the compound with the chemical shift at −478 ppm as a function of the VO(OCH₃)₃ concentration generated a polynomial ($x = 2$) (data not shown). We also recorded the spectra at higher
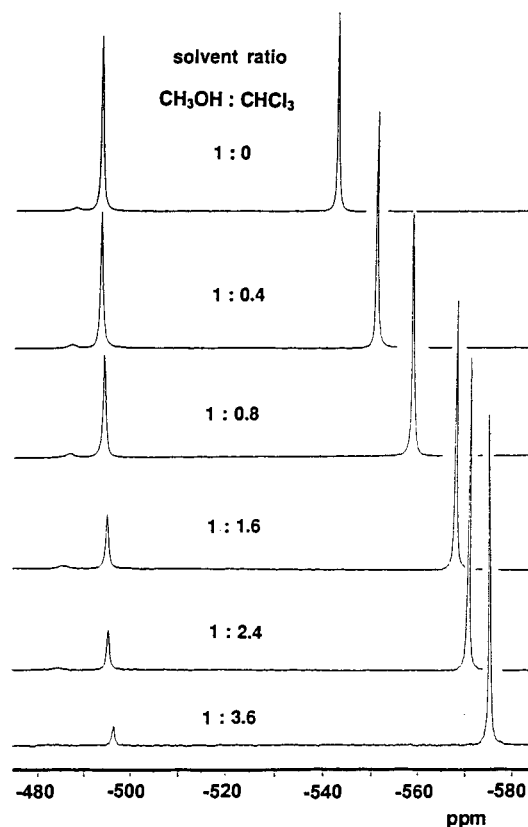
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Figure 4. Selected ⁵¹V NMR spectra (79 MHz) of 20 mM VO₂(acac) in 0.5 mL of CH₃OH with addition of 0.2 mL, 0.4 mL, 0.8 mL, 1.2 mL, and 1.8 mL of CHCl₃.
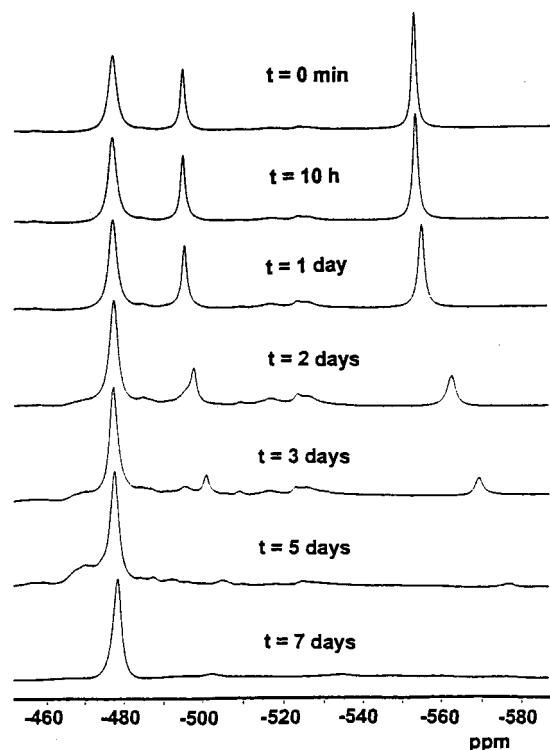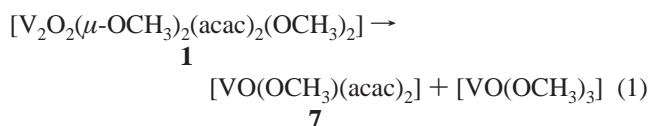

Figure 5. Complex **3** in CHCl₃ at room-temperature monitored by ⁵¹V NMR spectroscopy (79 MHz) at various times: 0 min, 10 h, 1 day, 2 days, 3 days, 5 days, 7 days.

concentrations where the known association between VO-(OCH₃)₃ molecules is likely to interfere with the linear relationship.[53,54,58] We concluded that the signal at −502 ppm is

attributed to a mononuclear vanadium compound and the signal at −478 ppm is attributed to a dinuclear compound. The formation of dimer from monomer is favored in CHCl$_3$ (at nearly stoichiometric methanol concentrations) over CH$_3$OH by a factor of 20. Despite the lower stability of the dimer in CH$_3$OH, both the dinuclear and tetranuclear complexes were best isolated from CH$_3$OH.

In view of the role this material can have as a building block, the structure of the mononuclear complex at −502 ppm was examined. On the basis of the structural information provided in this paper and the available data for vanadium–acac structures, it is very likely that the vanadium would be six-coordinate.[15,31,35−37,76] This expectation is supported by the abundant condensation reactions of ligand donors with either vanadium(IV)–acac or vanadium(V)–acac starting materials,[29,30,32,77,78] by the observation of six-coordinate vanadium in [VOL(acac)$_2$] complexes[32,39,77] and by the *cis*-VO(OCH$_3$) configuration in [VO(OCH$_3$)L$'_2$] complexes, in which L$'$ are analogous bidentate π-bonding ligands.[50,79] Thus, one likely formulation for the mononuclear species is the neutral complex with six-coordinate vanadium [VO(OCH$_3$)(acac)$_2$], **7**. In general V−O bonds in vanadium alkoxides trans to the V=O functionality are longer than the related V−O bonds in vanadium alkoxides cis to the V=O alkoxides, presumably reflecting the greater stability of the cis-adduct compared to the trans-adduct of a strongly coordinating ligand. Accordingly, we hypothesize that the most likely structure for such a complex has the methoxide ligand cis to the V=O oxo group, even though no precedent for such a *cis*-vanadium(V)−acac alkoxide was reported prior to this work.

$$[V_2O_2(\mu\text{-OCH}_3)_2(\text{acac})_2(\text{OCH}_3)_2] \rightarrow$$
$$\mathbf{1}$$
$$[VO(OCH_3)(\text{acac})_2] + [VO(OCH_3)_3] \quad (1)$$
$$\mathbf{7}$$

The ^{51}V NMR spectrum of **1** recorded in CDCl$_3$ shows that three complexes are present in solution, in very different ratios, readily allowing the assignment of the three different species by ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of the same CDCl$_3$ solution shows two types of coordinated acac$^-$, corresponding to two different molecules. Two or more signals for terminally coordinated methoxide groups are located at 79.1 and around 71 ppm. The 8 ppm difference in these chemical shifts is readily understood by the fact that three different terminally coordinated methoxide groups, one in each of compounds **1**, **7**, and VO(OCH$_3$)$_3$, should be present and one should be significantly less shielded than the others. ^{1}H NMR spectra are more complex. However, one broad peak at 4.84 ppm assigned to all three terminally coordinated methoxide groups and one sharp signal at 5.84 ppm assigned to the bridging methoxide can be identified. The ratio of these two signals is 3:1, which is consistent with the stoichiometry shown in eq 1 and with the assignments of the ^{13}C NMR spectra.

The chemical shifts for these species are very sensitive to solvents. Addition of CH$_3$OH to a solution of complex **1** in CHCl$_3$ shows significant (^{51}V) chemical shift changes for all

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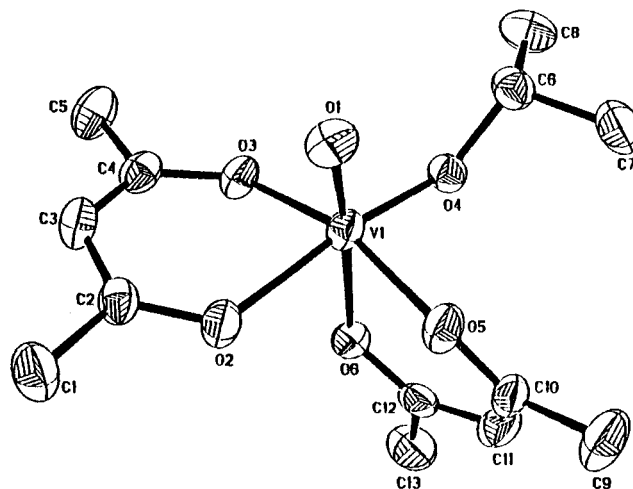

Figure 6. Molecular geometry and atomic labeling scheme for complex **6**, with ellipsoids drawn at the 50% probability level and hydrogen atoms omitted for clarity.

the vanadium atoms (up to 30 ppm). In addition to the change in chemical shift, the ratio of the isomers also changes. The −502 ppm signal shifts to −492 ppm while increasing its intensity, and the −478 and −573 ppm signals shift to −485 and −542 ppm, respectively, while their intensities decrease. The effect of solvent on stability of the −502 ppm signal was examined by the incremental addition of CHCl$_3$ to a solution containing 20 mM VO$_2$(acac) in CH$_3$OH (this mixture has the same signals as a solution of **1** in CH$_3$OH), Figure 4. The intensities of the signals at −502 and −478 ppm (−492 and −485 ppm in neat CH$_3$OH) decrease while the intensity of the VO(OR)$_3$ signal increases as the concentration of CHCl$_3$ increases. The addition of CHCl$_3$ to the reaction mixture accomplishes two things simultaneously; first, it decreases the concentration of CH$_3$OH, and second, it decreases the polarity of the medium. A polar monomeric complex such as VO-(OCH$_3$)(acac)$_2$ is likely to be favored in a more polar environment as well as under conditions of large excess of CH$_3$OH. This expectation is experimentally confirmed (Figure 4). Accordingly, the solvent effects and spectroscopic properties are consistent with the interpretation that the species at −502 ppm has the formula shown for compound **7**.

In attempts to obtain solid-state structural evidence for compound **7** we explored the preparation of mononuclear species with more bulky alcohols; below we describe our successful studies in 2-propanol.

Description of the Structure of 6. The vanadium atom in the neutral mononuclear complex **6** (see Figure 6) is surrounded by one isopropoxo ligand, two acac$^-$ ligands, and one oxo group. The complex exhibits a distorted octahedral coordination sphere with bond angles ranging from 99.02(12)° to 81.99(10)°. The two molecules of **6** found in the asymmetric unit are equal within experimental error, and we have only included bond distances and angles for one arbitrarily chosen molecule in Table 5.

As we proposed on the basis of the solution studies, the V=O and V−O(isopropoxo) groups are cis to each other. Unlike complexes **1**, **2**, and **5**, in which all of the V−O(acac) bonds are trans to alkoxide ligands and cis to the oxo group, **6** possesses an acac$^-$ oxygen atom (O6) trans to the strong V=O bond. As a result, V1−O6 (2.140(2) Å) is much longer than V1−O5 (1.951(2) Å) in the same acac$^-$ ligand and is the longest V−O(acac) bond length among the complexes in this study. However, this bond length is in the range of the bond distances for known oxovanadium complexes in which an acac$^-$ oxygen

Table 5. Selected Bond Distances (Å) and Angles (deg) for **6**

		Bond Lengths		
V1−O1	1.602(2)		O2−C2	1.270(4)
V1−O2	2.059(2)		O3−C4	1.295(4)
V1−O3	1.942(2)		O4−C6	1.450(4)
V1−O4	1.766(2)		O5−C10	1.300(4)
V1−O5	1.951(2)		O6−C12	1.259(4)
V1−O6	2.140(2)			

		Bond Lengths		
O1−V1−O2	91.85(12)		O2−V1−O6	83.24(10)
O1−V1−O3	97.73(12)		O3−V1−O4	94.83(10)
O1−V1−O4	99.02(12)		O3−V1−O5	163.23(11)
O1−V1−O5	95.01(12)		O3−V1−O6	81.99(10)
O1−V1−O6	175.10(12)		V1−O2−C2	126.8(2)
O2−V1−O3	84.50(10)		V1−O4−C6	127.1(2)
O2−V1−O4	169.10(11)		V1−O6−C12	126.4(3)
O2−V1−O5	84.23(10)			

Table 6. Distances (Å) of V−O Bonds to acac Ligands in **1**, **2**, **5**, **6**, and Other Complexes

compound	V−O- (short)	V−O- (long)	ref
[V$_2$O$_2$(μ-OCH$_3$)$_2$(acac)$_2$(OCH$_3$)$_2$], **1**	2.001(3)	2.025(2)	this work
[V$_4$O$_6$(μ-OCH$_3$)$_4$(acac)$_2$(OCH$_3$)$_2$], **2**	1.964(5)	2.015(4)	this work
[V$_3$O$_3$(μ,μ-thme)$_2$(acac)$_2$(OC$_2$H$_5$)], **5**	1.952(6)	2.038(6)	this work
	1.984(6)	1.995(6)	
[VO(OCH(CH$_3$)$_2$)(acac)$_2$], **6**	1.942(2)	2.059(2)	this work
	1.951(2)	2.140(2)^a	
[V$_4$O$_2$(μ-OCH$_3$)$_6$(acac)$_4$]	1.996(5)	1.997(6)	36
	1.985(5)	1.994(6)	
[VO(acac)$_2$]	1.955(8)	1.974(8)	67
	1.962(7)	1.983(7)	
[VCl$_2$(acac)$_2$]	1.904(15)	1.906(15)	35
	1.904(14)	1.916(14)	
[VO(acac)(Hbmid)]	2.002(3)	2.011(3)	33
[V$_2$(μ-O)(acac)$_2$(N$_3$C$_9$H$_{21}$)]	1.990(3)	1.994(2)	37
[VO(acac)$_2$(Phpy)]	1.96	1.97	39
	1.97	2.14^a	
[VO(acac)(Hshed)]	1.989(4)	2.149(4)^a	38
[VO$_2$(acac)(Phen)]	1.949	2.177^a	31
[VO(acac)(Salimh)]	1.966	2.203^a	34

^{a} Trans to oxo group.

Table 7. ^{51}V NMR Chemical Shifts of Complex **1** in Various Organic Solvents

			^{51}V signals (ppm)^a		
		time		VO(acac)$_2$-	VO-
solvent	concn (mM)	after dilution	**1**	(OCH$_3$)	(OCH$_3$)$_3$
CHCl$_3$	100	5 min	−478	−493	−542
CHCl$_3$	20	5 min	−478	−502	−573
CHCl$_3$	20	7 days	−478	−509	−583
CHCl$_3$	20	30 days	−478	ss	ss
CHCl$_3$	2	5 min	−478	−510	−582
CHCl$_3$	0.5	5 min	−478	ss	ss
CHCl$_3$/CH$_3$OH/CH$_3$CN, 3:1:1	20	5 min	−483	−496	−568
CHCl$_3$/CH$_3$OH, 4:1	20	5 min	−478	−491	−562
CHCl$_3$/CH$_3$OH, 3:2	20	5 min	−483	−491	−560
CH$_3$OH	20	5 min	−485	−491	−542

^{a} ss = small signal; less than 1% of total vanadium.

atom is trans to an oxo ligand (see Table 6).[31,34,38,39] Similarly, for the other acac$^-$ ligand of **6** the bond distance V1−O2 (2.059-(2) Å) trans to the isopropoxo group is also somewhat longer than the corresponding (and normal) V1−O3 bond distance (1.942(2) Å).

The bond to the isopropoxo ligand (V1−O4 = 1.776(2) Å) is similar in length to that in dimeric [VO(OiPr)L]$_2$ (1.803 Å) (L = N,N′-dihydroxy-N,N′-diisopropylheptanediamido)[49] and in [VO(OiPr)(8-hydroxyquinolinato)$_2$] (1.774(2) Å).[80] In the VO$_6$

core, the O2−O3−O4−O5 atoms are close to coplanar and the vanadium atom is 0.22 Å out of that plane toward the oxo group. The acac$^-$ coordinated axially to the vanadium (V1−O5−C10−C11−C12−O6) forms a highly planar six-membered chelate ring, while the acac$^-$ coordinated in the equatorial plane is slightly distorted toward a half-chair conformation, since the dihedral angle between the two planes defined by V1−O2−O3 and O2−C2−C3−C4−O3 is 167°. The fact that the acac$^-$ group with the longest V−O bond forms the more planar six-membered ring presumably reflects a greater need for electron delocalization of this unit.

Compound **6** represents the first structurally characterized mononuclear oxovanadium alkoxide-containing acac$^-$ complex. The characterization of this compound provides support for our mechanistic proposal relating to the structure of compound **7**. Although one previous mononuclear oxovanadium acac$^-$ complex has been structurally characterized, [VO(acac)$_2$(Phpy)],[39] it contained a nitrogen ligand in the sixth position. Perhaps, most importantly, none of these types of complexes had the sixth ligand cis to the oxo group. Many spectroscopic studies of VO(acac)$_2$ adducts have been devoted to the question of whether the sixth ligand is cis or trans.[81] This question was also entertained recently in a series of structural studies with the bis(maltolato)oxovanadium(V) complex.[79] We believe that these studies with compound **6** go beyond the mechanistic implications and synthetic applications of VO$_2$(acac) described in this paper and that the solid-state structural characterization of compound **6** and the solution studies presented here raise questions concerning the structures of vanadium(IV) and -(V) acac$^-$ and maltolato complexes.

Dissolved Crystalline Compound 6. A solution of **1** immediately generates three signals, in contrast to compound **6**, which at first generates only one signal at −495 ppm in CH$_3$-Cl. This CH$_3$Cl solution of **6** at ambient temperature is stable for about 10 h, but after 15 h, the solution changes color from red to brown. The brown solution contains signals at −517 (major), −556, and −562 ppm, in addition to the −495 ppm signal, which now reflects a minor component in the solution. In CH$_3$CN, the dissolved crystalline **6** is not stable for more than a few seconds, as evidenced by the rapid color change in this solvent.

Studies determining the stoichiometry and structure of the signal at −495 ppm employed a combination of ^{1}H, ^{13}C, and ^{51}V NMR studies of freshly prepared solution of both crystalline **6** and mixtures of VO$_2$(acac) and isopropyl alcohol in the presence or absence of excess Hacac in CHCl$_3$, CH$_3$CN, and isopropyl alcohol. The ^{13}C NMR spectra in CDCl$_3$ (and confirmed by ^{1}H NMR) contains one type of isopropoxide group and two types of acac$^-$ groups in a 1:1:1 ratio. The variety of combinations of **6**, isopropyl alcohol, and excess Hacac generated a series of solutions in which signals with ^{51}V NMR chemical shifts at −495, −517, and −625 ppm were present. The presence of excess 2-propanol increased the fractions of both the −517 and −625 ppm signals in the freshly prepared solutions. The −625 ppm signal is known to be VO(O-iPr)$_3$.[53,54,58] The ratio between the intensity of the −495 and −625 ppm signals remained constant in these studies indicative that the −495 ppm signals represent a mononuclear vanadium complex. In contrast, the ratio between the intensity of the signals at −495 and −517 ppm changed in accord with the latter containing two vanadium atoms. Since the ^{13}C and the ^{1}H NMR chemical shifts for the acac$^-$ group in the −495 ppm signal are

(80) Scheidt, W. R. *Inorg. Chem.* **1973**, *12*, 1758−1761.
(81) Kirste, B.; van Willigen, H. *J. Phys. Chem.* **1982**, *86*, 2743−2749.

very different, the acac$^-$ groups must be unsymmetrical. We conclude that the isopropoxide group is coordinated cis to the V=O group.

In solution, **6** was more sensitive to air than **1**. Only one signal for **6** was observed, −495 ppm (−506 ppm in neat 2-propanol) to a mononuclear species. It is reasonable that the mononuclear species is observed with the isopropoxide ligand and not with the methoxide ligand, since the former is likely to be stable. Indeed, the signal at −517 ppm (at −539 ppm in neat 2-propanol) may be for the corresponding isopropoxide-containing dinuclear species analogous to **1**. The isolation, structural characterization, and spectroscopic observation of the mononuclear **6** lend strong support to the proposed structure and existence of **7** in the corresponding methanol system.

Dissolved Crystalline Compounds 4 and 5. The further exploration of cluster formation by chelating alcohols to assist cluster assembly and stability was conducted in solution studies with **4** and **5**. At ambient temperature, **5** generated solutions giving rise to ^{51}V NMR spectra with three signals having 1:1:1 intensity at −462, −469, and −515 ppm. Thus, like the other thme^{3-}-containing oxovanadium complexes which maintain their solid-state structure in CHCl$_3$,[8,11,12,14,15] the trinuclear V−thme **5** shows a ^{51}V NMR spectrum reminiscent of its solid state structure. Since these two compounds only deviate by the one coordinated alkoxide group at V1, the ^{51}V NMR spectrum for **4** should essentially have three identical signals with **5**. However, ambient-temperature ^{51}V NMR spectra of **4** gave only two signals at a ratio of 2:1 at −459 and −514 ppm. The ^{13}C and ^{1}H NMR spectra show signals for free methanol at 49.6 and 3.46 ppm, respectively, when **4** is dissolved in CD$_3$-Cl at ambient temperature. At low temperature (233 K) the ^{51}V NMR spectrum of a solution with **4** gave three major peaks, suggesting that **4** is intact at these low temperatures. Decreased ratio of alcohol exchange at lower temperature can explain the observation. Furthermore, the greater stability of **5** is attributable to the slower alcohol exchange of the ethanoxide group compared to the methoxide group.

The hydrolytic stability of **4** and **5** in CDCl$_3$ was examined and followed by both ^{51}V and ^{1}H NMR spectroscopy. The latter is particularly convenient since the formation of free methanol/ethanol and Hacac can be easily monitored. Although most oxovanadium(V) alkoxide complexes readily hydrolyze, complexes **4** and **5**, which contain only one alkoxide coordinated to vanadium, are relatively stable in the presence of water at room temperature. Compounds **4** and **5** hydrolyzed so slowly at room temperature that neither precipitate formation nor color change was observed when these complexes were combined with up to 1 equiv of H$_2$O and stored in CDCl$_3$ for several weeks. In the presence of higher water concentrations (20 equiv of H$_2$O, Figure 7), the chemical shifts of hydrolysis products of 10 mM **5** were observed around the parent three ^{51}V NMR signals. At the same time, the 1.77 ppm signal from the coordinated C$_2$H$_5$O$^-$ ligand disappeared in the ^{1}H NMR spectrum, while the characteristic resonances at 1.23 and 3.69 ppm for the free C$_2$H$_5$OH were observed. In addition, the singlets at 5.49, 2.22, and 2.03 ppm for the free Hacac increased while the peaks assigned to coordinated acac$^-$ (5.65 (s), 5.61 (s) ppm) decreased. Formation of free alchohol as observed by ^{1}H NMR spectroscopy suggested that a hydroxide group replaced the monodentate alkoxide first, resulting in a species in which the three ^{51}V chemical shifts changed slightly, consistent with some signals which appeared in the ^{51}V NMR spectrum. In contrast to H$_3$thme, free Hacac was observed upon treatment of **5** with water. The fact that no free H$_3$thme could
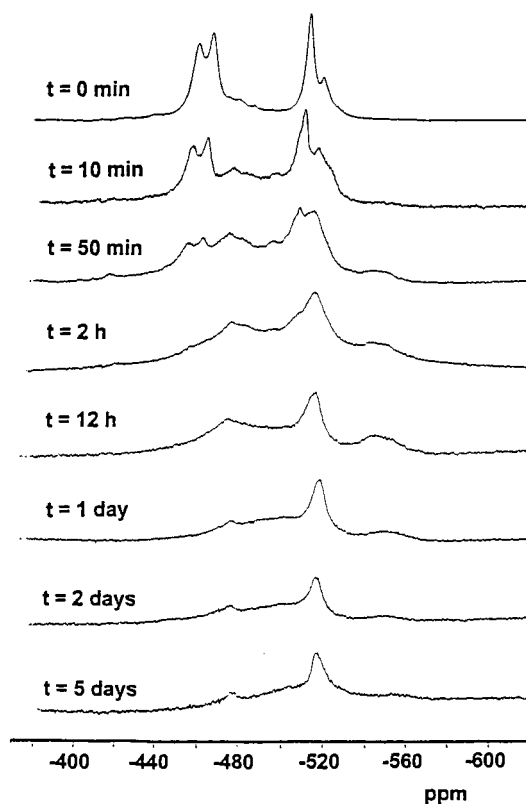

Figure 7. ^{51}V NMR spectroscopy (79 MHz) monitoring complex **5** with 20 equiv of H$_2$O in CHCl$_3$ at various times: 0 min, 10 min, 50 min, 2 h, 12 h, 1 day, 2 days, 5 days.

be observed in the ^{1}H NMR spectrum suggests the vanadium atoms in hydrolyzed species still had thme^{3-} attached. This point is substantiated by recognizing that the complex observed in aqueous solution between vanadate and H$_3$thme has a chemical shift near −520 ppm.[20] Furthermore, the variable reactivity of methoxide, ethoxide, and propoxide groups has previously been observed in tetranuclear vanadium species.[15] In addition, oxovanadium trialkoxides in which one alkoxide group had been exchanged by a hydroxide group had previously been inferred from spectroscopic studies.[58] In the presence of excess water (100 equiv), complexes **4** and **5** hydrolyzed. The color of such solutions changed quickly from orange to brown-yellow. In addition, the green solid formed was indicative of redox chemistry between the free ligand and free vanadium-(V). Complexes **1** and **3** hydrolyzed more easily than compounds **4** and **5**, presumably as a consequence of lacking the stabilizing effects that the thme^{3-} ligand provides.

At this time, a few points concerning the properties of compounds **1**−**6** will be summarized. The ^{1}H NMR spectra for complexes **1**−**6** contained a single sharp resonance in the narrow range 5.67−5.51 ppm, which is assignable to the β-proton of the acac$^-$ group (CH$_3$COC*H*COCH$_3$). A much wider range was observed in the ^{13}C chemical shift range for the α-carbon atoms of the acac$^-$ functionality. The approximately 10 ppm chemical shift range documents the different level of coordination to the vanadium atom of each acac$^-$ group, and the inequivalence of the two carbon atoms in each acac$^-$ group demonstrates the structural integrity of this portion of the molecule, even in the solution state. Solution-state ^{51}V NMR spectroscopy revealed that all methoxide-containing complexes, **1**, **3**, and **4**, only maintained their solid-state structures at low temperature in the solution state. The methoxide-containing complexes **1** and **3** in CHCl$_3$ showed excess numbers of ^{51}V signals at ambient temperature compared

Scheme 1. Proposed Relationships between Mononuclear and Oligometric Vanadium(V) Species in Organic Solvents Generated from $VO_2(acac)$ as a Vanadium Precursor
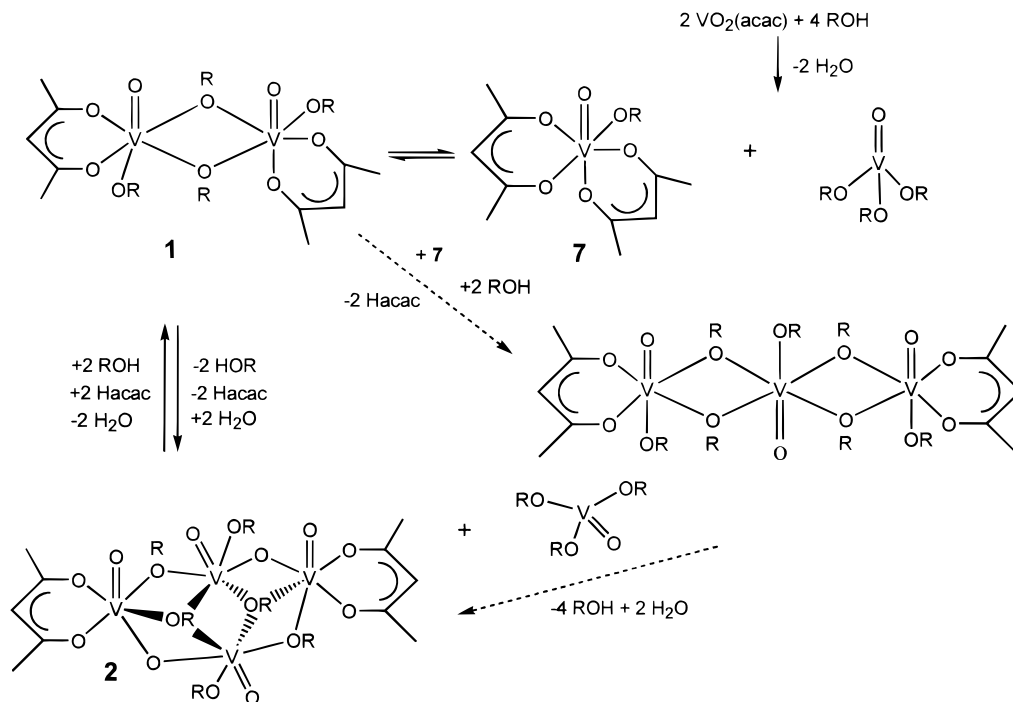
to the number of resonances expected from their structures, and this was consistent with a dynamic equilibrium involving several complexes. In contrast, the isopropoxide-containing mononuclear complex **6** had only one signal. The mixed ethoxide—thme^{3-} containing **5** had three peaks in CHCl$_3$ solution, as expected from its trinuclear structure with no crystallographically imposed symmetry. Compound **4** had a ^{51}V NMR spectrum with only two resonances, even though this compound contains three different types of vanadium atoms. This observation is explained by the dissociation of the terminally coordinated methoxide group in CHCl$_3$ solution at room temperature. In the ^1H NMR, the α-proton of bridging or terminally coordinated alkoxide groups in these complexes appeared in the range 6.73—4.05 ppm in CDCl$_3$. This chemical shift range is in accord with that expected for reported coordinated alkoxide groups.[15,42,58,75]

It is interesting to note that the 4.8 ppm signal of the solutions of **1** and **3** is very broad, in contrast to the sharp signal for the analogous peak of solutions containing pure $VO(OCH_3)_3$ (neat as well as in CDCl$_3$). Since only one broad signal is observed for all terminal methoxides, one can infer that these groups undergo dynamic exchange processes, regardless of the nature of the complexes, including dimeric and monomeric acac$^-$ complexes, as well as $VO(OCH_3)_3$. These exchange processes are observed even when crystalline **1** and **3** are dissolved in dry CHCl$_3$. The high lability of the terminally coordinated methoxide group is contrasted by the lower lability of the bridging methoxide groups. The latter show no lability on the time scale of the experiment, and the differences in the chemical shifts of free and bridging methoxides suggest that this part of the complex undergoes dynamic processes at a much slower rate. For comparison, it is interesting to note that none of the coordinated acac$^-$ groups undergo exchange on the time scale of the NMR experiments, even though hydrolytic cleavage of the acac$^-$ groups in compounds **4** and **5** was observed.

Mechanistic, Structural, and Semirational Synthetic Considerations of Cluster Preparation and Assembly. The available structural details and solution properties allow discus-

sion of and speculation relating to the solution assembly of these polynuclear oxovanadium alkoxide complexes. Complexes **1**, **2**, and **5** all contain the common V_2O_2 ring and can be considered as assemblies built up from a base unit $[V_2O_2]$, which is represented by the binuclear complex **1** in Scheme 1. Both the $[V_2O_2]$ unit and the mononuclear fragments, such as compound **6**, are likely intermediates and building blocks in the formation of trinuclear **4** and **5** and tetranuclear **2**. The trinuclear framework of **5** is composed of a V_2O_2 unit with an added mononuclear fragment to generate the V_3O_4 core in an extended linear-chain arrangement. Further addition of a mononuclear fragment, approaching the center vanadium and coordinating to the bridging methoxides of the V_3O_4 unit, would lead to the V_4O_6 unit in tetranuclear compound **2**, Scheme 1. During such cluster assembly, the bidentate acac$^-$ ligands are chelated to the two metal atoms which become the ends of the cluster framework. Presumably the stabilizing effects of the acac$^-$ ligand are a key factor in limiting the cluster size.[15,36,37]

The geometry of the mononuclear unit is likely to be very important for cluster assembly because the cis coordination of the alkoxide to the V=O group lends itself much more effectively to cluster building than the corresponding trans geometry. This point is particularly interesting when one considers the geometry of corresponding $VO(acac)_2$ condensation products and the fact that similar chemistry has not been reported with this precursor, despite the many more studies of such $VO(acac)_2$ adducts.[33,34,36−38] No solid-state structural characterization has been reported for systems with alkoxide or alcohol adducts; however, many studies employing EPR,[81,82] ENDOR,[81] and other methods[39,77] have been carried out. Although somewhat controversial, it is generally the consensus

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(83) Caravan, P.; Gelmini, L.; Glover, N.; Herring, F. G.; Li, H.; McNeill, J. H.; Rettig, S. J.; Setyawati, I. A.; Shuter, E.; Sun, Y.; Tracey, A. S.; Yuen, V. G.; Orvig, C. *J. Am. Chem. Soc.* **1995**, *117*, 12759−12770.

that an alcohol will add trans to V=O in VO(acac)$_2$.[81] It is, therefore, interesting that the solid-state structural evidence for the related oxovanadium(V) alkoxide complex has the alkoxide cis to the oxo group. Should the above observations prove to be general, they suggest a very subtle geometric preference between vanadium complexes of different oxidation states.

X-ray structures now exist for dinuclear [V$_2$O$_2$(thme)$_2$]$^{2+}$,[8] trinuclear [V$_3$O$_3$(thme)$_2$]$^{3+}$ (**5**), and tetranuclear [V$_4$O$_4$(thme)$_2$]$^{6+}$ [15] vanadium complexes containing the tridentate thme^{3-} ligand. Similar vanadium complexes containing the monodentate methoxide ligand include only the dinuclear [V$_2$O$_2$(OCH$_3$)$_4$]$^{2+}$ unit in **1** and the tetranuclear [V$_4$O$_4$(OCH$_3$)$_6$]$^{6+}$ unit in **2**. The latter complexes, however, illustrate that both thme^{3-} and methoxide are able to coordinate to vanadium using the same set coordination modes (chelating, doubly bridging, and triply bridging). The ability of the methoxide ligand to assume the same coordination modes as thme^{3-} may be important for cluster assembly. It is possible to speculate that a trinuclear complex analogous to **5** having a V$_3$O$_4$ framework but containing methoxide ligands in place of thme^{3-} could form in solution (see Scheme 1). One would expect that a trinuclear methoxide derivative would be of lower stability than the thme^{3-} analogue and that it may be difficult to observe by ^{51}V NMR spectroscopy. The lower stability of such a complex may explain why it was not readily isolated from these reaction mixtures.

The VO(acac)$_2$ derivative is a well-known and commonly used precursor in the synthesis of vanadium(IV) compounds[33−38] and can lead to vanadium(V) compounds as well.[26,30,31] From the work in this paper, there is no doubt that VO$_2$(acac) is an excellent vanadium(V) precursor with much potential. Several properties of this vanadium(V) compound are favorable for convenient use. It is a red-brown powdery solid, readily prepared from Na$_3$VO$_4$ and Hacac in H$_2$O at pH 1−2 in about 60% yield.[60] The compound is stable in air and easily dissolves in CH$_3$CN, DMF, DMSO, and CH$_3$OH. However, other solvents can be used successfully to generate compounds, as shown in this work by the reactions in C$_2$H$_5$OH and 2-propanol solvents, where VO$_2$(acac) dissolves slowly only when coordinating to a ligand dissolved in the solvent mixture. Reactions with VO$_2$(acac) can chelate both thme^{3-} and CH$_3$O$^-$ in contrast to most reported studies using CH$_3$OH as a solvent and VO(acac)$_2$ as a starting material, regardless of the reaction conditions.[29,31,34,38] This reagent doubtlessly can lead to many more clusters using related semirational approaches to cluster synthesis as these described here.

Supporting Information Available: Additional structural diagrams and tables listing crystal data, experimental parameters, bond lengths, bond angles, hydrogen coordinates, and anisotropic thermal parameters (29 pages). Ordering information is given on any current masthead page.

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