

Syntheses, X-ray Structures, and Solution Properties of $[V_4O_4\{(OCH_2)_3CCH_3\}_3(OC_2H_5)_3]$ and $[V_4O_4\{(OCH_2)_3CCH_3\}_2(OCH_3)_6]$: Examples of New Ligand Coordination Modes

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Tetranuclear vanadium complexes with alkoxy ligands, $[V_4O_4\{\mu,\mu,\mu_3-(OCH_2)_3CCH_3\}_2(OCH_3)_6]$ (**1**) and $[V_4O_4\{\mu-(OCH_2)_3CCH_3\}\{\mu,\mu_3-(OCH_2)_3CCH_3\}\{\mu,\mu,\mu_3-(OCH_2)_3CCH_3\}(OR)_3]$ ($R = C_2H_5$ (**2**), $R = CH(CH_3)_2$ (**3**), $R = CH_3$ (**4**)), were synthesized by reacting $VO(OR)_3$ and H_3 thme (H_3 thme = 1,1,1-tris(hydroxymethyl)ethane) in alcohol. Complex **1** crystallized in the monoclinic space group $P2_1/n$ with $a = 9.646(4)$ Å, $b = 11.502(3)$ Å, $c = 11.960(3)$ Å, $\beta = 90.20(3)^\circ$, $V = 1326.9(7)$ Å³, $Z = 2$ and R (wR_2) = 0.045 (0.143). Complex **2** also crystallized in the monoclinic space group $P2_1/n$ with $a = 8.290(8)$ Å, $b = 12.237(2)$ Å, $c = 29.118(4)$ Å, $\beta = 89.455(9)^\circ$, $V = 2954(3)$ Å³, $Z = 4$, and R (wR_2) = 0.049 (0.126). Both **1** and **2** are neutral, discrete complexes possessing a common $[V_4O_{16}]^{12-}$ core, which consists of four vanadium(V) atoms chelated by two (**1**) or three (**2**) tridentate $thme^{3-}$ ligands and by six (**1**) or three (**2**) RO^- groups. Compound **1** exhibits a crystallographically required inversion center; in contrast, complex **2** exhibits no crystallographically imposed symmetry, and its three trialkoxy ligands each coordinate differently (one $thme^{3-}$ is coordinated in a new coordination mode with the oxygens in a terminal, doubly-bridging and triply-bridging mode). Both compounds **1** and **2** maintain their structures in solution, although compound **1** also forms a second minor species upon dissolution. Sequential exchanges of the RO^- groups in complexes **2** and **3** were investigated by ⁵¹V and ¹H NMR spectroscopy. For example, $[V_4O_4(thme)_3(OC_2H_5)_3]$ will react with CH_3OH to generate $[V_4O_4(thme)_3(OCH_3)_3]$ (**4**). These reactions were found to be reversible. The time scale of the alcohol exchange reactions were found to vary depending on the vanadium center that is undergoing the exchange.

Introduction

The recent interest in vanadium alkoxide chemistry can be traced to applications in catalytic processes as well as their importance in the bioinorganic chemistry of vanadium.² We have had a long-term interest in structural solid state and solution characterization of various types of vanadium compounds including simple and complex alkoxide derivatives as well as the properties and reactivity of these compounds.^{3–8} We are particularly interested in vanadium complexes of polydentate ligands with oxygen donors, specifically the alkoxides. Our interest has been fueled by the observations that many weak vanadium complexes form with simple alcohols, diols, and carbohydrates and that some of these complexes induce very desirable biological effects.² In the present work we will describe the synthesis and structural characterization of two types of tetrameric oxovanadates. In addition, we describe how the alkoxide exchange processes of these complexes have been examined.

Many simple oxovanadium(V) alkoxides have been prepared, although characterization in both solid state and solution has only recently been accomplished for simple systems.^{9–12} Oxovanadium(V) alkoxides involving more complex ligands such as polydentate alcohols and carbohydrates are less well characterized, in part because such compounds often will form oligomeric or polymeric materials.^{13–17} Using tris(hydroxymethyl)methane ($thme^{3-}$) as a ligand and oxovanadium(V) alkoxides as vanadium precursor we find that tetranuclear oxovanadium alkoxides form containing both tridentate and monodentate alkoxide ligands. Previous reports of vanadium complexes with the $thme^{3-}$ ligands generated binuclear, hexanuclear, and decanuclear complexes^{16,18–22} in contrast to the family of complexes described in this work. While this work was in progress several reports of the structural characterization of related oxometalate systems appeared allowing a comparison of all the complexes currently available with this ligand.^{6,23–28}

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Among the tetranuclear oxovanadium complexes reported elsewhere^{6,23–28} and in this work, several types of metal and ligand connectivities can be identified, demonstrating the wide range of structural possibilities that are stable and tractable for these types of complexes. Although these complexes only contain four metal ions, it is becoming clear that even these simple oxometalates can support a wide range of structures.^{14,29} In this work we report four new complexes and solution studies in order to explore not only the new oxometalates and their form in solution, but also their reactivity toward exchange and hydrolytic reactions. We find that even these simple clusters are showing a surprising range in their ligand reactivity and may become useful models to explore catalytic reactivity of vanadium–oxide catalysts.

Experimental Section

Materials. Operations were carried out under nitrogen atmosphere using Schlenk, glovebox, or glovebag techniques depending on the sensitivity of the compound. Monoalcohols and organic solvents were purified by standard methods, stored under N₂ and over molecular sieves (3 Å).³⁰ VOCl₃ and tris(hydroxymethyl)ethane (H₃thme) were purchased from Aldrich. VO(OR)₃ (R = CH₃, C₂H₅ and CH(CH₃)₂) were prepared as described in the literature.^{31–33}

Methods. ¹H and ¹³C NMR were recorded at 300 and 76 MHz on a Bruker ACP 300 MHz instrument, employing routine parameters. The ⁵¹V NMR spectra were recorded at 79 MHz on a Bruker ACP-300 NMR spectrometer and chemical shifts were reported against an external neat VOCl₃ reference. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer. The UV spectroscopy was carried out on a Perkin-Elmer Lambda-4B spectrophotometer equipped with a constant-temperature cell. Elemental analyses were performed at Desert Analytics Laboratory.

[V₄O₄{(OCH₂)₃CCH₃]₂(OCH₃)₆], **1**. VO(OCH₃)₃ (0.32 g, 2.0 mmol) dissolved in 10 mL of methanol was added to a clear and colorless solution of H₃thme (0.12 g, 1.0 mmol) in 15 mL of methanol. The mixture was stirred for 2 h at ambient temperature at which time the solution had turned golden. After the solution was stored at –20 °C for several days a light yellow crystalline product had formed. Crystals of compound **1** (0.29 g) were collected, washed with pentane, and dried in vacuo. The yield was 84%. ⁵¹V NMR (78.9 MHz, 298 K, CDCl₃): δ major signals at –477, –484 ppm (minor signals at –468 and –491 ppm and elsewhere are not described further; see Figure 4A). ¹H NMR (300.1 MHz, 298 K, CDCl₃): δ 5.63 (6H, s, OCH₃), 5.21 (2H, d, (OCH₂)₃CCH₃), 5.15 (2H, d, (OCH₂)₃CCH₃), 5.10 (6H, s, OCH₃), 4.98 (6H, s, OCH₃), 4.72 (2H, d, (OCH₂)₃CCH₃), 4.63 (2H, d, (OCH₂)₃CCH₃), 4.42 (2H, d, (OCH₂)₃CCH₃), 4.21 (2H, d, (OCH₂)₃CCH₃), 0.66 (6H, s, (OCH₂)₃CCH₃). ¹³C NMR (75.6 MHz, 298 K, CDCl₃): δ 90.7 (2, (OCH₂)₃CCH₃), 88.7 (2, (OCH₂)₃CCH₃), 78.3 (2, (OCH₂)₃CCH₃), 76.8 (2, (OCH₃)), 73.0 (2, (OCH₃)), 72.8 (2, (OCH₃)), 37.8 (2, (OCH₂)₃CCH₃), 15.4 (2, (OCH₂)₃CCH₃) ppm. UV, λ_{max} (CHCl₃): 280 nm (ε 12 600 M^{–1} cm^{–1}). IR (KBr pellet cm^{–1}): 2920 (s), 2900 (vs), 2860 (s), 2800 (s), 1450 (m), 1420 (m), 1395 (m), 1205 (w), 1125

(m), 1075 (vs), 1015 (vs), 975 (vs), 647 (s), 618 (s), 560 (m), 510 (m), 474 (w). Anal. Calcd for C₁₆H₃₆O₁₆V₄: C, 27.92; H, 5.27; V, 29.61. Found: C, 28.25; H, 5.29; V, 28.62.

[V₄O₄{(OCH₂)₃CCH₃]₃(OC₂H₅)₃], **2**. H₃thme (0.12 g, 1.0 mmol) was dissolved in 15 mL of ethanol, and to this was added a solution of VO(OC₂H₅)₃ (0.28 g, 1.4 mmol) in 10 mL of ethanol. The clear colorless mixture turned orange over the course of 4 h of stirring at ambient temperature. A red crystalline product, compound **2**, had precipitated by this time; however, additional precipitation was facilitated by cooling at –20 °C for a few days. The crystalline compound was filtered off and washed with pentane. The solid was dried in vacuo, affording 0.16 g of **2** corresponding to a 63% yield. ⁵¹V NMR (78.94 MHz, 298 K, CDCl₃): δ major signals at –417, –482, –497, and –501 ppm. ¹H NMR (300.1 MHz, 298 K, CDCl₃): δ 6.10 (1H, d, (OCH₂)₃CCH₃), 5.53 (1H, d, (OCH₂)₃CCH₃), 5.42 (4H, q, OCH₂CH₃), 5.30 (4H, d, (OCH₂)₃CCH₃), 5.13 (2H, q, OCH₂CH₃), 5.16 (1H, d, (OCH₂)₃CCH₃), 4.95 (1H, d, (OCH₂)₃CCH₃), 4.72 (6H, d, (OCH₂)₃CCH₃), 4.55 (1H, d, (OCH₂)₃CCH₃), 4.44 (2H, d, (OCH₂)₃CCH₃), 4.33 (1H, d, (OCH₂)₃CCH₃), 1.44 (3H, t, OCH₂CH₃), 1.39 (3H, t, OCH₂CH₃), 1.37 (3H, t, OCH₂CH₃), 1.08 (3H, s, (OCH₂)₃CCH₃), 0.83 (3H, s, (OCH₂)₃CCH₃), 0.80 (3H, s, (OCH₂)₃CCH₃) ppm. ¹³C NMR (75.6 MHz, 298 K, CDCl₃): 96.4 ((OCH₂)₃CCH₃), 91.6 ((OCH₂)₃CCH₃), 91.1 ((OCH₂)₃CCH₃), 89.0 ((OCH₂)₃CCH₃), 88.0 ((OCH₂)₃CCH₃), 86.2 ((OCH₂)₃CCH₃), 81.6 ((OCH₂)₃CCH₃), 81.4 ((OCH₂)₃CCH₃), 80.7 ((OCH₂)₃CCH₃), 80.2 (OCH₂CH₃), 80.0 (OCH₂CH₃), 79.3 (OCH₂CH₃), 47.4 ((OCH₂)₃CCH₃), 38.8 ((OCH₂)₃CCH₃), 38.6 ((OCH₂)₃CCH₃), 18.0 (OCH₂CH₂), 17.9 (OCH₂CH₂), 17.8 (OCH₂CH₃), 15.6 (OCH₂)₃CCH₃, 15.4 (COCH₂)₃CCH₃, 15.3 (COCH₂)₃CCH₃) ppm. UV, λ_{max} (CHCl₃): 269 nm (ε 18 000 M^{–1} cm^{–1}). IR (KBr pellet, cm^{–1}): 2963 (s), 2927 (s), 2900 (s), 2856 (s), 1460 (s), 1420 (m), 1390 (m), 1370 (m), 1345 (m), 1190 (w), 1120 (m), 1090 (m), 1050 (vs), 1020 (vs), 975 (s), 960 (s), 905 (m), 655 (vs), 625 (m), 550 (s), 493 (m). Anal. Calcd for C₂₁H₄₂O₁₆V₄: C, 33.44; H, 5.61; V, 27.01. Found: C, 33.22; H, 5.44; V, 27.50.

[V₄O₄{(OCH₂)₃CCH₃]₃(OCH(CH₃)₂)₃], **3**. To the colorless solution of H₃thme (0.36 g, 3.0 mmol) in 60 mL of 2-propanol was added VO(OCH(CH₃)₂)₃ (0.98 g, 4.0 mmol), and the color of the solution turned to red. This solution was stirred for 4 h at room temperature and kept at –20 °C for several days to complete precipitation of product. After filtration, washing with pentane and drying in vacuum, 0.32 g of red crystalline product was isolated. This corresponded to a yield of 40%. ⁵¹V NMR (78.9 MHz, 298 K, CDCl₃): δ major signals at –414, –496, –500 and –514 ppm. ¹H NMR (300.1 MHz, 298 K, CDCl₃): δ 6.04 (1H, d, (OCH₂)₃CCH₃), 5.77 (3H, m, OCH(CH₃)₂), 5.52 (1H, d, (OCH₂)₃CCH₃), 5.24 (4H, d, (OCH₂)₃CCH₃), 5.13 (1H, d, (OCH₂)₃CCH₃), 4.88 (1H, d, (OCH₂)₃CCH₃), 4.60 (6H, d, (OCH₂)₃CCH₃), 4.48 (1H, d, (OCH₂)₃CCH₃), 4.39 (2H, d, (OCH₂)₃CCH₃), 4.28 (1H, d, (OCH₂)₃CCH₃), 1.50 (6H, d, OCH(CH₃)₂), 1.46 (6H, d, OCH(CH₃)₂), 1.30 (6H, d, OCH(CH₃)₂), 1.07 (3H, s, (OCH₂)₃CCH₃), 0.83 (3H, s, (OCH₂)₃CCH₃), 0.77 (3H, s, (OCH₂)₃CCH₃). ¹³C NMR (75.6 MHz, 298 K, CDCl₃): δ 96.1 ((OCH₂)₃CCH₃), 91.4 ((OCH₂)₃CCH₃), 90.9 ((OCH₂)₃CCH₃), 88.8 ((OCH₂)₃CCH₃), 87.7 ((OCH₂)₃CCH₃), 87.3 ((OCH₂)₃CCH₃), 87.2 ((OCH₂)₃CCH₃), 86.3 ((OCH₂)₃CCH₃), 86.2 ((OCH₂)₃CCH₃), 81.1 (OCH(CH₃)₂), 80.3 (OCH(CH₃)₂), 79.3 (OCH(CH₃)₂), 47.3 (COCH₂)₃CCH₃, 39.0 (COCH₂)₃CCH₃, 38.6 (COCH₂)₃CCH₃, 24.8 (2, (OCH(CH₃)₂)), 24.7 (OCH(CH₃)₂), 24.5 (OCH(CH₃)₂), 24.0 (2, (OCH(CH₃)₂)), 15.7 ((OCH₂)₃CCH₃), 15.5 ((OCH₂)₃CCH₃), 15.4 ((OCH₂)₃CCH₃). UV, λ_{max} (CHCl₃) 295 nm (ε 27 000 M^{–1} cm^{–1}). IR (KBr pellet cm^{–1}): 2965 (s), 2925 (s), 2860 (s), 1655 (m), 1465 (m), 1455 (s), 1394 (m), 1367 (m), 1321 (m), 1120 (s), 1066 (vs), 1024 (vs), 971 (vs), 842 (m), 655 (s), 561 (s). Anal. Calcd for C₂₄H₄₈O₁₆V₄: C, 36.19; H, 6.07; V, 25.59. Found: C, 36.50; H, 6.25; V, 26.19.

X-ray Crystallography. For **1** and **2**, diffraction data were collected (θ/2θ scans) on a Siemens P4 diffractometer (–100 °C for **1**, 21 °C for **2**) to (sin θ)/λ = 0.595 Å^{–1}. Both structures were solved by direct methods (TREF)^{3–8} and optimized by using full-matrix weighted least-squares refinement on F² (164 parameters for **1**, data/parameters = 14.3; 389 parameters for **2**, data/parameters = 13.4). Hydrogen atoms were included in the structural models at idealized positions (U(H) = 1.2U_{iso}(C)). Additional crystallographic details may be found in Table 1.

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Table 1. Crystallographic Data for Complexes **1** and **2**

	1	2
empirical formula	C ₁₆ H ₃₆ O ₁₆ V ₄	C ₂₁ H ₄₂ O ₁₆ V ₄
fw	688.2	754.3
cryst syst	monoclinic	monoclinic
space group	P2 ₁ /n	P2 ₁ /n
<i>a</i> (Å)	9.646(4)	8.290(8)
<i>b</i> (Å)	11.502(3)	12.237(2)
<i>c</i> (Å)	11.960(3)	29.118(4)
β (deg)	90.20(3)	89.455(9)
<i>V</i> (Å ³)	1326.9(7)	2954(3)
<i>Z</i>	2	4
<i>T</i> (K)	173	293
λ (Å)	0.7107	0.7107
D _{calc} (g cm ⁻³)	1.72	1.70
no. of reflns colld	2496	5306
no. of indep reflns	2351	5202
no. of data/restraints/params	2351/0/164	5202/0/389
<i>R</i> (I > 2 σ (I))	0.045	0.049
<i>wR</i> ₂	0.143	0.126
largest diff peak and hole (e Å ⁻³)	1.060 and -0.403	1.035 and -0.639

Results and Discussion

Synthesis and Properties of Compounds 1–3. Complexes **1–3** were synthesized as part of our systematic investigation into the reactions and complexes formed from vanadium(V) precursors and polydentate hydroxyl containing ligands.^{3–8} Compounds **1–3** were isolated from the ambient temperature reactions of VO(OR)₃ with the triols H₃thme in methanol, ethanol, and 2-propanol, respectively. When methanol is used in place of ethanol, the reaction mixture was cooled during the initial stage of crystallization to prevent decomposition of complex; compound **1** was not even stable in the mother liquor at ambient temperatures for periods beyond 1 h. The reactions leading to the products used for X-ray analysis were carried out using a 3-fold excess of vanadium precursor over H₃thme. However, studies aimed at optimizing the synthesis showed that the isolated products also formed at other vanadium to H₃thme ratios. Greater yields were, however, obtained with equimolar vanadium precursor and H₃thme ligand. Yields of crystalline materials could furthermore be improved to more than 90% if the filtrate was collected and most of the solvent removed by evaporation. Since the reaction mixture shows the presence of a minor complex, this complex must convert to the crystalline material upon crystallization given the high yield isolated on evaporation of filtrate. Given the simplicity of the synthesis, we describe only the preparations leading to optimum crystalline yields.

It is interesting that the same ligand in methanol will result in one type of oxometalate, (VO)₄[(OCH₂)₃CCH₃]₂(OCH₃)₆, **1**, and in ethanol or 2-propanol will form a second type of oxometalate, (VO)₄[(OCH₂)₃CCH₃]₃(OR)₃ (R = C₂H₅ (**2**), CH(CH₃)₂ (**3**)). The light yellow crystal of compound **1** was not thermally stable and would decompose in a few hours both in solid-state and solution-state at room temperature. Compounds **2** and **3** were stable when exposed to air at room temperature. In solution they were stable in solvents such as CHCl₃, DMF, DMSO; in other solvents, including CH₃CN, acetone, and even CH₃OH, C₂H₅OH, and (CH₃)₂CHOH, the compounds would decompose over the course of a few days.

Several polynuclear vanadium complexes with thme³⁻ have been recently reported, and some of those have been structurally characterized, including a dimer and several hexamers and decamers.^{16,18–22} Temperatures up to 180 °C in water for 21–50 h (hydrothermal synthesis) were necessary for the preparation of most of these compounds. Others were obtained in organic solvents from *n*-Bu₄ N⁺ salts of [H₃V₁₀O₂₈]³⁻, [V₅O₁₄]³⁻, and [VO₂Cl₂]⁻ as the vanadium(V) precursor. However, this is the

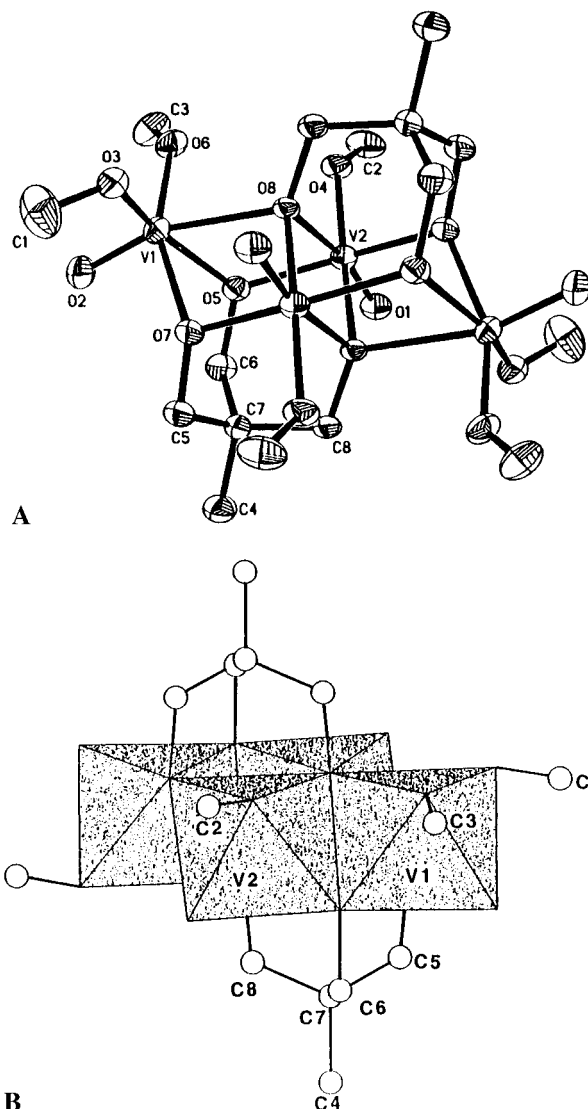


Figure 1. Molecular structure and numbering scheme for complex [V₄O₄((OCH₂)₃CCH₃)₂(OCH₃)₆], **1** (A). The complex is also shown using the polyhedral representation in a slightly rotated orientation (B). The polyhedral structure was drawn using SHELXP.

first report where a neutral vanadium(V) compound, such as VO(OR)₃, has been employed for preparation of these polynuclear vanadium complexes.

Crystallographic Studies. The structures and numbering schemes for **1** and **2** are shown in Figures 1a and 2a, respectively. In Figures 1b and 2b the structures of **1** and **2** are shown in slightly rotated orientations emphasizing the oxometalate core. The polyhedral representations of compounds **1** and **2** have been rotated somewhat in order to illustrate the connectivities in the metalate framework and the ligand connectivity to this framework. The atomic coordinates and selected bond lengths and angles are listed in Tables 2 and 3. Other results have been supplied as Supporting Information.

Compound 1. The discrete, neutral complex **1** consists of four vanadium atoms in a [V₄O₁₆]¹²⁻ core, two thme³⁻ ligands, and six CH₃O⁻ ligands; a crystallographic inversion center is imposed on the molecule in the solid state. The four oxovanadium units in **1** are doubly, O(5, 5a, 7, 7a), or triply, O(8, 8a), bridged by oxygen atoms of the two thme³⁻ ligands; each vanadium atom is also bound to one or two CH₃O⁻ groups to achieve a saturated octahedral coordination sphere. The four co-planar metal atoms are linked by four doubly-bridging, O5, O7, O5a and O7a, alkoxy arms of the two thme³⁻ ligands to

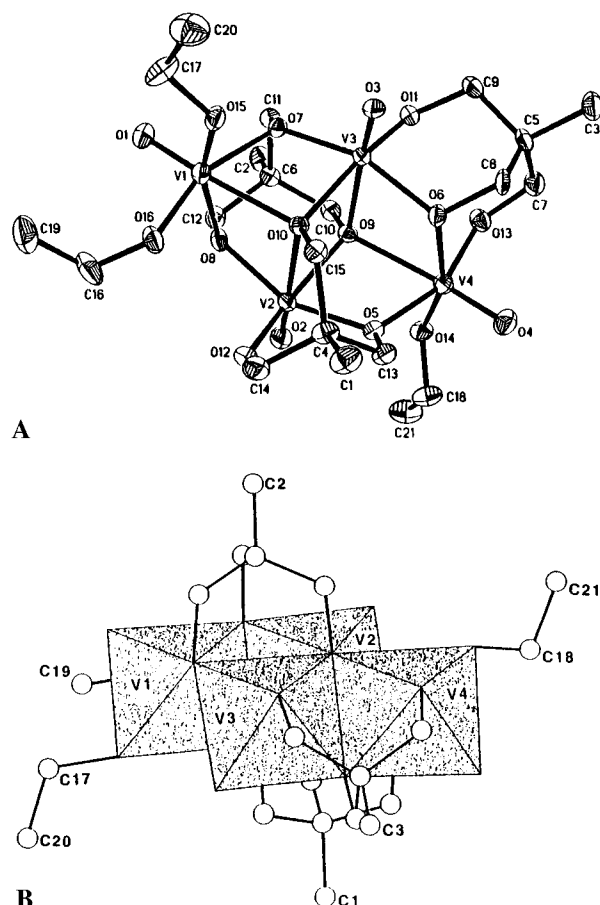


Figure 2. Molecular structure and numbering scheme for complex $[V_4O_4\{(OCH_2)_3CCH_3\}_3(OC_2H_5)_3]$, **2** (A). Thermal ellipsoids have been drawn at the 50% probability level, and hydrogen atoms have been omitted for clarity. The complex is also shown using the polyhedral representation in a slightly rotated orientation (B). The polyhedral structure was drawn using SHELXP.

form an eight-membered V₄O₄ ring. The eight-membered ring is in a chair-like configuration, with V1 and V1a occupying the puckering positions, and O5–V2–O7a/O5a–V2a–O7 representing the parallel two sides of the chair. In addition, V1, V2, V2a (and V1a, V2, V2a), are bridged by two μ_3 -O atoms of the thme³⁻ ligands.

The coordination sphere of V1 (and V1a) is completed by an oxo ligand and by two terminal, two doubly-bridging and one triply-bridging alkoxy oxygen donors, yielding a coordination mode O_tO_tO_{b-D}O_{b-D}O_{b-T}O_{b-T} (t = terminal, b = bridge, D for dinuclear, T for trinuclear), while the V(2) (and V(2a)) atom is surrounded by an oxo ligand and by one terminal, two doubly-bridging, and two triply-bridging alkoxy oxygen atoms, yielding the mode O_tO_{b-D}O_{b-D}O_{b-T}O_{b-T}. The ligand atoms in **1** are situated in distorted octahedral geometries about each vanadium atom, with O–V–O bond angles varying from 72.15 to 104.35°. The two tridentate thme³⁻ ligands in **1** exhibit the coordination mode (O_{b-D}O_{b-D}O_{b-T}), which is identical to one of the three coordination modes found in compound **2** (see below), and to coordination modes found in other complexes containing thme³⁻ ([V₁₀O₁₆(thme)₄]²⁻,^{16, 21} [Ti₄(thme)₂(O-*i*Pr)₁₀],²³ and [(MoO₂)₄(thme)₂(OC₂H₅)₂]²⁷). Complex **1** is structurally analogue of the tetramer [V₄O₄(SO₄)₂(H₂O)₂{(OCH₂)₃CR]₂²⁻, which also has the [V₄O₁₆] core and a chairlike V₄O₄ configuration.¹⁸

Compound 2. The discrete, neutral complex **2** also contains four vanadium atoms in a [V₄O₁₆]¹²⁻ core. The four crystallographically independent oxovanadium units are chelated by three tridentate thme³⁻ ligands and terminally coordinated by three C₂H₅O⁻ groups. All four vanadium atoms in **2** exhibit a

distorted octahedral coordination geometry. The shortest V–O bonds (1.596(4) Å) are to the oxo ligands; the V–O_t (1.786(8) Å), V–O_{b-D} (2.01(8) Å) and V–O_{b-T} (2.18(11) Å) bonds increase in length with increasing level of bridging. The two triangular faces V1, V2, V3 and V2, V3, V4 are capped by O10 and O9 see Figure 2a. O10 and O9 are two triply-bridging oxygen donors of the thme³⁻ ligands, one above and below the plane of the vanadium atom, respectively, and can be viewed as two edge-sharing trigonal pyramids. Furthermore, the tetrametallate core is doubly bridged by O5, O6, O7, and O8, which are also oxygen atoms in the thme³⁻ ligands.

Besides the terminal oxo moieties, V1 and V4 are each coordinated to two terminal alkoxy oxygen and three doubly-bridging alkoxy oxygen or triply-bridging alkoxy oxygen atoms in the O_tO_tO_{b-D}O_{b-D}O_{b-T} mode, while V2 and V3 each are surrounded by one terminal and by four doubly-bridged or triply-bridged alkoxy oxygen atoms in the O_tO_{b-D}O_{b-D}O_{b-T}O_{b-T} mode. The three tridentate thme³⁻ ligands chelate in three different coordination modes, O_tO_tO_{b-D} (terminal, terminal, doubly-bridging), O_tO_{b-D}O_{b-T} (chelating, doubly-bridging and triply-bridging), and O_{b-D}O_{b-D}O_{b-T} (doubly-bridging, doubly-bridging, triply-bridging). The former two of these chelation patterns, O12,5,10 and O11,13,6, are new and interesting modes of chelation. The bifunctional mode has been reported in one example, previously, [V₂O₂Cl₂{(OCH₂)₂C(R)(CH₂OH)}₂.¹⁸ This is the first time the trifunctional mode has been observed. These coordination modes are fairly unusual considering that one or two alkoxide functionalities of the tridentate thme³⁻ ligand are terminally coordinated to the vanadium atoms.

The bond distances of V=O (average 1.598(1), 1.596(4) Å) in **1** and **2** are clearly showing doubly bonded character. The average distances of V–O_{b-D}(5.5a,7.7a) (2.01(9) Å) in **1** and V–O_{b-D}(5.6,7.8) (2.01(8) Å) in complex **2** are comparable to the corresponding bonds in the vanadium–thme³⁻ complexes isolated from hydrothermal synthesis.^{16,20–22} Surprisingly, the average distances of V–O_{b-T}(8.8a) (2.18(9) Å) and V–O_{b-T}(9,10) (2.18(11) Å) in **1** and **2** are longer than those in the decamers where the average bond lengths are 2.02(9) Å.^{16,21} The possibility that the long V–O_{b-T} bonds in **1** and **2** are due to protonation is inconsistent with complex stoichiometry and elemental analysis. In addition this possibility was ruled out in a bond-valence calculation.³⁴ The possibility that intermolecular V···O contacts for oxygen atoms with long V–O bonds could explain the long bonds was ruled out since we see no evidence for intermolecular interactions in the tables of interatomic distances.

Comparison of the geometries of compounds **1** and **2** with those of other structurally characterized tetramers reveals several structural patterns (see Table 4). In general, the V₂O₂ unit (M₂O_c,M₃,O_{c1} shown in Table 4) that constitutes the center of the tetramer is very similar in **1**, **2**, and a previously characterized tetramer ([V₄O₈(OCH₃)₄(bipy)₂].²⁴ One bond is relatively short and the other (trans to the V=O) is relatively long. A chloro-substituted tetramer [(VOCl)₂(VO(OH))₂(DMPD)₄] shows a similar relationship between bond lengths, although the specific bond lengths are less similar.⁶ The outer ring (M₁O_aM₂O_{a2}M₄O_{a3}M₃O_{a1} in Table 4), on the other hand, shows significant differences between the different tetramers. The bond lengths of this type are similar in compounds **1** and **2** while the shorter bonds in [V₄O₈(OCH₃)₄(bipy)₂] reflect the fact that the outer metal ions are coordinated by nitrogen donors. In contrast, the complex [(VOCl)₂(VO(OH))₂(DMPD)₄] contains significantly longer bonds of these types as a result of chloride

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Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (\AA^2) for **1** and **2** ($U(\text{eq})$ Defined as One-Third of the Trace of the Orthogonalized U_{ij} Tensor)

	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq})$		<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq})$
For 1 ^a									
V1	0.20321(7)	0.32666(6)	0.47410(5)	0.0227(3)	O8	0.0441(2)	0.4518(2)	0.4092(2)	0.0179(6)
V2	0.12324(6)	0.60681(5)	0.49931(5)	0.0196(3)	C1	0.0955(6)	0.1010(4)	0.4230(5)	0.0519(14)
O1	0.1660(3)	0.7055(2)	0.5870(2)	0.0255(6)	C2	0.3219(5)	0.7354(4)	0.3680(3)	0.0347(10)
O2	0.3045(3)	0.2577(3)	0.5567(2)	0.0316(7)	C3	0.4571(4)	0.4157(4)	0.3748(4)	0.0359(11)
O3	0.1269(3)	0.2147(2)	0.3913(2)	0.0287(7)	C4	0.1047(5)	0.4403(4)	0.8649(3)	0.0322(10)
O4	0.2358(3)	0.6365(2)	0.3875(2)	0.0248(6)	C5	0.0477(4)	0.3234(3)	0.6959(3)	0.0260(9)
O5	0.2246(3)	0.4819(2)	0.5672(2)	0.0208(6)	C6	0.3293(4)	0.4760(4)	0.6879(3)	0.0265(9)
O6	0.3149(3)	0.3860(2)	0.3712(2)	0.0274(7)	C7	0.0896(4)	0.4445(3)	0.7366(3)	0.0227(8)
O7	0.0329(3)	0.3162(2)	0.5756(2)	0.0218(6)	C8	-0.0206(4)	0.5360(3)	0.7101(3)	0.0217(8)
For 2									
V1	-0.22156(9)	0.73445(6)	0.05076(3)	0.0192(2)	C2	-0.4026(6)	1.1183(4)	0.0609(2)	0.0288(11)
V2	0.05778(9)	0.89989(6)	0.09370(2)	0.0176(2)	C3	-0.3585(6)	0.8323(4)	0.3150(2)	0.0300(12)
V3	-0.26242(9)	0.80439(6)	0.15705(2)	0.0157(2)	C4	0.1912(5)	0.6826(4)	0.1341(2)	0.0218(10)
V4	0.01921(9)	0.96768(6)	0.20246(3)	0.0189(2)	C5	-0.2998(6)	0.8692(4)	0.26739(14)	0.0207(10)
O1	-0.3367(4)	0.7587(3)	0.00829(11)	0.0250(7)	C6	-0.3107(5)	1.0167(4)	0.07593(15)	0.0189(9)
O2	0.1212(4)	1.0177(3)	0.07927(11)	0.0261(7)	C7	-0.2295(6)	0.9841(4)	0.2716(2)	0.0268(11)
O3	-0.3299(4)	0.68812(2)	0.17289(10)	0.0192(7)	C8	-0.1682(6)	0.7902(4)	0.25162(14)	0.0222(10)
O4	0.1315(4)	0.9356(3)	0.24471(11)	0.0281(8)	C9	-0.4448(5)	0.8657(4)	0.23490(15)	0.0235(10)
O5	0.1471(3)	0.8783(2)	0.15520(10)	0.0188(7)	C10	-0.2147(5)	1.0444(4)	0.1193(2)	0.0203(10)
O6	-0.1059(4)	0.8170(2)	0.20590(10)	0.0181(7)	C11	-0.4326(5)	0.9253(4)	0.0849(2)	0.0195(10)
O7	-0.3602(3)	0.8230(2)	0.09784(10)	0.0176(7)	C12	-0.1968(6)	0.9831(4)	0.0360(2)	0.0229(10)
O8	-0.1047(4)	0.8867(2)	0.04753(10)	0.0194(7)	C13	0.2278(5)	0.7778(4)	0.1666(2)	0.0213(10)
O9	-0.1206(3)	0.9539(2)	0.13615(10)	0.0163(6)	C14	0.2583(6)	0.7085(4)	0.0858(2)	0.0267(11)
O10	-0.0811(3)	0.7482(2)	0.11519(10)	0.0153(6)	C15	0.0120(5)	0.6564(4)	0.1318(2)	0.0198(10)
O11	-0.3964(3)	0.8920(2)	0.18845(10)	0.0192(7)	C16	0.0041(7)	0.7008(5)	-0.0242(2)	0.0372(13)
O12	0.2096(4)	0.8136(3)	0.07038(11)	0.0251(7)	C17	-0.3814(6)	0.5289(4)	0.0476(2)	0.0330(12)
O13	-0.1557(4)	1.0236(3)	0.23031(10)	0.0236(7)	C18	0.2743(6)	1.1198(4)	0.1806(2)	0.0337(12)
O14	0.1078(4)	1.0894(2)	0.18038(11)	0.0226(7)	C19	-0.0578(8)	0.6140(5)	-0.0557(2)	0.046(2)
O15	-0.2994(4)	0.6087(3)	0.07342(10)	0.0220(7)	C20	-0.4153(7)	0.4285(5)	0.0763(2)	0.0411(14)
O16	-0.0470(4)	0.6789(3)	0.02242(11)	0.0250(7)	C21	0.2949(7)	1.2305(5)	0.1592(2)	0.0432(14)
C1	0.2764(6)	0.5803(4)	0.1524(2)	0.0284(11)					

^a Symmetry transformations used to generate equivalent atoms: $-x, -y + 1, -z + 1$.

coordination. Comparison of **1** and **2** with the similar molybdenum and titanium complexes shows close similarity in the conformation of the M_4O_4 unit, considering the differences in the bond lengths ($\text{Ti}-\text{O}_{\text{b-D}} = 2.04(8)$ Å and $\text{Mo}-\text{O}_{\text{b-D}} = 2.09(13)$ Å, respectively).^{23,27}

Complexes **1** and **2** have the four vanadium atoms in a single plane and the V_4O_4 ring in a "chair" conformation; this conformation has also been observed for $[(\text{VOCl})_2(\text{VO}(\text{OH}))_2(\text{DMPD})_4]$,⁶ $[\text{V}_4\text{O}_8(\text{OCH}_3)_4(\text{bipy})_2]$,²⁴ $[\text{V}_4\text{O}_4(\text{H}_2\text{O})_2(\text{SO}_4)_2\text{-}\{(\text{OCH}_2)_3\text{CR}\}_2]^{2-}$,¹⁸ $[\text{Ti}_4(\text{thme})_2(\text{O}-i\text{Pr})_{10}]^{23}$ and $[\text{Mo}_4\text{O}_8(\text{thme})_2(\text{OEt})_2]$ and is illustrated in Figure 3a using a polyhedral representation.²⁷ This type of tetranuclear core is generated by condensing four $[\text{VO}_6]$ units by edge-sharing each octahedron. This is a very compact polyhedral mode. There are, however, two fundamentally different types of edge-sharing polyhedral modes, the "chair" mode described in this work, and a "boat mode". The tetramers $[\text{V}_4\text{O}_8(\text{NO}_3)(\text{tca})_4]^{2-}$,²⁶ $[\text{V}_4\text{O}_8(\text{C}_2\text{O}_4)_4(\text{H}_2\text{O})_2]^{4-}$,²⁸ and $[\text{V}_4\text{O}_8(\text{O}_2\text{CCH}_2\text{tBu})_4]^{25}$ contain four vanadium atoms in a single plane and in a "boat" conformation. An entirely different geometry is observed for the closely related complex $[\text{V}_4\text{O}_4(\text{SNNS})_4]$ (where SNNS is *N,N'*-bis(*o*-mercaptophenyl)ethylenediamine). In this molecule of S_4 symmetry the boat conformation prevents the four vanadium atoms from being in a plane.³⁵ In Figure 3b one of the four reported "boat" modes is shown; the polyhedral core consists of two pairs of edge-sharing octahedra linked by two corner-sharing oxygen atoms. This geometry was reported in $[\text{V}_4\text{O}_4(\text{C}_2\text{O}_4)_4(\text{H}_2\text{O})_2]^{4-}$.²⁸ The two other "boat" modes were reported in $[\text{V}_4\text{O}_8(\text{O}_2\text{CCH}_2\text{-tBu})_4]^{25}$ and $[\text{V}_4\text{O}_8(\text{NO}_3)(\text{tca})_4]^{2-}$;²⁶ the polyhedral core consists of four corner-sharing $[\text{VO}_5]$ units and four edge-sharing $[\text{VO}_6]$

units, respectively. Parts a and b of Figure 3 clearly demonstrate the topological differences in these oxometalate complexes despite the fact that all these complexes maintain the four vanadium atoms in one plane. The three tetramers with the "boat" conformation have significantly shorter "external" V–O bonds regardless of their substitution and polyhedra core geometry. It is interesting here to note that the metavanadate ions, $\text{HV}_4\text{O}_{12}^{4-}$ and $\text{V}_4\text{O}_{12}^{4-}$ have also been crystallized in "chair",³⁶ "boat",³⁷ and planar³⁸ geometries, presumably reflecting the importance of the counterions on cluster formation.

IR Spectroscopy. The infrared spectra (KBr pellet) of oxovanadium tetramers **1**, **2** and **3** exhibited intense characteristic absorption bands for V=O in the expected range (from 975 to 955 cm^{-1}). The intense bands at 1075–1015 cm^{-1} are attributable to $\nu(\text{C}-\text{O})$ of the RO^- groups. The absorption bands, attributed to the coordinated thme³⁻ ligands, were at 1460–1420, 1395–1320, 655, and 560–510 cm^{-1} , as compared with that of the free ligands (1400, 1290, 665 cm^{-1}). More ligand absorption bands are observed for compounds **2** and **3** than for compound **1**. These characteristics suggest that compound **3** is more similar to **2** than to **1**. This is consistent with the fact that compound **1** only contains one type of ligand and compounds **2** and **3** contain three different types of ligands.

Solution Properties. The ⁵¹V NMR spectrum shows two major signals of equal intensity for compound **1** (Figure 4A) in CHCl_3 . The minor signals observed by ⁵¹V NMR spectroscopy for this compound are presumably reflecting hydrolysis and/or

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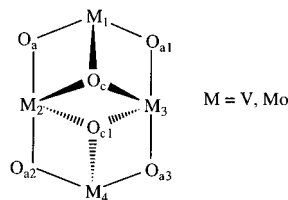
Table 3. Bond Lengths (Å) and Angles (deg) for Compounds **1** and **2**

For 1 ^a							
Bond Lengths							
V1–O2	1.597(3)	V2–O4	1.759(3)	O4–C2	1.428(5)	O8–V2	2.067(2)
V1–O6	1.775(3)	V2–O5	1.917(3)	O5–C6	1.446(4)	C4–C7	1.542(5)
V1–O3	1.782(3)	V2–O7	1.961(3)	O6–C3	1.414(5)	C5–C7	1.529(5)
V1–O7	2.050(3)	V2–O8	2.067(2)	O7–C5	1.448(5)	C6–C7	1.514(5)
V1–O5	2.114(3)	V2–O8	2.217(3)	O7–V2	1.961(3)	C7–C8	1.528(5)
V1–O8	2.241(3)	O3–C1	1.394(5)	O8–C8	1.451(4)	C8–O8	1.451(4)
V2–O1	1.599(3)						
Bond Angles							
O2–V1–O6	104.35(14)	O3–V1–O8	89.47(12)	O7–V2–O8	77.84(10)	C5–O7–V2	120.1(2)
O2–V1–O3	103.61(15)	O7–V1–O8	72.15(10)	O1–V2–O8	167.79(12)	C5–O7–V1	120.6(2)
O6–V1–O3	98.26(13)	O5–V1–O8	72.86(10)	O4–V2–O8	89.93(11)	V2–O7–V1	108.59(12)
O2–V1–O7	95.43(13)	O1–V2–O4	101.69(13)	O5–V2–O8	77.15(10)	C8–O8–V2	115.6(2)
O6–V1–O7	157.35(12)	O1–V2–O5	97.13(13)	O7–V2–O8	83.01(10)	C8–O8–V2	116.9(2)
O3–V1–O7	87.49(12)	O4–V2–O5	98.75(12)	O8–V2–O8	74.15(10)	V2–O8–V2	105.85(10)
O2–V1–O5	92.03(13)	O1–V2–O7	100.10(13)	C1–O3–V1	128.1(3)	C8–O8–V1	120.5(2)
O6–V1–O5	88.96(12)	O4–V2–O7	92.31(12)	C2–O4–V2	129.8(3)	V2–O8–V1	98.16(10)
O3–V1–O5	160.46(12)	O5–V2–O7	157.19(11)	C6–O5–V2	118.2(2)	V2–O8–V1	96.54(10)
O7–V1–O5	79.31(10)	O1–V2–O8	94.84(12)	C6–O5–V1	119.3(2)	O7–C5–C7	113.2(3)
O2–V1–O8	161.75(12)	O4–V2–O8	162.06(12)	V2–O5–V1	111.18(12)	O5–C6–C7	111.7(3)
O6–V1–O8	85.95(11)	O5–V2–O8	85.94(10)	C3–O6–V1	131.6(3)		
For 2							
Bond Lengths							
V1–O1	1.597(3)	V3–O11	1.789(3)	O7–C11	1.440(5)	C4–C15	1.522(6)
V1–O15	1.792(3)	V3–O7	1.925(3)	O8–C12	1.447(5)	C4–C14	1.540(7)
V1–O16	1.793(3)	V3–O6	1.941(3)	O9–C10	1.443(5)	C4–C13	1.533(6)
V1–O7	2.084(3)	V3–O10	2.045(3)	O10–C15	1.449(5)	C5–C8	1.525(7)
V1–O8	2.101(3)	V3–O9	2.255(3)	O11–C9	1.444(5)	C5–C7	1.527(6)
V1–O10	2.224(3)	V4–O4	1.599(3)	O12–C14	1.423(6)	C5–C9	1.537(6)
V2–O2	1.590(3)	V4–O14	1.779(3)	O13–C7	1.428(6)	C6–C11	1.528(6)
V2–O12	1.773(3)	V4–O13	1.790(3)	O14–C18	1.429(6)	C6–C10	1.537(6)
V2–O8	1.919(3)	V4–O5	2.046(3)	O15–C17	1.411(5)	C6–C12	1.546(6)
V2–O5	1.962(3)	V4–O6	2.118(3)	O16–C16	1.445(6)	C16–C19	1.496(8)
V2–O9	2.029(3)	V4–O9	2.268(3)	C1–C4	1.536(6)	C17–C20	1.512(7)
V2–O10	2.269(3)	O5–C13	1.439(5)	C2–C6	1.524(6)	C18–C21	1.501(7)
V3–O3	1.596(3)	O6–C8	1.461(5)	C3–C5	1.533(6)		
Bond Angles							
O1–C1–O15	103.2(2)	O2–V2–O10	168.64(14)	O13–V4–O5	157.08(13)	C10–O9–V4	121.0(2)
O1–V1–O16	101.5(2)	O12–V2–O10	88.57(14)	O4–V4–O6	92.2(2)	V2–O9–V4	99.63(13)
O15–V1–O16	97.5(2)	O8–V2–O10	76.50(12)	O14–V4–O6	161.25(13)	V3–O9–V4	95.73(11)
O1–V1–O7	94.74(15)	O5–V2–O10	80.37(12)	O13–V4–O6	85.25(14)	C15–O10–V3	116.9(2)
O15–V1–O7	90.55(13)	O9–V2–O10	74.54(11)	O5–V4–O6	79.42(12)	C15–O10–V1	120.4(2)
O16–V1–O7	159.62(14)	O3–V3–O11	99.9(2)	O4–V4–O9	160.57(15)	V3–O10–V1	98.07(13)
O1–V1–O8	94.54(15)	O3–V3–O7	102.42(14)	O14–V4–O9	88.12(13)	C15–O10–V2	117.1(2)
O15–V1–O8	160.37(13)	O11–V3–O7	97.01(14)	O13–V4–O9	89.75(14)	V3–O10–V2	104.94(12)
O16–V1–O8	86.89(14)	O3–V3–O6	95.37(14)	O5–V4–O9	69.72(12)	V1–O10–V2	95.61(11)
O7–V1–O8	79.62(12)	O11–V3–O6	89.66(14)	O6–V4–O9	73.83(11)	C9–O11–V3	120.7(3)
O1–V1–O10	163.86(14)	O7–V3–O6	159.56(13)	C13–O5–V2	120.4(3)	C14–O12–V2	128.3(3)
O15–V1–O10	86.80(12)	O3–V3–O10	97.26(14)	C13–O5–V4	122.7(3)	C7–O13–V4	126.2(3)
O16–V1–O10	89.44(14)	O11–V3–O10	162.80(13)	V2–O5–V4	110.12(14)	C18–O14–V4	127.7(3)
O7–V1–O10	72.27(12)	O7–V3–O10	79.60(13)	C8–O6–V3	114.7(3)	C17–O15–V1	124.9(3)
O8–V1–O10	74.07(11)	O6–V3–O10	88.32(13)	C8–O6–V4	114.0(2)	C16–O16–V1	126.2(3)
O2–V2–O12	101.9(2)	O3–V3–O9	169.10(14)	V3–O6–V4	111.40(14)	C15–C4–C1	107.2(4)
O2–V2–O8	97.1(2)	O11–V3–O9	88.34(13)	C11–O7–V3	121.1(3)	C15–C4–C14	110.3(4)
O12–V2–O8	100.48(15)	O7–V3–O9	83.41(12)	C11–O7–V1	120.5(2)	C1–C4–C14	108.7(4)
O2–V2–O5	103.7(2)	O6–V3–O9	77.47(12)	V3–O7–V1	107.05(14)	C15–C4–C13	112.8(4)
O12–V2–O5	89.80(14)	O10–V3–O9	74.54(11)	C12–O8–V2	118.0(3)	C1–C4–C13	108.1(4)
O8–V2–O5	154.36(13)	O4–V4–O14	104.0(2)	C12–O8–V1	119.3(3)	C14–C4–C13	109.6(4)
O2–V2–O9	95.91(15)	O4–V4–O13	102.7(2)	V2–O8–V1	111.71(14)	O5–C13–C4	114.3(4)
O12–V2–O9	159.70(14)	O14–V4–O13	100.01(15)	C10–O9–V2	115.8(3)	O12–C14–C4	111.9(4)
O8–V2–O9	86.67(13)	O4–V4–O5	94.8(2)	C10–O9–V3	115.6(2)	O10–C15–C4	112.0(3)
O5–V2–O9	76.54(13)	O14–V4–O5	89.73(14)	V2–O9–V3	105.97(13)		

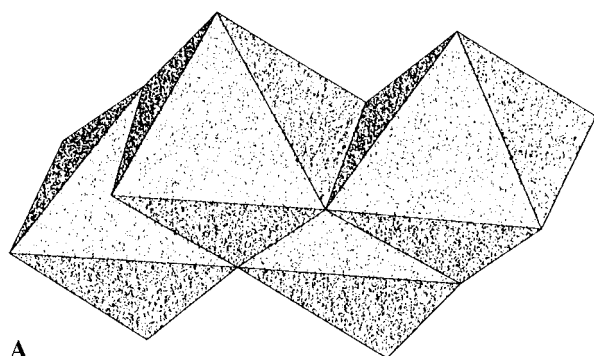
^a Symmetry transformations used to generate equivalent atoms: $-x, -y + 1, -2z + 1$.

decomposition products given the instability of this compound. Compound **1** is fairly unstable at room temperature, and no spectra were recorded without the minor signals. Precautions, such as drying CHCl₃ and a nitrogen atmosphere, did not change the ratio of the major doublet with respect to the minor doublet, suggesting the minor doublet may be an isomer of compound **1**. The minor downfield signals may be due to hydrolysis product(s), since these signals will increase upon exposure to

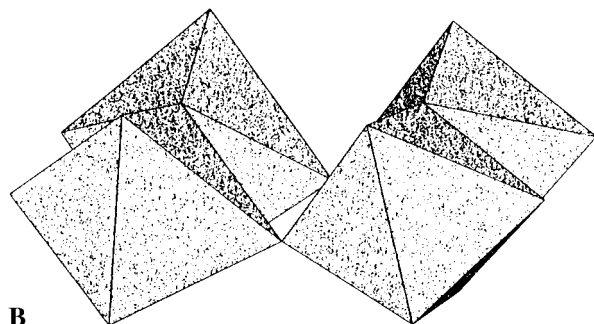
air and addition of small amounts of water. However, at this time we cannot rule out that these signals are due to decomposition products resulting from redox chemistry. The ¹³C NMR signals for the five inequivalent carbons in the symmetry-related thme³⁻ ligands of **1** appear at 15.4, 37.8, 78.3, 88.7 and 90.7 ppm, consistent with the structure characterized in the solid state for **1** for the major complex in solution. The four equal intensity signals for compounds **2** and **3** in the ⁵¹V NMR spectrum

Table 4. Structural Characteristics for a Series of Oxovanadium and Molybdenum Tetramers Including Compounds **1** and **2** and $(\text{VOCl})_2(\text{VO}(\text{OH}))_2(\text{DMPD})_4$,⁶ $\text{V}_4\text{O}_8(\text{OCH}_3)_4(\text{bipy})_2$,²⁴ $[\text{V}_4\text{O}_8(\text{NO}_3)(\text{tca})_4]^{2-}$,²⁶ $[\text{Mo}_4\text{O}_8(\text{thme})_2(\text{OC}_2\text{H}_5)_2]$,²⁷ $[\text{V}_4\text{O}_8(\text{C}_2\text{O}_4)_4(\text{H}_2\text{O})_2]^{4-}$,²⁸ $[\text{V}_4\text{O}_8(\text{O}_2\text{CCH}_2\text{tBu})_4]$,²⁵ and $[\text{V}_4\text{O}_4(\text{SNNS})_4]$ ³⁵

O – M (Å)	$[\text{V}_4\text{O}_4(\text{thme})_2(\text{OMe})_6]$	$[\text{V}_4\text{O}_4(\text{thme})_3(\text{OEt})_3]$	$[(\text{VOCl})_2(\text{VO}(\text{OH}))_2(\text{DMPD})_4]$	$[\text{V}_4\text{O}_8(\text{OCH}_3)_4(\text{bipy})_2]$	$[\text{Mo}_4\text{O}_8(\text{thme})_2(\text{OC}_2\text{H}_5)_2]^{27}$	$[\text{V}_4\text{O}_8(\text{NO}_3)(\text{tca})_4]^{2-}$	$[\text{V}_4\text{O}_8(\text{C}_2\text{O}_4)_4(\text{H}_2\text{O})_2]^{4-}$	$[\text{V}_4\text{O}_8(\text{O}_2\text{CCH}_2\text{tBu})_4]$	$[\text{V}_4\text{O}_4(\text{SNNS})_4]$
O_a-M_1	2.050(3)	2.101(3)	1.966(2)	1.709(1)	2.157(4)	1.783(12)	1.80(1)	1.789(7)	1.652(3)
O_a-M_2	1.961(3)	1.919(3)	1.832(2)	2.000(1)	2.001(4)	1.851(12)	1.79(1)	1.784(8)	2.014(3)
$\text{O}_{a1}-\text{M}_1$	2.114(3)	2.084(3)	2.305(1)	1.818(1)	2.256(4)	1.808(11)	1.84(1)	1.872(8)	2.014(3)
$\text{O}_{a1}-\text{M}_3$	1.917(3)	1.925(3)	2.009(2)	1.822(1)	1.972(4)	1.780(12)	1.84(1)	1.847(7)	1.652(3)
$\text{O}_{a2}-\text{M}_2$	1.917(3)	1.962(3)	2.009(2)	1.822(1)	1.972(4)	1.792(11)	1.82(1)	1.827(7)	1.652(3)
$\text{O}_{a2}-\text{M}_4$	2.114(3)	2.046(3)	2.305(1)	1.818(1)	2.256(4)	1.803(11)	1.82(1)	1.770(8)	2.014(3)
$\text{O}_{a3}-\text{M}_3$	1.961(3)	1.941(3)	1.832(2)	2.000(1)	2.001(4)	1.799(12)	1.80(1)	1.955(7)	2.014(3)
$\text{O}_{a3}-\text{M}_4$	2.050(3)	2.118(3)	1.966(2)	1.709(1)	2.157(4)	1.821(13)	1.79(1)	1.929(7)	1.652(3)
O_c-M_1	2.241(3)	2.224(3)	1.978(2)	2.274(1)	2.282(4)				
O_c-M_2	2.067(3)	2.269(3)	1.780(2)	2.299(1)	2.287(4)				
O_c-M_3	2.217(3)	2.045(3)	2.271(1)	2.039(1)	2.287(4)				
$\text{O}_{c1}-\text{M}_2$	2.217(3)	2.029(3)	2.271(1)	2.039(1)	2.287(4)				
$\text{O}_{c1}-\text{M}_3$	2.067(3)	2.255(3)	1.780(2)	2.299(1)	2.287(4)				
$\text{O}_{c1}-\text{M}_4$	2.241(3)	2.268(3)	1.978(2)	2.274(1)	2.282(4)				
conformation of M_4O_4 ring	chair	chair	chair	chair	chair	boat	boat	boat	boat



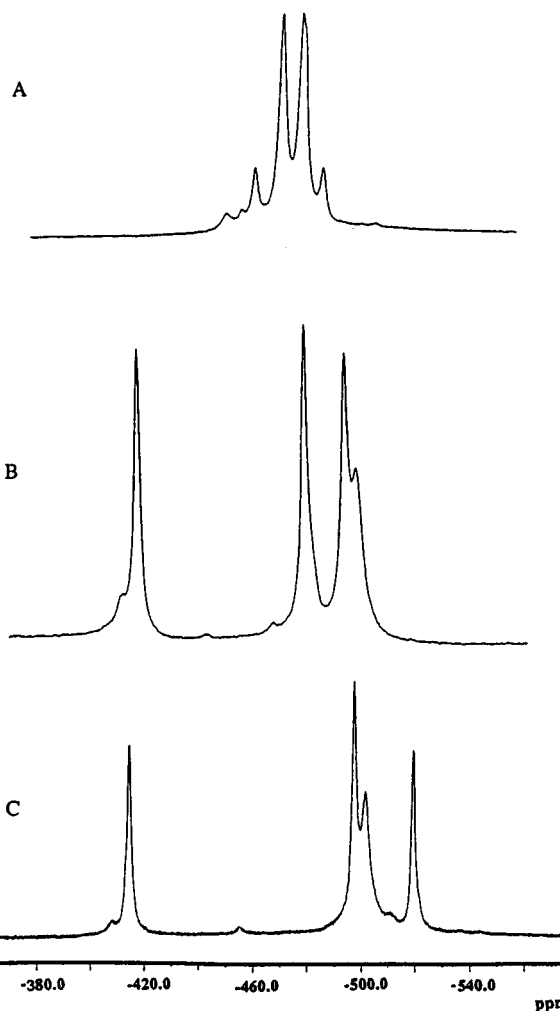
A



B

Figure 3. Polyhedral representation of “boat” (a) and “chair” (b) conformations of oxovanadium tetramers. The “boat” illustrated is the structure reported for $[\text{V}_4\text{O}_8(\text{C}_2\text{O}_4)_4(\text{H}_2\text{O})_2]^{4-}$.²⁸

suggest that these compounds may be related (Figure 4b,c). In cases where the resonances overlap, we find that the integrations still are of a 1:1:1:1 intensity upon closer analysis and comparison with the major resonances elsewhere in the spectra. Compound **2** contains four different vanadium atoms in the X-ray structure, and the ^{51}V NMR spectra show that four different vanadium atoms are present in solution. This is consistent with these expectations should compounds **2** and **3** remain intact in solution. Such a conclusion was supported by

**Figure 4.** ^{51}V NMR spectra (79 MHz) of compounds **1** (A), **2** (B) and **3** (C).

the ¹H and ¹³C NMR spectra, which albeit complicated show the fact that both compounds **2** and **3** contains three different types of thme³⁻ ligands coordinated to the vanadium atom. We conclude that the structures characterized for compounds **1** and **2** are maintained in CHCl₃ solution.

Perhaps the most interesting feature of the ¹H and ¹³C NMR spectra for compounds **2** and **3** is the observation that one of the thme³⁻ ligands shows unusually large differences in the chemical shifts of the β and γ carbons and protons. In the past it has been shown that ¹³C chemical shifts of carbon atoms adjacent to oxygen atoms coordinated to vanadium shift in the following order: C–O_t < C–O_{b-D} < C–O_{b-T}.⁶ Since the chemical shifts for the carbon atoms in two of the thme³⁻ in compound **2** are similar to the chemical shifts of the thme³⁻ in compound **1**, the downfield shifted signals can be attributed to the thme³⁻ coordinated in the O_tO_tO_{b-D} mode. The ¹³C signals of β carbons in thme³⁻ coordinated in the O_tO_tO_{b-D} mode are shifted downfield by 9 ppm in comparison to the other two thme³⁻ substituents in complexes **2** and **3**, which is the largest shift observed so far for a β carbon in a vanadium alkoxide. This work provides a counter example to previously observed greatest coordination induced shifts for carbon atoms adjacent to oxygen atoms bridging with vanadium atoms. The short V–O bond may explain the large observed shift. The chemical shifts for the additional thme³⁻ ligands can be assigned to the two other modes, which reflect great similarity in coordination induced shift. The fact that β and γ carbon atoms in thme³⁻ coordinated in the O_tO_{b-D}O_{b-T} and O_{b-D}O_{b-D}O_{b-T} modes are shifted upfield with respect to free ligand is, however, noteworthy. It appears from these observations that the short V–O bonds in the O_tO_tO_{b-D} mode have a greater effect on electron density of the β carbon than the cumulative effects of several vanadium atoms on bridging oxygen atoms.

Alkoxide Exchange Studies. Simple oxovanadium alkoxides in general show a high level of lability.^{5,9,39,40} The lability can be decreased by using sufficiently large bulky groups around the vanadium atom⁷ however, compounds **1–3** are likely to show some differences in their lability since they contain different alkoxy groups. All three tetramers would form VO(OR)₃ when dissolved in alcohol. However, when dissolved in CHCl₃ compound **2** and **3** were stable and even in the presence of excess alcohol did not revert to VO(OR)₃. It is therefore possible to examine the reactions of compound **2** with 2-propanol and methanol in CHCl₃ in order to determine the solution properties of these types of oxovanadium alkoxides.

The treatment of compound **2** with five equivalents of 2-propanol monitored by ⁵¹V NMR spectroscopy show that signals at –482 and –497 ppm in compound **2** disappear as a function of time while signals at –496 and –514 ppm appear. The latter two signals are characteristic for compound **3**. Since the chemical shifts for these compounds are somewhat sensitive to solvent (and thus the addition of alcohol), several spiking and titration experiments (see ref 41 for detail) were necessary to ensure that the signals correlate. Indeed, we find that the addition of (five or ten equivalents of) 2-propanol to compound **2** in CHCl₃ did show that the chemical shift for this vanadium atom immediately shifts by 2–3 ppm. During the first 50 min after mixing compound **2** and 2-propanol conversion of about 25% of the cluster was observed; at 5 h about 75% had converted (Figure 5), however, it took 24 h before complex **2** had completely converted to **3**. The addition of 10 equiv of ethanol to complex **3** in CHCl₃ generated **2**, thus demonstrating

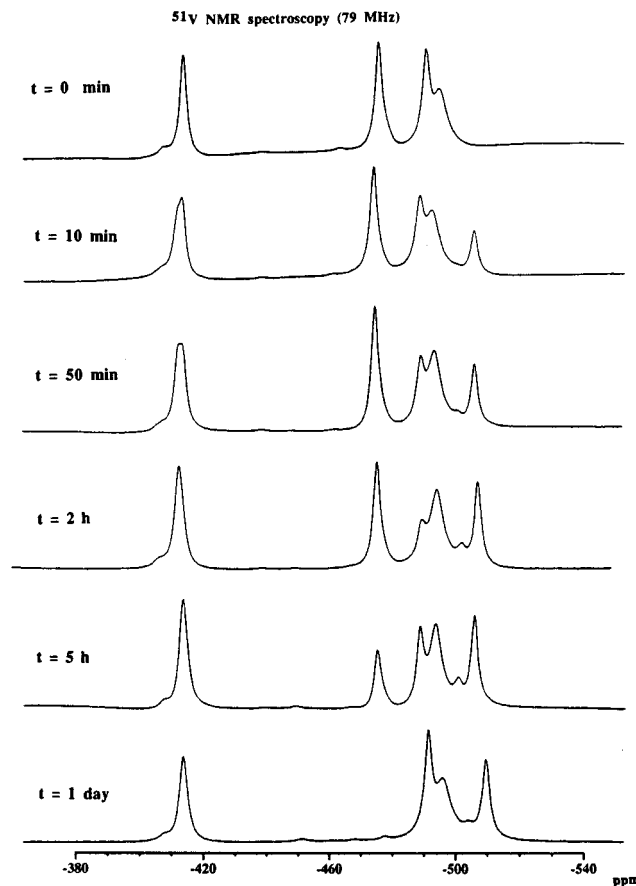


Figure 5. Exchange reaction of [V₄O₄((OCH₂)₃CCH₃)₃(OC₂H₅)₃] (**2**) with 5 equiv of 2-propanol in CDCl₃ monitored by ⁵¹V NMR spectroscopy (79 MHz) at various times: 0 min, 10 min, 50 min, 2 h, 5 h and 24 h.

that the alkoxide exchange reaction was reversible and that the monodentate alkoxide exchanged faster than the thme³⁻ exchange.

Why is the structure of **1** adapted in methanol solution when **2** and **3** form in ethanol and 2-propanol? From the reaction mixtures of compounds **2** or **3** it is clear that more than one oxovanadium alkoxide forms; however, upon isolation all material converts to compounds **2** or **3**. Is it possible that a tetrameric oxometalate containing three thme³⁻ and three CH₃O⁻ ligands (referred to as compound **4**, see Scheme 1) can form? The exchange reactions described above with compound **2** suggest that it may be possible to convert compound **2** to **4** upon treatment with CH₃OH should the latter compound be sufficiently stable. We examined the reaction of **2** with 5 equiv of CH₃OH using ⁵¹V NMR spectroscopy, and the results are shown in Figure 6. Within 1 h of adding CH₃OH to **2** the ⁵¹V NMR signal at –497 ppm converted to a signal at equal intensity at –485 ppm. Incubation of this reaction mixture for 24 h resulted in the conversion of the signal at –482 ppm to a signal at –469 ppm. The signals at –417 and –501 ppm in these solutions did not significantly change consistent with the fact that two vanadium atoms are not directly coordinated to the monoalkoxide. We conclude that these observations are consistent with the formation of a new oxovanadium tetramer containing three thme³⁻ and three CH₃O⁻ ligands, compound **4**.

We also examined the reaction of compound **2** with CH₃OH using ¹H NMR spectroscopy. As shown in Figure 7 two new CH₃O resonances at 5.05 and 5.15 ppm appeared within the first 1 h of the reaction consistent with formation of V–OCH₃ groups. In addition, the signal corresponding to two molecules

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Scheme 1. Proposed Alkoxide Exchange Reactions When $[\text{V}_4\text{O}_4\{(\text{OCH}_2)_3\text{CCH}_3\}_3(\text{OC}_2\text{H}_5)_3]$ (**2**) Is Added to CH_3OH

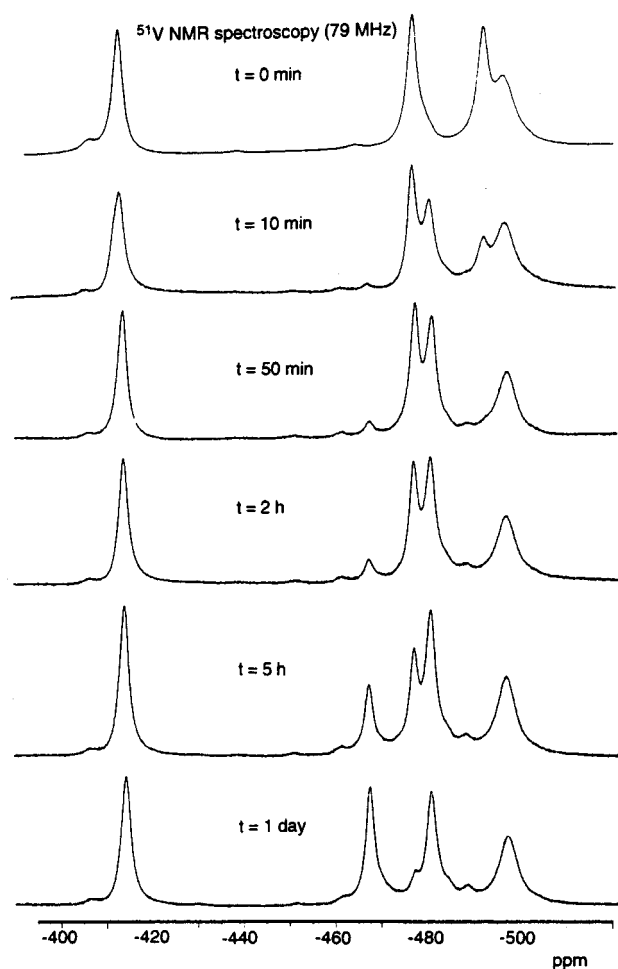
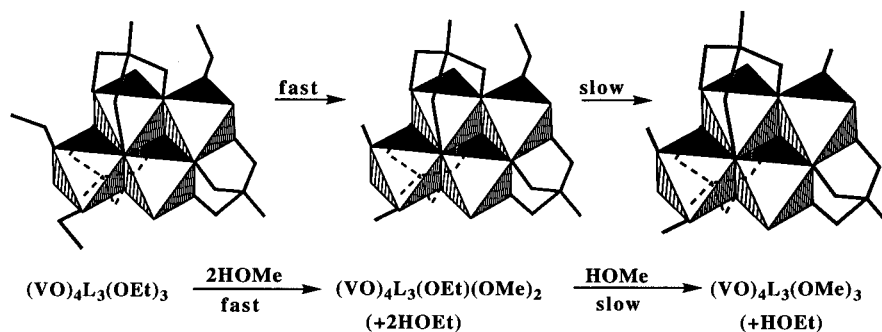


Figure 6. Exchange reaction of $[\text{V}_4\text{O}_4\{(\text{OCH}_2)_3\text{CCH}_3\}_3(\text{OC}_2\text{H}_5)_3]$ (**2**) with 5 equiv of CH_3OH in CDCl_3 monitored by ^{51}V NMR spectroscopy (79 MHz) at various times: 0 min, 10 min, 50 min, 2 h, 5 h, and 24 h.

of free $\text{C}_2\text{H}_5\text{OH}$ appeared. Further incubation of the reaction mixture for 24 h resulted in the disappearance of the $\text{V}-\text{OCH}_3$ groups and formation of three new $\text{V}-\text{OCH}_3$ groups. Additional signals in the spectra and the integration are consistent with the interpretation that two CH_3O^- groups exchange rapidly with two $\text{C}_2\text{H}_5\text{O}^-$ groups and one CH_3O^- group exchange more slowly with one $\text{C}_2\text{H}_5\text{O}^-$ group (Scheme 1). These results are therefore consistent with the interpretation that **4** forms. It appears that the red compound **4** can form from the red compounds **2** and **3** under reaction conditions in which the thm^{3-} ligand is in excess of the ratio found in **1**. The red solutions of compounds **1** and **4** will slowly turn brown in the absence of and rapidly in the presence of water. The fact compound **1** changes color in the absence of water suggests that not only hydrolysis, but also redox reactions are involved

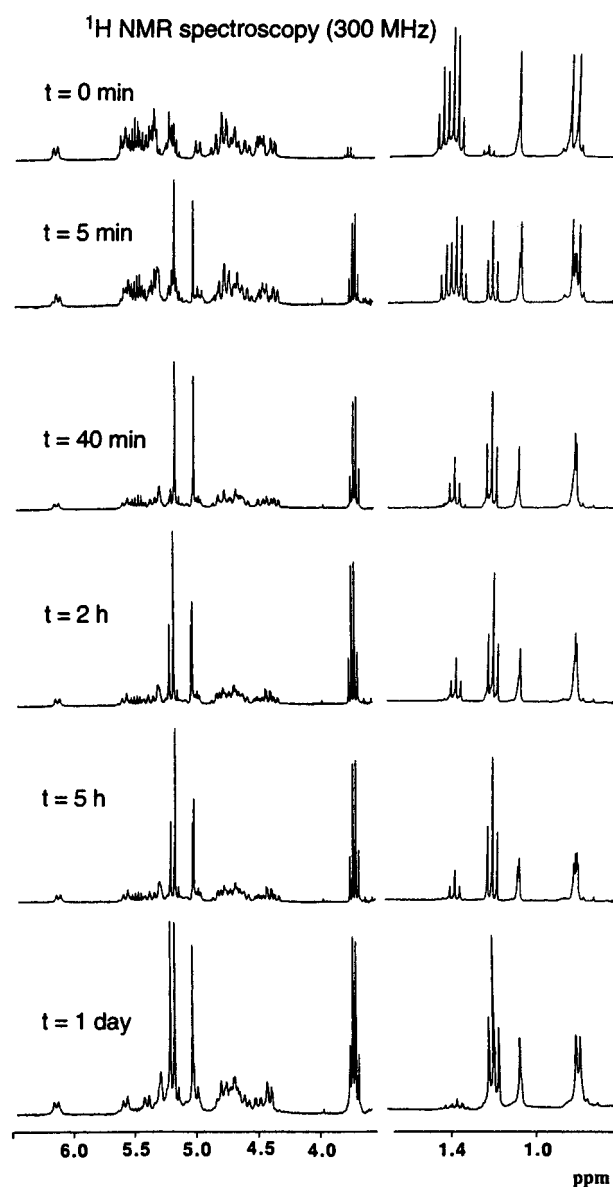


Figure 7. ^1H NMR spectra (300 MHz) monitoring the exchange reaction of $[\text{V}_4\text{O}_4\{(\text{OCH}_2)_3\text{CCH}_3\}_3(\text{OC}_2\text{H}_5)_3]$, **2**, with 5 equiv of CH_3OH in CDCl_3 at various times: 0 min, 5 min, 40 min, 2 h, 5 h, and 24 h.

in these processes. This is consistent with the reported one-electron electrochemical reduction of the red $[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CNO}_2\}_3]^{2-}$ to generate the dark brown $[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CNO}_2\}_3]^{3-}$,^{15,42} or the chemical reduction of this compound using organohydrazines to generate the brown hydroxy-bridged species.^{15,42} Since reaction mixtures for preparation of compounds **2** and **3** show two minor ^{51}V NMR

signals in the chemical shift range of the major signals for compound **1**, it is possible that a minor component of these reaction solutions are compounds with the [V₄O₄(thme)₂(OR)₆] geometry. In summary, the observations reported in this paper suggest that the type of oxovanadium tetramer represented by complex **1** may both be less thermodynamically stable and more redox active than the type of tetramer represented by **4**.

Hydrolysis Studies. Even though compounds **1–3** were not stable when dissolved in water we investigated the hydrolytic stability of **2** in CHCl₃ using ⁵¹V NMR and ¹H NMR spectroscopy. ¹H NMR spectroscopy was particularly useful for these studies at low water concentration since we can monitor the formation of free ethanol. In contrast, ⁵¹V NMR spectra of the hydrolysis products of **2** were not sufficiently separated from the parent compound; the four ⁵¹V NMR signals merely broadened upon hydrolysis. At 25 equiv of H₂O both complex **1** and **2** would hydrolyze quickly, and the resulting solutions contain the green-black precipitates characteristic of hydrolysis and redox reactions. In the presence of 5 equiv of H₂O, **1** would hydrolyze within 1 h, while it would take more than 24 h for complex **2** to hydrolyze. At low water concentration (0.1 and 0.5 equiv of H₂O) complex **2** hydrolyzed very slowly at room temperature. These reactions could furthermore be followed by the color change of the solution, since the red solution turned brown over the course of several days. Since no precipitates formed in these solutions we can infer that a possible hydrolysis product such as [V₄O₄{(OCH₂)₃CCH₃}₃(OC₂H₅)₂(OH)] is soluble in chloroform. This is consistent with the observation of the characteristic signals at 3.65 and 1.22 ppm for the free C₂H₅-OH generated from hydrolyzed complex **2** in ¹H NMR spectrum. NMR signals have previously been attributed to derivatives such as VO(OR)₂(OH) in organic solvents.⁷ Perhaps most importantly, these hydrolysis studies demonstrate the fact that compound **2** is stable for significant periods of time in the presence of small concentrations of H₂O.

Conclusion

Four new oxovanadium(V) alkoxide systems have been prepared representing two new types of oxometalates each of

which were characterized by X-ray crystallography. The complexes were spectroscopically characterized in CHCl₃ solution and were found to maintain the tetranuclear solid state structure. All tetramers contain vanadium atoms in octahedral geometry in a single plane thus outlining a “chair”-like geometry of the V₄O₄-backbone. The rest of the tetranuclear structures are made up by the tridentate ligand thme³⁻ and various monodentate alkoxides which are coordinated to the V₄O₄-backbone. One type of tetramer contains two symmetrically chelated thme³⁻ ligands and the second type contains three thme³⁻ ligands. The latter complexes, represented by [V₄O₈-(thme)₃(OC₂H₅)₃], were found to have an interesting and somewhat unusual structure since the three thme³⁻ ligands are chelated differently to the V₄O₄ backbone. The thme³⁻ ligand chelation modes are O_tO_tO_{b-D}, O_tO_{b-D}O_{b-T}, and O_{b-D}O_{b-D}O_{b-T}; the first coordination mode has not previously been observed for oxovanadium complexes.

In solution [V₄O₄(thme)₃(OC₂H₅)₃] will exchange the ethoxide ligands faster than the thme³⁻ ligands. Interestingly, the two ethoxide ligands exchange more rapidly than the third ethoxide ligand, thus reflecting the very different reactivity of the four vanadium atoms in the tetranuclear complex. In solution [V₄O₄(thme)₃(OC₂H₅)₃] will react with CH₃OH to generate [V₄O₄(thme)₃(OCH₃)₃]. This is of particular interest in view of the fact that the much less stable cluster containing two thme³⁻ and six CH₃O⁻ groups ([V₄O₄(thme)₂(OCH₃)₆]) forms in reaction solutions containing methanol. Furthermore, the reaction mixture generating [V₄O₄(thme)₃(OC₂H₅)₃] contains two additional signals in the ⁵¹V NMR spectrum consistent with the formation of a second cluster containing only two thme³⁻ ligands. These observations are consistent with the interpretation that both tetrameric clusters form in solution and that the redox properties of one may prevent formation of the second despite the greater stability of the latter.

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Supporting Information Available: Tables listing crystal data, experimental parameters, atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters and full structures of **1** and **2** (13 pages). Ordering information is given on any current masthead page.

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- (41) The chemical shift for one vanadium in pure compound **2** is -417 ppm and the corresponding chemical shift for this vanadium in CHCl₃ for pure compound **3** is -414 ppm when referenced against external VOCl₃. The vanadium atoms in question in these compounds were not resolved by ⁵¹V NMR spectroscopy at 79 MHz when both compounds were present in solution. Usually a 3 ppm difference in chemical shifts would have been observed. It is possible that the overlap of these signals is due to solvent shifts (such effects have been reported previously in several organic solvents), see: Rehder, D.; Weidemann, C.; Duch, A.; Pribsch, W. *Inorg. Chem.* **1988**, *27*, 584. Pribsch, W.; Rehder, D. *Inorg. Chem.* **1985**, *24*, 3058.
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