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Vanadium(V)–Protein Model Studies: Solid-State and Solution Structure

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Abstract: The structures of oxovanadium(V) triethanolaminate, **1**, and oxovanadium(V) tri-2-propanolaminate, **2**, have been determined. In each case the V(V) atom exhibits distorted trigonal bipyramidal coordination with the nitrogen atom and the oxo group in the axial positions. The distortion is observed because the vanadium atom is displaced out of the plane of the triethanolaminate oxygens in the direction of the doubly-bonded oxygen. Compound **1** crystallizes in the monoclinic space group $P2_1$ with $a = 7.051(2)$ Å, $b = 7.429(2)$ Å, $c = 7.980(2)$ Å, $\beta = 93.46(3)°$, $V = 417.2(2)$ Å^3, and $Z = 2$. The discrete complex exhibits a V–N bond length of 2.276(1) Å and an average VO(C) bond length of 1.794(3) Å. Compound **2** crystallizes in the hexagonal space group $P6_3$ with $a = 9.465(2)$ Å, $c = 7.493(2)$ Å, $V = 581.3(2)$ Å, and $Z = 2$. The discrete complex exhibits a V–N bond length of 2.297(15) Å and a VO(C) bond length of 1.794(5) Å. The multinuclear solution NMR parameters of **1** and **2** were determined and compared to the parameters for aqueous complexes of vanadate and triethanolamine and vanadate and tri-2-propanolamine, respectively. The results and analyses of these systems lead to structural characterization of the aqueous complexes. ^{13}C NMR and multinuclear NMR studies of related vanadium(V)–peptide complexes should assist in characterizing the coordination chemistry about the vanadium in complexes that resist structural analysis by X-ray diffraction.

Introduction

The existence of vanadium-requiring enzymes and the potent biological activities of vanadium in biological systems have increased the interest in the coordination chemistry of vanadium with protein-like ligands.[1] Some examples of these complexes with vanadium in the +4 oxidation state,[2] and related compounds with vanadium in other oxidation states, have been reported.[3,4] Both +4 and +5 oxidation states are biologically active forms of vanadium—the latter as a cofactor in the haloperoxidases and as an insulin mimetic agent.[1] Structurally characterized vanadium(V) complexes containing amino acid or peptide-like ligands are particularly rare.[5] The lack of structural information extends even to simple compounds such as oxovanadium(V) triethanolaminate (**1**), which has been known for decades[6] and used extensively as a polymerization catalyst.[7] Recently a vanadium(V) complex with *N*-(phosphonomethyl)iminodiacetic acid was found to produce *N*-(phosphonomethyl)glycine (the active agent in the herbicide Roundup) using molecular oxygen as a catalyst.[8] When complexed by such multidentate ligands, vanadium(V) is expected to acquire a pentacoordinate or octhedral geometry, but details of the coordination to vanadium in such cases remain to be determined.[5] Two simple models for vanadium(V)–peptide complexes, oxovanadium(V) triethanolaminate (**1**) and oxovanadium(V) tri-2-propanolaminate (**2**), have been prepared in organic solvents, and their solid-state structures are described in this paper.

Interactions between protein-like ligands and vanadium occurs in aqueous environments under biological conditions. Complexes between vanadium(V) and amino acids, peptides, or protein in aqueous environments may generate materials that cannot be isolated in crystalline form. The rapid exchange reactions that occur between vanadium oxoanions and organic vanadates cause problems when attempting to isolate these materials for structural characterization.[9] Although vanadate–peptide complexes can be much more stable,[10] the possibility for labile complexes with these types of ligands still exists. Since the composition and structure of aqueous complexes are of direct relevance to the mechanism by which vanadium interacts in biological systems, characterization of such complexes is important for understanding the role and mechanism by which vanadium acts. Recent ^{51}V NMR studies have described the composition of several new complexes, but very little information is available on the structure and the coordination about the vanadium in these materials.[10–13] In the present report we compare the structures of an oxovanadium(V) triethanolamine complex, **1**, and an oxovanadium(V) tri-2-propanolamine complex, **2**, which were generated in organic solvents with the corresponding aqueous complexes. The aqueous complexes were previously examined using ^{51}V NMR spectroscopy. On the basis of the chemical shift and the pH-dependent stability of the complex, it was deduced that one arm of triethanolamine (TEA) or tri-2-propanolamine (TPA) is free

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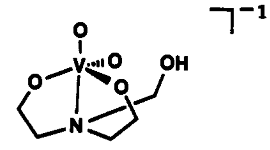
in these complexes.[14] ^{13}C and ^{1}H NMR studies of both complexes in aqueous and organic solutions show different patterns which lead to structural proposals **3** and **4** for the aqueous oxovanadium(V) triethanolamine complex on the basis of a comparison to structure **1**. In structures **3** and **4**, all bonds are represented equally by solid lines, although the V–O bonds are likely to be much stronger than the V–N bond. In these representations we merely show that a bond exists between the atoms but do not make any claims as to the strengths of these bonds. The structural characterization described in this work of **1** and **2** in the solid state and in solution provides a structural basis allowing for the characterization of the solution geometry of vanadium(V) peptide-like complexes using multinuclear NMR spectroscopy.



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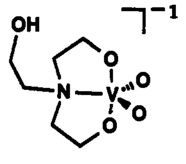

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Experimental Procedures

General Methods. The reagents used in this work were all reagent grade. Chemicals were purchased from Aldrich and dried before use unless stated otherwise. All solvents were dried by standard methods as described by Perrin and Armarego.[15] IR spectra were obtained in KBr pellets on a Perkin-Elmer 1600 FT-IR spectrophotometer. Mass spectra were obtained on a V6-MM 16 spectrometer at 453 K using EI.

Syntheses. Oxovanadium(V) Triethanolaminate, 1. In a 200-mL taper flask, a clear and colorless solution containing triethanolamine (TEA) (0.15 g, 1.0 mmol) was stirred in 100 mL methanol at 298 K. VO(OMe)$_3$ (0.16 g, 1.0 mmol) was added to the flask, and the clear and colorless solution turned golden. After about 10 days of stirring at ambient temperature, a light yellow needlelike crystalline material **1** formed (0.10 g, 0.47 mmol). After filtration and drying the yield was 47%. The compound was characterized as follows: Sublimes at 195 °C; ^{51}V-NMR δ(CD$_3$CN) −380.0 ppm; ^{1}H-NMR δ(CD$_3$CN) 4.56 (2H, triplet), 3.07 (2H, trplet) ppm; ^{13}C{^{1}H}-NMR δ(CD$_3$CN) 75.8, 53.8 ppm; IR (KBr) 2963 (s), 2932 (s), 2870 (s), 1458 (m), 1261 (m) 1056 (vs), 1025 (vs), 956 (vs), 925 (m), 896 (s), 743 (m), 629 (vs), 430 cm^{-1} (m); MS *m/e* 213 (M$^+$), 183 (M$^+$ − OCH$_2$), 153 (M$^+$ − 2OCH$_2$), 139 (M$^+$ − OCH$_2$ − OC$_2$H$_4$), 127 (M$^+$ − OCH$_2$ − NC$_3$H$_6$), 123 (M$^+$ − 3OCH$_2$), 109 (M$^+$ − 2OCH$_2$ − OC$_2$H$_4$), 95 (M$^+$ − 2OC$_2$H$_4$ − OCH$_2$), 81 (VON), 67 (VO), 56 (NC$_3$H$_6$), 44 (OC$_2$H$_4$) 30 (OCH$_2$). Anal. Found (calcd): C, 33.99 (33.82); H, 5.66 (5.68); N, 6.62 (6.57); V, 23.42 (23.90).

Compound **1** could also be prepared using the following procedure. A clear blue solution containing vanadyl acetylacetonate (VO(ACAC)$_2$) (0.265 g, 1.00 mmol) in 20 mL of ethanol was stirred at 298 K. TEA (0.15 g, 1.0 mmol) was added to the solution, which turned green. After stirring of the mixture at ambient temperatures for about 4 days, light yellow needles formed (0.181 g, 0.850 mmol). The yield was 85%. The compound sublimes at 195 °C and was characterized as above.

Oxovanadium(V) Tri-2-propanolaminate, 2. In a 200-mL flask, a clear and colorless solution containing tri-2-propanolamine (0.19 g, 1.0 mmol) (TPA, the commercial mixture of isomers *R,R,R/S,S,S* and *R,R,S* and *S,S,R*) was stirred in 100 mL of methanol at 298 K. VO(OMe)$_3$ (0.16 g, 1.0 mmol) was added to the flask, and the clear and colorless solution turned green. After stirring of the mixture for about 10 days at ambient temperatures, 0.089 g (0.35 mmol) of colorless crystalline needles were formed. The yield was 35%. The compound was characterized as follows: Sublimes at 170 °C; ^{51}V-NMR (CD$_3$CN) −387.0 ppm; ^{1}H-NMR (CD$_3$CN) 4.92 (1H, m), 3.06 (1H, dd), 2.62 (1H, dd), 1.11 (3H, d) ppm; ^{13}C{^{1}H}-NMR (CD$_3$CN) 82.0, 61.2, 20.6 ppm; IR (KBr) 2974 (s), 2927 (s), 2869 (s), 1459 (s), 1373 (s), 1331 (s), 1257 (m), 1128 (vs), 1078 (vs), 1052 (vs), 951 (vs), 921 (m) 658 (vs), 538 (w), 492 (w), 451 (m), 400 (m); MS *m/e* 255 (M$^+$), 225 (M$^+$ − OCH$_2$), 211 (M$^+$ − OC$_2$H$_4$), 181 (M$^+$ − OCH$_2$ − OC$_2$H$_4$), 167 (M$^+$ − 2OC$_2$H$_4$), 153 (M$^+$ − 2OC$_2$H$_4$ − CH$_2$), 139 (M$^+$ − 2OCH$_3$H$_7$), 124 (M$^+$ −2OC$_3$H$_7$ − CH$_3$), 67 (VO). Anal. Found (calcd): C, 41.96 (42.36); H, 7.09 (7.11); N, 5.45 (5.49); V, 20.20 (19.96). A yellow solid would precipitate in about 80% yield upon evaporation of solvent. This material contained two components, compound **2**, the major components as described above, and analogous complexes of the (*R,R,S*) and the (*S,S,R*) isomers of TPA. The ^{51}V NMR chemical shift of the small component is −391.7 ppm.

Table I. Details of the Crystallographic Experiment and Computations for Oxovanadium(V) Triethanolaminate (**1**) and Oxovanadium(V) Tri-2-propanolaminate (**2**)

	1	2
mol formula	C$_6$H$_{12}$NO$_4$V	C$_9$H$_{18}$NO$_4$V
fw	213.1	255.2
cryst system	monoclinic	hexagonal
space group	$P2_1$	$P6_3$
lattice consts		
a, Å	7.051(2)	9.465(2)
b, Å	7.429(2)	
c, Å	7.980(2)	7.493(2)
β, deg	93.46(3)	
V, Å^3	417.3(2)	581.3(2)
Z	2	2
ρ(calcd), g cm^{-3}	1.696	1.458
radiation (λ, Å)	Mo Kα (0.7107)	Mo Kα (0.7107)
abs coeff μ, mm^{-1}	1.16	0.848
2θ range, deg	4.0–50.0	4.0–50.0
no. of unique reflcns	799	372
no. of obsd reflcns	766	368
reflcns criterion	$F > 2.5\sigma(F)$	$F > 2.5\sigma(F)$
R(obsd data)	0.036	0.046
R_w	0.050	0.068

Oxovanadium(V) Diethanol-2-propanolaminate, 5. A 100-mL methanol solution containing *N,N*-bis(2-hydroxyethyl)-2-propanolamine (PDEA) (0.16 g, 1.0 mmol) was stirred at ambient temperatures in a 200-mL tapered flask. VO(OCH$_3$)$_3$ (0.16 g, 1.0 mmol) was added to the solution, which then turned golden. After about 10 days, colorless needle-shaped crystals formed (0.091 g, 0.40 mmol). After isolation the yield was found to be 40%. The compound was characterized as follows: Sublimes at 187 °C; ^{51}V-NMR δ(CD$_3$CN) −384.1 ppm; ^{1}H-NMR δ(CH$_3$CN) 4.95 (1H, m), 4.71 (2H, m), 4.41 (2H, m), 3.05 (5H, m), 2.65 (1H, dd), 1.12 (3H, d) ppm; ^{13}C{H}-NMR δ(CD$_3$CN) 82.3, 75.9, 75.7, 60.4, 55.0, 54.1, 20.6 ppm; IR (KBr) 2971 (m), 2924 (m), 2868 (m), 1471 (m), 1452 (m), 1374 (w), 1317 (w), 1264 (m), 1124 (m), 1080 (s), 1060 (vs), 1029 (s), 997 (m), 954 (vs), 913 (m), 886 (s), 859 (s), 774 (s), 661 (s), 634 (s), 586 (w), 442 (m); MS *m/e* 227 (M$^+$), 197 (M$^+$ − OCH$_2$), 183 (M$^+$ − OC$_2$H$_4$), 167 (M$^+$ − 2OCH$_2$), 153 (M$^+$ − 2OC$_2$H$_4$ − OCH$_2$), 139 (M$^+$ − 2OC$_2$H$_4$), 123 (M$^+$ − 2OCH$_2$ − OC$_2$H$_4$), 109 (M$^+$ − 2OC$_2$H$_4$ − OCH$_2$), 95 (M$^+$ − 3OC$_2$H$_4$), 81 (VON), 67 (VO), 56 (NC$_3$H$_6$), 44 (OC$_2$H$_4$), 30 (OCH$_2$). Anal. Found (calcd): C, 37.02 (36.84); H, 6.21 (6.05); N, 6.17 (6.04); V, 22.42 (22.80).

X-ray Structure Determination of Oxovanadium(V) Triethanolaminate, 1. Clear, pale yellow platelets were recrystallized from a saturated acetonitrile solution by slowly evaporating the solvent at ambient temperature. A clear yellow platelet (0.20 × 0.30 × 0.40 mm) was used for X-ray data collection. Intensity data were collected on a Siemens P4 diffractometer using Mo Kα (λ = 0.7107 Å) radiation. The unit cell constants reported in Table I were determined from a least-squares fit of the setting angles for 25 reflections ($2\theta_{av}$ = 18.07°). Data were collected ($\theta/2\theta$ scans) to $(\sin\theta)/\lambda$ = 0.5947 Å^{-1}, $-8 \le h \le 8$, $-8 \le k \le 0$, and $-9 \le l \le 0$. The intensities of three standard reflections (200, 020, 002) were examined every 97 reflections; no significant changes were noted. Lorentz and polarization corrections were applied. A total of 799 unique reflections were observed, and 766 reflections with $F_o < 2.5\sigma(F_o)$ were used in calculations.

The structure was solved by direct methods using the Siemens SHELXTL PLUS program library.[16] It was refined using full-matrix (108 parameters total, data/parameters = 7.1) weighted [$w = (\sigma^2(F) + gF^2)^{-1}$, $g = 1.2 \times 10^{-3}$] least-squares refinement on F. H atoms were placed in idealized positions (C–H = 0.96 Å, U(H) = 1.2 U_{iso}(C)). All non-H atoms were refined with anisotropic thermal parameters; at convergence (($\Delta/\sigma)_{max}$ = 0.073, $(\Delta/\sigma)_{mean}$ = 0.012 for last cycle)) R =

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Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for Compounds **1** and **2**

	x	y	z	U(eq)^a
		Compound **1**		
V(1)	2006(1)	0	7546(1)	18(0)
O(1)	2076(6)	−2196(8)	7504(5)	33(2)
O(2)	3027(6)	395(5)	9631(5)	31(1)
O(3)	−508(5)	329(6)	7220(5)	27(1)
O(4)	3431(5)	540(5)	5831(5)	25(1)
N(1)	1865(6)	3060(10)	7609(5)	20(1)
C(1)	3554(9)	2145(9)	10188(7)	33(2)
C(2)	2190(9)	3533(8)	9399(7)	29(8)
C(3)	−1385(8)	2037(9)	7422(8)	31(2)
C(4)	−47(8)	3521(8)	6917(7)	28(2)
C(5)	3493(8)	2318(8)	5159(7)	26(2)
C(6)	3375(8)	3679(8)	6555(7)	27(2)
		Compound **2**		
V(1)	3333	6667	2192	21(1)
O(1)	1605(6)	4697(5)	2648(6)	37(2)
O(2)	3333	6667	35(18)	32(3)
N(1)	3333	6667	5257(21)	24(3)
C(1)	2168(7)	4988(7)	5772(9)	32(2)
C(2)	871(9)	4193(9)	4409(12)	41(3)
C(3)	−14(8)	2345(8)	4516(10)	36(3)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Bond Lengths (Å) for Compounds **1** and **2**

	Compound **1**		
V(1)–O(1)	1.633(6)	V(1)–O(2)	1.797(4)
V(1)–O(3)	1.793(4)	V(1)–O(4)	1.792(4)
V(1)–N(1)	2.276(7)	O(2)–C(1)	1.416(8)
O(3)–C(3)	1.425(8)	O(4)–C(5)	1.427(7)
N(1)–C(2)	1.476(7)	N(1)–C(4)	1.466(7)
N(1)–C(6)	1.470(7)	C(1)–C(2)	1.520(9)
C(3)–C(4)	1.522(9)	C(5)–C(6)	1.510(8)
	Compound **2**		
V(1)–O(1)	1.794(4)	V(1)–O(2)	1.617(13)
V(1)–N(1)	2.297(15)	V(1)–O(1A)	1.794(5)
V(1)–O(1B)	1.793(2)	O(1)–C(2)	1.456(10)
N(1)–C(1)	1.462(7)	N(1)–C(1A)	1.462(8)
N(1)–C(1B)	1.461(5)	C(1)–C(2)	1.418(10)
C(2)–C(3)	1.517(10)		

Table IV. Bond Angles (deg) for Compounds **1** and **2**

	Compound **1**		
O(1)–V(1)–O(2)	99.9(2)	O(1)–V(1)–O(3)	99.4(2)
O(2)–V(1)–O(3)	116.7(2)	O(1)–V(1)–O(4)	100.9(2)
O(2)–V(1)–O(4)	117.3(2)	O(3)–V(1)–O(4)	117.0(2)
O(1)–V(1)–N(1)	179.2(2)	O(2)–V(1)–N(1)	80.3(2)
O(3)–V(1)–N(1)	79.8(2)	O(4)–V(1)–N(1)	79.6(2)
V(1)–O(2)–C(1)	121.6(3)	V(1)–O(3)–C(3)	122.5(3)
V(1)–O(4)–C(5)	121.7(3)	V(1)–N(1)–C(2)	104.7(4)
V(1)–N(1)–C(4)	105.4(4)	C(2)–N(1)–C(4)	113.2(5)
V(1)–N(1)–C(6)	105.4(4)	C(2)–N(1)–C(6)	113.8(5)
C(4)–N(1)–C(6)	113.1(5)	O(2)–C(1)–C(2)	110.2(5)
N(1)–C(2)–C(1)	107.3(5)	O(3)–C(3)–C(4)	109.6(5)
N(1)–C(4)–C(3)	107.6(5)	O(4)–C(5)–C(6)	109.7(4)
N(1)–C(6)–C(5)	106.7(5)		
	Compound **2**		
O(1)–V(1)–O(2)	101.0(2)	O(1)–V(1)–N(1)	79.0(2)
O(2)–V(1)–N(1)	180.0(1)	O(1)–V(1)–O(1A)	116.4(2)
O(2)–V(1)–O(1A)	101.0(2)	N(1)–V(1)–O(1A)	79.0(2)
O(1)–V(1)–O(1B)	116.5(2)	O(2)–V(1)–O(1B)	101.0(2)
N(1)–V(1)–O(1B)	79.0(2)	O(1A)–V(1)–O(1B)	116.5(1)
V(1)–O(1)–C(2)	123.4(4)	V(1)–N(1)–C(1)	105.3(6)
V(1)–N(1)–C(1A)	105.3(6)	C(1)–N(1)–C(1A)	113.3(6)
V(1)–N(1)–C(1B)	105.3(6)	C(1)–N(1)–C(1B)	113.3(6)
C(1A)–N(1)–C(1B)	113.3(5)	N(1)–C(1)–C(2)	110.7(7)
O(1)–C(2)–C(1)	108.6(5)	O(1)–C(2)–C(3)	108.9(7)
C(1)–C(2)–C(3)__	112.9(7)		

0.036, $R_w = 0.050$, and $S = 1.04$ ($(\Delta\rho)_{max} = 0.72$ e Å^{-3}, $(\Delta\rho)_{min} = -0.34$ e Å^{-3}). Neutral-atom scattering factors and anomalous dispersion corrections were used.[17] Table II gives the atomic coordinates and equivalent isotropic thermal parameters, while Tables III and IV give bond lengths and angles, respectively. Additional parameters are reported in the supplementary material.

X-ray Structure Determination of Oxovanadium(V) Tri-2-propanolaminate, 2. Structure determination parameters of compound **2** are similar to those of compound **1**, and experimental details are only provided if different from that used for compound **1**. A clear, colorless needle (0.20 × 0.21 × 0.80 mm) crystallized from a methanol solution was used for X-ray data collection. The unit cell constants reported in Table I were determined from a least-squares fit of setting angles for 12 reflections ($2\theta_{av} = 12.70°$). Data were collected ($\theta/2\theta$ scans) to $(\sin\theta)/\lambda = 0.5947$ Å^{-1}, $0 \leq h \leq 9$, $0 \leq k \leq 9$, and $0 \leq l \leq 8$. A total of 374 unique reflections were observed, and 368 reflections with $F_0 > 2.5\sigma(F_o)$ were used in calculations.

The structure was refined using full-matrix (45 parameters total, data/parameters = 8.2) weighted [$w = (\sigma^2(F) + gF^2)^{-1}$, $g = 6 \times 10^{-4}$] least-squares refinement on F. Table II gives the atomic coordinates and equivalent isotropic thermal parameters, while Tables III and IV give bond lengths and angles, respectively. Additional parameters are reported in the supplementary material.

^{51}V, ^{13}C, ^{1}H, ^{51}V, and ^{17}O NMR Spectroscopy. ^{51}V NMR spectra were acquired on a Bruker WPSY spectrometer (4.7 T) at 52.6 MHz and a Brucker ACP-300 NMR spectrometer (7.0 T) at 78.9 MHz. A spectral window of 150 ppm, a 90° pulse angle, and an acquisition time of 0.25 s with no relaxation delay was used. A 15-Hz line-broadening factor was typically applied before Fourier transformation. The spectra were recorded with an external lock, and the chemical shifts were recorded against a $VOCl_3$ reference (at 0 ppm).

^{1}H and ^{13}C NMR spectra were acquired on a Bruker ACP-300 NMR spectrometer (7.0 T) using standard parameters. A 2-Hz exponential line-broadening was applied to the FID before Fourier transformation. The spectra were recorded in deuterated solvents with TMS as an internal standard or in D_2O with DSS as an external standard.

^{17}O NMR spectra were recorded at 40.7 MHz on a Bruker ACP-300 NMR spectrometer (7.0 T) in 5% or 15% ^{17}O-labeled H_2O. The sweep width was 900 ppm, the accumulation time 0.02 s, and the relaxation delay 0.07 s. Standard baseline corrections were used to work up the spectra. No significant change was observed upon integration of spectra recorded with longer relaxation delays.

NMR Sample Preparation. All NMR samples were prepared at room temperature in distilled and dionized water or nondeuterated solvents. Complex, vanadate, and ligand concentrations were varied as needed. If the samples were recorded in water, no significant changes in pH were observed for each solution measured before and after the NMR spectrum had been acquired.

Results and Discussion

Synthesis of Oxovanadium(V) Triethanolaminate (1), Oxovanadium(V) Tri-2-propanolaminate (2), and oxovanadium(V) Diethanol-2-propanolaminate. Preparations of compound **1** and derivatives have been reported previously.[6] We used the reaction of oxovanadium(V) trialkoxides with triethanolamine (TEA) or tri-2-propanolamine (TPA), or *N*,*N*-bis(2-hydroxyethyl)-2-propanolamine (PDEA) in methanol to prepare **1**, **2**, and **5**, respectively. The low yields for formation of **2** can in part be explained by the distribution of TPA isomers described below. We also formed **1** by the reaction of $VO(ACAC)_2$ with TEA. Since $VO(ACAC)_2$ is commercially available and less expensive than any oxovanadium(V) compounds, this approach may be more convenient for laboratory preparations. We prepared compound **5** to examine a derivative with two types of hydroxy-substituted arms.

Structure of Oxovanadium(V) Triethanolaminate, 1. The numbering system and the molecular structure of **1** are shown in Figure 1. The complex exhibits a noncrystallographic C_3 symmetry with the 3-fold axis defined by the V–N bond of the molecule. The amino nitrogen and oxo atoms occupy the axial positions of a trigonal bipyramidal coordination array. The

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(17) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974, Vol. IV.

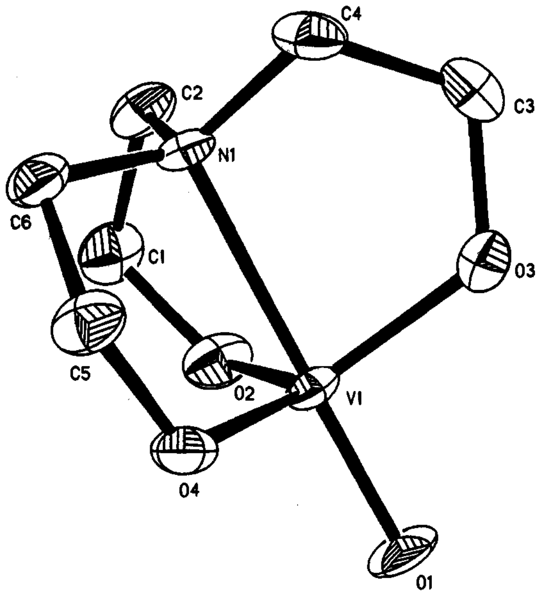

Figure 1. Structure of oxovanadium(V) triethanolaminate, **1**, and its numbering system.

vanadium atom is pulled out of the plane formed by the triethanolaminate oxygen atoms in the direction of the doubly-bonded oxygen by 0.342 Å. The distortion of the trigonal bipyramidal vanadium geometry is thus toward a tetrahedral geometry rather than a square planar geometry. The coordination observed for **1** could therefore in principle also have been obtained by distorting a tetrahedral vanadium atom (with four oxygen atoms) by providing the fifth ligand (the nitrogen atom).

The V–N bond length of 2.276(7) Å trans to the oxo group in structure **1** appears long when compared to V–N bond lengths in other pentacoordinate vanadium complexes. A vanadium(I)–TEA complex has been characterized with a V–N bond of 2.152(5) Å.[3] A dipicolinate complex with a nitrogen in length the equatorial plane, two oxygen ligands in the axial plane, and a VO_2^- unit in the equatorial plane has a V–N bond length of 2.089(6) Å.[4] Bond lengths around 2.3 Å have been observed in complexes with octahedral vanadium(V). In the case of the mixed-valence $[V_2O_3(\text{nitrilotriacetate})_2]^{3-}$ the V–N bond length was 2.297(6) Å and the nitrogen atom was trans to the oxo group (very similar to the configuration **1**).[18a] Other complexes with V–N bond lengths around 2.25 Å and up to 2.40 Å have the oxo atom cis to the nitrogen atom.[18,19] The distance of 1.79 Å observed for the V–O bonds is however within the range of that expected for V–O bonds as defined by V–O bond lengths reported in the literature.[20] After submission of this work for publication, it came to our attention that a related compound, $V(O)[N(CH_2CHC(CH_3)_3O)_3]$, had been structurally characterized with similar geometry.[21]

Solution Studies of Oxovanadium(V) Triethanolaminate. The solution structure of **1** was examined for comparison to the aqueous TEA complex, which has previously been described.[14] ^{51}V, ^{13}C, and ^{1}H NMR spectroscopy was used to characterize **1** dissolved in CD_3CN. The chemical shift differences in the ^{13}C and ^{1}H NMR spectra upon complexation are shown in Table V. The 1.3 and 15.7 ppm downfield shifts of the CH_2O protons and carbon, respectively, upon complexation suggest a strong bond between the O and the V. The 0.5 and −3.8 ppm downfield shifts of the CH_2N protons and the carbon, respectively, indicate a weak interaction between the N and the V. The solution structure therefore mimics the structure in the solid since the VO(C) bonds are of normal length and the V–N bond is long and weak. The NMR signals were sharp, and variable-temperature studies showed no evidence of inter- or intramolecular ligand exchange in **1** at ambient temperatures. We conclude that the structure of **1** in CH_3CN is similar to the structure in solid state.

The analogous spectroscopic parameters for the aqueous complex,[14a] in which one ethanol arm is free and the overall charge is −1, were obtained and are shown in Table V for comparison with the shifts for **1**. The aqueous complex shows a similar shift for the bound protons and carbon in CH_2O of 0.6 and 12.1 ppm, respectively. However, the carbon in the bound CH_2N is shifted to a higher frequency by 4.6 (+4.6) ppm, whereas the carbon in the free CH_2N is shifted to lower a frequency of 6.7 (−6.7) ppm. The analogous shifts for the protons are 0.2 and 0.6 ppm. In addition, this complex shows the intramolecular ligand exchanges in solution on the ^{13}C NMR time scale at elevated temperatures.[14b] Since the chemical shifts in the ^{51}V, ^{13}C, and ^{1}H spectra are significantly different in the aqueous complex compared to **1** dissolved in CH_3CN or methanol, some significant structural changes occur when **1** is converted to the aqueous complex. The spectroscopic observations suggest the VO(C) bonds in the bound ethanol arms in the aqueous complex may be longer than observed for **1**. The V–N bond is expected to be significantly shorter in the aqueous complex than in **1**. Two reasonable structural possibilities are shown in **3** and **4**. Both structures are consistent with the observed coordination induced shifts (CIS).[22] Structure **4** would be expected, should these types of complexes follow Bent's rule. The ^{13}C CIS reversal between the aqueous complex and **1** is then attributed to the substitution of an OR with an O^- group and a presumed change in coordination about the vanadium toward the ideal trigonal bipyramidal structure. Structure **3**, on the other hand, is consistent with the V–N bond in an axial position as observed by X-ray for **1**.

The structure for the aqueous TEA complex was previously suggested to be **3** on the basis of the ^{51}V NMR and UV spectroscopic studies of aqueous solutions containing the complex. Although **3** was drawn with a pentacoordinate vanadium, the possibility that an extra water molecule is associated with the vanadium was not excluded at the time.[14a] Even given the X-ray structures for **1** and **2**, it is still not possible to exclude the possibility that the aqueous complex contains octahedral vanadium without further characterization. We therefore resorted to ^{17}O NMR studies.

Potentially ^{17}O NMR studies could not only distinguish between structures **3** and **4** but also address the possibility whether the aqueous complex contains octahedral vanadium. Complexes between vanadate and related multidentate ligands were found to form with a second-order rate constant around 10^{-4} M^{-1} s^{-1}.[23,24] It would therefore be reasonable to expect that the aqueous vanadate complexes with TEA or TPA would also form with similar rate constants. This expectation has been experimentally confirmed and will be described elsewhere.[14b] Since the rate of formation is similar to the rate of exchange of the terminal oxo (with water) in the vanadium complex,[23,24] the two terminal oxo atoms in **3** would be recognized as different oxygen atoms on the time scale of the ^{17}O NMR experiment. ^{17}O NMR spectra of complex **3** would have two signals with quite different chemical

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(18) (a) Nishizawa, M.; Hirotsu, K.; Ooi, S.; Saito, K. J. *Chem. Soc., Chem. Commun.* **1979**, 707–8. (b) Ogino, H.; Shimoi, M.; Saito, Y. *Inorg. Chem.* **1989**, *28*, 3596–600. (c) Launay, J.-P.; Jeannin, Y.; Daoudi, M. *Inorg. Chem.* **1985**, *24*, 1052–9. (d) Kojima, A.; Okazaki, K.; Ooi, S.; Saito, K. *Inorg. Chem.* **1983**, *22*, 1168–74.

(19) (a) Scheidt, W. R.; Collins, D. M.; Hoard, J. L. *J. Am. Chem. Soc.* **1992**, *93*, 3873–7.

(20) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244–7.

(21) Nugent, W. A.; Harlow, R. Personal communication. Selected structural parameters (Å and deg) for $V(O)[N(CH_2CHC(CH_3)_3O)_3]$ are V═O (1.612(2)), V–N (2.269(3)), V–O(C) (1.810(2), 1.803(2), 1.799(3), ∠OVN (179.5(7)), ∠O(C)VN (79.2(1), 79.0(1), 78.6(1), ∠OVO(C) (101.0(1), 101.3(1), 100.9(1)), and ∠O(C)VO(C) (113.6(1), 117.1(1), 118.6(1)).

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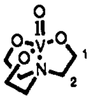
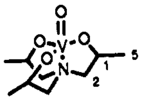
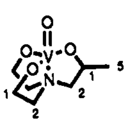
Table V. CIS Shifts upon Complexation of TEA, TPA, and PDEA to Vanadium(V) in Organic (CD_3CN) and Aqueous Solution[a]

	C^1		C^2		C^3 (free arm)		C^4 (free arm)		C^5	
compd	$\Delta\delta(^{13}C)$	$\Delta\delta(^{1}H)$	$\Delta\delta(^{13}C)$	$\Delta\delta(^{1}H)$	$\Delta\delta(^{13}C)$	$\Delta\delta(^{1}H)$	$\Delta\delta(^{13}C)$	$\Delta\delta(^{1}H)$	$\Delta\delta(^{13}C)$	$\Delta\delta(^{1}H)$
 1	15.7	1.3	−3.8	0.5						
aq oxovanadium(V) TEA complex[b]	12.1	0.6	4.6	0.2	+1.6	0.2	−6.7	0.6		
 2	16.3	1.2	−5.7	0.6/0.2					−0.1	0.1
aq oxovanadium(V) TIP complex[c]	11.4/10.8	0.85/0.73	4.2/3.5	1.24/0.90 −0.27/−0.34	1.1	0.44	−4.3	0.72	2.4	−0.2 0.1/0.2
 5	11.5 11.7 17.0	0.9 1.1 1.2	−4.1 −3.3 0.1	0.6 0.7 0.4/0.0					−0.1	0.1
aq oxovanadium(V) PDEA complex[d]	14.5 13.8		6.1 4.6		1.5		−4.0		−0.2	

[a] The chemical shift differences are all in ppm and the spectra recorded at ambient temperatures unless noted otherwise. [b] The sample contained 400 mM vanadate, 600 mM TEA, and 10% D_2O at pH 8.99 (±0.05). The concentration of vanadate TEA complex was 250 mM. [c] The sample contained 500 mM vanadate, 1.50 M TPA, and 10% D_2O at pH 9.50 (±0.05). The concentration of vanadate TPA complex was 420 mM. [d] The sample contained 200 mM vanadate, 300 M PDEA, and 10% D_2O at pH 7.95 (±0.05). The concentration of vanadate PDEA complex was 173 mM. The spectrum was recorded at 273 K.

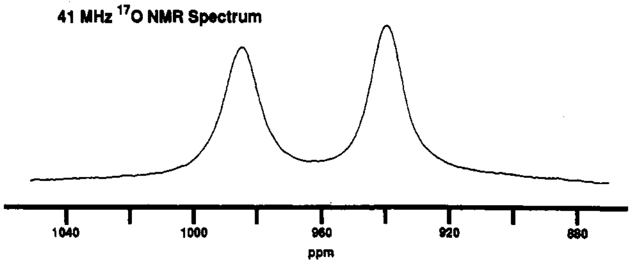


Figure 2. 41-MHz ^{17}O NMR spectrum of a solution containing 600 mM TPA, 200 mM vanadate, and 15% $H_2{}^{17}O$. The solution contains 170 mM complex and 30 mM vanadate oligomers. A section (from 870 to 1050 ppm) of the ^{17}O NMR spectrum with the complex resonances is shown.

shifts for the terminal-vanadium oxygen atoms whereas complex **4** would only have one resonance. A sample containing 5% ^{17}O-enriched H_2O, 250 mM TEA, or two resonances with very similar chemical shifts and 50 mM vanadate, which according to the ^{51}V NMR spectrum contain 90% of the vanadium as complex and 10% as vanadate oligomers, was examined. The ^{17}O-spectrum shows two signals from the complex (at 954 and 980 ppm), and they were of equal intensity. The ^{17}O NMR spectrum for the analogous aqueous complex of tri-2-propanol with vanadate (the two complex resonances are at 940 and 985 ppm) is shown in Figure 2. These spectra support a complex with the structure shown in **3**. A spectrum with two signals of equal intensity rules out an octahedral complex because such a complex would contain three terminal oxo or hydroxy ligands and results in one of the following spectra: (a) a two-to-one ratio between the intensities of two resonances, (b) only one resonance, or (c) three resonances. We therefore conclude that the solution structure of these complexes are shown in **3**.

The observed trend in the CIS changes of the carbons adjacent to the oxygen atoms described here are compared to the trend in a series of oxovanadium trialkoxides. $VO(OCH_3)_3$[24] and $VO(OCH_2CH_2Cl)_3$[25] are known to associate in solution at high concentrations;[25,26] nevertheless, their CIS of 21.7 and 19.6 ppm reflects the strong interactions between the vanadium atom and the alkoxide ligand. Each of these compounds has one long and two short V–O(C) bonds in the solid state; for the $VO(OCH_3)_3$ they are 2.04(6) Å and 1.84(5)/1.78(5) Å, and for $VO(OCH_2CH_2Cl)_3$ they are 1.857(1) Å and 1.771(2)/1.763(2) Å. In solution only one type of carbon is observed, presumably reflecting the exchange in these systems. More bulky alcohols such as in oxovanadium(V) tri-*endo*-norborneol, oxovanadium(V) tri-*exo*-norborneol and oxovanadium(V) tri-2-adamantanol induce slightly smaller ^{13}C CIS of 18.9, 19.0, and 19.4 ppm, respectively.[26] With the exception of the $VO(OCH_3)_3$, all the above complexes are believed to contain vanadium with a coordination number lower than six.[27,28] The CIS of oxovanadium(V) tri-*tert*-butyl alcohol and oxovanadium(V) tri-1-adamantanol were both found to be 15.5 ppm. Since these are the two oxovanadium(V) trialkoxides that are most likely to contain tetrahedral vanadium,[28] it is interesting that the CIS is smaller than for the other derivatives. These observations suggest association and coordination induce CIS to a certain magnitude. Large ^{13}C CIS are observed for vanadium complexes with geometries intermediate between trigonal bipyramidal and tetrahedral and for vanadium complexes with trigonal bipyramidal or octahedral geometries. The heteroatom (nitrogen), the negatively-charged oxygen atoms, the specific coordination around the vanadium, and association with other molecules may also affect the observed CIS. We recommend that all such possibilities be considered when examining the structures of complexes in solution.

Reactions of Oxovanadium(V) Triethanolaminate, 2. Compound **1** was stable at ambient temperature, but when the solid was exposed to air, it would slowly turn yellow over time. The complex was stable in CH_3CN in the presence of 10 equiv of water for a period of weeks. However, when dissolved in water (at pH ~5), the complex hydrolyzed to form the aqueous TEA complex and vanadate oligoanions.

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(26) Priebsch, W.; Rehder, D. *Inorg. Chem.* **1990**, *29*, 3013–9.

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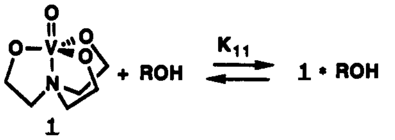
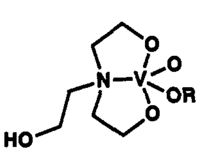
Dissolving compound **1** in methanol gives rise to three complexes as found by ^{51}V NMR spectroscopy. The major complex is **1** at −380 ppm, the second complex at −554 ppm is oxovanadium(V) trimethoxide, and the third complex at −413 ppm is presumably a reaction product between methanol and **1**. This expectation was confirmed by examining the reaction **1** with ethanol, 2-propanol, and *tert*-butyl alcohol. The reaction of **1** with ROH, as shown in eqs 1 and 2, generates solutions with three signals:



(1)

$$1 \cdot ROH + 2ROH \overset{K_{12}}{\rightleftharpoons} VO(OR)_3 + TEA \qquad (2)$$

1, the particular oxovanadium(V) trialkoxide, and a third complex with chemical shifts of −426 ppm (in ethanol), at −447 ppm (in 2-propanol), and −479 ppm (in *tert*-butyl alcohol). The intermediate complex is an adduct between **1** and one molecule of alcohol and presumably maintains the stable vanadate–diethanolamine component in its structure. Possible structures for the **1**·ROH complex with one free ethanol arm are shown in **6** and **7**. These two structures contain pentacoordinate vanadium and



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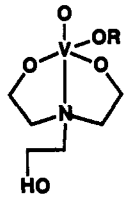

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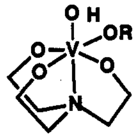

8

a V–N bond which is equatorial or axial, respectively. Analogous structures can be proposed that contain octahedral vanadium in **8**. The small formation constant (see below and Table IV) of the **1**·ROH complex with all four alcohols examined prevented characterization of ^{13}C NMR spectroscopy. The ^{51}V NMR chemical shift of −413 ppm for the **1**·CH_3OH complex is consistent with both octahedral and pentacoordinate complexes. We also measured the line width at half-height for these new complexes and found they increased rapidly. As described elsewhere, broad line widths are most consistent with complexes containing octahedral vanadium.[14b]

The equilibrium constant for the formation of **1**·ROH was calculated on the basis of the integrations in the ^{51}V NMR spectra. Only saturated concentrations of **1** were used for these measurements because the limited solubility of **1** (about 5 mM in methanol) prevented the use of an appropriate concentration range. These measurements are further complicated by the decreasing solubility of **1** as the bulk of the alcohol increase. The constants given in Table V were, however, obtained by approaching the equilibrium in solutions with compound **1** and in solutions of equimolar amounts of $VO(OR)_3$ and TEA. The formation constants of **1**·ROH increase in the series methanol, ethanol, and 2-propanol and then decrease with *tert*-butyl alcohol. The reactions attempting to generate $VO(OR)_3$ from **1** in various alcohols suggest that the complex **1**·ROH may be sensitive to steric hinderance. Sensitivity to sterically hindered alcohols is most consistent with the 1-ROH complex containing octahedral vanadium (**8**).

Structure of Oxovanadium(V) Tri-2-propanolaminate, 2. The numbering system and the molecular structure of **2** are shown in Figure 3. Compound **2** exhibits crystallographic C_3 symmetry with the 3-fold axis defined by the V–N bond of the molecule. The nitrogen and terminal oxo atoms are axial in the trigonal bipyramidal coordination sphere. The V═O bond length is 1.617(13) Å, and the V–N bond length is 2.297(15) Å. These parameters are indistinguishable from those observed for **1** within experimental uncertainty and similar to the corresponding parameter for $V(O)[N(CH_2CHC(CH_3)_3O)_3]$.[21] The unique V–O(C) bond length is the same as that for **1** at 1.794(4) Å, and the bond angles are very similar to those observed for **1**. The vanadium is again distorted away from a tetrahedral geometry toward a trigonal bipyramidal geometry as the vanadium atom is pulled out of the plane of the tri-2-propanolamine oxygen atoms in the direction of the doubly-bonded oxygen by 0.342 Å (as in **1** and in $V(O)[N(CH_2CHC(CH_3)_3O)_3]$[21]).

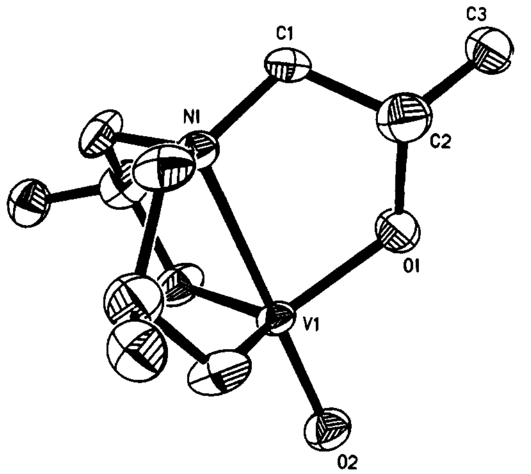

Figure 3. Structure of oxovanadium(V) tri-2-propanolaminate, **2**, and its numbering system.

Solution Studies of Oxovanadium(V) Tri-2-propanolaminate, 2. The reactions were carried out as described for oxovanadium(V) triethanolamine with the complication that the TPA preparation consists of a mixture of isomers: the enantiomeric pair of *R,R,R* and *S,S,S* and the enantiomeric pair of *R,R,S* and *S,S,R* of the ligand. On the basis of the ^{13}C NMR spectra, it appears that the *R,R,S*/*S,S,R* isomer constitutes about 60% of the sample. These assignments were made by analyzing INEPT, HETCOR, and ^{13}C spectra of ligand and hydrolyzed **2**. The X-ray structure was solved, and Figure 3 shows the structure of oxovanadium(V)–(*S,S,S*)-tri-2-propanolamine. The minor component, the oxovanadium(V) complex of the *R,R,S*/*S,S,R* isomer, was only observed when the product of the reaction was precipitated as a powder.

The chemical shift differences upon complex formation are reported in Table V. As in the case of **1**, the shifts 1.2 and 16.3 ppm for the CH_2O protons and carbons suggest the VO bond is strong. This is in contrast to the shifts of 0.6, 0.2, and −5.7 ppm for the CH_2N protons and carbons suggesting the V–N bond is even longer than that in **1**. We conclude that, in complex **2**, the ligand is coordinated to the vanadium in a tetradentate manner analogous to that observed for **1** by X-ray crystallography.

Given the chiral nature of the ligand, the potential to characterize the aqueous complex is even greater than in the case of triethanolamine. A solution containing 1.5 M TPA and 500 mM vanadate generates a solution containing 420 mM of the aqueous complex. The ^1H NMR is quite complex given that the two propanol arms attached to the vanadium are different from each other as well as the free arm. A drawing of the complex indicating the chemical shifts of each proton and the specific coupling patterns is shown in Figure 4. The ^{17}O NMR spectrum of a sample containing ^{17}O-enriched H_2O ligand and vanadate shows two signals of equal intensity for the complex (Figure 2). This ^{17}O-NMR spectrum shows that the aqueous complex has a structure analogous to **3**.

Given the experimental uncertainties, the V–N, V–O(C), and V═O bonds in compounds **1** and **2** were indistinguishable by

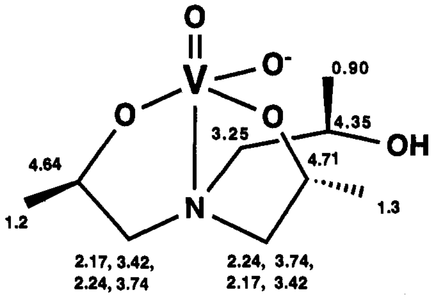

Figure 4. Proposed structure of the aqueous oxovanadium(V) tri-2-propanolaminate complex with indicated chemical shifts in the ^{1}H NMR spectrum.

X-ray crystallographic in the solid state. Spectroscopic studies in solution suggest, however, that the V–N bond in **2** is longer than the V–N bond in **1**. Although structural changes may have occurred upon dissolution, it is also possible that NMR spectroscopy is more sensitive to small structural changes than X-ray crystallography in these molecules. This is confirmed by IR characterization of the solids, which shows that the estimated V–N stretches for **1** (about 430 cm^{-1}) shifted to about 400 cm^{-1} for compound **2**. Such shifts would correspond to a difference in V–N bond length of about 0.03 Å, which is within the experimental uncertainties in the X-ray crystallographic determination of the V–N bond length in compounds **1** and **2**. Spectroscopic studies therefore appear to be very sensitive to the change in bond lengths and geometric arrangements around the vanadium in these materials.

Reactions of Oxovanadium(V) Tri-2-propanolaminate, 2. Compound **2** is, like compound **1**, fairly stable but will eventually hydrolyze when exposed to air. The reaction of **2** with various alcohols was explored as described above for compound **1**. The dissolution of **2** in methanol generates $VO(OCH_3)_3$ and a complex at −418 ppm. In ethanol $VO(OCH_2CH_3)_3$ is formed as well as a complex at −432 ppm. On the basis of the chemical shifts, we presume these materials are $\mathbf{2}\cdot CH_3OH$ and $\mathbf{2}\cdot CH_3CH_2OH$. The line widths at half-height for these complexes are 470 and 420 Hz, which compares to the line width of the V–TPA complex of 100 Hz. No complexes were formed in 2-propanol and *tert*-butyl alcohol. Given the larger steric bulk in **2**, approach of incoming alcohols would be particularly difficult if the complex were of the type described by structure **8**. It was therefore interesting that the reaction of **2** with $HOCH_3$ or $HOCH_2CH_3$ generates the alcohol adduct but with significantly more difficulty than **1** (Table VI).

The reactions of **1** and **2** with alcohols to generate **1**·ROH and **2**·ROH, respectively, is of interest for several reasons. First of all, the increased stability of the complex in an alcoholic or aqueous environment supports results suggesting that such arrangements will be stable inside a protein. Second, the partial reaction provides chemical evidence for the types of reactions the vanadium will support in for example the bromperoxidases.[29] In the presence of CH_3OH or CH_3CH_2OH both **1** and **2** will form the adduct which presumably contains TEA or TPA as well as one molecule of the alcohol. Reasonable structures for such complexes contain either pentacoordinate or octahedral vanadium and have been shown in **6**–**8**. The adduct was only characterized by ^{51}V NMR since the formation constant was not sufficiently favorable for other types of characterizations. However, the fact that no adduct formed between the more sterically congested **2** and 2-propanol or *tert*-butyl alcohol and the broad line widths would support the formation of an adduct containing octahedral vanadium.

Solution Structure of Oxovanadium(V) Diethanol-2-propanolaminate, 5, and Corresponding Aqueous Complexes. The reaction of *N,N*-bis(2-hydroxyethyl)-2-propanolamine (PDEA) with $VO(OCH_3)_3$ in methanol formed **5**. The solution structure of **5** was explored to examine the effects of one methyl group substitution. The CIS values are given in Table V. The substitution breaks the symmetry of the two ethanolamine arms in **5**, and the ^{13}C and ^{1}H NMR show such asymmetry. Indeed, two resonances were observed for the carbons in the ethanolamine arms. In both cases, the C1 CIS was above 10 ppm (11.5 and 11.7 ppm) and the C2 CIS was negative (−4.1 and −3.3 ppm). This pattern was also observable for the 2-propanol substituent since the C1 has a CIS of 17.0 and the C2 CIS was 0.1 ppm. It is, however, interesting to note that the C1 CIS in the ethanol arms are less than that for the TEA complex suggesting the V–O(C) bond in complex **5** may be stronger than those in complexes **1** and **2**. Furthermore, it appears that the V–N bond in complex **5** is between those of complexes **1** and **2**.

The aqueous complex (173 mM) forms in a solution containing 200 mM vanadate and 300 mM PDEA at pH 7.97 (±0.05). In the aqueous complex, one ethanol arm is free whereas the other ethanol and the 2-propanol arms are attached to the vanadium. The CIS for the C1 carbons are a few ppm higher than the aqueous complexes of TEA and TPA suggesting that these bonds may be stronger than the other complexes. Since the C2 CIS is −4.1 ppm, it is possible the V–N bond is weaker than the TPA complex and stronger than the TEA complex. The IR spectrum shows a V–N absorbance between that of the two other complexes and supportive of the solid-state structure between that of **1** and **2**. These results are consistent with the structural expectations defined by complexes **1** and **2** and support the conclusions derived from the application of NMR spectroscopy to examine solution structures of the oxovanadium(V) complexes.

Implications of These Model Studies to Interactions of Vanadium with Proteins. The triethanolamine and tri-2-propanolamine ligands are different from that of any peptides in that the nitrogen is not an amide nitrogen and that one hydroxyl group will be substituted with a terminal amine or amide group depending on the length of the peptide. Complexes of peptides and metal ions have been characterized in detail for other metal ions including Cu^{2+}, Ni^{2+}, and Zn^{2+}.[30,31] The substitution of the nitrogen with an amide nitrogen will stabilize a vanadium complex significantly,[10] and if the nitrogen is coordinating in the equatorial plane, the V–N bond is likely to be short. Although vanadium(V) does not generate structures with the vanadium in a square pyramidal arrangement as often as vanadium(IV), many oxovanadium(V) complexes show geometries intermediate to these two structures.[2,5] The vanadiums in **1** and **2** are in a distorted trigonal bipyramidal geometry, but the distortion is not toward square pyramidal geometry. The distortion observed in compounds **1** and **2** comes about by taking tetrahedral vanadium and bringing in one more ligand.

The substitution of one CH_2O group with a COO group in the ligand is expected to reduce the preference for the trigonal bipyramidal geometry and generate a complex containing octahedral vanadium.[14b] The oxovanadium(V) peptide complexes are therefore likely to be different from complexes **1** and **2**. The dramatic CIS shifts in compounds **1** and **2** compared to the aqueous complexes may be associated with changes in the geometry about the vanadium, and somewhat smaller changes may be observed with vanadium(V)–peptide complexes if similar coordination about the vanadium is observed.

Nevertheless, the studies shown here suggest that ^{13}C NMR spectroscopy in particular will be an effective tool to explore the coordination geometry of oxovanadium complexes. If indeed the amide nitrogen will coordinate in an equatorial position, one would expect that the adjacent carbon atoms will exhibit larger CIS than the carbon atoms adjacent to the axial ligands. Although the magnitude of the CIS still remains to be determined, the pattern expected has been defined by compounds **1** and **2** and

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Table VI. Equilibrium Constants for Formation of **1**-ROH (K_{11}) and **2**·ROH (K_{12}) Adducts and the Resulting Alcoholysis Reactions (K_{21} and K_{22})

alcohol	$\delta_{1\cdot ROH}$, ppm	$\Delta\delta_{1\cdot ROH}$[a]	K_{11},[b] M^{-1}	$\delta_{2\cdot ROH}$, ppm	$\Delta\delta_{2\cdot ROH}$[a]	K_{12},[c] M^{-1}	K_{21},[d] M^{-1}	$10^5 K_{22}$,[e] M^{-1}
CH_3OH	−413	95 (±10)	0.17	−418	455 (±15)	0.036	6×10^{-5}	1
CH_3CH_2OH	−426	265 (±15)	0.27	−432	405 (±15)	0.057	4×10^{-3}	6
$(CH_3)_2CHOH$	−447	225 (±15)	0.52	NOF[c]			3×10^{-3}	
$(CH_3)_3COH$	−479	195 (±20)	0.40	NOF[c]			2×10^{-2}	

[a] The $\Delta\delta$ values under these conditions are the following: V–TEA (65 ± 5 Hz), VP–TPA (95 ± 10 Hz), $VO(OCH_3)_3$ (95 ± 10 Hz), $VO(OCH_2CH_3)_3$ (32 ± 3 Hz), $VO(OCH(CH_3)_2)_3$ (16 ± 2 Hz), $VO(OC(CH_3)_3)_3$ (10 ± 2 Hz). [b] K_{11} = [**1**·ROH]/[**1**][ROH]; repeated measurements give K_{11} with ±0.03 M^{-1}. [c] K_{12} = [**2**·ROH]/[**2**][ROH]; repeated measurements give K_{12} with ±0.005 M^{-1}. [d] K_{21} = $[VO(OR)_3][TEA]/[\mathbf{1}\cdot ROH][ROH]^2$. [e] K_{22} = $[VO(OR)_3][TPA]/[\mathbf{2}\cdot ROH][ROH]^2$. [f] NOF = no observed formation of complex *2*·ROH by ^{51}V NMR spectroscopy.

their corresponding aqueous complexes. The results described here suggest that the coordination geometry in related vanadium(V)–peptide complexes can effectively be explored using these spectroscopic methods.

The formation of the complexes **1**·ROH and **2**·ROH from **1** and **2** is also very interesting, supporting the possibility that similar types of complexes can form inside proteins. It is possible that the catalytic role of the enzyme is related to the ability of the vanadium to change coordination number in an enzyme environment.

Conclusion

The structure of oxovanadium(V) triethanolaminate, **1**, and oxovanadium(V) tri-2-propanolaminate, **2**, was solved and shows distorted trigonal bipyramidal vanadium with the nitrogen and the oxo atoms in axial positions. The spectroscopic properties of both complexes were examined, and their solution structures in CH_3CN are identical to that observed in the solid state. The V–TEA and V–TPA complexes can increase their coordination number by binding an additional alcohol group. Such complexes demonstrate the ability of the vanadium to change coordination number in environment such as that found inside a protein. The spectroscopic studies were compared to analogous studies with aqueous complexes of vanadate and TEA or TPA. The CIS values provided evidence that the V–N bonds in the aqueous complexes were shorter than those in **1** and **2** and that the aqueous complexes are distinct from both **1** and **2**. The aqueous complexes contain a free arm and an overall −1 charge. The possibility that the N-atom may be an equatorial substituent in these complexes was explored but discarded. The aqueous complexes contain a nitrogen atom in axial position (**3**) and two different terminal oxygen atoms (an oxo and a $-O^-$). Oxygen-17 NMR spectroscopy furthermore provides evidence to rule out octahedral coordination in these complexes. CIS shifts ad IR absorbance bands of related vanadium(V)–peptide complexes could assist in characterizing the coordination about the vanadium in complexes resisting characterization by X-ray analysis.

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Supplementary Material Available: Tables containing parameters describing the crystallographic experiment, anisotropic displacement coefficients, H-atom coordinates, and isotropic displacement coefficients (3 pages). Ordering information is given on any current masthead page.