Inorg. Chem. **1992**, *31*, 4939–4949

Oxovanadium(V) 1,3-Propanediolate Chloride Complexes: Tetrameric Clusters

Debbie C. Crans,* Robert W. Marshman, Miri Shaia Gottlieb, Oren P. Anderson, and Mary M. Miller

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

Received May 8, 1992

The structure of the reaction product of $VOCl_3$ and various 1,3-propanediol derivatives was characterized in solution at various temperatures using multinuclear NMR spectroscopy. Although oxovanadium dialkoxide chlorides tend to be monomeric, 1,3-propanediol derivatives induce cluster formation generating tetrameric complexes with a molecular formula of $(VOClL)_4$ (where L is bidentate). The 1,3-propanediol derivatives preferred to bridge over two (or three) vanadium atoms rather than form a cyclic six-membered ring on one vanadium atom as found with the corresponding phosphorus compounds. When the 1,3-propanediol ligand was asymmetric, several complexes were observed in solution. A hydrolysis product was characterized by X-ray crystallography. The compound crystallizes in the triclinic space group $P\bar{1}$ with a = 10.003 (2) Å, b = 11.462 (3) Å, c = 11.699 (2) Å, α = 65.72 (2)°, β = 79.81 (2)°, γ = 81.89 (2)°, V = 1199.7 (4) Å^3, and Z = 1. The correlation between solution and solid-state structure was determined, and a possible pathway to the hydrolysis product was suggested. Vanadium is used as a reagent in organic synthesis; however, these studies suggest that altered reactivities may surface in the presence of 1,3-propanediol ligands or substrates. The studies show that the analogy between phosphorus and vanadium breaks down in complexes containing 1,3-propanediol derivatives, reducing the prospects of chemically preparing vanadium analogs of cAMP.

Introduction

Structural, spectroscopic, and catalytic studies of oxovanadium(V) alkoxide chlorides have shown that these compounds are monomeric and exhibit activities as oxidation catalysts and Lewis acids.[1,2] Monomeric derivatives have been characterized both in the solid state and in solution, with a variety of alcohols as ligands.[3,4] The corresponding oxovanadium(V) alkoxides, where all the chlorides have been replaced by alkoxides, are dimeric ($[(VO(OCH_2CH_2Cl)_3)_2]$)[5] or polymeric ($[((VO(OCH_3)_3)_2)_n]$)[6] and often have very complex structures.[7] However, the structures characterized in the solid state may not be the same as the structures in solution, since exchange and fluxional processes can occur in solution. Very little is known about the correlation between solution and solid-state structures of vanadium alkoxides. Given the structural preference of oxovanadium(V) alkoxide chlorides to exist as monomeric complexes, the possibility for generation of fairly simple compounds with more complex ligands should be significant. Structural characterization of solution species and examination of the fluxional processes within a complex should specifically assist in the understanding of the role of ligand in complex assembly in vanadium alkoxides. Herein we describe the solution structure of tetranuclear vanadium derivatives generated from the reaction of 1,3-propanediol derivatives and $VOCl_3$. The exchange and fluxional processes in these tetranuclear compounds are complex, and only a few of these processes lead to formation of structures that can be examined by X-ray crystallography. Nevertheless, the exploration of the solution properties of vanadium(V) alkoxide complexes is critical to the understanding of the catalytic properties of these compounds.

The analogy[8] between vanadate (pK_a's 3.7, 8.1, 12.7)[8b] and phosphorus (pK_a's 2.5, 7.0, 12.5) has been demonstrated structurally and electronically. The corresponding analogy between organic vanadates and organic phosphates has been suggested to hold on the basis of enzymatic studies showing that organic vanadate can substitute for organic phosphate with several dehydrogenases and isomerases.[9] Despite this analogy, vanadate does not form a cyclic derivative in aqueous solutions with 1,3-propanediol derivatives.[10] Since a cyclic vanadate ester forms in solutions containing vanadate and ethylene glycol,[11] we were interested in exploring the nature of the vanadium complexes which form with 1,3-propanediol derivatives. The structure of the cyclic-1,2-diol complex oxovanadium(V) pinacolate chloride[12] has some similarities to the five-membered cyclic phosphorus compound.[13] Structural characterization of cyclic organic phosphorus compounds formed with 1,3-diols suggests that six-membered rings centered at phosphorus can be either in a boat conformation (with the ligand extending from the axial to the equatorial position of the trigonal bipyramidal phosphorus atom) or in a chair conformation (with the ligands lying in the equatorial

---

(1) (a) Hirao, T.; Mori, M.; Ohshiro, Y. *J. Org. Chem.* **1990**, *55*, 358–360. (b) Hirao, T.; Ohshiro, Y. *Tetrahedron Lett.* **1990**, *31*, 3917–3918. (c) Meier, I. K.; Schwartz, J. *J. Am. Chem. Soc.* **1989**, *111*, 3069–3070. (d) Hirao, T.; Mori, M.; Ohshiro, Y. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2390–2400.

(2) Phan Viet, M. T.; Sharma, V.; Wuest, J. D. *Inorg. Chem.* **1991**, *30*, 3026–3032.

(3) (a) Toscano, P. J.; Schermerhorn, E. J.; Dettelbacher, C.; Macherone, D.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1991**, 933–934. (b) Feher, F. J.; Walzer, J. F. *Inorg. Chem.* **1991**, *30*, 1689–1694.

(4) Crans, D. C.; Chen, H.; Felty, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 4543–4550.

(5) Priebsch, W.; Rehder, D. *Inorg. Chem.* **1990**, *29*, 3013–3019.

(6) Caughlan, C. N.; Smith, H. M.; Watenpaugh, K. *Inorg. Chem.* **1966**, *5*, 2131–2134.

(7) Klemperer, W. G.; Marquart, T.; Yaghi, O. M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 49–51.

(8) (a) Pettersson, L.; Hedman, B.; Andersson, I.; Ingri, N. *Chem. Scr.* **1983**, *22*, 254–264. (b) Chasteen, N. D., Ed. *Vanadium in Biological Systems*; Kluwer: Dordrecht, The Netherlands, 1990. (c) Chasteen, N. D. *Struct. Bonding* **1983**, *53*, 105–138.

(9) (a) Drueckhammer, D. G.; Durrwachter, J. R.; Pederson, R. L.; Crans, D. C.; Daniels, L.; Wong, C.-H. *J. Org. Chem.* **1989**, *54*, 70–77. (b) Nour-Eldeen, A. F.; Craig, M. M.; Gresser, M. J. *J. Biol. Chem.* **1985**, *260*, 6836–6842. (c) Crans, D. C.; Simone, C. M.; Blanchard, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 4926–4928.

(10) Tracey, A. S.; Gresser, M. J. *Can. J. Chem.* **1988**, *66*, 2570–2574.

(11) Gresser, M. J.; Tracey, A. S. *J. Am. Chem. Soc.* **1986**, *108*, 1935–1939.

(12) Crans, D. C.; Felty, R. A.; Miller, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 265–270.

(13) (a) Reddy, B. S.; Saenger, W. *Acta Crystallogr.* **1978**, *B34*, 1520–1524. (b) Haque, M.-U.; Cauglan, C. N.; Moats, W. L. *J. Org. Chem.* **1970**, *35*, 1446–1448. (c) Baineke, T. A. *Chem. Commun.* **1966**, 860–861. (d) Newton, M. G.; Cox, J. R., Jr.; Bertrand, J. A. *J. Am. Chem. Soc.* **1966**, *88*, 1503–1506.

0020-1669/92/1331-4939$03.00/0

plane).[14] In addition, a cyclic six-membered phosphorus-containing ring is a fundamental structural unit for the activity of the second messenger and hormone cAMP.[15] It was therefore of both chemical interest and biological importance to explore the formation of six-membered oxovanadium(V) alkoxide derivatives.

Dissolving vanadate ($NaVO_3$ or Na_3VO_4) in aqueous solution led to mixtures of monomeric, dimeric, tetrameric, and pentameric vanadate anions.[16] The distribution of oligomers is sensitive to pH, ionic strength, vanadate concentrations, and temperature.[17] In the physiological pH range vanadate tetramer is the most stable species. Vanadate oligomeric oxyanions including dimers,[18] tetramers,[19] pentamers,[20] hexamers,[21] octamers,[22] and decamers[23] have recently been isolated from both aqueous and organic solvents and structurally characterized. Additional polyoxovanadates with organic ligands such as carboxylates[24] or other bifunctional[25] and polyfunctional[26] ligands have been characterized by X-ray crystallography; these complexes frequently occur as tetrameric units. We have found that with 1,3-propanediol derivatives as ligands, the most stable complex is a tetrameric cluster. NMR spectroscopic evidence suggests that several tetrameric forms exist in solution, and one such derivative has been characterized by X-ray crystallography. The present study shows that the preference for monomeric vanadium derivatives in vanadium(V) alkoxide chlorides can easily be counteracted by ligand substitution.

Experimental Procedures

General Methods. Reactions were carried out using standard air-sensitive techniques under nitrogen or argon unless otherwise stated. All solvents were dried over appropriate reagents as described previously and distilled under argon before use.[27] 2,2-Dimethyl-1,3-propanediol was dried under vacuum before use. Other reagent grade chemicals were obtained from Aldrich and used without further purification. NMR spectra were recorded on a Bruker AM-500 spectrometer operating at 131.5 MHz for ^{51}V, a Bruker ACP-300 spectrometer operating at 300 MHz for ^1H, 75.5 MHz for ^{13}C, or 79 MHz for ^{51}V, or a Bruker WSPY-200 spectrometer. For ^{51}V NMR on the ACP-300, a 50° pulse angle was used with an acquisition time ranging between 0.07 and 0.14 s with no relaxation delay between pulses. Integrations were determined using the software package provided by Bruker. No changes in integration were observed if longer relaxation delays were used. A 10-Hz line-broadening factor was applied to all spectra except those used in line width studies. ^{51}V chemical shifts are reported with respect to $VOCl_3$ (0 ppm) as an external standard. Variable-temperature spectra were recorded from −90 to 65 °C. Proton–proton homonuclear correlation (COSY) spectra were recorded at −95, −85, −78, and −65 °C. Resolution was enhanced by using a sweep width of 5 ppm, and although some peaks folded over, no effect in the region of interest was observed. Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR. Microanalysis was performed by Galbraith Laboratories, Inc., Knowville, TN.

$[(VOCl)(\mu\text{-}OCH_2CH_2CH_2O)]_4$ (1). A solution of 1,3-propanediol (H_2PD) was prepared by adding 125 mL of methylene chloride to 0.19 mL (2.6 mmol) of the diol. The solution was stirred for 45 min to ensure that the ligand was completely mixed since 1,3-propanediol is only slowly soluble in methylene chloride. A dilute $VOCl_3$ solution was prepared by adding 50 mL of methylene chloride to 0.25 mL of $VOCl_3$ (2.6 mmol). This solution was then added dropwise to the ligand solution over a period of 1 h and was accompanied by the solution turning orange brown. After addition the solution was stirred for 30 min and argon bubbled through the solution to remove HCl(g). Hexane (30 mL) was added, and the flask was placed under vacuum. Orange product precipitated when approximately one-quarter of the solvent had been removed and was collected by filtration yielding 0.22 g (0.31 mmol, 48%) of solid. Mp: 97 °C. ^{51}V NMR (52.6 MHz, $CDCl_3$, 298 K): δ −399.6, −405.2. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ 5.24 (br), 2.53 (br). IR (KBr pellet, cm^{-1}): 2967 (vw), 2951 (w), 2934 (vw), 2926 (w), 2876 (w), 2821 (vw), 1419 (w), 1376 (w), 1339 (w), 1274 (mw), 1221 (m), 1200 (w), 1162 (vw), 1110 (w), 1052 (vw), 1038 (vs), 1011 (vw), 949 (vs), 918 (w), 895 (vw), 836 (m), 651 (s), 616 (mw), 521 (s), 434 (s).

$[(VOCl)(\mu\text{-}OCH_2C(CH_3)_2CH_2O)]_4$ (2). A solution of 2,2-dimethyl-1,3-propanediol (H_2DMDP) (0.261 g, 2.48 mmol) in methylene chloride (25 mL) was prepared. Vanadium oxychloride (0.25 mL, 2.6 mmol) was added by syringe and the solution stirred for 30 min and then concentrated under vacuum until an orange solid precipitated. The precipitate was collected by filtration and washed twice with hexane (15 mL) to remove impurities yielding 0.338 g (0.414 mmol, 70.9%) of orange powder. Mp: 148–150 °C. Decomp pt: 158 °C. ^{51}V NMR (78.9 MHz, $CDCl_3$ 297 °C): δ −397.5 (1V), −404.0 (1V). ^1H NMR (200 MHz, $CDCl_3$, 290 °C): δ {5.104 (s, br), 4.953 (s, br), 3H}, 4.701 (s, br, 1H), {1.61 (s, very br) 1.209 (s, br), 1.103 (s, br), 6H}. $^{13}C\{^1H\}$ NMR (75.469 MHz, $CDCl_3$, 297 K): δ 92.27, 90.00, 41.92, 39.52, 21.94, 21.76, 21.00. IR (KBr pellet, cm^{-1}): 2971 (w), 2954 (w), 2932 (w), 2875 (w), 2852 (vw), 1464 (mw), 1439 (w), 1395 (mw), 1370 (mw), 1360 (mw), 1334 (w), 1302 (mw), 1275 (w), 1213 (vw), 1190 (w), 1174 (w), 1040 (vs), 1015 (s), 1000 (vs), 961 (s), 947 (vw), 924 (mw), 912 (w), 728 (w), 662 (s), 623 (s), 556 (s), 472 (s), 446 (s), 408 (m). Anal. Calcd for $C_{20}H_{40}Cl_4O_{12}V_4$: C, 29.36; H, 4.93; Cl, 17.33; V, 24.91. Found: C, 29.28; H, 5.01; Cl, 17.51; V, 25.52.

$[(VOCl)(\mu\text{-}OCH_2C(CH_3)(C_2H_5)CH_2O)]_4$ (3). A solution of 2-ethyl-2-methyl-1,3-propanediol (H_2EMPD) (0.308 g, 2.61 mmol) in methylene chloride (15 mL) was prepared. Vanadium oxy chloride (0.25 mL, 2.6 mmol) was added by syringe. The solution was stirred for one-half h, and hexane (15 mL) was added. The solution was stirred for one-half h, and then solvent was removed in vacuo. During the removal of the solvent, an orange solid precipitated from solution. The solid was collected and recrystallized from methylene chloride/pentane yielding 0.450 g (0.515 mmol, 79.0%) of orange crystalline solid. Mp: 87–89 °C. Decomp pt: 150 °C. ^{51}V NMR (78.94 MHz, $CDCl_3$, 297 K): δ −393.1 (1V), −397.5 (1V). ^1H NMR (300.1 MHz, $CDCl_3$, 298 °C): δ {5.05 (s, br), 4.99 (s, br), 3H}, 4.75 (s, br, 1H), 1.56 (m, br, 2H), {1.13 (s), 1.06 (s), 0.98 (tr, J = 6.8), 6H}. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 297 K): δ 91.15, 90.59, 88.55 (br), 44.93, 42.60, 27.93, 27.28, 26.42, 18.98, 18.38, 17.40, 7.84. IR (KBr pellet, cm^{-1}): 2967 (w), 2937 (w), 2877 (w), 2855 (w), 1458 (mw), 1422 (vw), 1386 (w), 1368 (w), 1339 (w), 1330 (w), 1314 (vw), 1262 (vw), 1244 (vw), 1206 (vw), 1184 (w), 1066 (w sh), 1032 (s), 999 (s), 968 (s), 948 (vw sh), 881 (w), 783 (w), 734 (vw), 662 (m), 626 (m), 558 (m), 486 (m), 479 (m), 419 (m). Anal. Calcd for $C_{24}H_{48}Cl_4O_{12}V_4$: C, 32.97; H, 5.71; Cl, 16.22; V, 23.31. Found: C, 32.69; H, 5.75; Cl, 17.26; V, 23.07.

$[(VOCl)(\mu\text{-}OCH_2C(CH_3)(n\text{-}C_3H_7)CH_2O)]_4$ (4). A solution of 2-methyl-2-propyl-1,3-propanediol (H_2MPPD) (0.702 g, 5.31 mmol) in methylene chloride (20 mL) was prepared. Vanadium oxy chloride (0.50 mL, 5.3 mmol) was added by syringe. The solution was stirred for 30 min, and

---

[14] (a) Huang, Y.; Arit, A. M.; Bentrude, W. G. *J. Am. Chem. Soc.* **1991**, *113*, 7800–7802. (b) Hans, J.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1991**, *30*, 3928–3936.

[15] Dugas, H.; Penney, C. *Bioorganic Chemistry, A Chemical Approach to Enzyme Action*; Springer-Verlag: New York, 1981; pp 129–135.

[16] Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: New York, 1983.

[17] Howarth, O. W.; Trainor, J. R. *Inorg. Chim. Acta* **1987**, *127*, L22–28.

[18] (a) Djordjevic, D.; Lee, M.; Sinn, E. *Inorg. Chem.* **1989**, 719–723. (b) Michine, Y.; Ichida, H.; Sasaki, Y. *Acta Crystallogr., Sect. C* **1987**, *C43*, 175–177. (c) Konnert, J. A.; Evans, H. T., Jr. *Acta Crystallogr., Sect. B* **1975**, *B31*, 2688–2690.

[19] (a) Day, V. W.; Klemperer, W. G.; Yagasaki, A. *Chem. Lett.* **1990**, 1267–1270. (b) Fuchs, J.; Mahjour, S.; Pickardt, J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 374–375.

[20] Day, V. W.; Klemperer, W. G.; Yaghi, O. M. *J. Am. Chem. Soc.* **1989**, *111*, 4518–4519. Bottomley, F.; Paez, D. E.; White, D. S. *J. Am. Chem. Soc.* **1982**, *104*, 5651–5657.

[21] (a) Chen, Q.; Zubieta, J. A. *Inorg. Chem.* **1990**, *29*, 1456–1458. (b) Chae, H. K.; Klemperer, W. G.; Day, V. W. *Inorg. Chem.* **1989**, *28*, 1423–1424.

[22] Chen, Q.; Liu, S.; Zubieta, J. A. *Inorg. Chem.* **1989**, *28*, 4433–4434.

[23] (a) Khan, M. I.; Chen, Q.; Goshorn, D. P.; Hope, H.; Parkin, S.; Zubieta, J. *J. Am. Chem. Soc.* **1992**, *114*, 3341–3346. (b) Day, V. W.; Klemperer, W. G.; Maltbie, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 2991–3002. (c) Capparelli, M. V.; Goodgame, D. M. L.; Hayman, P. B.; Skapski, A. C. *J. Chem. Soc., Chem. Commun.* **1986**, 776–777. (d) Debaerdemaeker, T.; Arrieta, J. M.; Amigo, J. M. *Acta Crystallogr.* **1982**, *B38*, 2465–2468. (e) Bino, A.; Cohen, S.; Heitner-Wirguin, C. *Inorg. Chem.* **1982**, *21*, 429–431.

[24] (a) Rieskamp, K.; Gietz, P.; Mattes, R. *Chem. Ber.* **1976**, *109*, 2090–2096. (b) Priebsch, W.; Rehder, D.; van Oeynhauser, M. *Chem. Ber.* **1991**, *124*, 761–764.

[25] Hambley, T. W.; Judd, R. J.; Lay, P. A. *Inorg. Chem.* **1992**, *31*, 345–351.

[26] Crans, D. C.; Chen, H. Manuscript in preparation.

[27] Perrin, P. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.

Table I. Summary of Crystallographic Data for $(VOCl)_2(VO(OH))_2(DMPD)_4{\cdot}4CHCl_3$ (**5**)

mol formula	$C_{20}H_{40}Cl_2O_{14}V_4{\cdot}4CHCl_3$	Z	1
		ρ(calcd) g cm^{-3}	1.74
fw	1256.7	radiation (λ, Å)	Mo Kα (0.7107)
cryst system	triclinic		
space group	$P\bar{1}$	abs coeff μ, cm	15.71
a, Å	10.003 (2)	scan range, deg	$4 < 2\theta < 50$
b, Å	11.462 (3)	no. of unique reflcns	3908
c, Å	11.699 (2)	no. of obsd reflcns $\lvert F_o\rvert > 2.5\sigma(\lvert F_o\rvert)$	3703
α, deg	65.72 (2)		
β, deg	79.81 (2)	R	0.032
γ, deg	81.89 (2)	R_w	0.038
V, Å^3	1199.7 (4)		

pentane (100 mL) was added by cannula to the solution. The solution was stirred for 1 h, and then the solvent was removed in vacuo. During the removal of solvent an orange solid precipitated from solution. The solid was collected by filtration yielding 0.954 g (1.03 mmol, 77.4%) of a light orange powder. Mp: 100–103 °C. Decomp pt: 140–150 °C. ^{51}V NMR (78.94 MHz, $CDCl_3$, 297 K): δ −394.2 (1V), −399.1 (1V). ^{1}H NMR (300.1 MHz, $CDCl_3$, 298 °C): δ {5.08 (s), 5.02 (d, br), 3H}, 4.74 (m, br, 1H), 1.41 (m br, 4H), {1.17 (s), 1.08 (s), 1.03 (s), 0.95 (m), 6H}. ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$, 297 K): δ 91.48, 90.78, 89.00 (broad), 44.83, 42.61, 37.79, 37.11, 36.29, 19.48, 18.99, 18.04, 16.78, 14.72. IR (KBr pellet, cm^{-1}): 2972 (vw), 2956 (w), 2935 (w), 2902 (w), 2872 (w), 1466 (mw), 1458 (mw), 1420 (vw), 1383 (w), 1364 (w), 1339 (w), 1321 (w), 1298 (w), 1962 (w), 1242 (vw), 1202 (vw), 1177 (w), 1091 (w), 1042 (m), 1028 (m), 998 (s), 977 (m), 944 (mw), 904 (w), 892 (vw), 804 (w br), 776 (w), 732 (w), 668 (m), 627 (mw), 578 (w), 562 (m), 498 (w), 472 (m), 440 (m). Anal. Calcd for $C_{24}H_{48}Cl_4O_{12}V_4$: C, 36.15; H, 6.07; Cl, 15.24; V, 21.90. Found: C, 36.06; H, 6.25; Cl, 16.26, V, 21.32.

X-ray Structure of $[C_{10}H_{20}ClO_7V_2]_2{\cdot}4CHCl_3$ (5). Crystals of **5** were grown over a period of several weeks by the slow evaporation of a chloroform solution of **2** at 4 °C. The thin, clear, amber, platelike crystal was mounted on the Nicolet R3m diffractometer. Unit cell parameters were obtained from a least-squares fit to the automatically centered settings for 25 reflections (20.17° ≤ 2θ ≤ 32.98°); those cell parameters and other crystallographic information are given in Table I along with additional details concerning the collection of the data. An empirical absorption correction was applied with $T_{min} = 0.575$, $T_{max} = 0.975$, and $R_{merge} = 0.053$ (before) and 0.030 (after). Correct positions for the vanadium atoms were deduced from a Patterson synthesis. Subsequent least-squares difference Fourier calculations revealed positions for the remaining non-hydrogen atoms. Hydrogen atoms were included in "idealized" positions (C–H = 0.95 Å, U(H) = 1.2U_{iso}(C)). All calculations were performed using the SHELXTL program library.[28] Neutral-atom scattering factors and anomalous dispersion corrections were used from ref 29. Atomic coordinates are given in Table II. Bond distances and angles are given in Tables III and IV.

Table II. Positional (×10^4) and Thermal Parameters and Their Estimated Standard Deviations for $(VOCl)_2(VO(OH))_2(DMPD)_4{\cdot}4CHCl_3$ (**5**)[a]

atom	x	y	z	U_{iso},[b] Å^2
V1	7299 (1)	665 (1)	5481 (1)	0.018 (1)
V2	5939 (1)	126 (1)	3747 (1)	0.017 (1)
O1	5614 (2)	1054 (1)	4683 (1)	0.018 (1)
O2	8378 (2)	1428 (2)	4337 (1)	0.024 (1)
O3	6975 (2)	899 (2)	2556 (1)	0.025 (1)
O4	8329 (2)	−57 (2)	6695 (1)	0.022 (1)
O5	4400 (2)	415 (1)	2992 (1)	0.020 (1)
O6	6340 (2)	−1518 (2)	3396 (2)	0.025 (1)
O7	7296 (2)	−770 (1)	4973 (1)	0.017 (1)
C1	1870 (3)	537 (3)	1949 (2)	0.031 (1)
C2	2974 (3)	1465 (3)	1295 (2)	0.025 (1)
C3	4360 (3)	812 (3)	1668 (2)	0.027 (1)
C4	3034 (3)	1829 (3)	−129 (2)	0.038 (1)
C5	2643 (3)	2652 (3)	1601 (2)	0.036 (1)
C6	7693 (2)	−2123 (2)	3225 (2)	0.024 (1)
C7	8438 (2)	−2532 (2)	4374 (2)	0.022 (1)
C8	8599 (2)	−1359 (2)	4636 (2)	0.021 (1)
C9	9880 (3)	−3061 (3)	4035 (3)	0.031 (1)
C10	7687 (3)	−3544 (2)	5520 (2)	0.031 (1)
C11	6431 (3)	4181 (2)	2855 (2)	0.030 (1)
C12	1803 (3)	7281 (2)	172 (2)	0.027 (1)
Cl1	6492 (1)	2351 (1)	6143 (1)	0.026 (1)
Cl2	5421 (1)	5328 (1)	3331 (1)	0.034 (1)
Cl3	5885 (1)	4193 (1)	1497 (1)	0.046 (1)
Cl4	8153 (1)	4494 (1)	2559 (1)	0.050 (1)
Cl5	3037 (1)	6696 (1)	1201 (1)	0.053 (1)
Cl6	953 (1)	8710 (1)	228 (1)	0.046 (1)
Cl7	626 (1)	6138 (1)	553 (1)	0.054 (1)

[a] Estimated standard deviations in the least significant digits are shown in parentheses. [b] U_{iso} is defined as one-third of the trace of the $\mathbf{U}_{ij}$ tensor.

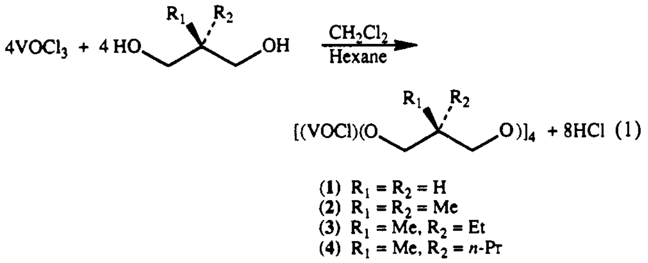
Table III. Bond Lengths (Å) for $(VOCl)_2(VO(OH))_2(DMPD)_4{\cdot}4CHCl_3$ (**5**)[a]

V1–O1	1.978 (2)	V1–Cl1	2.357 (1)
V1–O4	1.754 (2)	V1–O2	1.586 (1)
V1–O5a	2.305 (1)	V1–O7	1.966 (2)
V2–O3	1.592 (1)	V2–O1	1.780 (2)
V2–O6	2.060 (2)	V2–O5	1.832 (2)
V2–V2a	3.117 (1)	V2–O7	2.009 (2)
O1–V2a	2.271 (1)	V2–O1a	2.271 (1)
O5–C3	1.430 (3)	O4–C1a	1.435 (3)
O6–C6	1.451 (3)	O5–V1a	2.305 (1)
C1–C2	1.516 (4)	O7–C8	1.449 (3)
C2–C3	1.525 (3)	C1–O4a	1.435 (3)
C2–C5	1.524 (4)	C2–C4	1.534 (3)
C7–C8	1.531 (4)	C6–C7	1.524 (4)
C7–C10	1.522 (3)	C7–C9	1.534 (3)
C11–Cl2	1.757 (3)	C11–Cl3	1.764 (3)
C11–Cl4	1.755 (3)	C12–Cl5	1.747 (3)
C12–Cl6	1.756 (3)	C12–Cl7	1.752 (3)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

Results and Discussion

Synthesis. Vanadium oxychloride reacts with 1 equiv of several 1,3-propanediol derivatives including 1,3-propanediol (H_2PD), 2,2-dimethyl-1,3-propanediol (H_2DMPD), 2-ethyl-2-methyl-1,3-propanediol (H_2EMPD), and 2-methyl-2-propyl-1,3-propanediol (H_2MPPD) in methylene chloride to form deep red solutions which evolve HCl gas. The reactions are shown in eq 1. Addition



of hexane and removal of solvent in vacuo allows isolation of $(VOCl)_4(OCH_2C(R_1)(R_2)CH_2O)_4$ [$R_1 = R_2 = H$ (**1**); $R_1 = H$, $R_2 = CH_3$ (**2**); $R_1 = H$, $R_2 = C_2H_5$ (**3**); $R_1 = H$, $R_2 = n\text{-}C_3H_7$ (**4**)] in 50–80% yield. The reactions take several hours if nonforcing conditions are used but can be accelerated by bubbling inert gas through the solution or by removing solvent in vacuo.

The products are air-stable orange powders. Complex **3** sometimes forms as an orange microcrystalline solid. The PD complex (**1**) and the DMPD complex (**2**) are respectively considerably less soluble and slightly less soluble in organic solvents than their EMPD (**3**) and MPPD (**4**) counterparts. Conversely, the PD complex dissolves readily in water forming vanadate tetramer and decamer, while the others are water insoluble. The PD and DMPD complexes are slowly reduced upon prolonged exposure to moisture. The PD complex can be crystallized from the dilute reaction solution and forms a microcrystalline orange solid. A microcrystalline red solid was isolated from the reaction mixture of **2** when using concentrated (≥0.1 M in $VOCl_3$) methylene chloride solutions. Evaporation of a chloroform solution of **2** over a period of several weeks at 4 °C gave an amber

---

(28) Sheldrick, G. M. *SHELXTL, Rev. 5*; Nicolet XRD Corp.: Madison, WI, 1985.

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

Table IV. Bond Angles (deg) for $(VOCl)_2(VO(OH))_2(DMPD)_4 \cdot 4CHCl_3$ (**5**)[a]

Cl1–V1–O1	86.4 (1)	O1–V1–O2	102.5 (1)
Cl1–V1–O2	97.2 (1)	Cl1–V1–O4	92.1 (1)
O1–V1–O4	156.7 (1)	C2–V1–O4	100.7 (1)
O1–V1–O7	76.3 (1)	Cl1–V1–O7	160.3 (1)
O4–V1–O7	99.9 (1)	O2–V1–O7	95.8 (1)
Cl1–V1–O5a	83.9 (1)	O1–V1–O5A	72.3 (1)
O2–V1–O5A	174.7 (1)	O4–V1–O5a	84.4 (1)
O7–V1–O5a	81.8 (1)	O1–V2–O3	105.0 (1)
O3–V2–O5	100.0 (1)	O1–V2–O5	105.0 (1)
O1–V2–O6	156.5 (1)	O3–V2–O6	92.7 (1)
O5–V2–O6	86.6 (1)	O3–V2–O7	98.0 (1)
O1–V2–O7	79.8 (1)	O6–V2–O7	82.6 (1)
O5–V2–O7	159.3 (1)	O1–V2–O1a	80.1 (1)
O3–V2–O1a	174.2 (1)	O5–V2–O1a	75.7 (1)
O6–V2–O1a	83.2 (1)	O7–V2–O1a	85.6 (1)
V1–O1–V2a	104.0 (1)	V1–O1–V2	102.4 (1)
V1–O4–C1a	136.5 (1)	V1–O1–V2a	104.0 (1)
V2–O5–V1a	107.8 (1)	V2–O5–C3	125.8 (1)
V2–O6–C6	124.5 (2)	C3–O5–V1a	122.8 (1)
V1–O7–C8	117.9 (2)	V1–O7–V2	95.0 (1)
C2–C1–O4a	115.3 (2)	V2–O7–C8	122.9 (1)
C1–C2–C4	106.6 (2)	C1–C2–C3	110.7 (2)
C1–C2–C5	110.6 (2)	C3–C2–C4	107.3 (2)
C4–C2–C5	110.7 (2)	C3–C2–C5	110.8 (3)
O6–C6–C7	112.7 (2)	O5–C3–C2	111.6 (2)
C6–C7–C9	107.4 (2)	C6–C7–C8	109.9 (2)
C6–C7–C10	110.5 (2)	C8–C7–C9	106.7 (2)
C9–C7–C10	110.9 (1)	C8–C7–C10	111.3 (2)
Cl2–C11–Cl3	109.7 (1)	O7–C8–C7	112.0 (2)
Cl5–C12–Cl7	110.6 (1)	Cl2–C11–C14	110.3 (2)
Cl6–C12–Cl7	109.9 (1)		

[a] Estimated standard deviations in the least significant digits are given in parentheses.

crystalline solid, $[C_{10}H_{20}ClO_7V_2]_2 \cdot 4CHCl_3$ (**5**). The EMPD complex was recrystallized from methylene chloride/pentane. Attempts to crystallize the MPPD complex failed. Selected spectroscopic data are shown in Table V for compounds **1**–**4**.

X-ray Study of Compound 5. Coordinates and bond distances and angles for **5** are shown in Tables II–IV. The structure is shown in two views in Figure 1. Compound **5** is a tetranuclear complex containing four vanadium atoms and four dimethyl-1,3-propanediol ligands. Four molecules of chloroform cocrystallize with the compound. Only two of the four vanadium atoms and two of the dimethyl-1,3-propanediol ligands are crystallographically independent due to the crystallographically required inversion center present in the complex. Two of the chlorine atoms in **2** have been replaced by hydroxide groups. Although the hydrogen atoms of the hydroxide ligands were not observed in the X-ray structure determination, their presence can be inferred from a charge balance calculation.

Overall, the framework of vanadium and bridging oxygen atoms in **5** has the appearance of two connected face-sharing cubes, each with one vertex missing. Closer examination reveals systematic deviations from a cubic structure. The atoms on each "face" of the cube are strongly bound to each other, but the interaction between the two faces is weak. The vanadium–oxygen bond distances from the front to the back face (V1–O5a and V2–O1a) are 2.305 (1) and 2.271 (1) Å respectively. The ligands attached to the end vanadium atoms hold the tetramer together by bridging between the faces with V–O distances of 1.754 (2) (V1–O4) and 1.832 (2) (V2–O5) Å, respectively. The other ligand has longer V–O bonds (1.966 (2) (V1–O7) and 2.009 (2) (V2–O7) Å for the bridging oxygen, 2.060 (2) (V1–O6) Å for the nonbridging oxygen). The molecule can be viewed as two planar $V_2O_2(OH)Cl(DMPD)$ units tied together by two ligands (Figure 1). Each vanadium atom is six-coordinate. The structure has a tetranuclear core of close-packed edge-sharing octahedra. Similar structures has been observed for several molybdenum alkoxide complexes including $[n\text{-}Bu_4N]_2[Mo_4O_{10}(OMe)_4Cl_2]$.[30] From another perspective the complex has a layered structure. The four vanadium atoms are coplanar with a layer of oxygen atoms lying above and below this plane. This structure bears a marked resemblance to that in the decamer where six vanadium atoms are coplanar with alternating layers of oxygen and vanadium atoms above and below.[23]

Both oxygen atoms of each of the independent dimethyl-1,3-propanediol ligands are bound to one vanadium atom to generate a six-membered ring; additionally, one of the oxygen atoms bridges to another vanadium atom. The six-membered ring adopts the chair conformation with the central carbon (C2) and the vanadium atom (V1a) occupying the puckering positions in the chair. Each of the crystallographically independent vanadium atoms exhibit pseudooctahedral (VO_6, VO_5Cl) geometry, but the coordination geometry is significantly distorted. The average angle between the vanadium oxygen double bond (V1–O2, V2–O3) and the equatorial atoms (either oxygen or chlorine) is 99.0°. In addition, the V–O bonds trans to the doubly bonded oxygen (V1–O5a and V2–O1a) are very long. Similar coordination environments are observed for vanadium atoms in $K[VO_2(C_2O_4)]_4 \cdot 2H_2O$[24a] and $PV_{14}O_{42}$.[31] Each hydroxide oxygen atom bridges between three vanadium atoms in a nonsymmetric fashion: one bond (V2a–O1) is much longer (2.271 (1) Å) than the other two (1.780 (2) and 1.978 (2) Å for V2–O1 and V1–O1, respectively). These bond distances are similar to vanadium–oxygen bond lengths in $[V(O)(OCH_2CH_2Cl)_3]_2$[5] and $([VO(OMe)_3]_2)_n$.[6]

Solution Structure of Compounds 1–4. Although compound **5** was crystallized from a solution of **2**, it is a hydrolyzed derivative of compound **2** since the two compounds differ in their molecular formula. The proximity of the ^{51}V NMR chemical shifts of solutions of **2** and **5** suggests structural similarities around the (VOClL) unit in these compounds. Efforts to generate X-ray-quality crystals from compounds 1–4 were unsuccessful. NMR studies (vide infra) indicate that some fluxional processes are occurring in solution and that several clusters may exist.

We have evidence based on the solution chemistry that compounds **2**–**4** are tetranuclear in solution. All of these compounds were generated under forcing conditions so equilibrium methods could not be used directly to determine stoichiometry. At equilibrium additional species are observed, including complexes with 2:1 and 2:2 metal to ligand ratios. We have solution studies and solid-state characterization of these complexes and their conversion into compounds **2**–**4**.[32] This system is very complex and beyond the scope of this work; however, analysis, including all species present in solution, indicates that compounds **2**–**4** are tetranuclear complexes. Compound **1** remains more elusive since it is not very soluble in organic solvents and consequently resists the extensive characterization methods we have used with the other compounds. These studies will be detailed elsewhere.[32]

^{51}V NMR Solution Studies. Compounds **2**–**4** are characterized in the ^{51}V NMR by two peaks of equal area in the region between –390 and –405 ppm, with the downfield peak slightly broader than the upfield one (see Table V and Figure 2). In compound **1**, the ratio of the integrations of the two signals is 2:3. The two resonances suggest the existence of two types of vanadium atoms in compounds **1**–**4**. The chemical shifts for these atoms are midway between those observed for tetracoordinate vanadium alkoxides with one and two chlorines, $V(O)Cl_2(OR)$ (–315 ppm) and $V(O)Cl(OR)_2$, (–520 ppm),[33] considerably upfield from the pentacoordinate vanadium in the pinacol complex $[(VOCl)(\mu\text{-}OC(CH_3)_2C(CH_3)_2O)]_2$ (–324 ppm),[12] and close to that observed for the hexacoordinate vanadium in $[H_3V_{10}O_{28}]^{3-}$ (–396 ppm).[23b] The ^{51}V chemical shifts of compounds **1**–**4** are consistant with a hexacoordinate vanadium atom with one oxo and one chloride substituent.

---

(30) Kang, H.; Liu, S.; Shaihk, S. N.; Nicholson, T.; Zubieta, J. *Inorg. Chem.* **1989**, *28*, 920–933.

(31) Kato, R.; Kobayashi, A.; Sasaki, Y. *Inorg. Chem.* **1982**, *21*, 240–246.

(32) Crans, D. C.; Marshman, R. W.; Chen, H.; Anderson, O. P.; Miller, M. M. Manuscript in preparation.

(33) Priebsch, W.; Rehder, D. *Inorg. Chem.* **1985**, *24*, 3058–3062.

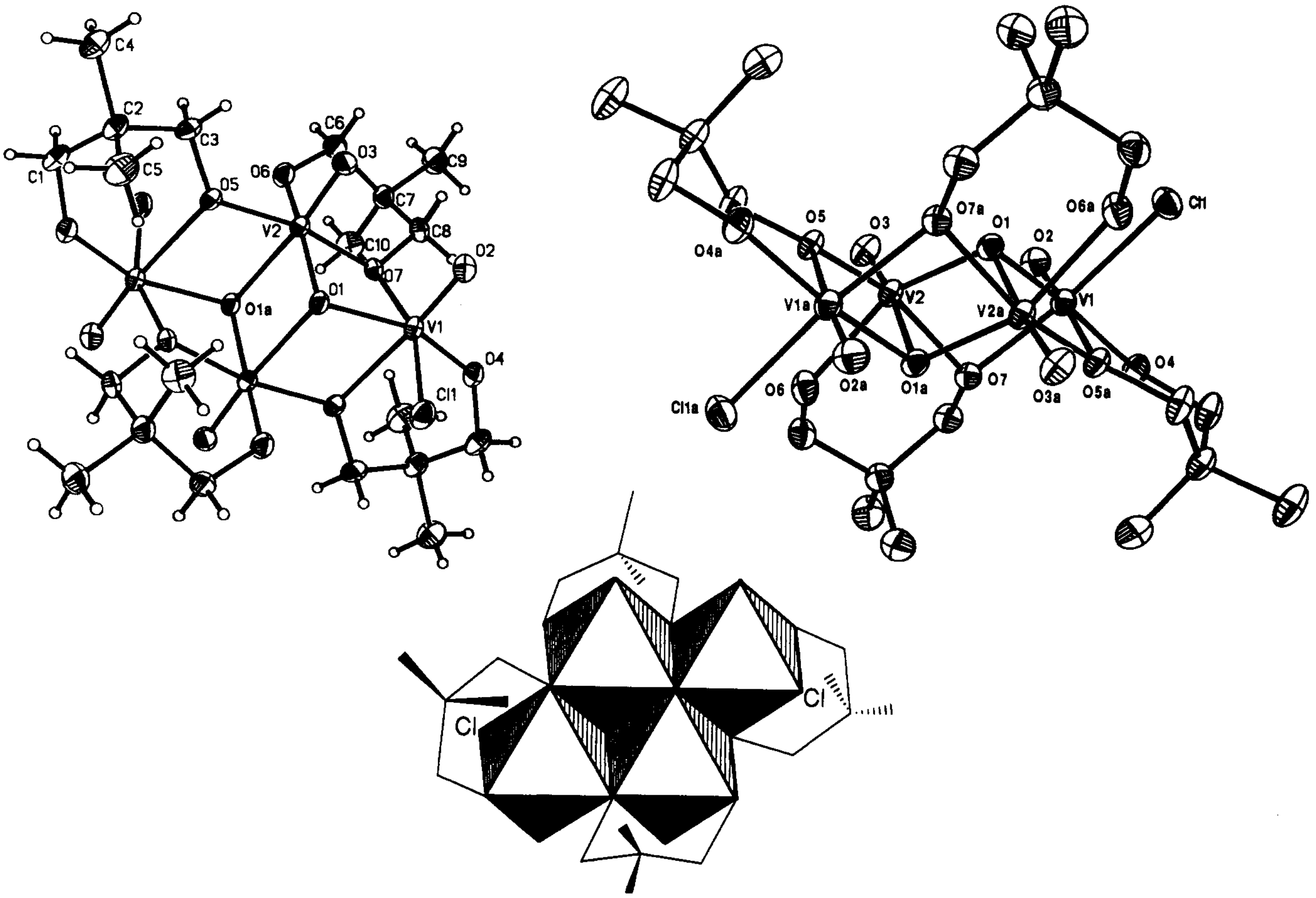


Figure 1. Thermal ellipsoid plots with atom-labeling scheme for $[C_{10}H_{20}ClO_7V_2]_2\cdot 4CHCl_3$ (**5**) shown in two views (30% thermal ellipsoids). An idealized polyhedral model is shown below in an alternative view.

Table V. Spectroscopic Properties of the Vanadium Tetramers **1**–**4**

	compd			
	[(VOCl)(PD)]$_4$ (**1**)[a]	[(VOCl)(DMPD)]$_4$ (**2**)	[(VOCl)(EMPD)]$_4$ (**3**)	[(VOCl)(μ-MPPD)]$_4$ (**4**)
^{51}V NMR (δ)	−399.5, −405.2	−397.7, −404.0	−393.1, −397.5	−394.2, −399.1
^{13}C NMR (δ)				
VOCH$_2$		92.72	91.15	91.48
		90.00	90.59	90.78
			88.54	89.00
CH$_2$C(CH$_3$)(R)CH$_2$		41.92	44.93	44.83
		39.52	42.60	42.61
C(CH$_3$)(CH$_2$C)			27.93	37.79
			27.28	37.71
			26.42	36.27
C(CH$_3$)(R)		21.94	18.98	19.48
		21.76	18.38	18.99
		21.00	17.40	18.04
others			7.84	16.78
				14.72
IR[b] (cm^{-1})	1038	1040	1032	1042
	1011	1015		1028
		1000	999	998
	949	961	968	977
	651	662	662	668
	616	623	626	627
	521	556	558	562
		472	486	472
			479	
	434	446	419	440

[a] No ^{13}C data was obtained for **1** because of low solubility in organic solvents. [b] Principal peaks only.

The line widths of both ^{51}V NMR resonances for compounds **1**–**4** at half-height are up to 3 times wider than those expected on the basis of relaxation times (T_1). Assuming quadrupolar relaxation is the dominant mechanism for relaxation and the molecule is within the motional limit, T_1 values approximate T_2 values and T_1 can be used to calculate line widths. The possibility that dynamic conformational motion or exchange reactions were broadening the signal was therefore explored at high and low temperature (Figure 2). Heating compound **4** to 62 °C results in the coalescence of the two vanadium signals, showing that the

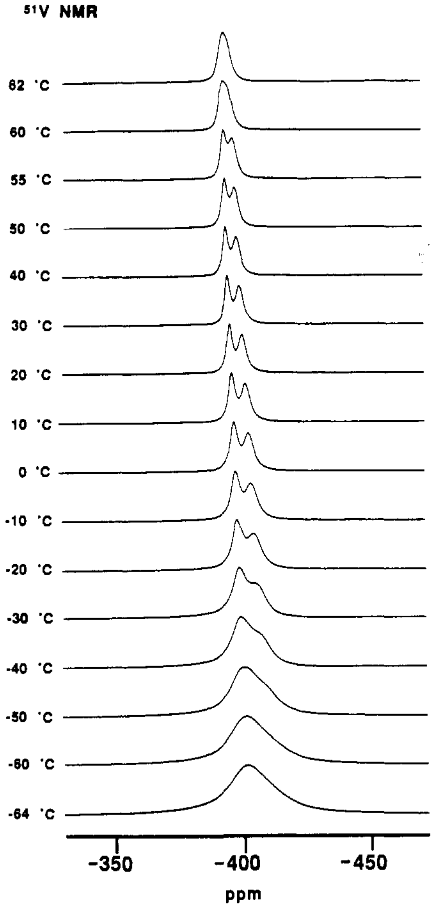


Figure 2. ^{51}V NMR spectra of $[(VOCl)(DMPD)]_4$ (**2**) recorded from 62 to -64 °C in $CDCl_3$ at 79 MHz.

Table VI. Possible Tetramer Ligand Arrangements

structure	nonbridging (μ_1) O	doubly bridging (μ_2) O	triply bridging (μ_3) O	symmetry	no. of V atoms
A	0	8	0	D_{4h}	1
B	1	6	1	C_s	3
C	2	4	2	C_{2h}	2
D	3	2	3	C_s	3
E	4	0	4	T_d	1

two vanadium atoms appear identical at higher temperature. The low-temperature ^{51}V NMR behavior for **2**–**4** was investigated by slowly cooling a $CDCl_3$ solution of each compound. At room temperature each spectrum consists of two lines, with the upfield resonance slightly broader. The signals are best resolved for **2** with the second resonance broadening into the baseline at -60 °C. For compound **3** the disappearance of the second resonance occurred between -10 and -20 °C, while for **4** the signal disappears between -50 and -60 °C. Line widths for compounds **1**–**4** range from 140 to 450 Hz at room temperature up to 1400 Hz for the downfield resonance at -60 °C. The single resonance present at low temperatures was asymmetric, indicating that some component of the upfield resonance was still present. Extreme broadening of ^{51}V NMR signals caused by the quadrupolar moment of the vanadium is often observed at low temperature. The temperature studies show that compounds **1**–**4** have very similar behavior in solution: The four vanadium atoms are identical at high temperature, and two types of vanadium atoms are observed at intermediate temperatures. No concentration effects, either on the line widths or the peak areas, were observed. This implies that if exchange is occurring, it is either intramolecular or between species of equal nuclearity. In aqueous solution, the relative proportion of vanadate oligomers and consequently the peak areas observed in the ^{51}V NMR are concentration dependent.[16]

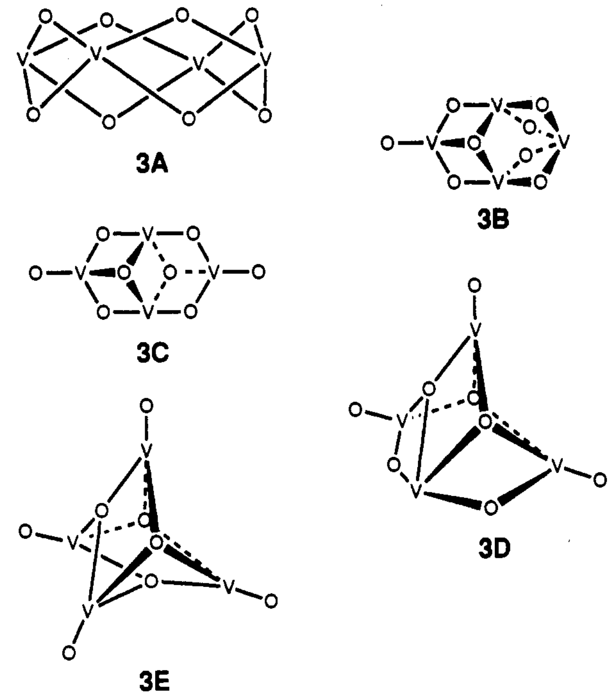


Figure 3. Structural frameworks for vanadium tetranuclear complexes: (A) 8 μ_2-O; (B) 1 μ_1-O, 6 μ_2-O, 1 μ_3-O; (C) 2 μ_1-O, 4 μ_2-O, μ_3-O; (D) 3 μ_1-O, 2 μ_2-O, 3 μ_3-O; (E) 4 μ_1-O, 4 μ_3-O.

Solution Structures. Compound **1**–**4** presumably contain four octahedral or distorted octahedral vanadium atoms, each with one Cl and one oxo substituent. Assuming each vanadium atom is six-coordinate, four additional bonds are required. These additional bonds must come from the four bidentate 1,3-propanediols. A total of 16 bonding interactions is required for a tetrameric complex, distributed among the 8 oxygens of the propanediol ligands. To satisfy these requirements, some of the ligand oxygens must be doubly bridging (μ_2-O) and possibly triply bridging (μ_3-O). The five possibilities are described in Table VI. For clarity, nonbridging ligand oxygen atoms are referred to as "μ_1". Drawings of the possible vanadium framework arrangements omitting ligands are shown in Figure 3. The structures range from one with only doubly bridging oxygens (Figure 3A) to one with only nonbridging and triply bridging oxygens (Figure 3E). Each structural framework has been illustrated in its highest possible symmetry in Figure 3, although attachment of the ligand bridge can reduce the symmetry. If we consider these structures in light of the ^{51}V NMR results, some may be excluded. Structures 3B and 3D have three different types of vanadium atoms whereas experimentally only two types are seen. Since the proposed types of vanadium are significantly different, the possibility that two signals are superimposed is unlikely. This eliminates structures 3B and 3D. Structure 3A, if of D_{4h} or C_{4v} symmetry, can also be excluded since all vanadium atoms would be equivalent. Likewise if structure 3E were of maximum symmetry, all vanadium atoms are equivalent, and it too can be excluded. The possibilities remaining are thus structures of the type 3A, 3C, and 3E in which the vanadium to ligand oxygen bonds are of variable length.

In the structure of $(VOCl)_2(VO(OH))_2(DMPD)_4$ (**5**), the vanadium oxygen bond lengths to the bridging oxygen atoms vary from 1.754 (2) to 2.305 (1) Å. This structure is a variation on 3C, where the symmetry has been reduced from C_{2h} to C_i because of the loss of the C_2 and σ symmetry elements. Vanadium–oxygen bond lengths can vary significantly in these complexes. In the case of **5** the bonds from vanadium to nonbridging oxygen atoms (V1–O4 and V2–O6) are 1.754 (2)

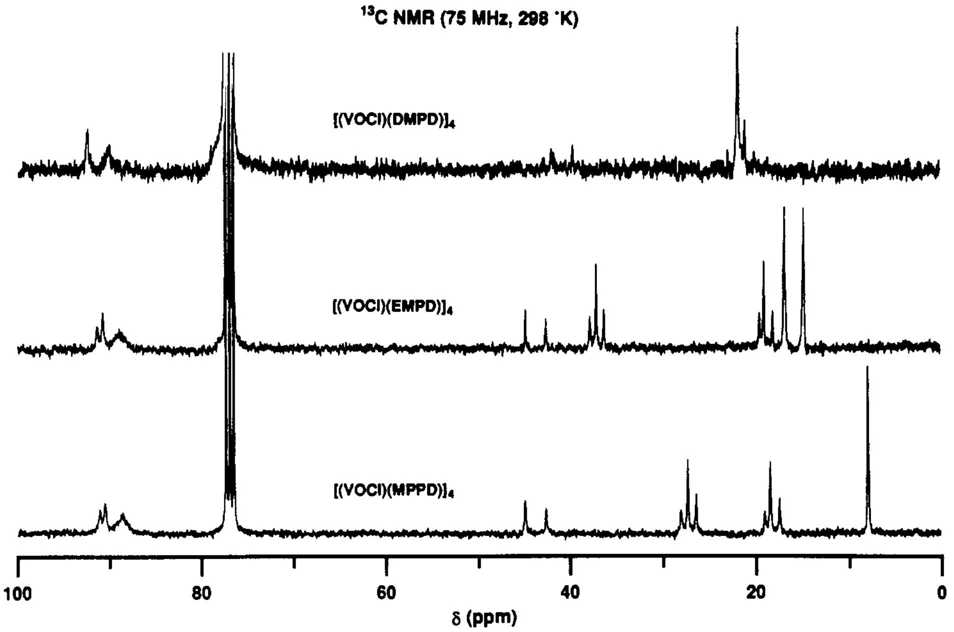


Figure 4. ^{13}C spectra of compounds $[(VOCl)(DMPD)]_4$ (**2**), $[(VOCl)(EMPD)]_4$ (**3**), and $[(VOCl)(MPPD)]_4$ (**4**), recorded at 75.5 MHz and 298 K.

and 2.060 (2) Å, respectively, while for the triply bridging hydroxide oxygens short, medium, and long vanadium oxygen bonds are observed. Doubly bridging ligand oxygens also show variability in bond lengths to vanadium ranging from 1.832 (2) (V2–O5) to 2.305 (1) Å (V1–O5a). Variations in vanadium–oxygen bond lengths place the two crystallographically independent vanadium atoms in different environments. Since ^{51}V chemical shifts are sensitive to vanadium oxygen bond distances,[34] ^{51}V NMR can provide structural information on the solution structure of compounds **1**–**4**. This leaves a low-symmetry structure 3A, structure 3C, or low-symmetry structure 3E as possible structures for the complex. The cationic complex $K[(VO_4(\mu\text{-}O)_4(\mu\text{-}O_2CCMe_3)]_4$ has C_{4v} symmetry with bridging oxygen and carboxylate ligands and is analogous to structure 3A.[24b] A sulfur analogue of structure 3C, $(NEt_4)_2[(V_4S_2(SCH_2CH_2S)_6]$, has also been reported.[35] VT ^{13}C and ^{1}H NMR should distinguish between these possibilities and allow for the characterization of the solution structure of compounds **1**–**4**.

^{13}C NMR Solution Studies. The ^{13}C NMR spectrum of compound **2** at ambient temperature gives five resonances at 92.7, 90.0, 41.9, 39.5, and 21.8 ppm and two lower intensity resonances at 21.9 and 21.0 ppm (Figure 4). Only three signals, at 71.3, 36.5, and 21.3 ppm, are observed for the free ligand suggesting that at least two inequivalent ligands are present in complex **2**. The two ^{13}C signals observed at 92.7 and 90.0 ppm are assigned to carbons adjacent to a bridging oxygen. Both resonances are somewhat broadened, which could be explained by an averaging of signals from carbons adjacent to bridging and nonbridging oxygen atoms. Carbons attached to nonbridging oxygens in vanadium alkoxides have chemical shifts around 80 ppm, while carbons attached to bridging oxygens have chemical shifts ranging from 86 to 96 ppm.[36] Two signals of equal intensity are observed for the quaternary carbons, at 41.9 and 39.5 ppm, suggesting that two types of ligands are present in the complex. One strong and two lower intensity signals are observed for the methyl carbons. The relative intensities of the signals are concentration dependent and not related to each other by simple integral ratios. This correlates well with the methyl signals observed in the proton NMR (infra vide) and indicates that at room temperature some fluxional process is occurring.

The ^{13}C NMR spectra for compounds **3** and **4** at ambient temperature show similar patterns, but three signals are observed in the *C*–O–V region. The signal at 89 and 88 ppm for **3** and **4**, respectively, is broad and presumably reflects the rapid exchange of two carbons; by integration this signal is the result of two carbon atoms. The added complexity in these spectra over that observed for compound **2** suggests that more than one complex exists in these solutions, a likely possibility as both these ligands are asymmetrically substituted at the quaternary carbons. Two ^{13}C resonances for the quaternary carbons support the interpretation that two different types of ligands are present in solutions of compounds **3** and **4**. If more than two major complexes are present in solution, they are sufficiently similar so that the ^{13}C resonances are overlapping. The remaining resonances in the ^{13}C spectrum define how the four ligands can be bound to the four vanadium atoms. Three signals are observed for the methyl group and for the methylene carbon of the ethyl and propyl groups attached directly to the ring. Only one signal is observed for the terminal carbon of the ethyl group and the other two carbons of the propyl group indicating that these protons are identical regardless of the nature of ligand attachment. The chemical shift differences presumably arise because of the different spatial relationships of the ligands in the complex.

At high temperature (60 °C), coalescence of the carbon signals centered at 90 ppm and those due to the methyl and adjacent methylene groups was observed. Low-temperature spectra of compound **4** show that the three resonances at 91, 90, and 89 ppm separate out into two groups of signals, one centered around 96 ppm and the other centered around 86 ppm.[37] Thus at −80 °C, signals from carbon atoms attached to triply, doubly, and nonbridging oxygens are observed. This precludes structural possibilities for complexes **1**–**4** containing only doubly bridging oxygens (structure 3A) or containing no doubly bridging oxygens (structure 3E). The low-temperature spectra are consistent with a complex containing two triply bridged, two singly bridged, and four doubly bridged oxygen atoms (structure 3C). The complexity of the spectrum suggests that at low temperature more than one isomer exists in solution.

---

(34) Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1977**, *99*, 3544–3545.

(35) Money, J. K.; Huffman, J. C.; Christou, G. *J. Am. Chem. Soc.* **1987**, *109*, 2210–2211.

(36) Preuss, F.; Ogger, L. *Z. Naturforsch.* **1982**, *37b*, 957–964.

(37) The observed signals in the region of interest at −80 °C are 97.99, 97.17, 96.50, 96.14, 95.63, 94.64, 94.1, 92.49, 90.76, 87.86, 86.93, 86.23, 84.30, and 83.30 ppm. Comparison with known structures suggests that the signals furthest downfield (97.99, 97.17 ppm) are due to carbons attached to triply bridging oxygens and the remainder due to carbons attached to doubly and nonbridging oxygens. The signal to noise ratio of this spectrum was low so the above assignments are not definitive.

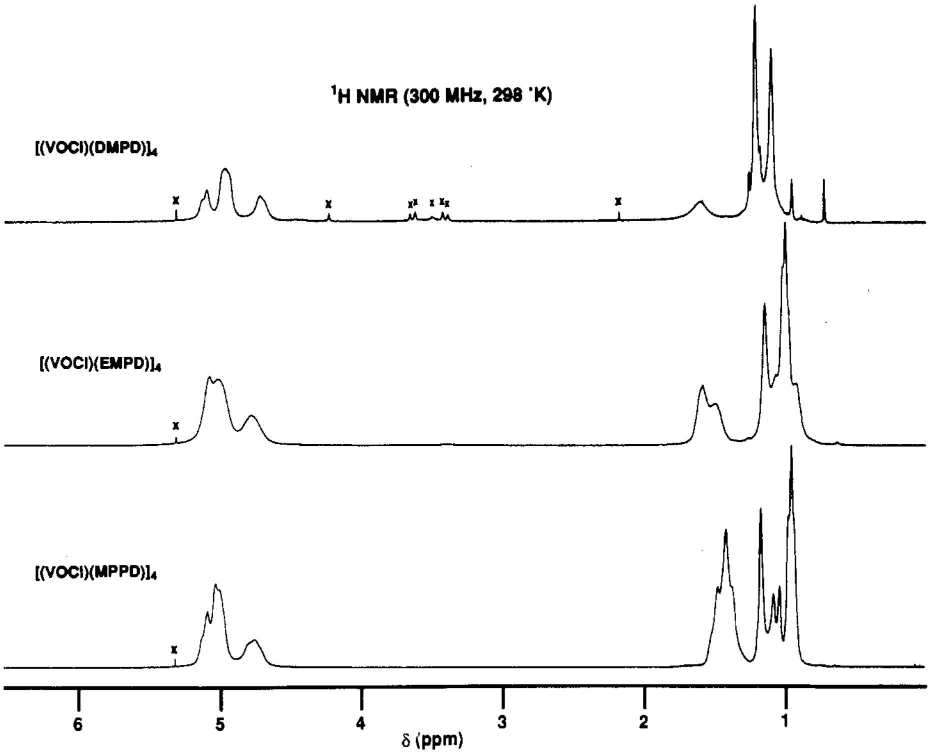


Figure 5. ^{1}H spectra of compounds [(VOCl)(DMPD)]$_4$ (2), [(VOCl)(EMPD)]$_4$ (3), and [(VOCl)(MPPD)]$_4$ (4), recorded at 300 MHz and 298 K.

^{1}H NMR Solution Studies. The complexes 1–4 are all characterized by broad resonances centered around 4.9 ppm for the VOCH$_2$ protons at 298 K (Figure 5). A more complex pattern is observed for the remaining ligand protons below 1.6 ppm. Even for the highly symmetric ligand DMPD the pattern cannot be easily interpreted. The resonances assigned to the methylene protons adjacent to the oxygen are very broad indicating that fluxional processes are occurring. Low-temperature spectra for these compounds show an even more complex pattern. Figure 6 shows a series of partial proton NMR spectra for compound 4 in CH$_2$Cl$_2$ recorded from -90 to 30 °C. Below -30 °C, the broad signals present at room temperature resolve into several doublets, with coupling constants of about 11.3 Hz, characteristic of geminal coupling. As shown above by the ^{13}C NMR spectra, some asymmetry in the ligand is expected and presumably will be observable in ^{1}H NMR spectra. An asymmetric tetranuclear complex can have 32 signals (16 protons). The spectra at -60 and -80 °C for 4 show more than 16 lines. Closer examination of the spectrum suggests that two different sets of resonances are present in the spectrum supporting the possibility that two different isomers are present in solution. This is illustrated by the VT (variable temperature) spectra of compound 4 in the region between 5.5 and 6.5 ppm (Figure 6). At -60 °C a broad multiplet at 5.96 ppm appears. As the temperature decreases, this signal shifts downfield and sharpens into a doublet. As the temperature is lowered further, a doublet at 5.50 ppm appears and continues to move downfield. No change is observed when the ratio of the doublets at 5.5 and 5.96 ppm are compared at various temperatures, and this suggests that the equilibrium distribution is not affected by temperature.

By comparison, the spectrum for complex 2 is fairly simple (Figure 7). At -70 °C, the five groups of peaks in the spectrum are doublets or multiplets; the signal centered around 5.1 ppm appears to be an AB quartet. The multiplet centered about 4.9 ppm integrates to three protons. Overall, the integral ratio of the peaks is 1:2:3:1:1, indicating that a total of eight protons are present in the complex. This observation is consistent with a structure possessing a 2-fold symmetry axis or a center of inversion. As the temperature is lowered below -70 °C, the AB quartet becomes a singlet but otherwise the spectrum remains the same.

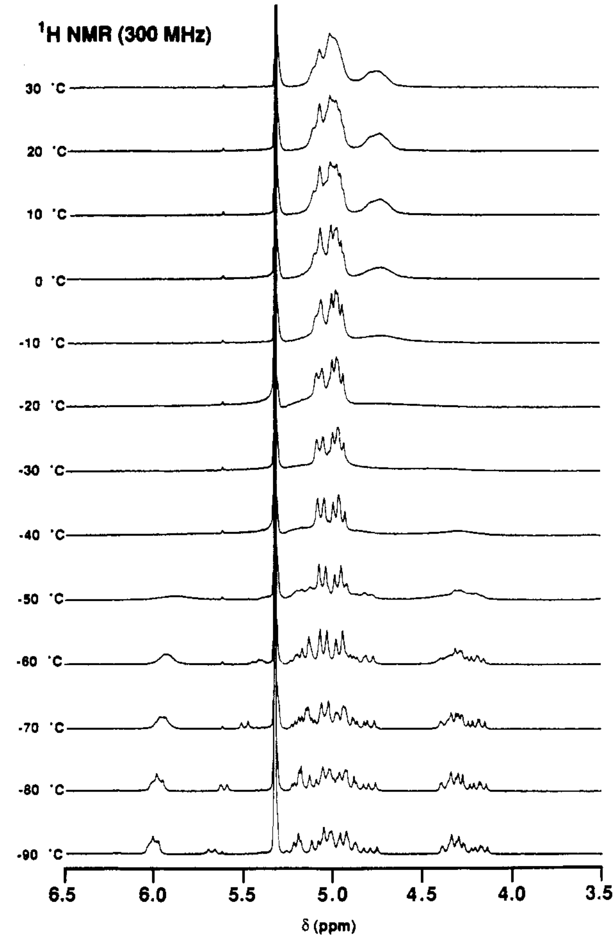


Figure 6. Partial ^{1}H spectra of [(VOCl)(MPPD)]$_4$ (4), recorded from -90 to 30 °C in CD$_2$Cl$_2$ at 300 MHz.

Low-temperature proton–proton correlation (COSY) spectra were recorded to resolve the coupling patterns observed in compounds 2 and 4. A COSY spectrum of 2 recorded at -78 °C is shown in Figure 8. Three doublets, at 6.08, 4.38, and 4.16 ppm

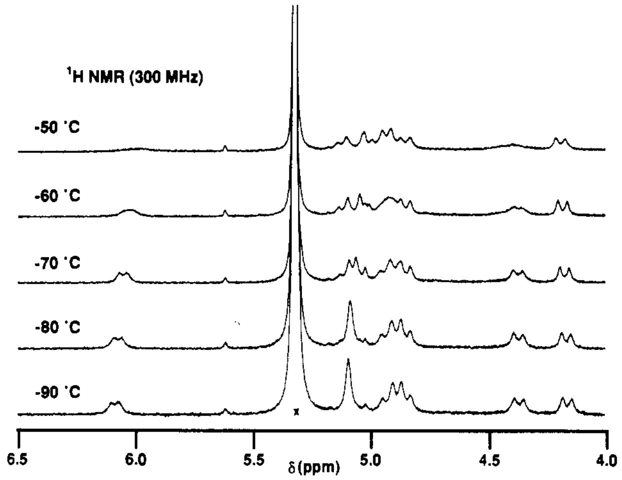


Figure 7. Partial ¹H spectra of $[(VOCl)(DMPD)]_4$ (**2**), recorded from −90 to −50 °C in CD_2Cl_2 at 300 MHz.

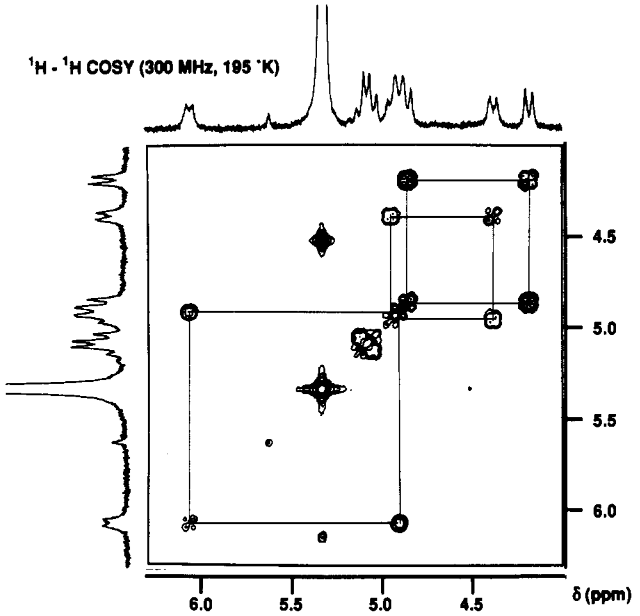


Figure 8. ¹H–¹H COSY spectrum of $[(VOCl)(DMPD)]_4$ (**2**), recorded at −78 °C in CD_2Cl_2.

were coupled with the three overlapping doublets at 4.88 ppm. As expected, the signal centered at 5.1 ppm contains two coupled protons with nearly identical chemical shifts (Figure 8). The eight correlations observed in these spectra indicate that only one tetranuclear complex is present in solution at low temperature for complex **2**, $[(VOCl)(DMPD)]_4$. The complex contains two independent ligands with all the methylene protons magnetically inequivalent. For a tetranuclear complex, these spectra require the presence of a center of inversion or a C_2 axis in the complex.

An analogous COSY study with complex **4** shows that more than one compound is present in solution (supplementary material). Several COSY spectra were recorded of complex **4** at varying temperatures, and overlapping signals observed in the 1D spectrum were resolved into several sets of doublets. For example, the resonance at 6.0 ppm consists of two overlapping doublets that are coupled to resonances at 5.04 and 4.94 ppm. A total of 11 correlations are identified in this spectrum, implying that at least 22 different proton environments exist for the tetranuclear complex in solution. These observations at low temperatures reflect the low activation barrier toward rearrangements between isomers and the existence of additional species in solution. Eight correlations are expected for tetranuclear complexes with a C_2 axis or an inversion center. The observed 22 correlations in the COSY of compound **4** suggest that either a minimum of three different symmetric complexes form in solution or that one of two complexes in solution is completely asymmetric having 16 different proton signals. The appearance of a doublet at 5.75 ppm at −70 °C well separated from the signals at 6.0 ppm suggests one complex is somewhat different from the two. Complexes with a C_2 axis or an inversion center are in accord with the ^{13}C and ^{51}V NMR spectroscopic studies described above and support solution structures for complexes **1**–**4** as illustrated by structure 3C.

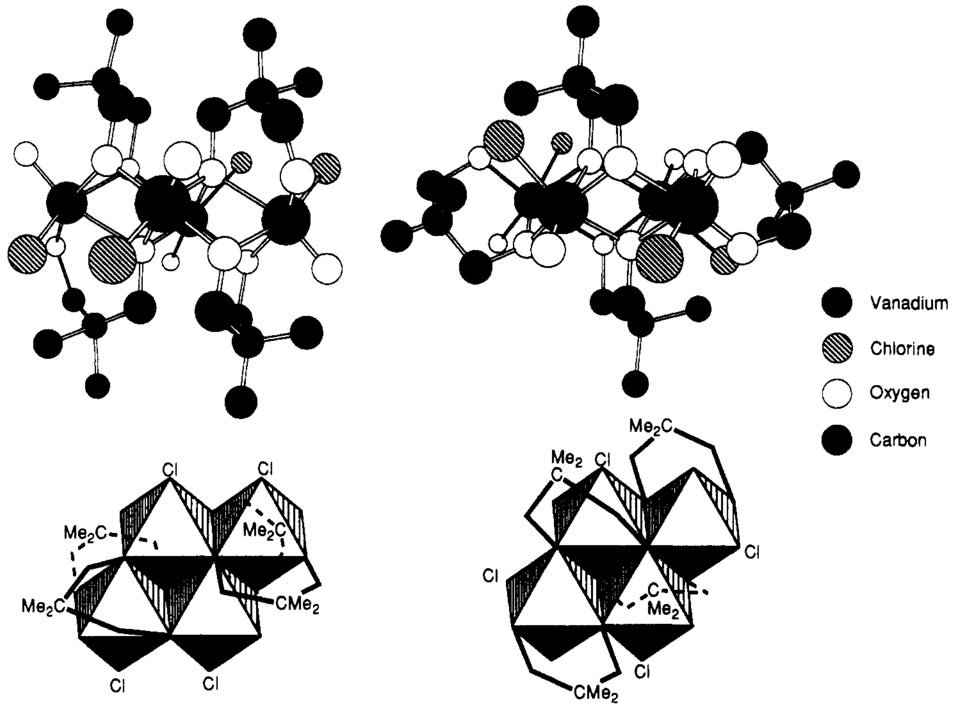
Proposed Solution Structure of Tetranuclear Complex. Two structures, shown in Figure 9, have a backbone of type 3C and are possible candidates for the solution structure of the tetranuclear vanadium complex. Both structures have a C_2 axis and an inversion center, two oxygens that are triply bridging, four oxygens that are doubly bridging, and two oxygens that are nonbridging. Structure 9A has one ligand with a nonbridging and triply bridging oxygen (μ_1-μ_3) and the other ligand with two doubly bridging oxygens (μ_2-μ_2). Structure 9B has one ligand with a nonbridging and doubly bridging oxygen (μ_1-μ_2) and the other ligand with a doubly and triply bridging oxygen (μ_2-μ_3). The proton NMR spectrum showed that one proton is in an environment which is particularly electron poor. Related complexes characterized in the solid state by X-ray crystallography and NMR spectroscopy show that such chemical shifts are only observed for protons in very restricted environments.[26] It is likely that such a proton is connected to a carbon adjacent to a doubly bridging oxygen atom because this would limit the geometry of the ligand. It is possible that a short distance between the methylene proton and the oxo group on the vanadium coupled with a relatively short V–O bond would produce a proton signal around 6 ppm. At the present time neither structure 9A nor structure 9B can be ruled out. Structure 9B has fewer steric constraints than structure 9A, suggesting that 9B may be more stable than 9A. In structure 9B, the possibility for isomers arises when the central carbon in the ligand (as in H_2EMPD and H_2MPPD) has two different groups attached to the central carbon. Symmetric and asymmetric variations on structure 9B are likely to have very similar ^{51}V chemical shifts, whereas modifications on structure 9A are likely to yield ^{51}V chemical shifts with greater differences.

Motional Processes of Tetranuclear Vanadium Complexes in Solutions. The fluxional processes are rapid at ambient temperatures. Several possibilities exist including distortions in the vanadium–oxygen framework, ligand rearrangement, or some type of pseudorotation about the vanadium. One possibility that modifies the V–O framework is a symmetric distortion of the molecule where the two vanadium atoms close together are pulled apart and vice versa. This process would also require simultaneous shifts in ligand bridging. If indeed this process was occurring rapidly, the vanadium, carbon, and proton chemical shifts should be identical. This is inconsistent with the finding that three isomers of $[(VOCl)(MPPD)]_4$ (**4**) are present in solution. Distortions based on shifts in the ligand include shifting the connectivity of one ligand from μ_1-μ_3 to μ_2-μ_2 to produce an intermediate structure similar to structure 3B. This complex would then undergo another shift to re-form structure 3C. The conversion of one isomer to another could occur in two stages, the first where one set of μ_1-μ_3 and μ_2-μ_2 ligands shift (interchanging) and the second where the other set of ligands shift. Alternately both parts of the molecule could shift forming structure 3A as an intermediate or a transition state. Several steps in the conversion could be slow and rate limiting. If the entire process was rapid on the NMR time scale, different complexes would not be observed.

The possibility that pentacoordinate vanadium complexes can undergo pseudorotation has previously been proposed.[38] Although octahedral coordination around the vanadium is observed in many

---

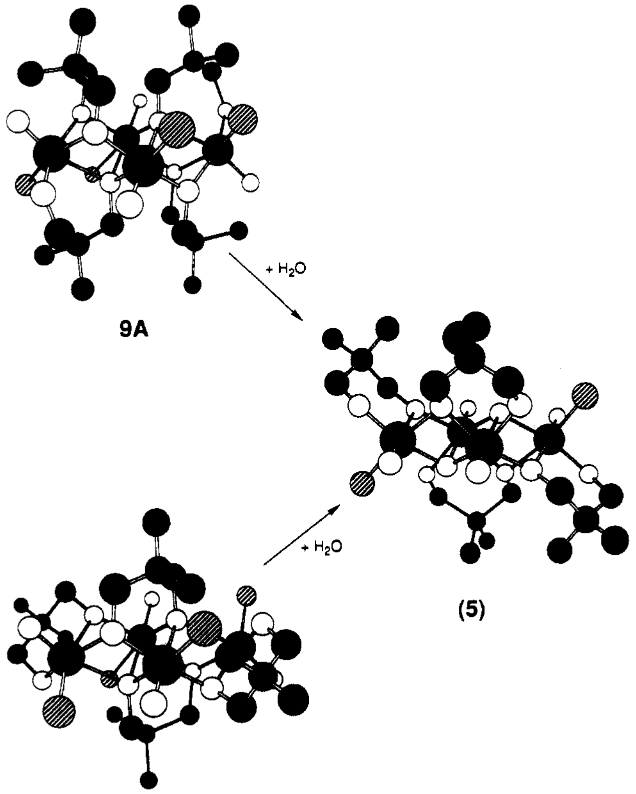
(38) Tracey, A. S.; Leon-Lai, C. H. *Inorg. Chem.* **1991**, *30*, 3200–3204.



9A **9B**

Figure 9. Computer-generated drawings and idealized polyhedral models for the two proposed structures of $[(VOCl)(DMPD)]_4$ in solution. Structure A contains two μ_1-μ_3 ligands and two μ_2-μ_2 ligands. Structure B contains two μ_1-μ_2 ligands and two μ_2-μ_3 ligands. See text for a description.

Scheme I



vanadium(V) structures, one very long bond to a ligand or a solvent molecule is often found trans to the oxo group.[5,6,12,23,30] It is possible that such interaction is sufficiently weak in solutions so that vanadium complexes behave as though they contained pentacoordinate vanadium in solution instead of hexacoordinate vanadium. The variable-temperature ^{1}H NMR spectrum for **2** bears a remarkable resemblance to those observed for the 5-coordinate phosphorous compounds $P(OR)_3(DMPD)$. At high temperature, pseudorotation was rapid and an average spectrum was observed, while at low temperatures different conformations were observed.[39] If indeed pseudorotation does occur and interchange the vanadium substituents, such a process would presumably occur while maintaining the tetrameric framework intact. Changes in ligand connectivity in the tetranuclear complex **2** have been observed since a symmetric five-coordinate dinuclear vanadium(V) compound can be isolated from a solution of complex **2**.[32] The crystalline dimer precipitates over a period of 12 h and is only slowly soluble in organic solvents, in contrast to the powdery compound **2**, which rapidly dissolves. The solution NMR of this compound is identical to the orange powder (tetranuclear compound) indicating that solubilizing the dinuclear vanadium(V) compound causes rearrangement to regenerate tetranuclear **2**.

Hydrolysis Reaction. In the presence of excess water **1** and **2** rapidly hydrolyze whereas **3** and **4** are quite stable. However, upon addition of 1 equiv of water, complex **2** reacts very slowly to generate a compound with a single ^{51}V NMR resonance around -309 ppm. The ^{51}V chemical shift of -309 ppm suggests that the vanadium in this compound still has chloride attached and that possibly a hydroxide has replaced part of the ligating diol. This and other hydrolysis products can be generated depending upon the particular reaction conditions. One of these may be the hydrolysis product of compound **2**, which undergoes ligand rearrangement and loss of chloride to generate compound **5**. Scheme I illustrates the hydrolysis reaction and accompanying ligand rearrangements could take place from structure 9A or 9B to **5**. Rearrangements to form **5** would not be as facile should 9A be the structure of the tetranuclear complex in solution as compared to 9B. Octahedral coordination around the vanadium suggests that the reaction may be rate limited by a dissociative

---

(39) (a) Day, R. O.; Kumara Swamy, K. C.; Fairchild, L.; Holmes, J. M.; Holmes, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 1629–1635. (b) Burton, S. D.; Kumara Swamy, K. C.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6104–6115. (c) Kumara Swamy, K. C.; Day, R. O.; Holmes, J. M.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6095–6103.

loss of a ligand generating a vanadium susceptible to attack by a water molecule. Such a process would be expected to be slow in agreement with our observations. Complexes **3** and **4** only react with water if forcing conditions are employed, and as described, complex **2** forms complex **5** over the course of several weeks at 4 °C in the presence of adventitious water.

Conclusions

The 1,3-propanediol derivatives act as bidentate ligands and induce cluster formation in vanadium(V) chloro complexes. The tetranuclear complexes of a series of vanadium(V)–propane-1,3-diol derivatives were characterized and their solution behavior examined using multinuclear spectroscopic methods. The structure of one of these compounds was determined using X-ray crystallography. The 1,3-propanediol ligand bridges over two vanadium atoms, suggesting that a six-membered ring containing one vanadium atom is not a stable structural arrangement as was found for the five-membered ring formation with the 1,2-diols. The tendency for 1,3-propanediols to bridge over two vanadium atoms in organic solvents parallels the finding that six-membered rings containing vanadate rarely form in aqueous solutions. Organic compounds with 1,3-propanediol moieties may show altered reactivities with vanadium(V) oxidation reagents as evidenced by a recent application of vanadium reagents in organic synthesis.[1]

Acknowledgment. We thank the NIH for funding this research (to D.C.C.). We thank The Center for Application of NMR Spectroscopy for access to the ^{1}H 500-MHz NMR spectrometer. The X-ray diffractometer and computing system at Colorado State University were purchased with funds provided by the National Science Foundation.

Supplementary Material Available: Tables VII–IX, giving complete experimental crystallographic details, anisotropic thermal parameters of all non-hydrogen atoms, and fractional atomic coordinates for hydrogen atoms for **5**, and Figures S1 and S2, showing low-temperature COSY spectra for **4** (5 pages). Ordering information is given on any current masthead page.