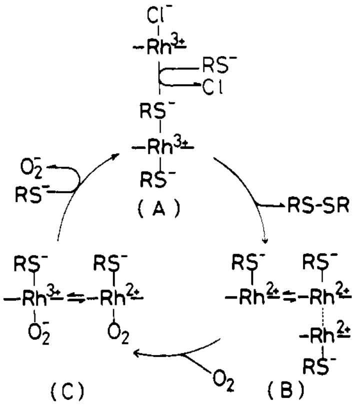
Scheme I. Possible Reaction Mechanism for Superoxide Generation by a Bis(thiolato)rhodium(III) Octaethylporphyrin[a]



[a] –Rh– represents rhodium(III) octaethylporphyrin.

In order to gain insight into the reaction mechanism between (TGE-S$^-$)$_2$Rh^{III}(OEP) and molecular oxygen, the ESR spectra of the complex prepared in benzene and THF in vacuo were measured by repeating freeze–thawing under molecular oxygen (Figure 4). As seen in Figure 4, the generation of free superoxide anion was found for the complexes on gradual exposure to oxygen. On the other hand, when Rh^{II}(OEP), prepared from Rh^{III}(OEP)Cl on a zinc mirror, was added to the TGE solution, followed by Bu$_4$NOH in vacuo,[23] no ESR signals due to Rh(II) species were detectable.

Possible Reaction Mechanism for Generating the Superoxide Anion in a Bis(thiolato)–Rh^{III}(OEP) Complex in the Presence of Molecular Oxygen. On the basis of electronic absorption and ESR spectral studies on a bis(thiolato)–Rh^{III}(OEP) complex in the presence of molecular oxygen in organic solvents, we speculate that the reaction mechanism for generating the superoxide anion in the complex is as shown in Scheme I, considering the mechanism for the corresponding Co^{III}-[14a,b] and Fe^{III}(TPP)[13d] complexes. A is a new hyperporphyrin spectral complex having a bis(thiolato)–Rh^{III}(OEP) coordination mode, deduced by electronic absorption spectrometry. B is a speculative and ESR-silent complex. C is also a speculative complex, being very unstable with a very short half-life. The generation of superoxide anion will continue until the available thiolato ligand is oxidized to the disulfide form in the system. We are now conducting studies to establish the structures and physicochemical natures of the complexes proposed in Scheme I.

Conclusion. Characteristic hyperporphyrin spectral features that appear upon bis(thiolato) ligation to Rh^{III}(OEP)Cl showed a marked similarity to those observed for thiolato adducts of P-450cam, cobalt-substituted P-450cam, and bis(thiolato)–Fe^{III}(TPP), –Co^{III}(TPP), and –Cr^{III}(TPP) complexes. The bis(thiolato)–Rh^{III}(OEP) complexes containing various types of aliphatic and aromatic thiol compounds were stable at room temperature under air, their half-lives being over 30 min. The positions of the characteristic split Soret band correlated linearly with the dielectric constants of alcohols as solvent and with the Hammett σ values of the substituents of thiophenol derivatives as axial ligands on Rh^{III}(OEP) in both acetone and benzene solvents. The unusual HP spectra with metalloporphyrins having 4d and 5d electrons are already known for antimony(III) and bismuth(III) porphyrins.[3a] However, the present bis(thiolato)–Rh^{III}(OEP) complex is the first example for HP spectra due to the formation of the coordination mode by bis(thiolato) metalloporphyrins having 4d electrons. Under the conditions observed for the formation of a hyperporphyrin spectrum, the generation of free superoxide anion was detectable at 77 K by ESR spectrometry. On the basis of the results, a possible reaction mechanism generating the superoxide anion by a bis(thiolato)–Rh^{III}(OEP) complex is proposed.

---

[23] The zinc mirror, Rh^{III}(OEP)Cl (0.5 mM in benzene, 0.25 mL), TGE (10 mM in acetone, 0.1 mL), and Bu$_4$NOH (80 mM in methanol, 0.04 mL) were prepared in four cuvvettes connected to an anaerobic ESR tube.

Contribution from the Department of Chemistry,
Simon Fraser University, Burnaby, BC, Canada V5A 1S6

Vanadium(V) Oxyanions. Interactions of Vanadate with Cyclic Diols and Monosaccharides

Alan S. Tracey* and Michael J. Gresser*

Received January 20, 1988

^{51}V nuclear magnetic resonance studies have shown that the vanadium(V) oxyanion, vanadate, reacts with *cis*- and *trans*-1,2-cyclohexanediols and the glucose, galactose, and mannose methyl pyranosides to give a variety of products including vanadate esters, divanadate esters, both binuclear mixed and symmetrical pentacoordinate anhydrides, and in the case of the methyl α- and β-galactopyranosides a previously unobserved binuclear product. The equilibrium constant for formation of esters with hydroxyls of the six-membered rings was found to be comparable to that observed for the formation of ethyl vanadate. In the case of the cyclohexanediols the formation of the pentacoordinate products was more highly favored for the *cis*-diol as compared to the *trans*-diol by a factor of about 10. For the glucosides only a very small proportion of pentacoordinate products was formed and then only for the α-anomer, while the formation of this product with the other monosaccharides was comparable to that of the cyclohexanediol system. A mixed pentacoordinate/tetrahedral binuclear vanadate product was formed in the presence of methyl galactopyranoside but not with methyl mannopyranoside. A third binuclear species was also observed. The latter product was formed with incorporation of two methyl galactopyranosides but was found to readily incorporate a third.

Introduction

The interactions of vanadate with carbohydrates have been a topic of developing interest since it was first proposed that oxovanadium complexes with uridine formed and that these products acted as transition-state analogues for enzymic reactions of phosphorylated uridine.[1] Subsequent nuclear magnetic resonance (NMR) studies[2,3] supported this conclusion, and X-ray and neutron diffraction studies showed the proposed transition-state geometry in a vanadate/uridine/ribonuclease complex.[3,4] Further

---

[1] Lindquist, R. N.; Lynn, J. L., Jr.; Lienhard, G. E. *J. Am. Chem. Soc.* **1973**, *95*, 8762–8768.

[2] Gresser, M. J.; Tracey, A. S.; Nour-Eldeen, A. F. *Fed. Proc., Fed. Am. Soc. Exp. Biol.* **1985**, *44*, 1400.

[3] Borah, B.; Chen, C.-W.; Egan, W.; Miller, M.; Wlodawer, A.; Cohen, J. S. *Biochemistry* **1985**, *24*, 2058–2067.

[4] Wlodawer, A.; Miller, M.; Sjölin, L. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 3628–3631.

0020-1669/88/1327-2695$01.50/0

evidence for the role of vanadate as a phosphate analogue was obtained when it was shown that glucose, in the presence of vanadate, acts as an enzyme substrate when combined with glucose-6-phosphate dehydrogenase.[5] Similarly, studies with phosphoglycerate mutase have shown that, in the presence of vanadate, mutase activity can be reduced because of inhibitory interactions resulting from the occurrence of a transition-state analogue.[6,7] The spontaneous formation of vanadate derivatives of hydroxylic compounds leading to analogues of phosphate esters has potential in preparative procedures that utilize enzymes and may have industrial significance.

The spontaneous formation of vanadate esters in aqueous solution has been studied in considerable detail, for ethanol[8] and for both phenol and tyrosine,[9] and similar reactions may be responsible for some of the physiological effects of vanadium.[8-12] The interactions between ethylene glycol and vanadate have also been studied, and the formation of bipyramidal coordination geometry about vanadate has been proposed.[13] The occurrence of similar products has also been reported for the aqueous vanadate/lactate and vanadate/glycerate systems.[14] In aqueous solvent such derivatives give rise to ^{51}V NMR signals near −520 ppm. Vanadate, in the presence of uridine, also gives rise to an NMR signal near −520 ppm, which, upon the addition of ribonuclease, decreases in magnitude, indicating the formation of a vanadate/uridine/ribonuclease complex.[2,3] A crystalline product, which presumably is the same enzyme derivative found in solution, shows a trigonal-bipyramidal coordination geometry about vanadium.[3,4] It should be noted that the uridine derivative of vanadate, described above, is a dimeric product[15] similar to that formed with ethylene glycol,[13] not monomeric as is the case with lactate.[14] Studies of alkyl esters of the type $OV(OR)_3$ in nonaqueous solution have indicated that there is a degree of dimerization in such systems and that the dimerization to an extent is dependent on the size of the alkyl group.[16,17] Similar triesters have not been observed in aqueous solution although their formation may be favored under strongly acidic conditions and low water concentrations.

The spontaneous formation in aqueous solution of trigonal-bipyramidal products, requiring, as it seemingly does, either vicinal hydroxyls, α-hydroxy carbonyls or α-hydroxy carboxylates, must be partially governed by conformational and steric requirements of the ligand. Such properties have, to a small extent, been investigated in acyclic ligand systems.[13,14] This investigation is now extended to various cyclic systems including the *cis*- and *trans*-1,2-cyclohexanediols and several monosaccharides. The methyl D-pyranosides were utilized in this study in order to eliminate problems of oxidation and to have only a single structural form in solution.

Information concerning the formation of pentacoordinate vanadate complexes with the vicinal hydroxyls of cyclic systems may be relevant to understanding possible effects that vanadate may have on the metabolism of inositol phosphates[18,19] and cyclic phosphates.[20]

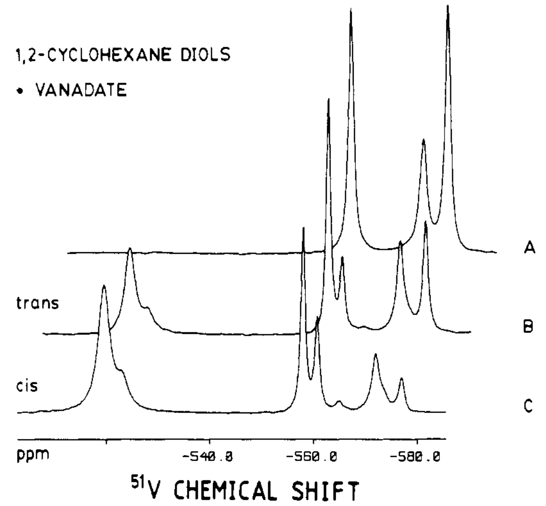


Figure 1. ^{51}V NMR spectra showing the formation of acyclic and cyclic products from the reaction of *cis*- and *trans*-1,2-cyclohexanediols with vanadate: (A) no added diol; (B) as for (A) but with 0.86 M *trans*-1,2-cyclohexanediol; (C) as for (A) but with 0.22 M *cis*-1,2-cyclohexanediol. The three solutions contained 3.0 mM vanadate and 20 mM HEPES buffer at pH 7.5.

Experimental Section

Materials. All materials used in this study were obtained from commercial sources. Their purity was checked by ^{13}C or ^{1}H NMR spectroscopy, and they were used as supplied. Stock vanadate solutions were prepared from vanadium pentoxide (Aldrich Gold Label 99.999%). All solutions were prepared as previously described.[15] Note that the pH of the solutions was regulated with HEPES buffer instead of the Tris (tris(hydroxymethyl)aminomethane) buffer used in previous work.[8,9,13,14] The Tris buffer was replaced with the HEPES buffer because use of the Tris buffer resulted in the formation of mixed-ligand products containing Tris.[21]

Spectroscopy. ^{51}V NMR spectra were obtained at 105 MHz from the multinuclear facility of a Bruker WM-400 NMR spectrometer. All spectra were obtained at ambient temperatures (21 °C). 2K data set sizes, 60° pulse widths, and 0.05 s acquisition times were used for all spectra. The time domain spectrum was zero-filled to 8K. A 30-Hz line-broadening factor was applied to all spectra before transforming to the frequency domain. Signal intensities were obtained by using the integration routine supplied by the instrument manufacturer.

Results and Discussion

1,2-Cyclohexanediols. Vanadate reacts with both *cis*- and *trans*-1,2-cyclohexanediols in aqueous solution to give a variety of products. The products formed include both acyclic tetrahedral mono- and diesters of vanadate and dimeric pentacoordinate cyclic derivatives. The formation of the pentacoordinate products is strongly favored in the case of *cis*-1,2-cyclohexanediol (c-CHD) over that of the *trans*-1,2-cyclohexanediol (t-CHD) ligand, but the nature of products is not significantly different. Figure 1 shows NMR spectra from vanadate solutions with no cyclohexanediol (Figure 1A), with 0.86 M t-CHD (Figure 1B), and with 0.22 M c-CHD (Figure 1C). The bottom two spectra clearly are very similar, particularly in the region of the spectra near −520 ppm. This observation has some relevance to the assignment of coordination geometry to these products. It has been shown that the analogous products formed with acyclic diols have pentacoordinate geometry and partly on the basis of NMR studies have been assigned a trigonal-bipyramidal structure.[13] The evidence here, although not definitive, is consistent with that assignment.

For the case of trigonal-bipyramidal geometry, the *cis*- and *trans*-cyclohexanediols could both give rise to two products, assuming anhydride linkage is through the apical positions of the two bipyramids. If the pentacoordinate structure were square

---

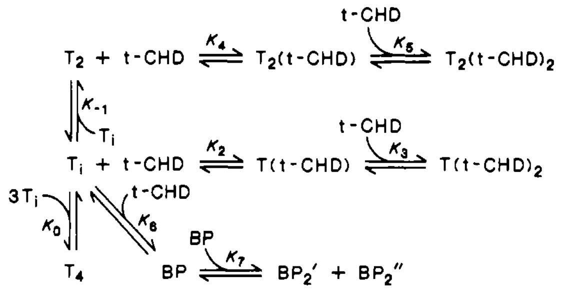
(5) Nour-Eldeen, A. F.; Craig, M. M.; Gresser, M. J. *J. Biol. Chem.* **1985**, *260*, 6836–6842.
(6) Tracey, A. S.; Gresser, M. J. *Fed. Proc., Fed. Am. Soc. Exp. Biol.* **1986**, *45*, 1647.
(7) Stankiewicz, P. J.; Hass, L. F. *Fed. Proc., Fed. Am. Soc. Exp. Biol.* **1986**, *45*, 1649.
(8) Gresser, M. J.; Tracey, A. S. *J. Am. Chem. Soc.* **1985**, *107*, 4215–4220.
(9) Tracey, A. S.; Gresser, M. J. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 609–613.
(10) Ramasarma, T.; Crane, F. L. *Curr. Top. Cell. Regul.* **1981**, *20*, 247–301.
(11) Chasteen, N. D. *Struct. Bonding (Berlin)* **1983**, *53*, 105–138.
(12) Gresser, M. J.; Tracey, A. S.; Stankiewicz, P. J. *Adv. Protein Phosphatases* **1987**, *4*, 35–57.
(13) Gresser, M. J.; Tracey, A. S. *J. Am. Chem. Soc.* **1986**, *108*, 1935–1939.
(14) Tracey, A. S.; Gresser, M. J.; Parkinson, K. M. *Inorg. Chem.* **1987**, *26*, 629–638.
(15) Tracey, A. S.; Gresser, M. J.; Liu, S. *J. Am. Chem. Soc.*, in press.
(16) Paulsen, K.; Rehder, D.; Theonnes, D. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmosphys.* **1978**, *33A*, 834–839.
(17) Howarth, D. W.; Trainor, J. R. *Inorg. Chim. Acta* **1987**, *127*, L27–L28.
(18) MaCara, I. G.; Marinetti, G. V.; Balduzzi, P. C. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 2728–2732.
(19) Sugimoto, Y.; Whitman, M.; Cantley, L. C.; Erikson, R. L. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 2117–2121.
(20) Dixon, J. F.; Hokin, L. E. *J. Biol. Chem.* **1985**, *260*, 16068–16071.
(21) Tracey, A. S.; Gresser, M. J. *Inorg. Chem.* **1988**, *27*, 1269–1275.

Table I. Concentrations of Vanadate Products Formed from the Reaction of Vanadate with *trans*-1,2-Cyclohexanediol in Aqueous Solution[a-c]

[V(t)]	[t-CHD]	[T_i]	[$T\ell$]	[$T\ell$]$_2$	[BP(t)]	[T_2]	[T_4]
			Concentration of t-CHD Varied				
3.00	0.043	1.056	0.073		0.009	0.700	1.161
3.00	0.086	0.941	0.106		0.035	0.697	1.221
3.00	0.129	1.010	0.118		0.081	0.689	1.102
3.00	0.172	1.003	0.148		0.134	0.685	1.029
3.00	0.215	0.983	0.160		0.204	0.696	0.958
3.00	0.258	0.946	0.180		0.298	0.645	0.930
3.00	0.344	0.957	0.222		0.428	0.649	0.713
3.00	0.516	0.844	0.270	0.031	0.829	0.566	0.460
3.00	0.688	0.768	0.293	0.051	1.071	0.505	0.312
3.00	0.860	0.674	0.308	0.064	1.401	0.420	0.133
			Concentration of Vanadate Varied				
0.10	0.215	0.083	0.010		0.001	0.006	
0.50	0.215	0.327	0.058		0.028	0.072	0.015
0.75	0.215	0.453	0.073		0.042	0.131	0.051
1.00	0.215	0.549	0.092		0.071	0.202	0.086
1.50	0.215	0.703	0.117		0.097	0.332	0.251
2.00	0.215	0.815	0.134		0.138	0.476	0.436
2.50	0.215	0.894	0.165		0.176	0.609	0.655
6.00	0.215	1.276	0.203		0.335	1.223	2.963

[a] Conditions of the experiments were as follows: pH, 7.50; buffer, 20 mM HEPES; temperature, ambient (21 °C). [b] Concentrations of all vanadate derivatives are given as vanadium atom concentrations in millimolar units. The ligand concentrations are in molar units. [c] Identification of symbols: V(t) total vanadate in solution; t-CHD, 1,2-*trans*-cyclohexanediol; T_i, inorganic vanadate; $T\ell$, vanadate ester with t-CHD; $T\ell_2$, vanadate diester with t-CHD; BP(t), total of trigonal-bipyramidal products; T_2, divanadate; T_4, tetravanadate.

Scheme I



pyramidal, then t-CHD would again give rise to two products; however, with c-CHD there is the possibility of three products, two with the vanadium atoms equivalent by symmetry and one with no symmetry. As a consequence, four NMR signals might be expected from the equilibrium mixture with c-CHD and two signals from that with t-CHD. The close similarity between the two spectra and the observation of only two signals are indicative of trigonal-bipyramidal coordination geometry.

The spectrum displayed as Figure 1B was obtained under conditions of 3.0 mM vanadate, 0.86 M racemic *trans*-1,2-cyclohexanediol, pH 7.5, and 20 mM HEPES buffer. Table I gives the vanadium atom concentrations in the products giving rise to these NMR signals as a function of total vanadate and of cyclohexanediol concentrations. As discussed above, those resonances occurring near −520 ppm are attributed to pentacoordinate products. The resonance at −558.2 ppm corresponds to tetrahedral monomeric vanadate, T_i. The resonance at −561.6 ppm derives from the *trans*-1,2-cyclohexanediol acyclic tetrahedral ester (T(t-CHD)) of vanadate, analogous to ethyl vanadate,[8] while the low-intensity signal at −566.1 ppm arises from the bis(*trans*-1,2-cyclohexanediol) tetrahedral vanadate diester (T(t-CHD)$_2$). The resonance at −572.9 ppm is attributed to the tetrahedral divanadate anhydride, T_2, and that at −578.1 ppm to the tetramer, T_4. Like T_i, T_2 has positions available for ester formation, and the product, T_2(t-CHD), may be formed. Similar products cannot form from T_4.

On the basis of this assignment of products, Scheme I can be written and the results of the concentration studies given in Table I used to test this scheme and provide the equilibrium constants. In the experiments the water concentration was not changed significantly, and water stoichiometry cannot be obtained. Scheme I therefore ignores water requirements, and this factor has accordingly been dropped in the determination of equilibrium constants. On this basis the constants of Scheme I are given by eq 1–9, where ℓ refers to the ligand, BP to the monomeric pentacoordinate product, and BP_2 to the total of the two pentacoordinate anhydrides, that is, $[BP_2] = [BP_2'] + [BP_2'']$. For the purposes of this paper, BP_2' refers to the product giving rise to an NMR signal at −524.4 ppm, and BP_2'', to the product with a signal at −520.9 ppm.

$$4T_i \xrightleftharpoons{K_0} T_4 \qquad [T_i]^4K_0 = [T_4] \tag{1}$$

$$2T_2 \xrightleftharpoons{K_1} T_4 \qquad [T_2]^2K_1 = [T_4] \tag{2}$$

$$T_i + \ell \xrightleftharpoons{K_2} T\ell \qquad [T_i][\ell]K_2 = [T\ell] \tag{3}$$

$$T\ell + \ell \xrightleftharpoons{K_3} T\ell_2 \qquad [T\ell][\ell]K_3 = [T\ell_2] \tag{4}$$

$$T_2 + \ell \xrightleftharpoons{K_4} T_2\ell \qquad [T_2][\ell]K_4 = [T_2\ell] \tag{5}$$

$$T_2\ell + \ell \xrightleftharpoons{K_5} T_2\ell_2 \qquad [T_2\ell][\ell]K_5 = [T_2\ell_2] \tag{6}$$

$$T_i + \ell \xrightleftharpoons{K_6} BP \qquad [T_i][\ell]K_6 = [BP] \tag{7}$$

$$2BP \xrightleftharpoons{K_7} BP_2 \qquad [BP]^2K_7 = [BP_2] \tag{8}$$

$$BP_2' \xrightleftharpoons{K_8} BP_2'' \qquad [BP_2']K_8 = [BP_2''] \tag{9}$$

Scheme I indicates that as inorganic vanadate (T_i) concentration is varied, the concentrations of the two tetrahedral vanadate esters, T(t-CHD) and T(t-CHD)$_2$, should maintain a constant proportionality with the concentration of T_i. With a change in *trans*-1,2-cyclohexanediol concentration, the two products should not maintain a direct proportionality but change as the first or second power of the t-CHD concentration in accord with eq 3 and 4. From eq 3 it is seen that if [T(t-CHD)]/[t-CHD] is plotted against [T_i], a straight line of slope K_2 should be obtained. The experimental data (Table I) provided a good straight line from which $K_2 = 0.68 \pm 0.07\ M^{-1}$ was obtained. Similarly, a straight line was obtained when the appropriate quantities of eq 4 were plotted. The equilibrium constant K_3 for formation of T(t-CHD)$_2$ from T(t-CHD) in combination with t-CHD was found to be $0.24 \pm 0.03\ M^{-1}$. The factor of about 3 between these equilibrium constants is similar to the analogous factor for the case of formation of 2-hydroxyethyl vanadate and bis(2-hydroxyethyl) vanadate, where the proportion is about 4.[13]

Since the products T(t-CHD) and T(t-CHD)$_2$ are readily formed, it can be expected that similar products will be formed

Table II. Formation Constants Determined for the Various Products Formed from the Reaction of Vanadate with *cis*- and *trans*-1,2-Cyclohexanediol

equil eq		equil const t-CHD	 c-CHD
$4T_i \rightleftharpoons T_4$	K_0	$(2.5 \pm 0.1) \times 10^8$ M^{-3}	$(3.3 \pm 0.2) \times 10^8$ M^{-3}
$2T_i \rightleftharpoons T_2$	K_{-1}	$(2.8 \pm 0.2) \times 10^2$ M^{-1}	$(3.4 \pm 0.3) \times 10^2$ M^{-1}
$2T_2 \rightleftharpoons T_4$	K_1	$(3.2 \pm 0.3) \times 10^3$ M^{-1}	$(2.9 \pm 0.3) \times 10^3$ M^{-1}
$T_i + \ell \rightleftharpoons T\ell$	K_2	0.68 ± 0.07 M^{-1}	0.24 ± 0.06 M^{-1}
$T\ell + \ell \rightleftharpoons T\ell_2$	K_3	0.24 ± 0.03 M^{-1}	
$T_2 + \ell \rightleftharpoons T_2\ell$	K_4	1.0 ± 0.2 M^{-1}	<0.15 M^{-1}
$2T_i + 2\ell \rightleftharpoons BP_2$	K_5'	$(2.3 \pm 0.2) \times 10^3$ M^{-3}	$(1.9 \pm 0.2) \times 10^4$ M^{-3}
$BP_2' \rightleftharpoons BP_2''$	K_8	4.0 ± 0.3	2.9 ± 0.2

from the anhydride, T_2. Close inspection of the spectra obtained at the high ligand concentrations revealed the formation of a product that gives rise to a signal occurring about 1 ppm to the high field side of the T_2 resonance but not at all well separated from it. The NMR signals from T_2, T_2(t-CHD), and T_2(t-CHD)$_2$ were treated as a superposition of signals, and eq 5 and 6 were combined with eq 2, summed, and rearranged to give eq 10. A

$$\frac{[T_2] + [T_2\ell] + [T_2\ell_2]}{[T_4]^{1/2}} = K_1^{-1/2} + K_1^{-1/2}K_4[\ell] + K_1^{-1/2}K_4K_5[\ell]^2 \quad (10)$$

plot of the term on the left of this equation vs $[\ell]$ should give a line of intercept $K_1^{-1/2}$ and, if T_2(t-CHD)$_2$ is formed, of upward curvature. In practice, the formation of T_2(t-CHD)$_2$ is not observable except at very high ligand concentrations since K_5 is generally quite small. As a consequence, the graph is linear within the error of the experiment, and the intercept provides $K_1^{-1/2}$, and the slope, $K_1^{-1/2}K_4$. The values obtained were intercept $K_1^{-1/2} = (1.8 \pm 0.1) \times 10^{-2}$ $M^{1/2}$ ($K_1 = (3.2 \pm 0.3) \times 10^3$ M^{-1}) and slope $K_1^{-1/2}K_4 = (1.9 \pm 0.3) \times 10^{-2}$ M^{-2} from which $K_4 = 1.0 \pm 0.2$ M^{-1}. Thus the formation of T_2(t-CHD) is slightly favored over the formation of T(t-CHD).

On the basis of Scheme I, it can be expected that the bipyramidal products BP_2' and BP_2'' will maintain a constant proportionality with each other irrespective of vanadate concentration. Inspection of spectra obtained over a 10-fold range in total vanadate concentration indicated this was the case. It is, however, possible to test in a more quantitative manner for the presence of bipyramidal products, mononuclear in vanadium, by investigating in detail the equilibria of Scheme I.

If the monomer, BP, exists, it must have an NMR signal under that from the dimer, BP_2, since no other signal attributable to such a species is observed and there is no reason to expect it to show a large chemical shift difference from that of BP_2. On the basis of superposition of signals, eq 7 and 8 can be combined with eq 1, then summed, and rearranged to give eq 11. The factor of

$$\frac{[BP] + 2[BP_2]}{[T_4]^{1/4}K_0^{-1/4}[\text{t-CHD}]} = K_6 + 2K_0^{-1/4}K_6^2K_7[T_4]^{1/4}[\text{t-CHD}] \quad (11)$$

2 in this equation is to allow for the factor of 2 in the vanadium atom concentrations. The tetramer, T_4, is used in this equation instead of T_i since partial overlap of the NMR signal of T_i with $T\ell$ occurs. This is particularly critical at the lower concentration of ligand if an intercept is to be well determined. The slope of the plot of the values obtained for $[T_i]$ vs $[T_4]^{1/4}$ gave $K_0^{1/4} = (1.27 \pm 0.03) \times 10^2$ $M^{-3/4}$, the inverse of which was utilized in eq 11. The plot of the relevant parameters of eq 11 is shown in Figure 2. There clearly is no indication of a nonzero intercept, indicating that K_6 is probably less than 0.05 M^{-1}. Thus, there is no detectable monomeric pentacoordinate product. The least-squares intercept is −0.012, but of course the true value cannot be less than zero. The slope was $(4.6 \pm 0.3) \times 10^3$ M^{-3}, which is twice the overall formation constant of BP_2 from two vanadates and two ligands ($2K_6^2K_7$ in terms of eq 7 and 8).

The NMR spectra clearly reveal at least two products giving rise to signals near −520 ppm. There is no indication from any of this work that these products are other than stereoisomers.

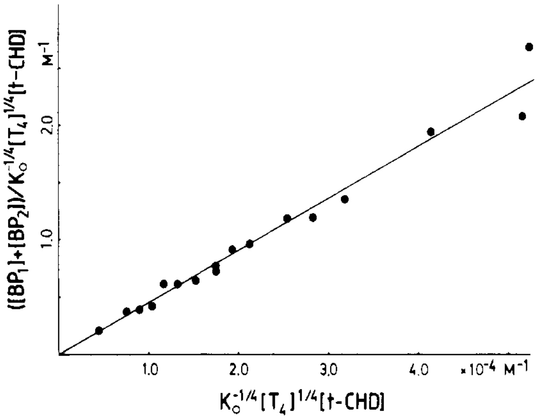


Figure 2. Graph showing that there is no observable formation of a mononuclear vanadium product among the *trans*-1,2-cyclohexanediol derivatives giving rise to the ^{51}V NMR signals centered at −520 ppm. Experimental conditions: 20 mM HEPES buffer; pH 7.5; varying amounts of total vanadate and t-CHD as indicated in Table I.

Stereoisomers have previously been observed for the analogous BP_2 products formed from 1,2-propanediol.[13] Samples prepared from optically resolved *trans*-cyclohexanediol should help establish this point for the present system. If we accept that the two signals observed derive from stereoisomers BP_2' and BP_2'', then the equilibrium between them is given simply by their proportions (~1:4) or $K_8 = 4.0 \pm 0.3$.

The interactions of vanadate with *cis*-1,2-cyclohexanediol are not significantly different from those with the *trans*-diol. The products formed, as is evident from Figure 1B,C, must be very similar. The major difference lies in the formation constants for these products. The analysis for the equilibrium constants proceeds identically with that discussed for the trans compound. The constants are summarized in Table II.

Of interest here are the formation constants for the ester, $T\ell$. The formation of the ester from the *trans*-diol is favored by almost a factor of 3 over that of the cis derivative. This may indicate that the equatorial hydroxyl of the *cis*-cyclohexanediol is preferentially esterified relative to the axial hydroxyl. The *trans*-diol of course has two equatorial hydroxyls in its preferred conformation.

A further interesting point is that, under the conditions of these experiments, there was no observable formation of the divanadate ester $[T_2\ell]$ of the *cis*-diol whereas in the trans case the formation of this product was favored relative to that of the mono ester, $T\ell$. The result indicates the presence of destabilizing interactions in the case of the *cis*-diol.

The remaining products formed are the pentacoordinate derivatives. Their formation from the *cis*-cyclohexanediol is favored by a factor of 10 over that from the *trans*-cyclohexanediol. This result presumably is a reflection of the unfavorable stereochemistry of the *trans*-diol, where ring flattening causes the adjacent carbon–oxygen bonds to project at an angle to each other that leads to ring strain in the cyclic products. This behavior is even more pronounced in the methyl glycopyranosides.

Methyl α- and β-D-Glucopyranosides. The interactions of vanadate with methyl α- or β-D-glucopyranosides might be expected to be similar to those with *trans*-1,2-cyclohexanediol since this

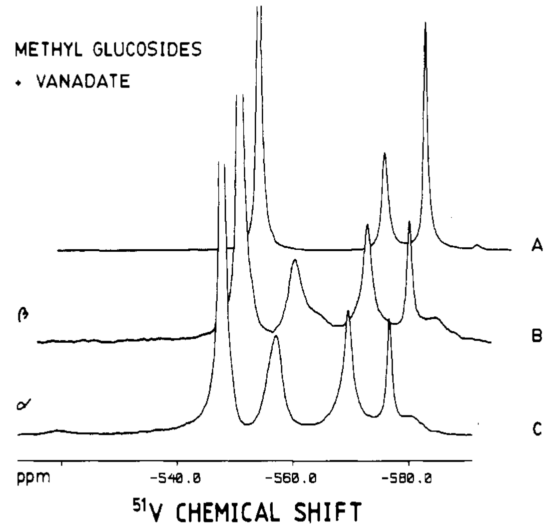


Figure 3. ^{51}V NMR spectra showing the formation of complexes formed from vanadate in the presence of methyl β-D-glucopyranoside (B) or methyl α-D-glucopyranoside (C). Trace A shows a spectrum of a vanadate solution obtained under similar conditions but with no glucoside present. Experimental conditions: 3.0 mM total vanadate; 0.82 M glucoside; 20 mM HEPES buffer; pH 8.50.

glycoside has three ring hydroxyls in a trans arrangement. In addition, there is the primary hydroxyl at C-6. Traces B and C of Figure 3 show ^{51}V NMR spectra of the α- and β-glucosides under conditions of 3.0 mM vanadate, 0.82 M glucoside, 20 mM HEPES buffer, and pH 8.50. The top trace of this figure shows the NMR spectrum obtained under similar conditions but in the absence of a glucoside. The spectra clearly show that a variety of new products are formed. From vanadate and glucoside concentration studies, assignments of the resonances have been made for the β-glucoside products (Figure 3B). All possible products cannot be assigned since an insufficient number of signals were resolved. Three signals derive from vanadate itself, as is clear from Figure 3A. The intense signal at −549.1 ppm derives from monomeric vanadate, and those at −569.9 and −577.8 ppm derive from divanadate and tetravanadate, respectively.

Three new signals are clearly observable in the NMR spectrum of the β-anomer (Figure 3B). Those at −557.7 and −562 ppm are assigned to esters of vanadate with the secondary hydroxyls of methyl glucoside. The third signal, at −582 ppm, apparently derives from esters of divanadate since this signal decreases in relative magnitude, as does that from divanadate, when the total vanadate concentration is decreased. Also, at low vanadate concentrations, where there is little divanadate in solution to obscure the signal, a fourth signal ascribed to diesters can be observed at −573 ppm. The intensity of this signal is comparable to that occurring at −562 ppm and is of comparable width. One further signal can be identified in the spectrum. This signal occurs just to high field of the vanadate signal at −551 ppm and is assigned to the primary vanadate ester, which is formed with the hydroxyl group at C-6 of the glucoside. At pH 6.8 this signal is much more clearly resolved and occurs at −558.6 ppm whereas that from vanadate is found at −559.9 ppm. The assignment of this signal to the primary ester is based on our general observation that vanadate primary esters, when measured at neutral pH, give rise to NMR signals to low field of the lowest field secondary esters and also our finding that the vanadate ester of 2-(hydroxymethyl)tetrahydropyran gives a signal in this region of the NMR spectrum.

Assignment of structures to the vanadate derivatives giving rise to the signals assigned to secondary esters is aided somewhat by comparison of the spectrum of vanadate in the presence of methyl α-D-glucopyranoside (Figure 3C) with that of the β-derivative (Figure 3B). The only significant difference between the two spectra is that the −562 ppm signal of the β-anomer moves position, presumably to −558 ppm, where it is superimposed on the signals ascribed to vanadate esters of the other secondary hydroxyls already in that position. The −562 ppm signal of the β-derivative is then assigned to a vanadate at the 2-position of the glucose ring, as only this position is expected to be significantly affected by the shift of the methoxy group from an axial to an equatorial position. The signals at −558 ppm can then be assigned to the vanadate esters at the 3- and 4-positions of the β-glucoside and to the 2-, 3-, and 4-positions of the α-derivative.

Table III. Concentrations of Products Formed from the Reaction of Vanadate with Methyl β-D-Glucopyranoside in Aqueous Solution[a–c]

[V(t)]	[β-glu]	$[T_i]$ + $[T\ell']$	$[T\ell']$	$[T_2(t)]$	$^1/_2([T_2\ell'] + [T_2\ell'_2])$	$[T_4]$
3.0	0.0	1.534		0.544		0.888
3.0	0.515	1.421	0.436	0.589	0.181	0.358
3.0	0.773	1.358	0.594	0.591	0.190	0.266
3.0	1.030	1.221	0.719	0.631	0.247	0.182
3.0	1.288	1.132	0.857	0.626	0.286	0.098
3.0	1.545	1.060	0.933	0.649	0.295	0.064
0.5	1.545	0.236	0.193	0.061	0.010	
1.0	1.545	0.414	0.374	0.163	0.049	
2.0	1.545	0.798	0.662	0.379	0.146	0.015
4.0	1.545	1.269	1.159	0.935	0.440	0.197

[a] Conditions of the experiments were as follows: pH, 8.50; buffer, 20 mM HEPES; temperature, ambient (21 °C); the indicated concentrations of vanadate and methyl β-D-glucopyranoside. [b] Concentrations of all vanadate derivatives are given as vanadium atom concentrations in millimolar units. The glucoside concentrations are given in molar units. [c] Identification of symbols: V(t), total vanadate in solution; β-Glu, methyl β-D-glucopyranoside; T_i, inorganic vanadate; $T\ell$, vanadate ester formed with the primary hydroxyl of the glucoside; $T\ell'$, vanadate esters formed with secondary hydroxyls of the glucoside; $T_2(t)$, dimeric vanadate plus esters of divanadate with ^{51}V NMR signals under the T_2 signal, including $T_2\ell$, $T_2\ell_2$, and $^1/_2T_2\ell'$, where the ℓ refers to primary hydroxyl and ℓ' to secondary hydroxyl products; $T_2\ell'$, divanadate esters formed with secondary hydroxyls (only the vanadium with the ligand attached is expected to give an NMR signal separated from that from T_2 here); $T_2\ell'_2$, divanadate diesters from secondary hydroxyls of the glucoside; T_4, tetravanadate.

It is interesting to note from the spectra of Figure 3 that no pentacoordinate vanadate product is observed with the β-glucoside. This presumably reflects the ring flattening (compared to cyclohexane) associated with the replacement of carbon by oxygen in the cyclohexane ring. There is however a small amount of pentacoordinate product formed with the α-anomer.

There are some problems associated with determining equilibrium constants for the formation of all products since there are many overlapping signals. Table III gives the results of vanadate and methyl β-D-glucopyranoside concentration studies. These data allow formation constants for the primary and secondary vanadate esters to be readily obtained.

The NMR signal from the primary ester lies under that from monomeric vanadate. As a consequence, the sum of the concentrations of these two species must be utilized. Combination of eq 1 with eq 3 and then rearrangement give eq 12. A plot

$$\frac{[T_i] + [T\ell]}{[T_4]^{1/4}} = K_0^{-1/4} + K_0^{1/4}K_2[\ell] \qquad (12)$$

of the ratio on the left of this equation vs $[\ell]$ gave a line of intercept $K_0^{-1/4} = (1.29 \pm 0.06) \times 10^{-2}$ M$^{3/4}$ and slope $K_0^{-1/4}K_2 = (2.5 \pm 0.2) \times 10^{-3}$ M$^{-1/4}$, from which $K_2 = 0.19 \pm 0.02$ M^{-1}. This value for K_2 is very close to that determined for the formation of ethyl vanadate, 0.20 at pH 7.5.[6] Having determined K_2, one can readily calculate the proportion of T_i of the total measured concentrations of $T_i + T\ell$ (referred to below as $T_i(t)$) for any of the concentrations of Table III. However, $[T_i]$ is just equal to $K_0^{-1/4}[T_4]^{1/4}$, and thus either $[T_i(t)]$ or $[T_4]$ can be used to give the formation constant K_2', which represents the sum of the formation constants for the three secondary vanadate esters, $T\ell'$, formed at the 2-, 3-, and 4-positions of the glucoside. On plotting the relevant parameters of eq 13, the value for K_2' of 0.72 ± 0.06

$$\frac{[T\ell']}{K_0^{-1/4}[T_4]^{1/4}} = [\ell]K_2' \qquad (13)$$

Table IV. Concentrations of Products Formed from the Reaction of Vanadate with Methyl β-D-Galactopyranoside[a-c]

[V(t)]	[β-gal]	$[T_i] + [T\ell]$	$T\ell'$	$[T_2] + [T_2\ell]$	$[T_4]$	[−544]	[−517]	[−502]
4.0	0.026	1.769		0.682	1.350		0.078	
4.0	0.103	1.665		0.680	1.028	0.283	0.288	0.024
4.0	0.155	1.659		0.601	1.854	0.393	0.416	0.055
4.0	0.258	1.619	0.048	0.534	0.544	0.508	0.598	0.141
4.0	0.309	1.553	0.069	0.486	0.451	0.554	0.691	0.196
0.5	1.545	0.285	0.048	0.011		0.019	0.065	0.071
1.0	1.545	0.485	0.099	0.022		0.061	0.157	0.174
2.0	1.545	0.767	0.127	0.067		0.146	0.428	0.464
3.0	1.545	0.961	0.130	0.088		0.277	0.726	0.818
4.0	1.545	1.337	0.211	0.174		0.332	0.889	1.057

[a] Conditions of the experiments were as follows: pH, 8.5; buffer, 20 mM HEPES; temperature ambient; the indicated concentrations of vanadate and methyl β-D-galactopyranoside. [b] Concentrations of all vanadate derivatives are given as vanadium atom concentrations in millimolar units. The galactoside concentrations are given in molar units. [c] Identification of symbols: β-gal, methyl β-D-galactopyranoside; −544, product giving rise to the vanadium NMR signal at −544 ppm; −517, products giving rise to the NMR signals at −516.5 and −521 ppm; −502, products giving rise to the vanadium NMR signals centered at −502 ppm. Other symbols are as for Table III except that ℓ now refers to the galactoside.

M^{-1} was obtained. Since there are three secondary hydroxyls, this averages to 0.24 ± 0.2 M^{-1} for each position. This value is very close to that for the primary hydroxyl and is in accord with our general observation that primary and secondary esters are formed equally well.

Divanadate esters are also readily formed, but the complexity of the spectra resulting from overlapping transitions precludes a reliable determination of the various formation constants. In principle, the problem can be solved and has been above for *trans*-1,2-cyclohexanediol, and elsewhere for methanol,[22] albeit in these cases either only primary or only secondary divanadate esters are formed.

The chemistry associated with the α-glucoside is not expected to differ significantly from that of the β-anomer, so it has not been studied in detail. The α-derivative does, however, form observable amounts of the pentacoordinate product. From the spectra obtained, a value of $K_6{}^2K_7 = 8.6$ M^{-3} was estimated for the formation of this product from two ligands and two vanadates by utilizing eq 11 and assuming no significant concentrations of monomeric products. This formation constant is very small, being only 0.4% of the analogous value determined from *trans*-1,2-cyclohexanediol. Not surprisingly, the situation is very different when one of the hydroxyls on the pyranose ring is in an axial position. In such cases the formation of cyclic products is highly favored as observed for the methyl α- and β-D-galactopyranosides.

Methyl α- and β-D-Galactopyranosides. D-Galactose is the 4-epimer of D-glucose and as such has an axial hydroxyl at position 4 of the pyranose ring when the galactopyranoside is in its preferred conformation. The galactoside readily reacts with vanadate. The formation of a variety of products is evident from the spectra of Figure 4. The conditions for these spectra are the same as for those of the glucosides displayed in Figure 3.

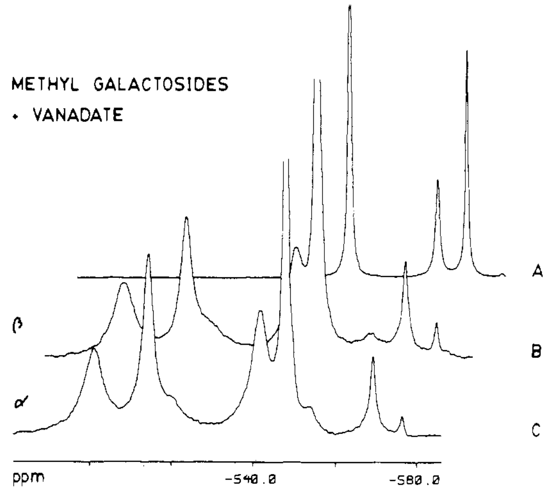


Figure 4. Formation of a variety of vanadate complexes of methyl β- (B) and α-D-galactopyranosides (C) are indicated by these ^{51}V NMR spectra, which are compared to a spectrum (A) obtained under similar conditions but with no galactoside present. Experimental conditions are as for the glucoside spectra (Figure 3) but with 0.515 M galactoside in solution to replace the glucoside.

It is evident from these spectra that there is little difference between the reactions of the α- (Figure 4C) and the β-anomers (Figure 4B) with vanadate. As was similarly observed for the glucosides, a signal occurring at −562 ppm with the β-galactoside disappears (is absent with the α-anomer) and a different ^{51}V signal occurs at −552 ppm. These signals are assigned to the vanadate esters formed at the 2-positions of the two monosaccharides. The NMR signals from the remaining vanadate esters occur under the signal from T_i at −547 ppm.

Four other NMR signals are observed in the ^{51}V spectrum, only two of which occur at resonance positions similar to those observed for the cyclohexanediols. One signal occurs at −516.5 ppm, and this is superimposed on a much broader signal that is centered near −521 ppm. These two signals throughout the remainder of the discussion are referred to as the −517 ppm signal. Another signal occurs at −544 ppm, and the fourth, at −502 ppm.

Table IV gives the results of vanadate and methyl β-D-galactopyranoside concentration studies at pH 8.5. As for the cyclohexanediols, signals for all the esters are not observed, but rather there is a superposition of NMR signals from vanadate and three of the vanadate esters. Application of eq 12 to the data of Table IV gives a value for K_2 of 0.67 ± 0.07 M^{-1} or, on division by 3, an average of 0.22 M^{-1} for ester formation on hydroxyl groups. A value of $K_0{}^{-1/4} = (1.26 \pm 0.05) \times 10^{-2}$ $M^{3/4}$ was obtained from the *y* intercept of this plot.

The value of 0.67 M^{-1} can be used to calculate the proportions of T_i and $T\ell$ giving rise to the signal at −547 ppm at the various concentrations of Table IV. The calculated concentrations of T_i and the measured concentrations of the ester giving rise to the ^{51}V signal at −561 ppm ($T\ell'$ of Table IV) can then be utilized with eq 3 to provide a determination of K_2 for the formation of this product. The value measured was $K_2 = 0.16 \pm 0.03$ M^{-1}, a value in excellent agreement with the above determination for the other three hydroxyls of the galactose ring.

A measure of the overall formation constant for the esters of divanadate was obtained through application of eq 10. A value for K_4 of 0.8 ± 0.2 M^{-1} was obtained. This value of K_4 is similar to the sum of four K_2 values, as expected, since there are four hydroxyls at which condensation can occur. No information concerning the formation of either $T\ell_2$ or $T_2\ell_2$ was obtainable from the results of this study.

The prominent signals of major interest in Figure 4 are those occurring at −544, −517, and −502 ppm. As is evident from Table IV, these signals maintained a constant proportionality in their intensities as the total vanadate concentration was varied. This establishes that the products giving rise to these signals all contain the same number of vanadium nuclei, which can easily be shown to be 2. A constant proportionality between the −517 and −502

---

(22) Tracey, A. S.; Gresser, M. J.; Galeffi, B. *Inorg. Chem.* **1988**, *27*, 157–161.

ppm signals was not maintained as the ligand concentration was varied, with the product giving rise to the −502 ppm resonance being favored at the higher ligand concentrations.

Analysis of the change in concentration of the −544 ppm product indicated that this compound was formed according to eq 14, where ℓ refers to the ligand, methyl β-D-galactopyranoside. Since

$$2T_i + \ell \overset{K_9}{\rightleftharpoons} -544 \qquad [T_i]^2[\ell]K_9 = [-544] \tag{14}$$

$[T_i]^2 = K_0^{-1/2}[T_4]^{1/2}$, a plot of [−544] vs $K_0^{-1/2}[T_4]^{1/2}[\ell]$ using the concentrations in Table IV gave a line of slope (1.06 ± 0.06) × 10^3 M^{-2}, where for the purposes of this plot it was initially assumed that only one of the two vanadium nuclei of the −544 ppm product gave a signal at this chemical shift. The second vanadium signal from this compound then occurs under either the −544, −517, or −502 ppm signal, and this assumption can be examined. The product giving rise to the −544 ppm signal was first assumed to be a mixed anhydride with one ^{51}V signal occurring at −544 ppm and the other most probably at either −516.5 or −521 ppm. Similar mixed anhydrides have been found for the lactate system, where an octahedral/tetrahedral product has been proposed,[14] and for the tris(hydroxymethyl)aminomethane system, where it has been proposed that a trigonal-bipyramidal/tetrahedral mixed anhydride is formed.[21] As for the case here, both of these latter products have two vanadates and one ligand. The formation of such products is not surprising since the products, $T_2\ell$, are readily formed and, unless bridging by the ligand from one vanadate moiety to the other occurs, cyclization gives the proposed product directly.

If the second vanadium NMR signal of the −544 product arises at −516.5 ppm, then its formation can be inferred from examination of the behavior of the −517 ppm resonance as a function of ligand and vanadate concentrations. The broad NMR signal occurring at −521 ppm might be the symmetrical anhydride formed from the −544 product by addition of a second ligand, and then eq 15 is obtained where BP_2 identifies this product as a

$$-544 + \ell \overset{K_{10}}{\rightleftharpoons} BP_2 \qquad [-544][\ell]K_{10} = [BP_2] \tag{15}$$

pentacoordinate derivative with a presumed trigonal-bipyramidal coordination, as discussed above for the 1,2-cyclohexanediols and previously for ethylene glycol.[13]

Combination of eq 14 with eq 1 and 15 followed by rearrangement gives eq 16. The factor of 2 arises because only

$$\frac{[-544] + 2[BP_2]}{K_0^{-1/2}[T_4]^{1/2}[\ell]} = K_9 + 2K_9K_{10}[\ell] \tag{16}$$

vanadium ion concentrations are measured. The quantity [−544] + $2[BP_2]$ corresponds to [−517] of Table IV, since this set of signals is assumed to consist of the resonance from the two vanadium atoms of BP_2 and the resonance from one of the two vanadium atoms of the −544 product. On plotting the ratio on the left of eq 16 vs $[\ell]$, one obtains a line of intercept K_9 = (0.99 ± 0.05) × 10^3 M^{-2} and a slope $2K_9K_{10}$ = (1.01 ± 0.06) × 10^3 M^{-3} (=$2K_6{}^2K_7$ of eq 11), from which K_{10} = 0.51 ± 0.04 M^{-1}. This value of K_9 is well determined and agrees exceptionally well with that previously measured from the −544 ppm signal, K_9 = (1.06 ± 0.06) × 10^3 M^{-2}. At 0.515 M methyl β-D-galactopyranoside, these values give the proportion 1:3.8 for the $[BP_2]$:[−544] ratio or 1:1.9 for the vanadium atom concentrations for the NMR signals at −516.5 and −521 ppm. This proportion agrees well with that observed. The −516.5 ppm signal then derives from the pentacoordinate moiety of the bipyramidal/tetrahedral mixed anhydride, while the much broader −521 ppm signal is from the two vanadium atoms of the symmetrical anhydride. The structure of this latter product is assumed to be similar to that of the analogous product formed from the cyclohexanediols. Of course, the possibility of stereoisomers in this product cannot be ignored.

The product giving rise to the ^{51}V NMR signal at −502 ppm is different from previously observed products. This product contains two vanadium atoms and two ligands and can incorporate a third ligand. The chemical shift is lower than previously observed for products containing only oxygen ligands. A product giving rise to a similar ^{51}V chemical shift has been observed with the buffer 1,1,1-tris(hydroxymethyl)aminomethane, but this product was mononuclear in vanadium, and it is possible that the amine group acts as a ligand in this complex.[21]

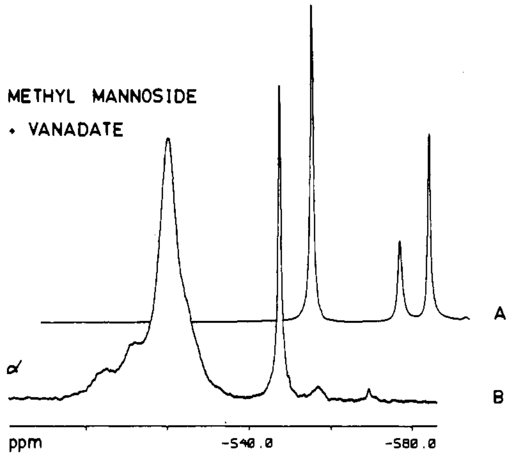


Figure 5. ^{51}V NMR spectra of vanadate in the absence (A) and presence (B) of methyl β-D-mannopyranoside (0.515 M) obtained under conditions similar to those for the glucoside (Figure 3) and galactoside (Figure 4) spectra.

The present compound is formed according to eq 17 and 18, where 2[−502′] + 2[−502″] = [−502]. Summation of eq 17 and 18 followed by combination with eq 1 and rearrangement provides

$$2T_i + 2\ell \overset{K_{11}}{\rightleftharpoons} -502' \qquad [T_i]^2[\ell]^2K_{11} = [-502'] \tag{17}$$

$$-502' + \ell \overset{K_{12}}{\rightleftharpoons} -502'' \qquad [-502'][\ell]K_{12} = [-502''] \tag{18}$$

eq 19. From the values for [−502] in Table IV, the various ligand

$$\frac{[-502]}{2K_0^{-1/2}[T_4]^{1/2}[\ell]^2} = K_{11} + [\ell]K_{11}K_{12} \tag{19}$$

and T_4 concentrations, and the known $K_0^{-1/2}$, the ratio on the left of eq 19 versus the concentration of methyl β-D-galactopyranoside was plotted to give the intercept K_{11} = (3.7 ± 0.2) × 10^2 M^{-3} and slope $K_{11}K_{12}$ = (7.8 ± 0.7) × 10^2 M^{-4}, from which K_{12} = 2.1 ± 0.3 M^{-1}. Thus, incorporation of the third ligand is quite favorable compared to formation of the acyclic tetrahedral esters. It, unfortunately, is not possible to tell whether the third galactoside is acting as other than a monodentate ligand.

If it is accepted that previous studies, in their assignment of trigonal-bipyramidal and octahedral coordination to vanadium(V) nuclei giving rise to signals at ∼−520 and ∼−535 ppm, are correct for hydroxyl-bearing ligands, then it may be that the −500 ppm signals, observed here for the galactoside and previously for the Tris buffer, derive from complexes having a different coordinate geometry, such as square-pyramidal pentacoordinate. No information concerning possible bridging from one vanadium to another by these ligands is provided by these studies.

Methyl β-D-Mannopyranoside. Methyl β-D-mannopyranoside has an axial hydroxyl in the 2-position of the pyranose ring rather than the 4-position as for the galactoside. Other than this, there is little difference between the two isomers, and reaction with vanadate might be expected to be similar for the two compounds. Figure 5 shows the ^{51}V NMR spectrum of vanadate in the presence of the methyl mannoside under conditions similar to those for the glucosides and the galactosides.

It is evident from Figure 5 that the formation of the bipyramidal dimer, BP_2 (−522 ppm), is much more favored with the mannoside than with the galactoside. Interestingly, there is no signal corresponding to the −544 ppm signal of the galactoside system. This may be an indication that the mixed pentacoordinate/tetrahedral anhydride of the galactoside system is in fact a bridged system with the bridging occurring via the hydroxymethyl group at C-5 of the carbohydrate ring. A similar stereochemistry is not available for the mannoside. Clearly, more studies on this aspect of complex formation are required. Low-intensity ^{51}V NMR signals were also observed at −506 and −514 ppm in the mannoside system. Because of the line widths of the various signals, no effort was made to quantitatively assess the spectra.

Conclusions

The hydroxyl groups of six-membered cyclic molecules such as pyranosides and 1,2-cyclohexanediols form acyclic vanadate esters and cyclic complexes analogous to those observed earlier with ethylene glycol.[13] However, the geometric constraints imposed by the cyclic ligands strongly influence the equilibrium constants for formation of the various complexes and are probably responsible for the formation of some types of complexes not previously observed with ligands containing only hydroxyl groups. Esterification of axial hydroxyls by vanadate is disfavored, while formation of cyclic complexes is strongly favored for ligands with cis compared to those with trans vicinal hydroxyl groups. Although cyclic complexes were not detected with methyl β-D-glucopyranoside, such a complex was observed to form with methyl α-D-glucopyranoside, however, with a formation constant about 60 times smaller than that for the analogous complex with methyl β-D-galactopyranoside. This observation is in keeping with the occurrence of ring flattening associated with the replacement of a carbon of the cyclohexane ring by an oxygen. Ring flattening increases the dihedral angle between the adjacent diequatorial C–O bonds of the trans hydroxyls from the nominal 60° of the unperturbed system. The corresponding angles between the hydroxyls in the cis arrangement are decreased from 60°. The smaller angle favors formations of a five-membered cyclic product. On this basis, it is expected that cyclic products formed from the methyl glucosides will be less favored than those from the methyl galactosides and mannosides, and this is observed.

A complex, binuclear in vanadium, but with mixed-coordination structure is formed with the methyl D-galactosides, but there is no evidence for such a complex with methyl α-D-mannopyranoside, possibly because the vicinal *cis*-hydroxyls of the galactosides are sufficiently close to the 6-hydroxyl group for some interaction that is not possible with the mannoside.

It is apparent from these studies that both the types and the stabilities of the vanadate complexes formed from these ligands are very sensitive to subtle changes in ligand structure.

The formation of 5-coordinate vanadate complexes with the vicinal hydroxyls of six-membered cyclic molecules may be relevant to possible effects of vanadate on the metabolism of inositol phosphates and phosphatidyl inositol,[18,19] which is thought to involve, in some cases, the formation of an inositol 1,2-cyclic phosphate.[20] The pentacoordinate uridine vanadate complex presumably inhibits the function of ribonuclease because the complex resembles the transition state for formation and hydrolysis of the uridine 2′,3′-cyclic phosphate intermediate of the enzymatic reaction. Analogous behavior might be expected for enzymes that catalyze formation or hydrolysis of inositol cyclic phosphates.

Acknowledgment. Thanks are gratefully extended to the Natural Sciences and Engineering Research Council of Canada (M.J.G.), the Medical Research Council of Canada (M.J.G.), and the British Columbia Heart Foundation (A.S.T.) for their financial support of this work.

Contribution from the Department de Quimica Inorganica and Department de Fisica, Universitat de Barcelona, 08028 Barcelona, Spain, and Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204

Importance of Metal–Metal Interactions through the P–P Bonds for the Multidimensional Electrical Properties of MP_4 (M = V, Cr, Mo)

Santiago Alvarez,[*,1a] Josep Fontcuberta,[*,1b] and Myung-Hwan Whangbo[*,1c]

Received January 22, 1988

The electronic structures of MP_4 (M = V, Cr, Mo) were examined by performing tight-binding band calculations on VP_4. The MP_4 phase has a structure in which metal atom chains are sandwiched between P_4^{2-} layers. Despite this apparently one-dimensional character, the t_{2g}-block bands of VP_4 are dispersive not only along the chain but also along the interchain and interlayer directions. Our study shows that the multidimensional nature of those bands originates from the fact that metal atom chains interact with one another through the P–P bonds of the P_4^{2-} layers. Our Fermi surface calculations reveal that VP_4 is a three-dimensional metal, while CrP_4 and MoP_4 are semimetals.

In the past two decades, the series of transition-metal phosphides MP_4 (M = V; M = Cr, Mo, W; M = Mn, Tc, Re; M = Fe, Ru, Os) have been obtained.[2] The first member of the series, VP_4, contains one-dimensional chains of metal atoms parallel to the *c* axis[3] and shows metallic conductivity. The same structure is found for CrP_4 and MoP_4, both of which exhibit metallic properties.[4a] WP_4 is observed to be a poor metal, but its exact structure has not been determined yet.[4b] MnP_4, TcP_4, and ReP_4 do not form chains of metal atoms but consist of metal–metal dimers.[5-8] Three different structural modifications exist for MnP_4, all of which are semiconductors and differ in the way the Mn_2 dimers are connected to one another. FeP_4, RuP_4, and OsP_4 have structures with no metal–metal bonds,[9-11] and all of them are diamagnetic semiconductors. MP_4 phases for M = Ti, Co, Ni, and Cu have not been made, whereas non-transition-metal MP_4 phases are known (e.g., CdP_4,[12] MgP_4,[13] and $MgAs_4$[14]).

---

(1) (a) Departament de Quimica Inorganica, Universitat de Barcelona. (b) Departament de Fisica, Universitat de Barcelona. (c) North Carolina State University.

(2) For a recent review, see: Jeitschko, W.; Florke, M.; Moller, M.-H.; Ruhl, R. *Ann. Chim. Fr.* **1982**, *7*, 525.

(3) Jeitschko, W.; Florke, M.; Scholz, M. D. *J. Solid State Chem.* **1984**, *52*, 320.

(4) (a) Jeitschko, W.; Donohue, P. C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 1893. (b) Kinomura, N.; Terao, K.; Kikkawa, S.; Koizumi, M. *J. Solid State Chem.* **1983**, *48*, 306.

(5) Jeitschko, W.; Donohue, P. C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 574.

(6) Ruhl, R.; Jeitschko, W. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 39.

(7) Ruhl, R.; Jeitschko, W.; Schwochau, K. *J. Solid State Chem.* **1982**, *44*, 134.

(8) Jeitschko, W. Ruhl, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 1953.

(9) (a) Jeitschko, W.; Braun, D. J. *Acta Crystallogr., Sect B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 3196. (b) Sugitani, M.; Kinomura, M.; Koizumi, M.; Kume, S. *J. Solid State Chem.* **1978**, *26*, 195. (c) Grandjean, F.; Gerard, A.; Kriger, M.; Heiden, C.; Braun, D. J.; Jeitschko, W. *Solid State Commun.* **1980**, *33*, 261.

(10) (a) Evain, M.; Broc, R.; Fiechter, S.; Tributsh, H. *J. Solid State Chem.* **1987**, *71*, 40. (b) Fiechter, S.; Tributsch, H.; Evain, M.; Brec, R. *Mater. Res. Bull.* **1987**, *22*, 543.

(11) (a) Braun, D. J.; Jeitschko, W. *Z. Anorg. Allg. Chem.* **1978**, *445*, 157. (b) Florke, M.; Jeitschko, W. *J. Less-Common Met.* **1982**, *86*, 247.

(12) Krebs, H.; Muller, K.-H.; Zurn, G. *Z. Anorg. Allg. Chem.* **1956**, *285*, 15.

(13) (a) Gibinski, T.; Cisowaska, E.; Zdanowivz, W.; Henkie, Z.; Wojakowski, A. *Krist. Tech.* **1974**, *9*, 161. (b) El Maslout, A.; Zanne, M.; Jeannot, F.; Gleitzer, Ch. *J. Solid State Chem.* **1975**, *14*, 85. (c) von Schnering, H. G.; Menge, G. *Z. Anorg. Allg. Chem.* **1976**, *422*, 219.

0020-1669/88/1327-2702\$01.50/0