Synthesis, characterization and crystal structure of cyclic vanadate complexes with monosaccharide derivatives having a free adjacent diol system

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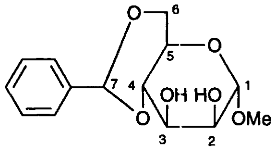
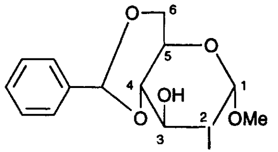
A new approach to the study of reactions between vanadate and monosaccharide derivatives by introducing them into an acetonitrile medium has been elaborated. Based on this approach, a crystalline product of the reaction of $[NBu^n_4][H_2VO_4]$ with methyl *O*-4,6-benzylidene-α-D-mannopyranoside (H_2L^1) has been obtained, $[NBu^n_4]_2[(VO_2L^1)_2]$, and its structure has been determined by X-ray crystallography. The anion comprises a dinuclear $V_2(\mu\text{-}O)_2$ centre and two deprotonated H_2L^1 molecules. Each vanadium atom is bound to the deprotonated vicinal *cis*-diol of one mannopyranoside ring resulting in a five-membered ring cyclic complex. The geometry of the two five-co-ordinated vanadium(v) atoms is intermediate between a square pyramid and a trigonal bipyramid. A complex with a similar formula $[NBu^n_4]_2[(VO_2L^3)_2]$ {H_2L^3 = 5′-*O*-[(*p*-methoxyphenyl)diphenylmethyl]uridine}, has also been prepared and spectroscopically characterized. Multinuclear NMR studies and conductivity measurements in acetonitrile provided strong evidence that the dimeric structure of both complexes is maintained in solution. Vanadium-51 NMR titration studies in acetonitrile solutions showed that the chelation ability follows the order $L^3 > L^1 > L^2$ (H_2L^2 = methyl *O*-4,6-benzylidene-α-D-glucopyranoside). Molecular modelling suggested that the $O^- \cdots O^-$ distance and dihedral angle between the adjacent hydroxyl groups in a sugar ring are the determining factors for vanadium chelation.

The recent interest in the reaction between vanadate and carbohydrates is due mostly to the discoveries of various biological responses induced by vanadate, *i.e.* the inhibitive activities for ribonucleases[1] and almost all the ATPases,[2] insulin-mimetic activity[2] and cardiovascular effects.[3] These biological effects are commonly interpreted in terms of the analogy of vanadate to phosphate, including the vanadate esterification with carbohydrates and their derivatives.[2] However, the exact role and details of the mechanism in these systems are often not fully understood. The approaches currently used to study the formation of vanadate esters with monosaccharides[4–7] and nucleosides[7–12] were mostly confined to characterization in aqueous solutions. The presence of several hydroxyl groups with various configurations in the carbohydrate molecules and various oligomeric forms of vanadate in the solution complicate the study. Thus there was some debate as to the characterization of the reaction products.[6–10] To our knowledge, no crystal structure of a vanadate complex with carbohydrate has been reported except those of the adenosine–[13] and quinic acid–(1,3,4,5-tetrahydroxycyclohexanecarboxylic acid) vanadate[14] systems. Such structural characterization is needed,[12] particularly in view of the important role of these types of reactions in vanadium(v) biochemistry.

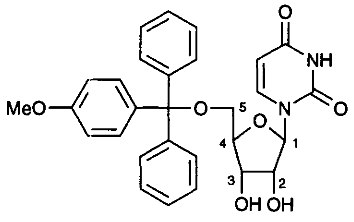
Reactions between vanadate and diol derivatives have been studied as models of the vanadate esterification of carbohydrates. As indicated by Crans and co-workers[7,15–18] and others,[5,19] the structures of the reaction products between vanadate or chlorovanadate and 1,2- or 1,3-diols are dramatically dependent on the subtle geometry and substituent groups of these diols. For instance, the dinuclear complex of pinacol chlorovanadate, $[\{VOCl(OCMe_2CMe_2O)\}_2]$,[15] contains a VOVO four-membered ring with each vanadium in a distorted trigonal-bipyramidal arrangement. The dimeric chlorovanadate complex with ethylene glycol, $[\{VOCl(OCH_2CH_2O)\}_2]$,[16] features a macrocyclic arrangement of tetrahedral vanadium, while the reactions between $VOCl_3$ and propane-1,3-diol derivatives gave tetrameric vanadium(v) clusters.[18] Evidently, the interpretation of the various modes of vanadate esterification with carbohydrates is exceedingly complex.



H_2L^1



H_2L^2



H_2L^3

In order to gain an insight into the relation between the mode of vanadate esterification and the number and configurations of free hydroxyl groups in carbohydrate residues in biological molecules, we blocked certain hydroxyl groups of some monosaccharides and studied their esterification. Instead of an aqueous medium, acetonitrile was used as solvent and thus the reactions were controlled. We obtained vanadate complexes of monosaccharide derivatives having a free vicinal *cis*-diol structure. The crystal structure of the vanadate complex with methyl 4,6-*O*-benzylidene-α-D-mannopyranoside (H_2L^1) has been elucidated by X-ray analysis, and ^{51}V NMR spectroscopy was used to characterize the species in acetonitrile.

Experimental

Materials

Vanadium pentaoxide (99.9%) and tetra-*n*-butylammonium iodide (A.R.) were obtained from Shanghai Chemical Co., uridine (99%) and benzaldehyde (redistilled before use) from Sigma, D-mannose from Serva and chloro(*p*-methoxyphenyl)-diphenylmethane (97%) from Aldrich; anhydrous D-glucose (A.R.), CD_3CN (> 99%) and spectragrade acetonitrile were from Beijing Chemical Co. and used without further purification. Other organic solvents were purified by conventional methods.[20]

Physical measurements

The UV/VIS spectra were obtained on a Shimadzu UV-260 spectrophotometer, diffuse-reflectance spectra in a $BaSO_4$ matrix using a Shimadzu UV-3100 UV/VIS/NIR recording spectrophotometer, IR spectra (as KBr pellets) on a Perkin-Elmer 983G spectrometer and ^{13}C and ^1H NMR spectra on a Varian VXR 300 MHz instrument with $SiMe_4$ as an internal standard for the non-aqueous systems. The conductivities of the products were measured in $\approx 10^{-3}$ mol dm^{-3} solutions using a model DDS-11A conductometer and a DJS-1 conducting glass electrode from Shanghai Analytical Instruments. Elemental analyses (C, H, N) were performed by a Perkin-Elmer 240C instrument. The vanadium content was determined complexometrically and spectrophotometrically [molar absorption coefficient 17.26 dm^3 mol^{-1} cm^{-1} for $VOCl_2$ aqueous solutions at 760 nm (0.0–0.02 mol dm^{-3})].

Vanadium-51 NMR spectroscopy

The ^{51}V NMR spectra were scanned on a Varian XL-400 NMR spectrometer with a broad-band facility at about 20 °C. The measurements were conducted at 105 MHz, using a 90° pulse width, a 0.10 s acquisition time and 5000 average scans. A line-broadening factor of 20 Hz was applied to all spectra before Fourier transformation. The vanadium chemical shifts are given in ppm relative to external $VOCl_3$ (δ 0) and the error in the chemical shift is estimated to be ± 1 ppm for resonances with a linewidth $\leqslant 1000$ Hz and ± 3 ppm for those with > 1000 Hz. The relative peak areas were obtained with the instrument integration routine. The concentrations of various vanadate species in each sample were calculated on the basis of the corresponding peak areas along with the total vanadium concentrations and expressed in molarities of vanadium.

The solutions for ^{51}V NMR titration were prepared by dissolving directly tetra-*n*-butylammonium vanadate and the monosaccharide derivatives in acetonitrile at various molar ratios and then 10% (v/v) CD_3CN was added as field lock. Before measurement, the solutions were incubated for a certain time as indicated in the figure legends.

Syntheses

The salt $[NBu^n{}_4][H_2VO_4]$ was prepared according to the patent[21] with some modifications. To a mixture of water (5 cm^3) and $NBu^n{}_4I$ (3.69 g, 0.01 mol) dissolved in dichloromethane (50 cm^3) was added freshly prepared silver metavanadate (2.07 g, 0.01 mol) with stirring at room temperature. Stirring was continued for 4 h in the dark. The reaction mixture was filtered by suction and the precipitate washed thoroughly with dichloromethane. The washing liquid was combined with the filtrate. The dichloromethane layer was separated and dried over anhydrous $CaCl_2$ overnight. The solution was filtered and the solvent was removed under vacuum. The nearly colourless solid obtained was lyophilized at −40 °C. Owing to its hygroscopic nature the product was maintained in a desiccator; yield 1.87 g (52%). It was characterized by elemental analysis and infrared spectroscopy (Found: C, 54.3; H, 10.45; N, 3.90; V, 13.9. Calc. for $C_{16}H_{38}NO_4V$: C, 53.95; H, 10.6; N, 3.90; V, 14.2%). IR (KBr pellet): $\tilde{\nu}_{max}$/cm^{-1} 782s, 922s (sh), 1027w, 1054m, 1105w, 1151w, 1379m, 1482s (sh), 1664m, 2870s, 2956vs and 3391m (br). UV(MeCN): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 233 (6.02×10^4) and 282 (3.76×10^3).

The compounds methyl 4,6-*O*-benzylidene-α-D-mannopyranoside (H_2L^1) [m.p. 142–144 °C (lit.,[22] 140–143 °C); UV(MeCN): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 216 (1.54×10^3) and 242–268 nm (five peaks, ε 245–430)], methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (H_2L^2) [m.p. 163–164 °C (lit.,[23] 163–164 °C)] and 5′-*O*-[(*p*-methoxyphenyl)diphenylmethyl]uridine (H_2L^3) [m.p. 103–105 °C (lit.,[24] 103–105 °C); UV(MeCN): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 233 (1.46×10^4) and 259 (9.28×10^3)] were prepared according to the literature procedures[22,24] from D-mannose, D-glucose and uridine, respectively. Their identities were confirmed by IR and elemental analysis.

$[NBu^n{}_4]_2[(VO_2L^1)_2]$ 1. A solution of H_2L^1 (0.42 g, 1.5 mmol) in MeCN (15 cm^3) was added with stirring to a solution of $[NBu^n{}_4][H_2VO_4]$ (0.45 g, 1.3 mmol) in MeCN (10 cm^3). The mixture was stirred at 50–60 °C for about 12 h, then the dark green solution was concentrated to *ca.* 10 cm^3 by distillation under reduced pressure on a 60 °C water-bath. Diethyl ether (20 cm^3) was then added at room temperature with stirring. The product was filtered off and washed with diethyl ether. Recrystallization from acetonitrile–diethyl ether gave a dark green powder in 80% (0.65 g) yield which was dried in vacuum over phosphorus pentaoxide overnight. Pale green X-ray-quality crystals were obtained from the dark green solution of the vanadate complex in mixed acetonitrile–diethyl ether after standing in a tightly closed flask in a dark place at ambient temperature for 2 weeks. They were slightly moisture-sensitive (Found: C, 59.15; H, 8.60; N, 2.15; V, 8.35. Calc. for $C_{60}H_{104}N_2O_{16}V_2$: C, 59.5; H, 8.65; N, 2.30; V, 8.4%). IR (KBr pellet): $\tilde{\nu}_{max}$/cm^{-1} 700m, 756s, 806m, 876s, 913vs, 931vs, 969s, 1045–1126s, 1211m, 1302m, 1377vs, 1477vs, 1642w, 2869vs and 2957vs. UV/VIS(MeCN): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 216 (2.60×10^4), 280 (5.10×10^3), 523 (sh) (47.5) and 840 (br) (48.4). δ_V(105 MHz, CD_3CN) −497. δ_H(300 MHz, CD_3CN) 0.96 (24 H), 1.36 (16 H), 1.59 (16 H), 3.09 (16 H), 3.34 (3 H), 3.42 (3 H), 3.50–3.88 (m, 6 H), 4.08–4.22 (4 H), 4.22–4.38 (t, 2 H), 4.66 (2 H), 5.59 and 5.60 (2 H), 7.34–7.38 (m, 5 H) and 7.45–7.74 (m, 5 H). δ_C(75 MHz, CD_3CN) 13.76, 20.22, 24.19, 55.01, 55.11, 59.05, 62.48, 64.31, 69.02, 69.48, 78.57, 79.63, 80.90, 89.07, 101.9, 102.2, 102.4–102.8 (m), 127.0–129.6 (m) and 139.3.

$[NBu^n{}_4]_2[(VO_2L^3)_2]$ 2. This complex was synthesized by the same method in 70% yield as a dark green powder (Found: C, 64.1; H, 7.50; N, 4.85; V, 6.10. Calc. for $C_{90}H_{124}N_6O_{18}V_2$: C, 64.35; H, 7.45; N, 5.00; V, 6.05%). IR (KBr pellet): $\tilde{\nu}_{max}$/cm^{-1} 701s, 763s, 829m, 916vs, 985m, 1032s, 1088vs, 1177m, 1249vs, 1377s, 1459vs, 1504s, 1604m, 1685s (br), 2869vs, 2956vs, 3053s and 3190w (br). UV/VIS (MeCN): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 231 (4.18×10^4), 258 (2.69×10^4), 603 (100.6) and 865 (141.7). δ_V(105 MHz, CD_3CN) −497. δ_H(300 MHz, CD_3CN) 0.96 (24 H), 1.35 (16 H), 1.59 (16 H), 3.09 (16 H), 3.26–3.56 (m, 4 H), 3.77 and 3.78 (6 H), 4.00–4.30 (2 H), 4.44 (br, 2 H), 4.71–4.82 (2 H), 5.26 and 5.28 (2 H), 6.86–6.90 (m, 4 H), 7.24–7.74 (m, 28 H) and 10.98 and 11.05 (2 H). δ_C(75 MHz, CD_3CN): 13.78, 20.24, 24.20, 55.79, 59.07, 63.48, 65.21, 83.54, 87.19, 87.52, 90.39, 102.2, 127.6–131.3 (m), 135.7, 136.1, 141.3, 144.9–145.4 (m), 151.2, 159.3 and 163.9.

X-Ray crystallography

A suitable crystal of complex **1** was mounted in a glass capillary and measured at 295 K.

Crystal data. $C_{60}H_{104}N_2O_{16}V_2$, $M = 1211.3$, orthorhombic, space group $P2_12_12_1$, $a = 10.588(2)$, $b = 21.121(4)$, $c = 29.038(6)$ Å, $U = 6492(2)$ Å^3 [by least-squares refinement of diffractometer angles for 25 independent reflections, $\lambda = 0.710\,73$ Å (Mo-Kα)], $Z = 4$, $D_c = 1.239$ g cm^{-3}, $F(000) = 2608$. Pale green, slightly air-sensitive cube. Crystal dimensions $0.2 \times 0.3 \times 0.3$ mm, $\mu = 3.39$ cm^{-1}.

Data collection and processing. Rigaku AFC6S diffractometer, ω–2θ mode with 2θ scan range = 0.50°, ω-scan speed 4.00–32.00° min^{-1}, graphite-monochromated Mo-Kα radiation; Three standard reflections measured every 150. 5688 Reflections collected in the range 2θ 3.0–48.0°, 5655 independent, giving 4198 with $F > 4.0\sigma(F)$.

Structure analysis and refinement. Data reduction and the application of Lorentz-polarization and absorption corrections were carried out using the Siemens SHELXTL PLUS(VMS) system.[25] The structure was solved by direct methods using SHELXS 86.[26] Hydrogen atoms were calculated and included in ideal positions by using the riding model with U_{iso} fixed at 0.08 Å^2, and all other atoms were refined anisotropically. Full-matrix least-squares methods were used to refine an overall scale factor and positional and thermal parameters. The computations were carried out on a microVAX-II computer, and the plots were drawn using the XP subprogram of ref. 25. In the subsequent refinement, the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized where F_o and F_c are the observed and calculated structure-factor amplitudes. The indices $R = \Sigma(|F_o| - |F_c|)/(\Sigma|F_o|)$ and $R' = [\Sigma(w|F_o - F_c|)^2/\Sigma(w|F_o|)^2]^{\frac{1}{2}}$ with $w = [\sigma^2(F) + 0.00001F^2]^{-1}$ were 0.0791 and 0.0683, respectively.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/121.

Results and Discussion

Syntheses

The reactions of tetra-*n*-butylammonium vanadate in acetonitrile with H_2L^1 and H_2L^3 in 1.1 : 1 molar ratios (slight excess of proligand) give the dark green products of $[NBu^n{}_4]_2[(VO_2L^1)_2]$ **1** and $[NBu^n{}_4]_2[(VO_2L^3)_2]$ **2**, respectively. Both complexes are diamagnetic and EPR silent. Although attempts to grow crystals of **2** suitable for X-ray crystallography were unsuccessful, based on the identity of its ^{51}V NMR spectrum with that of complex **1** and the electronic, IR, ^{1}H and ^{13}C NMR spectra and conductivities, we suggest that the complex has a dinuclear structure similar to that observed for **1**. The recent report on the crystal structure of $[NEt_4]_2[\{VO_2(ado)\}_2]$[13] (ado = adenosine dianion) supports this conclusion.

Under the same conditions, however, the reactions of $[NBu^n{}_4][H_2VO_4]$ with H_2L^2 and methyl 2,3-di-*O*-acetyl-α-D-glucopyranoside lead to a mixture of reaction products. This is reasonable, because the two free adjacent hydroxyl groups in H_2L^2 are in *trans* configuration, while the two free hydroxyl groups in methyl 2,3-di-*O*-acetyl-α-D-glucopyranoside are not in adjacent positions. In both cases, the esterification is much more complicated.

The successful synthesis of the vanadate complexes with two monosaccharide derivatives having two free vicinal *cis*-hydroxyl groups in the sugar rings indicates that the condensation reaction between vanadate and hydroxyl groups is more favourable in acetonitrile than in aqueous solution. The high preference and selectivity of formation of the dioxovanadium(v) complex with the monosaccharide derivatives studied here represents a characteristic property of vanadate as an anion of an early transition element in higher oxidation state.[27] It is becoming clear that the high-valent oxovanadium ions such as $V^{IV}O^{2+}$, V^VO^{3+} and $V^VO_2{}^+$ have a strong affinity towards two oxo ligating atoms occupying adjacent *cis* positions to each other. The salts $M_2[V^{IV}O\ (C_6H_4O_2\text{-}1,2)_2]$ (M = NH_4 or Na) can be obtained from alkaline aqueous solutions.[28] Compounds of general formula $V^VOL(L')$, where L is a tridentate ligand and L′ a bidentate ligand with *cis*-dioxo ligating atoms (*e.g.* catechol, *N*-acetylhydroxylamine, salicylhydroxamic acid, *etc.*) have been prepared and spectroscopically characterized. Three of these complexes have been structurally characterized by X-ray crystallography.[29] Complexes of the cation $V^VO_2{}^+$ with ligands having adjacent dioxo ligating atoms were found with an α-hydroxy acid[19] and quinic acid.[14] In practice, the complexes studied here are further examples of such complexes.

X-Ray structural analysis

The crystal structure analysis of complex **1** revealed the presence of discrete $[NBu^n{}_4]^+$ cations and $[(VO_2L^1)_2]^{2-}$ anions. The molecular structure of the complex anion with the atom-labelling scheme is shown in Fig. 1. Selected bond lengths and angles of the anion are listed in Table 1. The anion $[(VO_2L^1)_2]^{2-}$ comprises a dinuclear $V_2(\mu\text{-}O)_2$ centre and two deprotonated H_2L^1 molecules. Each vanadium atom has two terminally bonded oxygen atoms [O(t)] and incorporates a vicinal *cis*-diol from one L^1 molecule resulting in a five-membered ring, namely a cyclic vanadate complex, with a stable twist conformation. The two vanadium atoms are bridged by two triply bonded oxygens [O(2) and O(7)] from two separate L^1 molecules, forming a VOVO four-membered ring. Each vanadium and its two terminal and one bridged oxygen atoms are coplanar to within 0.09 Å, and the sum of the three angles of the coplanar atoms is approximately 360°. The two vanadium atoms are each chelated by the deprotonated adjacent oxygens (O^-, O^-) in the same way from the two L^1 molecules, giving a plausibly symmetric structure to the complex. The two distorted 'axial' oxygens have O(2)–V(1)–O(8) and O(1)–V(2)–O(7) angles of 146.3(3) and 143.7(3)°, repectively. All the four six-membered rings, *i.e.* two α-D-mannopyranoside rings and two rings generated from the benzylidene-protected groups, adopt stable chair conformations. These general characteristics indicate that the two vanadium atoms are likely co-ordinated in a similar way and both have a distorted trigonal-bipyramidal geometry.

However, a further comparison of the data reveals that the arrangements of the ligating atoms about the two vanadium atoms in the anion are significantly divergent. For example, the bond V(1)–O(7) 2.002(8) Å deviates from V(2)–O(2) [2.061(7) Å]; and V(1)–O(8) [1.919(7) Å] from V(2)–O(1) [1.896(7) Å]. Moreover, C(15)–C(16) [1.586(15) Å] and C(16)–C(17) [1.420(17) Å] in one mannopyranoside ring

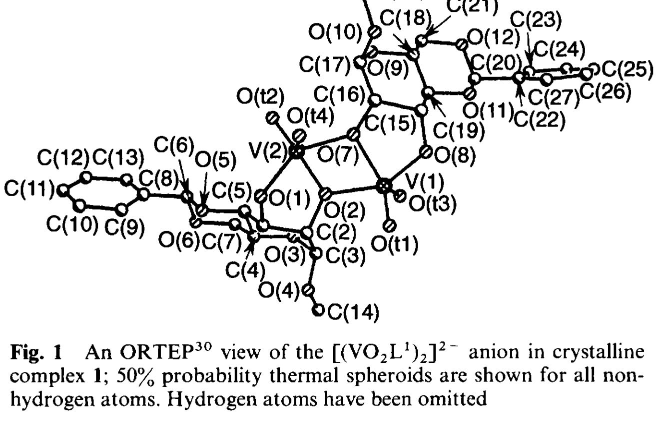


Fig. 1 An ORTEP[30] view of the $[(VO_2L^1)_2]^{2-}$ anion in crystalline complex **1**; 50% probability thermal spheroids are shown for all non-hydrogen atoms. Hydrogen atoms have been omitted

Table 1 Selected bond lengths (Å) and angles (°) for $[NBu^n{}_4]_2[(VO_2L^1)_2]$

V(1)–O(t1)	1.610(7)	V(2)–O(t2)	1.596(8)
V(1)–O(t3)	1.630(7)	V(2)–O(t4)	1.631(7)
V(1)–O(2)	2.014(6)	V(2)–O(7)	1.995(6)
V(1)–O(7)	2.002(8)	V(2)–O(2)	2.061(7)
V(1)–O(8)	1.919(7)	V(2)–O(1)	1.896(7)
O(7)–C(16)	1.474(12)	O(2)–C(2)	1.449(12)
O(8)–C(15)	1.361(17)	O(1)–C(1)	1.395(12)
O(9)–C(17)	1.458(12)	O(3)–C(3)	1.470(13)
O(9)–C(18)	1.443(12)	O(3)–C(4)	1.439(11)
C(15)–C(16)	1.586(15)	C(1)–C(2)	1.532(13)
C(16)–C(17)	1.420(17)	C(2)–C(3)	1.529(15)
C(18)–C(19)	1.418(19)	C(4)–C(5)	1.463(14)
C(15)–C(19)	1.551(15)	C(4)–C(7)	1.509(15)
O(t1)–V(1)–O(t3)	108.9(4)	O(t2)–V(2)–O(t4)	108.2(5)
O(t1)–V(1)–O(2)	94.8(3)	O(t2)–V(2)–O(7)	102.2(3)
O(t1)–V(1)–O(7)	128.4(3)	O(t2)–V(2)–O(2)	117.7(3)
O(t1)–V(1)–O(8)	98.7(3)	O(t2)–V(2)–O(1)	105.5(3)
O(t3)–V(1)–O(2)	100.7(3)	O(t4)–V(2)–O(7)	94.6(3)
O(t3)–V(1)–O(7)	121.9(4)	O(t4)–V(2)–O(2)	133.2(4)
O(t3)–V(1)–O(8)	103.6(4)	O(t4)–V(2)–O(1)	98.8(3)
O(2)–V(1)–O(7)	69.3(3)	O(2)–V(2)–O(7)	68.3(3)
O(2)–V(1)–O(8)	146.3(3)	O(1)–V(2)–O(7)	143.7(3)
O(7)–V(1)–O(8)	78.5(3)	O(1)–V(2)–O(2)	78.1(3)
V(1)–O(7)–V(2)	107.4(3)	V(1)–O(2)–V(2)	104.4(3)
V(1)–O(2)–C(2)	122.5(6)	V(2)–O(7)–C(16)	120.9(5)
V(1)–O(7)–C(16)	117.8(5)	V(2)–O(2)–C(2)	115.7(5)
V(1)–O(8)–C(15)	118.5(6)	V(2)–O(1)–C(1)	118.1(5)
O(7)–C(16)–C(15)	101.9(8)	O(2)–C(2)–C(1)	104.2(8)
O(7)–C(16)–C(17)	113.0(8)	O(2)–C(2)–C(3)	111.4(8)
O(8)–C(15)–C(16)	107.4(8)	O(1)–C(1)–C(2)	107.7(7)
O(8)–C(15)–C(19)	115.7(10)	O(1)–C(1)–C(5)	112.4(9)
O(9)–C(17)–C(16)	115.2(9)	O(3)–C(3)–C(2)	109.5(9)
O(9)–C(17)–O(10)	108.7(8)	O(3)–C(3)–O(4)	110.6(8)
O(9)–C(18)–C(19)	112.9(9)	O(3)–C(4)–C(5)	110.5(7)
O(11)–C(19)–C(18)	110.4(9)	O(5)–C(5)–C(4)	108.0(7)
C(16)–C(15)–C(19)	106.8(9)	C(2)–C(1)–C(5)	107.4(8)
C(15)–C(16)–C(17)	117.2(9)	C(1)–C(2)–C(3)	118.0(8)
C(16)–C(15)–C(19)	106.8(9)	C(2)–C(1)–C(5)	107.4(8)
C(17)–O(9)–C(18)	110.6(8)	C(3)–O(3)–C(4)	111.7(7)
C(15)–C(19)–C(18)	114.3(10)	C(1)–C(5)–C(4)	111.6(9)

are quite different from C(1)–C(2) [1.532(13) Å] and C(2)–C(3) [1.529(15) Å] in another (deviations are 0.054 and 0.109 Å, respectively). The differences in bond lengths and angles (Table 1) between the two mannopyranoside rings induced by vanadium chelation reveal that the co-ordination environments about the two vanadium(v) atoms are different.

The distorted trigonal-bipyramidal vanadium geometry of the cyclic vanadate complex (or ester) with the adjacent diol from the mannopyranoside ring or ribofuranose ring provides a further transition-state analogue of pentavalent phosphorus in trigonal-bipyramidal geometry in enzymatic cleavages of phosphodiester bonds.[31] However, the degrees of trigonality of the two five-coordinate vanadium atoms in $[(VO_2L^1)_2]^{2-}$ (Fig. 1) are different, as given by the parameter τ defined by Addison *et al.*,[32] $\tau = (\beta - \alpha)/60$, where atom A is simply chosen as the axial ligand by the criterion that it should not be any of the four which define the two largest angles, α and β. For a perfect square-pyramidal geometry $\tau = 0$, while it becomes unity for a perfect trigonal-bipyramidal geometry. The τ values in $[(VO_2L^1)_2]^{2-}$ are 0.300 [V(1)] and 0.175 [V(2)], where the two terminal oxygen atoms O(t3) and O(t2) are the axial ligands A for V(1) and V(2), respectively. In the cholorovanadate–pinacol complex,[15] which was the first model compound presumed to be a good transition-state analogue for enzyme-catalysed reactions involving phosphate transfer, the τ value is 0.230 [V(1)] with chloride as the axial ligand. The τ values of $[\{VO_2(ado)\}_2]^{2-}$[13] were calculated to be 0.323 [V(1)] and 0.015 [V(2)]. They indicate that the geometries of the two vanadium atoms diverge more significantly than in $[(VO_2L^1)_2]^{2-}$. In crystalline trimethyl vanadate, $[VO(OMe)_3]$,[33] the spontaneously formed dimer has two five-co-ordinate vanadium centres with $\tau = 0.083$ [V(1)] and 0.067 [V(2)], which show almost perfectly square-pyramidal geometries. We can postulate from these results that five-co-ordinate vanadium(v) favours a square-pyramidal geometry.

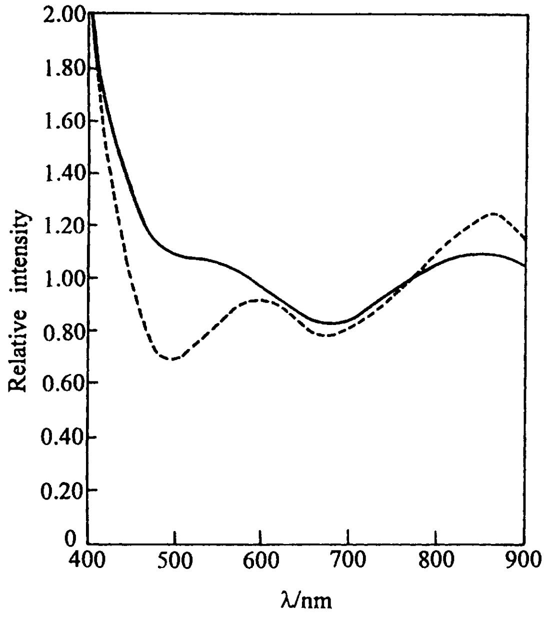


Fig. 2 Visible spectra of complexes **1** (——, 22.6 mmol dm^{-3}) and **2** (- - -, 9.03 mmol dm^{-3}) in acetonitrile

In the anion of $[(VO_2L^1)_2]^{2-}$ (Fig. 1) the two triply bonded oxygen atoms [O(2) and O(7) from two mannose rings] and two vanadium atoms are not coplanar (deviations ±0.22 Å), but an irregular quadrilateral ring is formed. The internal angles are 69.1(3) [at V(1)], 68.3(3) [at V(2)], 104.4(3) [at O(2)] and 107.4(3)° [at O(7)]. In contrast, the VOVO ring in an adenosine complex was reported[13] to have a geometry close to that of a regular parallelogram with the one pair of sides of length 2.04 Å and the other 1.98 Å.

Spectroscopy

The electronic spectra of complexes **1** and **2** are both characterized by strong absorption bands in near-UV and the relatively weak bands in the visible region (Fig. 2). The green colour of the acetonitrile solutions is attributed to these absorptions. The λ_{max} values of the near-UV absorptions are similar to those of tetrahedral vanadate which is typical of vanadate complexes. Based on their intensities, we assign these transitions as ligand-to-metal charge-transfer (l.m.c.t.) excitations.[34] In general, the l.m.c.t is facilitated when the co-ordination sphere is composed of polarizable ligands or ligands with high electron-donating ability. Under these conditions, a bathochromic effect can be observed as the result of esterification. Increasing the co-ordination number of the central metal ion gives the contrary result, because it renders the electron transfer difficult by increasing the energy of the d orbitals of the metal ion.[34] For complexes **1** and **2**, since the co-ordination number of vanadium increases from four (tetrahedral vanadate) to five (distorted trigonal bipyramid) upon complex formation, the bathochromic effect resulting from the esterification (or the complex formation) was almost counteracted.

As shown in Fig. 2, the characteristic broad absorptions in the visible region with molar absorption coefficients near 100 dm^3 mol^{-1} cm^{-1} are not observable for simple vanadate or ligand solutions and are rarely reported for dioxovanadium(v) complexes. Since the protecting group benzylidene or (p-methoxyphenyl)diphenylmethyl in the sugar ring increases its electron-donating capacity to the vacant 3d shell of a vanadium(v) configuration, the two weak absorptions are tentatively assigned as electronically forbidden l.m.c.t bands. It is interesting that six-co-ordinated monooxovanadium (V^VO^{3+}) complexes with catecholate derivatives have two very intense electronically allowed charge-transfer bands in the visible region.[29]

The diffuse reflectance spectra of both complexes dispersed in $BaSO_4$ matrices show similar features [λ_{max}/nm = 578, 850 (sh) and 615, 840, respectively], which suggest that the integrities of the complexes are maintained in acetonitrile solutions.

The IR spectra of complexes **1** and **2** have strong bands in the 900–950 cm^{-1} region representing the V=O stretches.[35] Crystalline complex **1** has two bands at 913 and 931 cm^{-1}, while the uridine derivative **2** has a single band at 916 cm^{-1}. Strong bands at 911 and 919 cm^{-1} were reported in the spectrum of crystalline $[NEt_4]_2[\{VO_2(ado)\}_2]$.[13] They were tentatively assigned to the V=O stretches of this dinuclear five-co-ordinated dioxovanadium(v) complex. Compared with the IR spectra of the proligands, the broad strong absorption at about 3400 cm^{-1} (OH) is not present for the complexes.

At ambient temperature the ^1H-decoupled ^{13}C NMR spectra of complexes **1** and **2** have four sharp lines at δ 13.8, 20.2, 24.2 and 59.1. They are assigned to four different kinds of carbon atoms in the tetra-*n*-butylammonium cation. The signals in the range δ 127–131 are characteristic of benzene rings. The downfield resonance lines with shifts at δ 102.2, 141.3, 151.2 and 163.8 in the ^{13}C spectrum of **2** correspond to the four atoms of the uracil group.[36]

After metal chelation, significant downfield shifts of $\Delta\delta(\delta_{\alpha\text{-carbon in complex}} - \delta_{\alpha\text{-carbon in free ligand}})$ = 10–18 are observed for the tertiary carbons, C(2) and C(3) (see Table 2) (note the atom numbering here is different from that given in Fig. 1). They are in accordance with reported Δδ values of 15–30 for the α-carbon in oxovanadium(v) alkoxides.[17] In the case of carbohydrates, since *gauche* interactions (shielding) hamper the co-ordination effects (deshielding),[37] the Δδ induced by co-ordination is less than that for alkoxides. As shown in Table 2, no significant difference in chemical shift was observed for non-α-carbon atoms in the sugar ring compared to those of the free proligands. Some carbon atoms in the sugar rings have two ^{13}C chemical shift values (Table 2) for each complex. This may be due to the two ligand molecules having slightly different chemical environments after metal binding. Two chemical shift values are also observed for some protons in the ^1H NMR spectra of the two complexes. These observations are consistent with the structure analysis for complex **1**.

The molar conductivities in acetonitrile and nitromethane were Λ_m = 249.6 (MeCN), 162.1 ($MeNO_2$) for complex **1** and 203.1 (MeCN), 140.1 ($MeNO_2$) ohm^{-1} cm^2 mol^{-1} for **2**. These results show that both complexes are 2:1 electrolytes in acetonitrile and nitromethane,[38] and that the divalent complex anions $[(VO_2L^1)_2]^{2-}$ and $[(VO_2L^3)_2]^{2-}$ remained intact in these organic solvents.

^{51}V NMR studies in acetonitrile solutions

The nearly colourless acetonitrile solution of $[NBu^n{}_4][H_2VO_4]$ contains various mono- and oligo-meric vanadium species in millimolar concentrations, according to ^{51}V NMR spectroscopy [see Figs. 3 and 4(*a*)]. According to the distribution of the vanadate species in aqueous solution,[12] and considering the downfield shifts due to the solvent effect, the resonances at δ −533, −551, −566 and −570 were assigned to tetrahedral mono-(V), di-(V_2), tetra-(V_4) and penta-meric vanadates (V_5), respectively. The assignments were confirmed by titration results. Upon increasing the total concentration of $[NBu^n{}_4][H_2VO_4]$ from 0.1 to 50.0 mmol dm^{-3} the resonance at δ −566 (V_4) became predominant in place of that at δ −533(V). The intensities of the signals at δ −566 (V_4) and −570 (V_5) increased concomitantly with the decrease in those at δ −533 (V) and −551 (V_2). These changes are similar to those of vanadate in neutral aqueous solutions.[12] The species are involved in oligomerization–deoligomerization equilibria in acetonitrile. The most upfield resonance (V_x) appears at about δ −608. No resonance was observed in this position for an aqueous solution of vanadate. According to the literature,[39] it is assigned to peroxovanadate, which is the likely reaction product of vanadate and molecular oxygen in acetonitrile. The co-ordination of solvent MeCN to vanadate resulting in the V_x species cannot be ruled out.

Table 2 Selected ^1H-decoupled ^{13}C NMR chemical shifts (δ) of complexes **1** and **2** and their ligands in CD_3CN

Compound	C^1	C^2	C^3	C^4	C^5	C^6	C^7	CH_3O
H_2L^1	102.4	71.7	68.9	79.5	64.2	69.2	102.6	55.1
1	101.8	89.1	78.6	79.6	62.5	69.0	102.4	55.0
	102.2			80.9	64.3	69.5	102.8	55.1
H_2L^3	90.4	75.2	70.3	87.6	63.3			55.8
	90.4	87.2	83.5	87.5	63.5			55.8
2					65.2			

The assignments of the resonance lines of H_2L^3 and H_2L^1 were according to refs. 36 and 37, respectively.

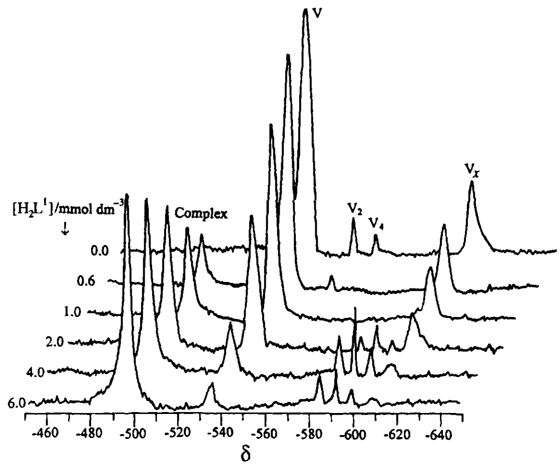


Fig. 3 Stacked plot of ^{51}V NMR spectra showing the products in acetonitrile solutions of $[NBu^n{}_4][H_2VO_4]$ with varying concentrations of H_2L^1. The signal at about δ −497 is due to the binuclear dioxovanadium(v) complex with two L^1; those at δ −533, −551, −566 and −570 are from mono-, di-, tetra- and penta-meric vanadate species, respectively. The solutions contained 1.0 mmol dm^{-3} vanadate and the indicated concentrations of H_2L^1. These ^{51}V NMR spectra were obtained in 2 h after incubating the solutions for 12 h at 20 °C

The stoichiometries of complexes **1** and **2** were further confirmed by ^{51}V NMR titration experiments. The spectra of a series of acetonitrile solutions containing 1.0 mmol dm^{-3} vanadate and H_2L^1 varying from 0 to 6.0 mmol dm^{-3} (Fig. 3) indicate that the reaction gives rise to one species with a ^{51}V NMR resonance at δ −497 the intensity of which increases during the titration with H_2L^1. Three sharp signals ranging from δ −580 to −600 occur simultaneously when the concentration of H_2L^1 was increased to some extent (Fig. 3). We can assign the three signals based on the study of Crans *et al.*[17] Their presence and changes in intensities are concurrent, therefore we postulate that they result from only one oligomeric vanadate complex.

The equilibrium between monomeric vanadate(v) and the complex species exhibiting the resonance at δ −497 was studied. Supposing that the species is a complex of stoichiometry (M:L) either 1:1 or 2:2, then we obtain the expressions (1) and (2). To testify the stoichiometry, the data were processed according to either equation (1) or (2). For

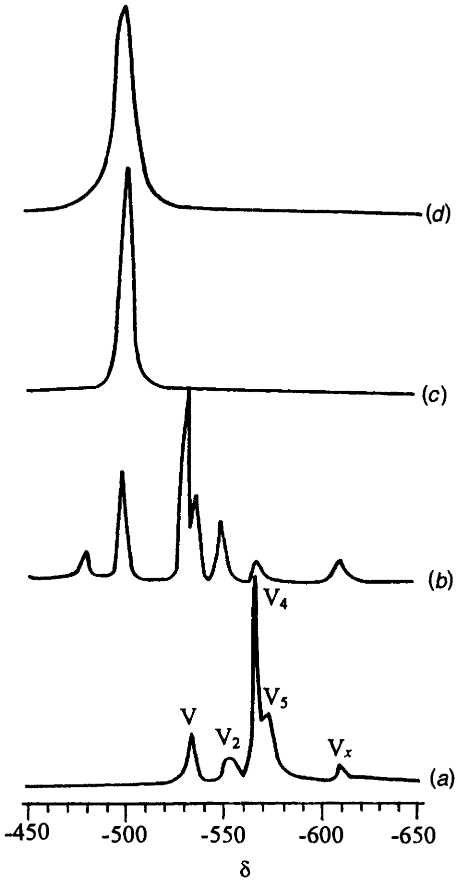


Fig. 4 The ^{51}V NMR spectra of acetonitrile solutions of 30 mmol dm^{-3} $[NBu^n{}_4][H_2VO_4]$ in the absence (*a*) and presence (*b*) of 45 mmol dm^{-3} H_2L^2, (*c*) 45 mmol dm^{-3} H_2L^1, and (*d*) 45 mmol dm^{-3} H_2L^3 at 20 °C. Each spectrum was measured after incubating the mixture in a 50–60 °C bath for 12 h

$$V + L \rightleftharpoons VL \quad [VL] = K_1[V][L] \qquad (1)$$

$$2V + 2L \rightleftharpoons V_2L_2 \quad [V_2L_2] = K_2[V]^2[L]^2 \qquad (2)$$

equation (1), $[L] = [L]_T - [VL]$ was used to obtain the equilibrium concentration of [L], where $[L]_T$ is the total concentration of H_2L^1. When the computation was based on equation (2), $[L] = [L]_T - 2[V_2L_2]$ was used to obtain [L]. By linear regression based on equation (1), the correlation coefficient $r = 0.24$ ($n = 10$) obtained is too low to represent a real case, while a plot of $[V_2L_2]$ on the left of equation (2) *versus* the product $[V]^2[L]^2$ gives a satisfactory linear regression with $r = 0.90$ ($n = 10$). Hence we conclude that the stoichiometry of the complex exhibiting the ^{51}V signal at δ −497 in acetonitrile is 2:2. This is consistent with the results of spectroscopy and conductivity measurements. The formation constant obtained is $K_2 = 2.2 \times 10^9$ dm^9 mol^{-3}.

Similar analyses were performed for the vanadate–H_2L^3 system. The stoichiometry of the corresponding complex was determined to be 2:2 too, and its formation constant was 3.6×10^{12} dm^9 mol^{-3}, which is *ca.* 10^3 times that of vanadate–H_2L^1, indicating H_2L^3 has a stronger chelating ability toward dioxovanadium(V).

The ^{51}V NMR titration experiments were performed after incubating the mixtures of vanadate and proligands in acetonitrile for 12 h at room temperature (≈20 °C). When the molar ratio of vanadate to proligand is 1:1.5, and the incubation time was extended to a week or the reaction temperature increased to 50–60 °C for 12 h, the ^{51}V NMR spectra gave a resonance at δ −497 as shown in Fig. 4(*c*) and 4(*d*). It should be noted that the signal of H_2L^3 is broader than that of H_2L^1. Since the co-ordination of the two vanadium atoms in the L^3 complex is presumably similar to that in the adenosine complex, the significant divergence of τ values between V(1) and V(2) may be one cause of the broadening of the ^{51}V NMR resonance. In addition, because of the low energy barriers between the envelope and twist conformers,[40] L^3 is thought to undergo rapid interconversions between them even after metal chelation. These are the reasons why the signal at δ −497 of the L^3 complex is broader than that of the L^1 complex in acetonitrile solution. In the case of H_2L^2, under the same conditions, one or more of its consecutive vicinal *trans*-diol groupings react with vanadate, also giving the dinuclear compound with a resonance at δ −497 but as a minor product [Fig. 4(*b*)].

Based on these results of these ^{51}V NMR studies, we may conclude that, when the monosaccharide derivatives react with vanadate as described above, the complexation ability follows the order $L^3 > L^1 > L^2$. For a reasonable explanation the structural properties of these ligands must be taken into account. The stereochemistry was predicted by molecular modelling, performed on a SGI XS24 computation station using the DISCOVER software (Biosym).[41] In the most stable staggered conformation, the distance ($O^- \cdots O^-$) and dihedral angle between the two free adjacent hydroxyl groups in a monosaccharide derivative are 2.66 Å and 34.57° for L^3, 2.72 Å and 48.09° for L^1, 2.86 Å and 66.32° for L^2, respectively. It is noteworthy that the increasing distances and torsion angles in the sugar $^-$O–C–C–O$^-$ moiety is opposite to that of the chelation ability. This indicates that the distance and dihedral angle are determinants for closure of the five-membered chelate ring. Moreover, the conformational freedom of the ribofuranose ring even after metal binding, as mentioned above, is an entropic factor which favours chelation of L^3. In L^2, the 4,6-benzylidene substituent stabilizes the chair conformation of the mannopyranoside ring and its freedom to interconvert becomes less. Meanwhile, the distance and dihedral angle in crystalline $[NBu^n{}_4]_2[(VO_2L^1)_2]$ presented here (Fig. 1) are close to 2.49 Å and 40°, respectively. This indicates that L^1 in its most stable staggered conformation is not suitable for chelation and must be tuned up in the metal-binding process. In the case of L^2, a limited number of ligand conformers, having distances and dihedral angles in the *trans*-diol suitable for metal chelation, contribute to the chelated species. Hence only a small amount of the dinuclear complex having the ^{51}V NMR resonance at δ −497 is produced in the mixture of vanadate and H_2L^2 in acetonitrile [Fig. 4(*b*)]. These considerations were also used to interpret the interactions between the vanadyl ion (VO^{2+}) and simple sugars in aqueous solutions.[42]

Conclusion

In the present work the interaction between vanadate and monosaccharide derivatives was studied successfully in an acetonitrile medium. Based upon this method, we have synthesized, characterized, and solved the crystal structure of the dinuclear complex $[NBu^n{}_4]_2[(VO_2L^1)_2]$. All the proligands utilized comprise two free adjacent hydroxyl groups on the carbohydrate rings. They react with vanadate to give dimeric five-co-ordinate complexes in acetonitrile with different affinities. The high selectivity and preference of H_2L^3 to react with vanadate to give the five-co-ordinate distorted trigonal-bipyramidal vanadium(V) geometry provides evidence of why uridine–vanadate is a strong inhibitor of ribonuclease A.[43] By ^{51}V NMR titration studies, we are able to report for the first time the assignments of vanadate species in acetonitrile solutions.

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