Carbohydrate Binding to VO^{3+}. Sugar Vanadate Esters Incorporating L-Amino Acid Schiff Bases as Coligands†

Kajal Krishna Rajak, Sankar Prasad Rath, Sujit Mondal, and Animesh Chakravorty*

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India

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The glycosides methyl-2,6-dimethoxy-β-D-galactopyranoside (β-D-H_2Me_3GP), methyl-4,6-dimethoxy-α-D-mannopyranoside (α-D-H_2Me_3MP), and methyl-5-methoxy-β-D-ribofuranoside (β-D-H_2Me_2RF) have been synthesized, and their reaction with VO(L-Asal)(OMe)(OHMe) in dichloromethane has afforded esters of the type VO(β-D-HMe_3GP)(L-Asal), VO(α-D-HMe_3MP)(L-Asal), and VO(β-D-HMe_2RF)(L-Asal) as dark-colored solids (red in solution). Here, L-$Asal^{2-}$ is the deprotonated salicylaldimine of L-alanine (A = a), L-valine (A = v), and L-phenylalanine (A = p). The X-ray structures of VO(β-D-HMe_3GP)(L-vsal)·H_2O and VO(α-D-HMe_3MP)(L-psal)·H_2O have revealed five-membered (O,O)-chelation by monoionized carbohydrates, the undissociated hydroxyl group lying trans to the oxo oxygen atom. In the carbohydrate frame, the alkoxidic oxygen atom is axial in the former ester and equatorial in the latter. The V−O(alkoxidic) and V−O(alcoholic) distances are, respectively, ∼1.80 and ∼2.30 Å. The ONO coordinating tridentate salicylaldimine ligand is folded (by ∼35°) along a C−N bond. The chiral configuration of the metal site corresponds exclusively to the endo disposition of the V═O and the amino acid C−R (R = Me, $CHMe_2$, CH_2Ph) bonds. In VO(β-D-HMe_3GP)(L-vsal)·H_2O two ester molecules constitute the asymmetric unit and these along with the two water molecules form a macrocyclic supramolecule (diameter, ∼6.1 Å) held by hydrogen bonds involving alcohol and an OMe function as well as water (O···O distance, 2.59−2.86 Å). On the other hand, in VO(α-D-HMe_3MP)(L-psal)·H_2O the water molecule bridges two symmetry-related ester molecules via alkoxide···water and alcohol···water hydrogen bonds forming an infinite chain structure (O···O lengths, 2.65 and 2.85 Å). The molecular structures observed in the solid state are preserved in solution (^1H and ^{51}V NMR). No isomerization is detectable either at the metal site or at the anomeric carbon atom, and the V−O(alkoxidic) and V−O(alcoholic) sites and the metal−carbohydrate binding remain in tact. The VO(β-D-HMe_2RF)(L-Asal) species did not afford single crystals but NMR results are consistent with (O,O)-chelation by the ribose fragment, the alkoxidic carbon being C3. Crystal data are as follows. VO(β-D-HMe_3GP)(L-vsal)·H_2O: chemical formula, $C_{21}H_{32}NO_{11}V$; crystal system, orthorhombic; space group, $P2_12_12_1$; a = 13.146(7) Å, b = 15.142(5) Å, c = 25.631(9) Å; Z = 8. VO(α-D-HMe_3MP)(L-psal)·H_2O: chemical formula, $C_{25}H_{32}NO_{11}V$; crystal system, monoclinic; space group, $P2_1$; a = 13.645(4) Å, b = 7.022(2) Å, c = 15.500(4) Å; β = 113.98(2)°; Z = 2.

Introduction

The pentavalent state of vanadium, like that of phosphorus, is prone to facile ester formation with alcohols.[1−5] This enables vanadates to bind enzymes for which the normal substrates are sugar phosphates or derivatives thereof. Examples are the activation of glucose-6-phosphate dehydrogenase[6] and the inhibition of RNase[7,8] and ATPase.[9] The usefulness of the ester analogy has in turn prompted research into the sparsely developed chemistry of sugar vanadates.[10−15] Much of the activity has so far been in the solution phase where the presence of complex equilibria has often vitiated structurally definitive

* Author to whom correspondence should be addressed.

† Dedicated to Professor R. C. Mehrotra on the occasion of his 77th birthday.

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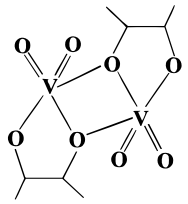
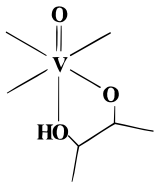
speciation. Isolation of authentic esters in the pure state has been rare, and only two systems have so far been structurally characterized, both revealing binucleation of VO_2^+ as in **1** via alkoxide chelation and bridging promoted by diionized sugars—adenosine in one case[16] and a mannopyranoside in the other.[17]



1

The paucity of well-characterized solid sugar vanadates has prompted us to search for new systems. Herein we describe a hitherto unknown family of mononuclear esters of VO^{3+} chelated to monoionized sugar as in **2** wherein the vacant

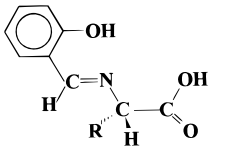


2

coordination sites are for occupation by a coligand. The synthesis and properties of the new family are reported. The X-ray structures of two representative esters have been determined, revealing the induction of chiral specificity at the metal site by ligands. NMR results are consistent with preservation of the gross solid-state structures in solution.

Results and Discussion

A. Synthesis. a. Sugar Ligands and Schiff Base Coligands. The three sugar ligands (general abbreviation H_2SUG) used in the present work are methylated β-D-galactopyranoside, **3**, α-D-mannopyranoside, **4**, and β-D-ribofuranoside, **5** (Chart 1). These were synthesized from the parent glycosides as outlined in Scheme 1 for the case of β-D-H_2Me_3GP, **3**. The coligands L-H_2-Asal, are salicylaldimines, **6**, of the chiral α-amino acids



R	
Me	L-H_2asal
$CHMe_2$	L-H_2vsal
CH_2Ph	L-H_2psal

6

L-alanine, L-valine, and L-phenylalanine. These were generated in situ from salicylaldehyde and the acids.

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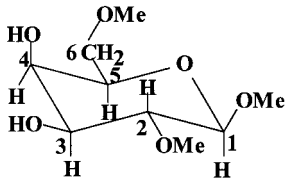
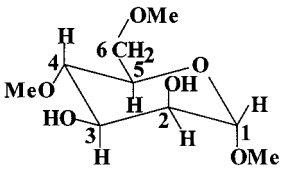
Chart 1

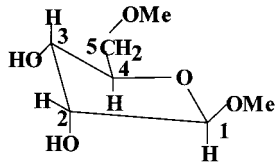
Sugar Ligands



β-D-H_2Me_3GP , **3**



α-D-H_2Me_3MP , **4**

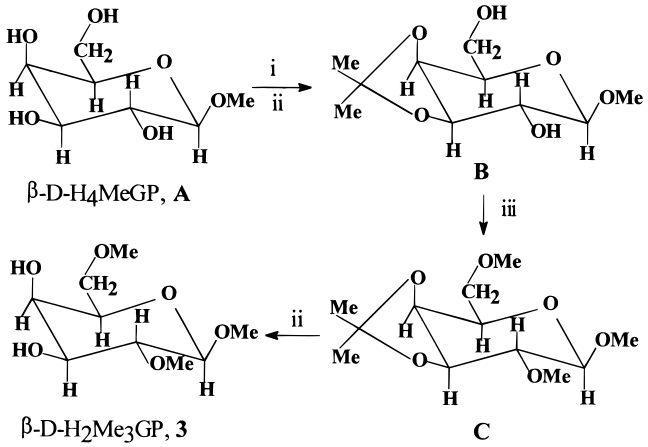


β-D-H_2Me_2RF , **5**

Esters

VO(β-D-HMe_3GP)(L-asal), **7a**
VO(β-D-HMe_3GP)(L-vsal), **7b**
VO(β-D-HMe_3GP)(L-psal), **7c**
VO(α-D-HMe_3MP)(L-asal), **8a**
VO(α-D-HMe_3MP)(L-vsal), **8b**
VO(α-D-HMe_3MP)(L-psal), **8c**
VO(β-D-HMe_2RF)(L-asal), **9a**
VO(β-D-HMe_2RF)(L-vsal), **9b**
VO(β-D-HMe_2RF)(L-psal), **9c**

Scheme 1[a]



[a] Conditions: (i) 2,2-dimethoxypropane in dmf, stir; (ii) p-toluenesulfonic acid, stir; (iii) Ag_2O, MeI in dmf, stir.

b. Vanadate Esters. Each sugar ligand is so methylated that only two vicinal hydroxyl groups having cis disposition (i.e., one axial and the other equatorial) remain free. This geometrical feature was introduced so as to facilitate chelation-stabilized ester formation. The L-H_2Asal coligand was used to engage three of the oxovanadium (VO^{3+}) coordination sites, leaving just two for possible chelation in a mononuclear configuration. Application of this design strategy to sugars was preceded by model experiments with linear polyols.[4]

Treatment of a dichloromethane solution of VO(L-Asal)(OMe)(OHMe)[18] with a slight excess of H_2SUG followed by layering with *n*-hexane and subsequent slow diffusion afforded the dark-colored vanadate esters VO(HSUG)(L-Asal) in excellent yields. In a solution of VO(L-Asal)(OMe)(OHMe) the dimer

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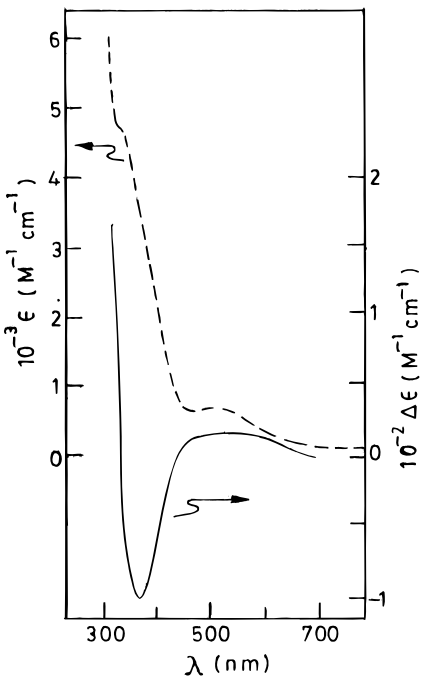

Figure 1. CD(—) and electronic (– – –) spectra of VO(β-D-HMe$_3$GP)(L-vsal) in dichloromethane solution.

V_2O_3(L-Asal)$_2$ is also present[18b] and the reactions involved in ester synthesis are stated in eqs 1 and 2. The nine esters prepared

$$\text{VO(L-Asal)(OMe)(OHMe)} + \text{H}_2\text{SUG} \rightarrow \text{VO(HSUG)(L-Asal)} + 2\text{MeOH} \quad (1)$$

$$\text{V}_2\text{O}_3\text{(L-Asal)}_2 + 2\text{H}_2\text{SUG} \rightarrow 2\text{VO(HSUG)(L-Asal)} + \text{H}_2\text{O} \quad (2)$$

in the present work are listed in Chart 1. Characterization data are collected in the Experimental Section.

Solution studies were performed in dichloromethane/chloroform for **7** and **8** and in dimethyl sulfoxide for **9**. The red color of such solutions is due to a band occurring near 500 nm (ϵ, 500−800 M^{-1} cm^{-1}) assigned to O^-(sugar) → V LMCT excitation.[4,5a,19] The band is circularly dichroic, and CD spectra reveal the presence of overlapping components (Figure 1).

The sugar hydroxyl stretch is observed near 3200 cm^{-1}. The V═O stretch occurs in the range 970−990 cm^{-1}, suggesting hexacoordination.[20] Carboxylate monocoordination is consistent with the presence of three stretches in the range 1300−1700 cm^{-1}.[21] The esters display an irreversible, presumably metal-centered ($VO^{3+} \rightarrow VO^{2+}$) reductive voltammetric response in the range −0.2 to −0.3 V vs SCE.

B. Crystal and Molecular Structure. a. Geometrical Features. The structures of VO(β-D-HMe$_3$GP)(L-vsal), **7b**, and VO(α-D-HMe$_3$MP)(L-psal), **8c**, both crystallizing as monohydrates have been determined. Molecular views excluding the water molecule and hydrogen atoms are shown in Figures 2 and 3. Selected bond parameters are given in Tables 1 and 2.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for VO(β-D-HMe$_3$GP)(L-vsal)·H$_2$O

molecule 1		molecule 2	
V1−O4	2.357(9)	V51−O54	2.297(8)
V1−O5	1.810(9)	V51−O55	1.805(9)
V1−O7	1.585(8)	V51−O57	1.591(8)
V1−O8	1.938(9)	V51−O58	1.946(9)
V1−O10	1.847(9)	V51−O60	1.851(8)
V1−N1	2.084(9)	V51−N51	2.079(10)
O4−V1−O5	77.2(3)	O54−V51−O55	77.0(3)
O4−V1−O7	177.4(4)	O54−V51−O57	178.1(4)
O4−V1−O8	81.8(4)	O54−V51−O58	83.3(4)
O4−V1−O10	82.8(4)	O54−V51−O60	82.8(3)
O5−V1−O7	100.2(4)	O55−V51−O57	101.1(4)
O5−V1−O8	92.0(4)	O55−V51−O58	93.2(4)
O5−V1−O10	100.8(4)	O55−V51−O60	100.6(4)
O7−V1−O8	97.9(4)	O57−V51−O58	97.0(4)
O7−V1−O10	98.2(4)	O57−V51−O60	97.5(4)
O8−V1−O10	157.3(4)	O58−V51−O60	157.7(4)
O4−V1−N1	79.9(4)	O54−V51−N51	80.4(3)
O5−V1−N1	155.7(4)	O55−V51−N51	155.9(4)
O7−V1−N1	102.5(4)	O57−V51−N51	101.5(4)
O8−V1−N1	76.6(4)	O58−V51−N51	76.0(4)
O10−V1−N1	84.3(4)	O60−V51−N51	84.5(4)

The asymmetric unit of **7b** consists of two metrically similar but crystallographically distinct molecules and two water molecules. In Figure 2 only molecule 1 is shown. The membering of the corresponding atoms in molecules 1 and 2 are, respectively, *n* and *n* + 50, e.g., V1−O7 and V51−O57 (Table 1).

The monoionized carbohydrate ligands β-D-HMe$_3$GP$^-$ and α-D-HMe$_3$MP$^-$ are bonded in five-membered chelate mode **2**. The alkoxidic and alcoholic oxygen atoms lie trans to the azomethine nitrogen atom of L-Asal^{2-} and the oxo-oxygen atom, respectively. The alcoholic hydrogen atom was directly observed in difference Fourier maps along with a few hydrogen atoms in both **7b** and **8c**. The alkoxide oxygen atom O5 in **7b** and O4 in **8c** are, respectively, disposed axially and equatorially in the carbohydrate frame.

The tridentate L-Asal^{2-} coligand spans meridionally forming one five-membered and one six-membered chelate ring. In both **7b** and **8c** the coligand consists of the excellently planar parts (mean deviation < 0.05 Å) CCO_2 and OC_6H_4CHN, intersecting along the C11−N1 bond. The dihedral angles between the two planes is 39.7° in **7b** (molecule 1), 35.0° in **7b** (molecule 2), and 33.6° in **8c**.

b. The VO_5N Coordination Sphere. In the distorted octahedral VO_5N coordination sphere the metal atom is displaced by ∼0.32 Å toward the oxo-oxygen from the equatorial plane (mean deviation < 0.07 Å) defined by three oxygen (alkoxide, phenoxide, and carboxylate) and one nitrogen atoms. The five V−O bonds are all unequal and span the range 1.58−2.36 Å. The shortest bond is with oxo-oxygen (1.58−1.59 Å), and the longest is with alcohol oxygen (2.30−2.36 Å). The lengths of the remaining V−O bonds, each involving a monoanionic oxygen donor, are in the order alkoxidic < phenoxidic < carboxylic (approximately 1.81, 1.85, and 1.95 Å, respectively) paralleling their order of acidity. The bond length trend qualitatively reflects the extent of O → V donation. To diminish competition for the same metal acceptor orbitals, the weakly donating alcohol function rather than the strongly donating alkoxide function of the carbohydrate is positioned trans to the oxo-oxygen atom.

c. Chiral Configuration of the Metal Site. The sugar ligands as well as Schiff base coligands are chiral. The anomeric configuration of each sugar ligand is preserved in both **7b**

(19) (a) Clague, M. J.; Keder, N. L.; Butler, A. *Inorg. Chem.* **1993**, *32*, 4754. (b) Arber, J. M.; de Boer, E.; Garner, C. D.; Hasnain, S. S.; Wever, R. *Biochemistry* **1989**, *28*, 7986.
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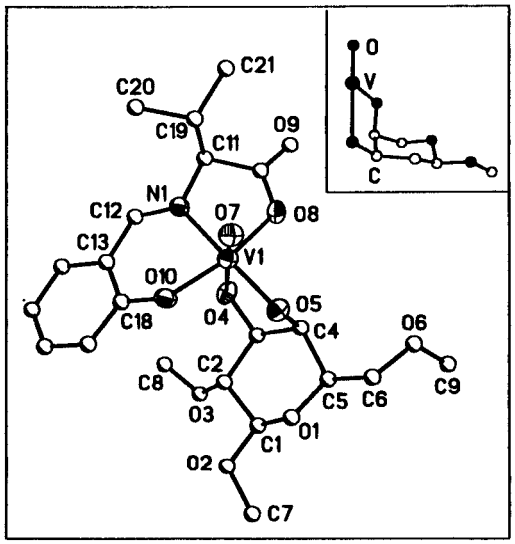
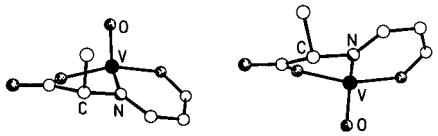


Figure 2. Perspective view and atom-labeling scheme for molecule 1 in VO(*β*-D-HMe$_3$GP)(L-vsal)·H$_2$O (water excluded); the alkoxide function is O5. The inset highlights the stereochemistry of the anomeric carbon atom and of the alkoxide−alcohol metal binding site.

(equatorial 1-OMe) and **8c** (axial 1-OMe). The L-amino acid residue has *S* configuration. The metal site lacks symmetry and can in principle occur in two optically isomeric forms affording two diastereoisomers. These correspond to endo and exo disposition of the V=O and C−R (in L-Asal^{2-}) bonds as in **10** and **11**, respectively. However, in both the structures the endo form alone is observed. This exclusive chiral preference can be related to the steric advantage of the endo form arising out of L-Asal^{2-} nonplanarity.[4a]



d. Hydrogen Bonding. The water molecules in the esters are involved in strong hydrogen bonding. In the monohydrate of **7b** the two ester molecules of the asymmetric unit along with the two water molecules constitute a macrocyclic supramolecule (Figure 4a) held by alcohol···water (O···O, 2.586(12) Å), water···water (2.863(14) Å), water···ether (2.840(13) Å), and alcohol···ether (2.660(12) Å) hydrogen bonds. The approximate diameter of the macrocyclic cavity is ∼6.1 Å. In the case of **8c** monohydrate each water molecule bridges two symmetry-related ester molecules via alkoxide···water and alcohol···water hydrogen bonds of O···O lengths 2.850(11) Å and 2.647(10) Å, respectively. This results is an infinite chain structure, Figure 4b. The alkoxide oxygen is strongly bonded to the metal site and is less available for hydrogen bonding. It is thus logical that the O···O lengths follow the order alkoxide···water > alcohol···water. In this context we note that in **7b** the alkoxide oxygen atom is not at all involved in hydrogen bonding.

C. Solution Structure. The solid-state structures of **7** and **8** are grossly preserved in solution as revealed by ^{1}H and ^{51}V NMR. No isomerization is detectable either at the metal site or at the anomeric carbon site. Further, the mode of metal−carbohydrate binding remains unaltered. The NMR results also

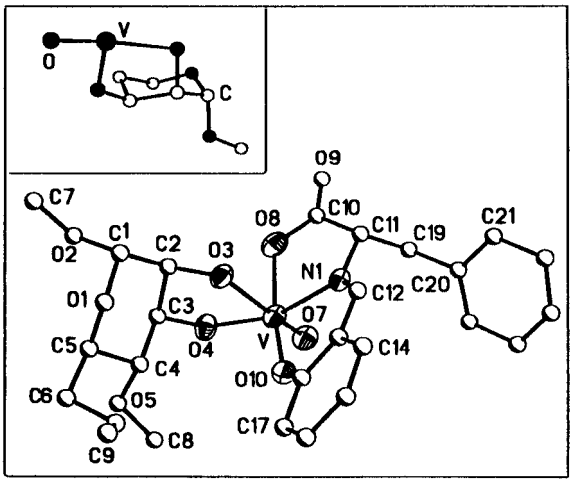


Figure 3. Perspective view and atom-labeling scheme of VO(α-D-HMe$_3$MP)(L-psal)·H$_2$O (water excluded); the alkoxide function is O4. The inset highlights the stereochemistry of the anomeric carbon atom and of the alkoxide−alcohol metal binding site.

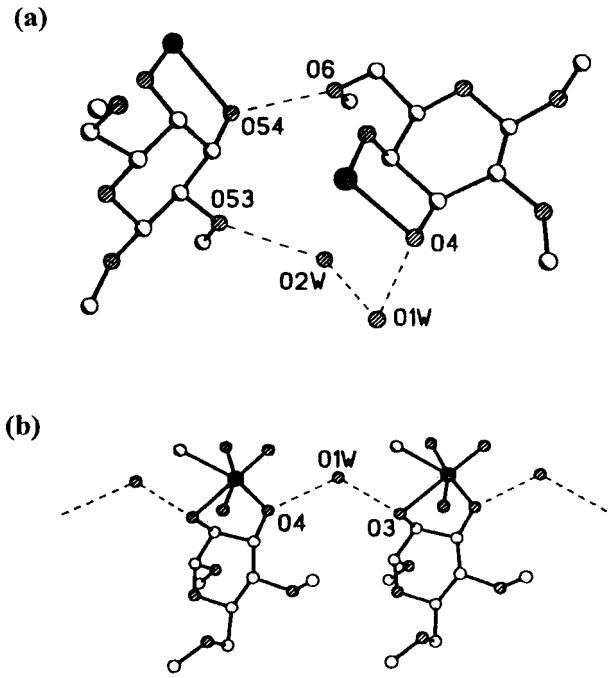


Figure 4. Hydrogen bonding in (a) VO(*β*-D-HMe$_3$GP)(L-vsal)·H$_2$O, and (b) VO(α-D-HMe$_3$MP)(L-psal)·H$_2$O.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for VO(α-D-HMe$_3$MP)(L-psal)·H$_2$O

V−O3	2.304(6)	V−O8	1.972(5)
V−O4	1.802(6)	V−O10	1.851(5)
V−O7	1.581(6)	V−N1	2.907(7)
O3−V−O4	76.5(2)	O7−V−O10	100.1(3)
O3−V−O7	175.2(3)	O8−V−O10	157.4(2)
O3−V−O8	81.2(2)	O3−V−N1	80.2(2)
O3−V−O10	84.4(2)	O4−V−N1	155.8(3)
O4−V−O7	101.0(3)	O7−V−N1	101.8(2)
O4−V−O8	93.7(3)	O8−V−N1	76.2(2)
O4−V−O10	99.8(3)	O10−V−N1	84.3(2)
O7−V−O8	94.9(3)		

clarify some aspects of vanadium−ribose binding in **9** which did not afford single crystals. Selected spectral data are collected in Table 3.

a. The Metal Site. Each ester displays a single ^{51}V line near −545 ppm assignable to the endo isomer. The exo form, if

Table 3. Selected NMR Spectral Data[a] [δ, ppm (J, Hz)]

esters	H(anomeric)	−C*H*OV	−C*H*(OH)V	−CH(O*H*)V	−O*Me*[b]	^{51}V, ppm
7a	4.12[c](7.8)	5.17[d]	4.06[d]	7.17[e]	3.54;[f] 3.48[g]	−546
7b	4.10[c](7.8)	5.10[d]	4.04[h](4.2,8.4)	7.22[c,e](5.1)	3.52;[f] 3.46[g]	−542
7c	4.14[c](7.8)	5.21[d]	4.12[d]	7.39[e]	3.54;[f] 3.50[g]	−545
8a	4.60[i]	4.97[h](4.2,8.4)	4.28[d]	7.36[e]	3.43;[j] 3.79[k]	−542
8b	4.68[i]	4.93[h](4.7,8.3)	4.23[d]	7.21[e]	3.43;[j] 3.78[k]	−545
8c	4.67[i]	5.01[h](3.3,8.1)	4.34[d]	7.20[e]	3.46;[j] 3.80[k]	−543
9a	4.24[i]	5.36[d]	3.89[d]	7.12[c,e](4.4)	3.37[l]	−544
9b	4.23[i]	5.23[d]	3.86[d]	7.07[c,e](4.5)	3.36[l]	−546
9c	4.28[i]	5.38[d]	3.88[d]	7.15[c,e](4.2)	3.39[l]	−545

[a] Solvents used are $CDCl_3$ for **7** and **8** and $(CD_3)_2SO$ for **9**. [b] For numbering, see Chart 1. [c] Doublet. [d] Center of ill-resolved multiplet. [e] Broad signal. [f] 1-O*Me* (free ligand value, 3.60). [g] 2-O*Me* (free ligand value, 3.55). [h] Doublets of doublet. [i] Center of ill-resolved doublet. [j] 1-O*Me* (Free ligand value, 3.46). [k] 4-O*Me* (free ligand value, 3.44). [l] 1-O*Me* (free ligand value, 3.48).

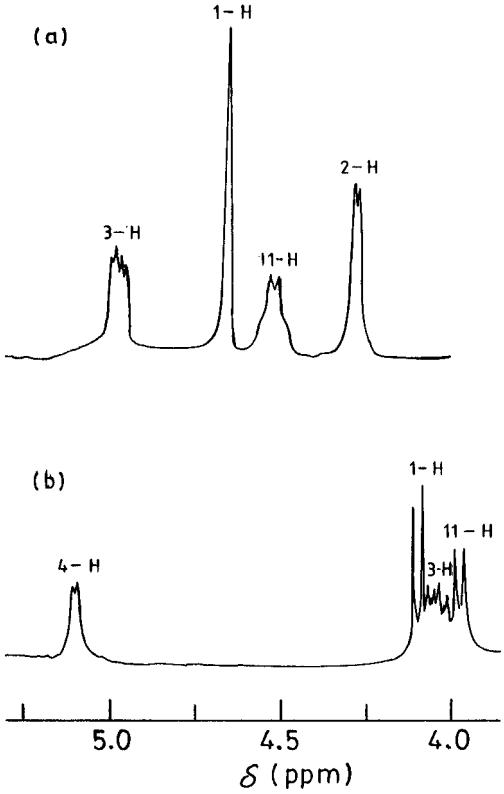
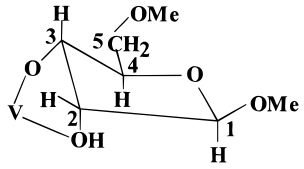


Figure 5. ^{1}H NMR spectra ($CDCl_3$, 4.0−5.3δ) of (a) VO(α-D-HMe$_3$-MP)(L-asal), and (b) VO(β-D-HMe$_3$GP)(L-vsal). The numbering scheme is as in Figures 2 and 3.

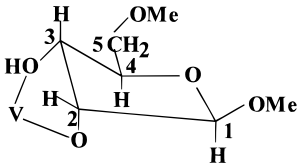
present, would have resonated at lower field.[4a] There is no diastereoisomeric splitting of any of the ^{1}H resonances either. The chiral preference at the metal site is more strongly expressed in the carbohydrate esters than in glycol and glycerol esters where the exo isomer is observed as a minor constituent in both ^{51}V and ^{1}H NMR studies in solution.[4a]

b. The Anomeric Proton. The spin−spin splitting of the anomeric proton is expected to be relatively large (6−8 Hz) only when axial−axial coupling is present; otherwise, it would be small.[22] In galactose esters it occurs as a doublet ($J \sim 8$ Hz) (Figure 5) signifying preservation of β-configurations (axial−axial H1 H2 coupling) in solution. For the mannose (Figure 5) and ribose esters spin−spin structure is only poorly resolved, consistent with α (equatorial−equatorial coupling) and β (axial−equatorial coupling) configurations, respectively.

c. Alkoxide-Alcohol Chelation. The ring OMe chemical shifts in the vanadate esters generally lie close to those in the corresponding free carbohydrates except when the OMe function lies adjacent to an alkoxide function. In **8c** (Figure 3) the 4-OMe group is so disposed, the alkoxide oxygen occurring at C3. The preservation of this structural feature in solution is reflected in the downfield shift of the 4-OMe signal from the free ligand value by ∼0.3 ppm. The possibility that C2 (instead of C3) has become alkoxidic in solution is thus excluded. The lack of any sizable shift of the 1-OMe signal from the free ligand value suggests the binding mode **12** (alkoxide oxygen at C3) as opposed to **13** (alkoxide oxygen at C2) in the case of the ribose esters.



12



13

The alkoxidic CH proton occurs as an isolated signal downfield[23,4] (by 1−2 ppm) from the alcoholic CH signal (Figure 5). In the mannose esters this signal is observed as a doublet of doublets due to axial−axial (H3 H4, $J \sim 8$ Hz) and equatorial−axial (H2 H3, $J \sim 4$ Hz) coupling. For the galactose esters no axial−axial interaction is present and an ill-resolved multiplet is obtained. In the structural type **12** of ribose esters an axial−axial (H3 H4) interaction is present, but here the alkoxidic CH signal is quite broad and the spin−spin structure is poorly resolved.

The hydroxyl proton of the esters occurs near 7.2 ppm, the signal expectedly disappearing upon shaking with D_2O. The doublet splitting of the signal due to coupling within the CHOH group is best resolved in the ribose group of complexes.

Concluding Remarks

The monoionized form of methyl-2,6-dimethoxy-β-D-galactopyranoside, methyl-4,6-dimethoxy-α-D-mannopyranoside, and methyl-5-methoxy-β-D-ribofuranoside, each having two free vicinal hydroxyl groups, has been successfully chelated to VO^{3+} which is coligated to chiral *N*-salicylidene-α-amino acids affording VO(β-D-HMe$_3$GP)(L-Asal), **7**; VO(α-D-HMe$_3$MP)(L-Asal), **8**; and VO(β-D-HMe$_3$RF)(L-Asal), **9**. The species represent the first examples of structurally characterized sugar vanadate esters incorporating VO^{3+}.

In the environment of chiral ligands and coligands, the metal site in **7**−**9** also assumes a specific chiral configuration ("endo") that is sterically favored by the folded structure of the coligand.

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NMR studies (^{1}H and ^{51}V) have demonstrated that no isomerization at metal or anomeric carbon sites occurs in solution and that the carbohydrates bind in the same manner in the solid and solution phases. Our search for new carbohydrate esters of vanadium is continuing.

Experimental Section

Materials. Methyl β-D-glactopyranoside, methyl α-D-mannopyranoside, and D-ribose were purchased from Sigma Chemical. Methyl β-D-ribofuranoside was prepared from D-ribose.[24] The VO(L-Asal)(OMe)(OHMe) were synthesized using reported methods.[18] Tetraethylammonium perchlorate (TEAP) was prepared as before.[25] Dimethylformamide was dried over P_4O_{10} for 72 h and then distilled in a vacuum. All other chemicals and solvent were analytical grade and used as received.

Physical Measurement. Spectral measurements were carried out with Perkin-Elmer 783 (IR), Hitachi 330 (UV-vis), and JASCO J-500 (CD) spectrometers. Electrochemical measurements were performed on a PAR model 370-4 system as previously.[26] A Perkin-Elmer elemental analyzer was used to collect microanalytical data (C,H,N). ^{51}V NMR were recorded at 25 °C on a Varian spectrometer at 78.8 MHz with $VOCl_3$ as the external reference. Proton NMR spectra were recorded on a Bruker FT300 MHz spectrometer. The numbering scheme used for ^{1}H NMR is the same as those in Chart 1 and Figures 2 and 3. Ligands **3**, **4**, and **5** have nine, nine, and seven carbon atoms, respectively. To retain a uniform numbering scheme for the L-Asal^{2-} ligand in all three groups of esters, no carbon atoms are numbered 8 and 9 in the ribose esters.

Synthesis of H_2SUG Ligands. The synthesis consisted of protection of two cis hydroxyl groups of the glycoside as the isopropylidene derivative, methylation of the remaining hydroxyl groups, followed by hydrolysis regenerating the pair that was protected.[27−29] The procedure given below for β-D-galactopyranoside is representative (see Scheme 1).

To a solution of β-D-H_4MeGP, **A** (5.00 g, 25.74 mmol) in dry *N*,*N*-dimethylformamide (30 mL), 2,2-dimethoxypropane (3.35 g, 32.17 mmol) and a catalytic amount of *p*-toluenesulfonic acid were added at room temperature. The mixture was stirred for 24 h, neutralized with triethylamine, and then evaporated to dryness under reduced pressure followed by chromatography on a silica gel column (70 g, 60−120 mesh) using ethyl acetate as eluent. Removal of solvent afforded the 3,4-isopropylidene derivative **B** as a colorless solid. Yield: 3.00 g (50%) on the basis of **A**. Anal. Calcd for $C_{10}H_{18}O_6$: C, 51.28; H, 7.68. Found: C, 51.11; H, 7.74. ^{1}H NMR ($CDCl_3$, δ): 4.18 (1-H, d, 7.5); 3.57 (1-O*Me*, s); 1.53, 1.36 (C*Me*$_2$, s).

B was dissolved in dry *N*,*N*-dimethylformamide (25 mL). Iodomethane (10.90 g, 76.80 mmol) and silver oxide (13.30 g, 57.60 mmol) were added followed by stirring for 12 h. The reaction was then quenched by adding chloroform (150 mL). After removal of solvent under reduced pressure, the pasty mass was subjected to chromatography on a silica gel column (60 g, 60−120 mesh) using an ethyl acetate−toluene (5:3) mixture as the eluent. Removal of the solvent under reduced pressure afforded 2.35 g of **C**. Yield: 70% on the basis of **B**. Anal. Calcd for $C_{12}H_{22}O_6$: C, 54.96; H, 8.40. Found: C, 54.84; H, 8.45. ^{1}H NMR ($CDCl_3$, δ): 4.19 (1-H, d, 7.6); 3.57 (1-O*Me*, s); 3.60 (2-O*Me*, s); 3.42 (6-O*Me*, s); 1.53, 1.36 (C*Me*$_2$, s).

C was dissolved in a 1:1 mixture (30 mL) of ethyl acetate and methanol, and *p*-toluenesulfonic acid was added followed by stirring for 4 h at room temperature. The solution was then neutralized with triethylamine, and the solvent was removed under reduced pressure. The residue was chromatographed on a silica gel column (50 g, 60−120 mesh) with an ethyl acetate−methanol (5:1) mixture to yield methyl-2,6-dimethoxy β-D-galactopyranoside, **3**, after removal of solvent. Yield: 1.47 g (74% on the basis of **C**). Anal. Calcd for $C_9H_{18}O_6$: C, 48.64; H, 8.10. Found: C, 48.51; H, 8.16. ^{1}H NMR ($CDCl_3$, δ): 4.19 (1-H, d, 7.8); 3.24, 3.22 (2-H, dd, 7.8, 9.3); 3.60 (1-O*Me*, s); 3.55 (2-O*Me*, s); 3.42 (6-O*Me*, s); 3.02, 2.98 (6-H, d, 3.6, 4.8).

Preparation of Complexes. The VO(β-D-HMe_3GP)(L-Asal), VO(α-D-HMe_3MP)(L-Asal), and VO(β-D-HMe_2RF)(L-Asal) were prepared by using a general method. Details are given below for a representative case.

(Methyl-2,6-dimethoxy β-D-galactopyranosideato(1−)-*O*^{1},*O*^{2})oxo-(*N*-salicylidene-L-alaninato)vanadium(V), VO(β-D-HMe_3GP)(L-asal), 7a. To a dichloromethane solution (10 mL) of VO(L-asal)(OMe)(OHMe) (0.10 g, 0.31 mmol) was added a slight excess of methyl-2,6-dimethoxy-β-D-galactopyranoside (0.075 g, 0.34 mmol). A dark-red solution was formed. Upon layering with *n*-hexane followed by slow diffusion it afforded a dark-colored crystalline compound within 2 days. The compound was filtered off, washed with a little of water, and then dried in vacuo over P_4O_{10}. Yield: 0.122 g (82%). Anal. Calcd for $C_{19}H_{26}NO_{10}V$: C, 47.60; H, 5.43; N, 2.92. Found: C, 47.63; H, 5.45; N, 2.89. IR (KBr, cm^{-1}): $\nu_{(V=O)}$ 980; $\nu_{(CO_2)}$ 1315 (sym), 1610 (asym), 1645 (asym); $\nu_{(OH)}$ 3170. UV−vis (CH_2Cl_2, λ_{max}, nm (ε, M^{-1} cm^{-1})): 500 (610), 340 (4620). CD (CH_2Cl_2, λ_{max}, nm (ε, M^{-1} cm^{-1})): 550 (10), 375 (−70). $VO^{3+}-VO^{2+}$ couple ($CH_2Cl_2-CH_3CN$ (1:1), $E_{1/2}$, V): −0.20 (irr). ^{1}H NMR ($CDCl_3$, δ): 3.77 (2-H, 5-H, m); 3.02, 2.98 (6-H, d, 3.7, 5.0); 2.96 (6-O*Me*, s); 4.50 (11-H, q, 7.2); 8.40 (12-H, s); 7.50 (14-H, d, 7.5); 6.95 (15-H, t, 7.2); 7.57 (16-H, t, 7.2); 6.98 (17-H, d, 8.4); 1.75 (11-Me, d, 6.0).

The following compounds were prepared using the similar procedure.

VO(β-D-HMe_3GP)(L-vsal), 7b. Yield: 85%. Anal. Calcd for $C_{21}H_{30}NO_{10}V$: C, 49.70; H, 5.91; N, 2.76. Found: C, 49.62; H, 5.94; N, 2.80. IR (KBr, cm^{-1}): $\nu_{(V=O)}$ 975; $\nu_{(CO_2)}$ 1310 (sym), 1615 (asym), 1650 (asym); $\nu_{(OH)}$ 3150. UV−vis (CH_2Cl_2, λ_{max}, nm (ε, M^{-1} cm^{-1})): 500 (660); 340 (4700). CD (CH_2Cl_2, λ_{max}, nm (ε, M^{-1} cm^{-1})): 540 (18); 360 (−103). $VO^{3+}-VO^{2+}$ couple ($CH_2Cl_2-CH_3CN$ (1:1), $E_{1/2}$, V): −0.28 (irr). ^{1}H NMR ($CDCl_3$, δ): 3.76 (2-H, 5-H, m); 3.00, 2.95 (6-H, d, 3.8, 5.2); 2.89 (6-O*Me*, s), 3.96 (11-H, d, 7.5); 8.27 (12-H, s); 7.50 (14-H, d, 7.8); 6.95 (15-H, t, 7.2); 7.57 (16-H, t, 8.5); 6.99 (17-H, d, 6.4); 2.52 (19-H, m); 1.18, 1.08 (19-Me, d, 6.0, 6.0).

VO(β-D-HMe_3GP)(L-psal), 7c. Yield: 83%. Anal. Calcd for $C_{25}H_{30}NO_{10}V$: C, 54.05; H, 5.41; N, 2.52. Found: C, 54.11; H, 5.46; N, 2.48. IR (KBr, cm^{-1}): $\nu_{(V=O)}$ 978; $\nu_{(CO_2)}$ 1305 (sym), 1610 (asym), 1650 (asym); $\nu_{(OH)}$ 3160. UV−vis (CH_2Cl_2, λ_{max}, nm (ε, M^{-1} cm^{-1})): 500 (550), 340 (4000). CD (CH_2Cl_2, λ_{max}, nm (ε, M^{-1} cm^{-1})): 550 (20), 370 (−80). $VO^{3+}-VO^{2+}$ couple ($CH_2Cl_2-CH_3CN$ (1:1), $E_{1/2}$, V): −0.28 (irr). ^{1}H NMR ($CDCl_3$, δ): 3.79 (2-H, 5-H, m); 3.00, 2.96 (6-H, d, 3.8, 5.1); (6-O*Me*, s); 4.38 (11-H, m); 7.00 (12-H, s); 7.25 (14-H, 21−25-H, m); 6.82 (15-H, t, 7.5); 7.51 (16-H, t, 7.2); 6.97 (17-H, t, 8.7); 3.41 (19-H, m).

VO(α-D-HMe_3MP)(L-asal), 8a. Yield: 84%. Anal. Calcd for $C_{19}H_{26}NO_{10}V$: C, 47.60; H, 5.43; N, 2.92. Found: C, 47.47; H, 5.48; N, 2.96. IR (KBr, cm^{-1}): $\nu_{(V=O)}$ 982; $\nu_{(CO_2)}$ 1308 (sym), 1630 (asym), 1680 (asym); $\nu_{(OH)}$ 3190. UV−vis (CH_2Cl_2, λ_{max}, nm (ε, M^{-1} cm^{-1})): 500 (600); 340 (4570). $VO^{3+}-VO^{2+}$ couple ($CH_2Cl_2-CH_3CN$ (1:1), $E_{1/2}$, V): −0.27 (irr). ^{1}H NMR ($CDCl_3$, δ): 3.90 (4-H, dd, 4.2, 8.5); 3.58 (5-H, 6-H, m); 3.34 (6-O*Me*, s); 4.52 (11-H, q, 7.4); 8.41 (12-H, s); 7.49 (14-H, d, 7.2); 7.00 (15-H, t, 7.5); 7.59 (16-H, t, 8.4); 6.90 (17-H, d, 8.4); 1.77 (11-Me, d, 6.9).

VO(α-D-HMe_3MP)(L-vsal), 8b. Yield: 85%. Anal. Calcd for $C_{21}H_{30}NO_{10}V$: C, 49.70; H, 5.92; N, 2.76. Found: C, 49.59; H, 5.88; N, 2.80. IR (KBr, cm^{-1}): $\nu_{(V=O)}$ 990; $\nu_{(CO_2)}$ 1290 (sym), 1620 (asym), 1660 (asym); $\nu_{(OH)}$ 3190. UV−vis (CH_2Cl_2, λ_{max}, nm (ε, M^{-1} cm^{-1})): 500 (680); 340 (4600). $VO^{3+}-VO^{2+}$ couple ($CH_2Cl_2-CH_3CN$ (1:1), $E_{1/2}$, V): −0.28 (irr). ^{1}H NMR ($CDCl_3$, δ): 3.85 (4-H, 11-H, m); 3.57 (5-H, 6-H, m); 3.35 (6-O*Me*, s); 8.25 (12-H, s); 7.46 (14-H, d, 7.5); 6.98 (15-H, t, 7.2); 7.59 (16-H, t, 7.5); 6.91 (17-H, d, 8.4); 2.59 (19-H, m); 1.16, 1.02 (19-Me, d, 5.7, 6.2).

VO(α-D-HMe_3MP)(L-psal), 8c. Yield: 86%. Anal. Calcd for $C_{25}H_{30}NO_{10}V$: C, 54.05; H, 5.40; N, 2.52. Found: C, 53.98; H, 5.44; N, 2.55. IR (KBr, cm^{-1}): $\nu_{(V=O)}$ 980; $\nu_{(CO_2)}$ 1320 (sym), 1615 (asym), 1680 (asym); $\nu_{(OH)}$ 3170. UV−vis (CH_2Cl_2, λ_{max}, nm (ε, M^{-1} cm^{-1})):

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500 (460); 340 (4370). $VO^{3+}-VO^{2+}$ couple ($CH_2Cl_2-CH_3CN$ (1:1), $E_{1/2}$, V): −0.25 (irr). ^1H NMR ($CDCl_3$, δ): 3.93 (4-H, dd, 4.6, 8.2); 3.59 (5-H, 6-H, m); 3.34 (6-O*Me*, s): 7.01 (12-H, s); 7.05 (14-H, d, 7.5); 6.85 (15-H, t, 7.5); 7.54 (16-H, t, 7.4); 6.89 (17-H, d, 8.5); 3.40 (19-H, m); 7.26 (21−25-H, m).

VO(β-D-HMe$_2$RF)(L-asal), 9a. Yield: 87%. Anal. Calcd for $C_{17}H_{22}NO_9V$: C, 46.89; H, 5.06; N, 3.22. Found: C, 46.76; H, 5.10; N, 3.25. IR (KBr, cm^{-1}): $\nu_{(V=O)}$ 980; $\nu_{(CO_2)}$ 1310 (sym), 1620 (asym), 1700 (asym); $\nu_{(OH)}$ 3160. UV−vis (Me_2SO, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 510 (690); 335 (5400). $VO^{3+}-VO^{2+}$ couple (Me_2SO, $E_{1/2}$, V): −0.28 (irr). ^1H NMR ($(CD_3)_2SO$, δ): 3.15 (4-H, 5-H, m); 3.32 (5-O*Me*, s); 4.60 (11-H, q, 7.3); 8.91 (12-H, s); 7.65 (14-H, d, 7.8); 6.98 (15-H, t, 7.2); 7.60 (16-H, t, 8.1); 6.87 (17-H, d, 8.1); 1.61 (11-Me, d, 7.1).

VO(β-D-HMe$_2$RF)(L-vsal), 9b. Yield: 85%. Anal. Calcd for $C_{19}H_{26}NO_9V$: C, 49.24; H, 5.61; N, 3.02. Found: C, 49.13; H, 5.65; N, 3.05. IR (KBr, cm^{-1}): $\nu_{(V=O)}$ 972; $\nu_{(CO_2)}$ 1305 (sym), 1610 (asym), 1675 (asym); $\nu_{(OH)}$ 3180. UV−vis (Me_2SO, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 510 (640); 330 (4000). $VO^{3+}-VO^{2+}$ couple (Me_2SO, $E_{1/2}$, V): −0.24 (irr). ^1H NMR ($(CD_3)_2SO$, δ): 3.16 (4-H, 5-H, m); 3.31 (5-O*Me*, s); 4.20 (11-H, d, 6.9); 8.85 (12-H, s); 7.66 (14-H, d, 7.8); 6.97 (15-H, t, 7.2); 7.60 (16-H, t, 7.8); 6.76 (17-H, d, 8.4); 2.34 (19-H, m). 1.10, 1.01 (19-Me, d, 6.6, 6.9).

VO(β-D-HMe$_2$RF)(L-psal), 9c. Yield: 86%. Anal. Calcd for $C_{23}H_{26}NO_9V$: C, 54.01; H, 5.08; N, 2.73. Found: C, 53.89; H, 5.12; N, 2.76. IR (KBr, cm^{-1}): $\nu_{(V=O)}$ 978; $\nu_{(CO_2)}$ 1300 (sym), 1610 (asym), 1680 (asym); $\nu_{(OH)}$ 3200. UV−vis (Me_2SO, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 510 (760); 330 (5650). $VO^{3+}-VO^{2+}$ couple (Me_2SO, $E_{1/2}$, V): −0.29 (irr). ^1H NMR ($(CD_3)_2SO$, δ): 3.20 (4-H, 5-H, m); 3.36 (5-O*Me*, s); 4.68 (11-H, dd, 4.2, 8.2); 7.98 (12-H, s); 7.23 (14-H, 21−25-H, m); 6.87 (15-H, t, 7.5); 7.56 (16-H, t, 7.8); 6.83 (17-H, d, 8.4); 3.45 (19-H, dd, 4.5, 7.8).

X-ray Structure Determination. Crystals of VO(β-D-HMe$_3$GP)(L-vsal)·H_2O (0.3 mm × 0.4 mm × 0.3 mm) and VO(α-D-HMe$_3$MP)(L-psal)·H_2O (0.4 mm × 0.3 mm × 0.3 mm) were grown by slow diffusion of hexane into dichloromethane solution in the former and into benzene solution in the latter case. During crystallization the water molecules are picked up from the wet solvents. For both complexes cell parameters were determined by a least-squares fit of 30 machine-centered reflections (2θ, 15−30°). Data were collected by the ω-scan technique in the 2θ range 3−50° on a Siemens R3m/V four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Two check reflections measured after every 98 reflections showed no intensity reduction. Data were corrected for Lorentz−polarization effects and an empirical absorption correction was performed on both sets of data on the basis of azimuthal scans[30] of six reflections. For VO(β-D-HMe$_3$GP)(L-vsal)·H_2O, 5114 reflections were collected, 4997 were unique and 2936 satisfying $I > 2.0\sigma(I)$ used for structure solution. In the case of VO(α-D-HMe$_3$MP)(L-psal)·H_2O the corresponding numbers are 2782, 2626, and 1912, respectively.

All calculations for data reduction, structure solution, and refinement were done using the programs of SHELXTL, Version 5.03.[31] Both structures were solved by direct methods and were refined by full-matrix least-squares on F^2. The available observed data did not permit anisotropic refinement of all nonhydrogen atoms. In the case of VO(β-D-HMe$_3$GP)(L-vsal)·H_2O the metal, nitrogen, and oxygen atoms were made anisotropic (data/parameter = 6.9). For VO(α-D-HMe$_3$MP)(L-psal)·H_2O the same atoms (except H_2O oxygen) and the carbohydrate carbon atoms were made anisotropic (data/parameter = 6.8). The remaining atoms were refined isotropically. For both compounds the alcoholic and the anomeric hydrogen atoms were directly located in difference Fourier maps along with a few other hydrogen atoms. The remaining hydrogen atoms were included in calculated positions. Significant crystal data are listed in Table 4.

Table 4. Crystallographic Data for VO(β-D-HMe$_3$GP)(L-vsal)·H_2O and VO(α-D-HMe$_3$MP)(L-psal)·H_2O

	VO(β-D-HMe$_3$GP)(L-vsal)·H_2O	VO(α-D-HMe$_3$MP)(L-psal)·H_2O
chemical formula	$C_{21}H_{32}NO_{11}V$	$C_{25}H_{32}NO_{11}V$
fw	525.42	573.46
crystal system	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1$
a, Å	13.146(7)	13.645(4)
b, Å	15.142(5)	7.022(2)
c, Å	25.631(9)	15.500(4)
β, deg	90.00	113.98(2)
U, Å^3	5102(3)	1356.9(7)
Z	8	2
T, °C	22	22
λ, Å	0.710 73	0.710 73
D_c, g cm^{-3}	1.371	1.404
μ(Mo Kα), cm^{-1}	4.46	4.25
F(000)	2208	600
R1,[a] wR2[b] [$I > 2\sigma(I)$]	8.06, 16.81	6.30, 13.75
goodness of fit on F^2	1.024	1.030

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

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Supporting Information Available: For VO(β-D-HMe$_3$GP)(L-vsal)·H_2O and VO(α-D-HMe$_3$MP)(L-psal)·H_2O, tables of crystal data, complete atomic coordinates and thermal parameters, bond distances and angles, anisotropic thermal parameters, and hydrogen atom positional and thermal parameters. For VO(β-D-HMe$_3$GP)(L-vsal), VO(α-D-HMe$_3$MP)(L-asal), and VO(β-D-HMe$_2$RF)(L-asal) ^1H NMR spectra and for VO(β-D-HMe$_3$GP)(L-asal), VO(α-D-HMe$_3$MP)(L-vsal), and VO(β-D-HMe$_2$RF)(L-asal) cyclic voltammograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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