1598 *Inorg. Chem.* **2000,** *39,* 1598−1601

Notes

Sugar Binding to VO^{3+}. Synthesis and Structure of a New Mannopyranoside Vanadate

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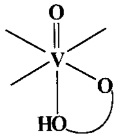
Received August 30, 1999

Introduction

Carbohydrate coordination chemistry is a notable frontier of inorganic research.[1,2] The case of vanadium is inherently interesting because sugar vanadates are potential analogues of sugar phosphates,[3−10] and this finds expression in, e.g., enzymatic action[11−13] and insulin-like function.[14] Very few crystalline sugar vanadates are, however, known.[15,16] The first VO^{3+} esters incorporating monoionized carbohydrate chelation as stylized in **1** were recently isolated and structurally characterized.[17−19]



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We report here a new crystalline vanadate ester wherein sugar modification selectively elongates the V−O(alcohol) bond in **1** to a state of virtual cleavage resulting in effective pentacoordination. In the crystal lattice the ester molecules are aggregated into helical chains via intermolecular hydrogen bonding.

Results and Discussion

Synthesis. The relevant sugar ligands, Schiff base coligands, and vanadate esters are listed in Chart 1. The most concerned sugar ligand is 4,6-benzylidine-α-D-mannopyranoside, α-D-H_2MeBMP, **2**, in which the two hydroxyl groups are correctly oriented (cis) for metal chelation. The diionized form of the hydrazone H_2bsal, **4**, was used to engage three equatorial sites in **1**. Thus the reaction of VO(bsal)(OMe)(OHMe)[20] with **2** in methanol afforded the ester **6** as a dark-colored crystalline solid in excellent yields, eq 1. Ligand **2** has been shown earlier to

$$\mathrm{VO(bsal)(OMe)(OHMe)} + \mathbf{2} \rightarrow \mathbf{6} + 2\mathrm{MeOH} \qquad (1)$$

furnish alkoxide-bridged dimeric esters of VO_2^+.[16] We have also explored the use of the salicylaldimine of glycine, H_2gsal, **5**, as a coligand to **2**. By replacing VO(bsal)(OMe)(OHMe) with VO(gsal)(OMe)(OHMe)[21] in the reaction of eq 1, the ester **7** has been isolated but only as an amorphous solid, whose characterization data are given in the Experimental Section. On the other hand, the methylated mannopyranoside, **3**, along with **5** is known to afford the crystalline vanadate **8**.[19] Attempts to synthesize VO(α-D-HMe_3MP)(bsal) by reacting VO(bsal)(OMe)(OHMe) with **3** furnished only an oily material which could not be characterized. These observations highlight the specificity of the ligand−coligand combination in promoting crystal formation in this class of sugar vanadates.

In **6,** the V═O and OH stretches occur respectively at 980 cm^{-1} (sharp) and 3185 cm^{-1} (broad). In solution **6** displays a relatively weak absorption band at 550 nm (ϵ, 240 $mol^{-1}\ cm^{-1}$) assigned to O^-(sugar) → V LMCT excitation.[18,19] In dichloromethane solution **6** undergoes irreversible one-electron voltammetric reduction ($VO^{3+} \rightarrow VO^{2+}$), the peak potential being −0.10 V versus SCE.

Structure. The X-ray structure of **6** has been determined; a view of the molecule is shown in Figure 1, and selected bond parameters are listed in Table 1. The VO^{3+} moiety is coordinated to the alkoxidic O3 atom of α-D-$HMeBMP^-$ and to O8, N1, and O9 atoms of the meridionally tridentate $bsal^{2-}$ ligand, the N1 atom lying trans to O3.

The V═O (1.592(5) Å) and V−O(alkoxidic) (1.795(4) Å) distances in **6** are similar to those in polyol[20,22−25] and carbohydrate[18,19] esters incorporating motif **1**. In the later esters the V−O(alcoholic) distance is lengthened by the V═O trans influence so as to lie within the range 2.34 ± 0.03 Å. A remarkable feature of **6** is the unusually long V···O(alcoholic)

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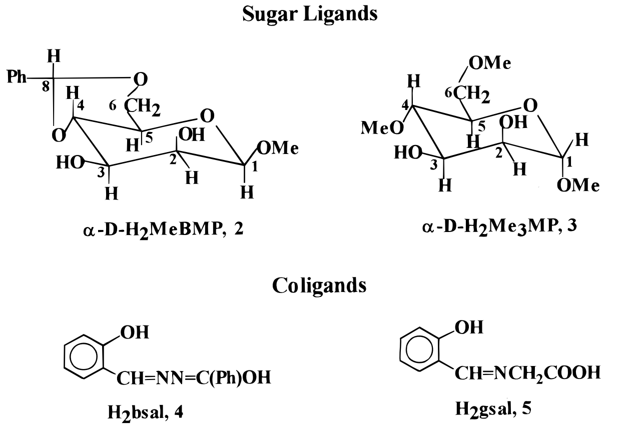
10.1021/ic9910460 CCC: $19.00 © 2000 American Chemical Society
Published on Web 03/17/2000

Chart 1



Esters

VO(α-D-HMeBMP)(bsal), 6

VO(α-D-HMe$_3$MP)(gsal), 8

VO(α-D-HMeBMP)(gsal), 7

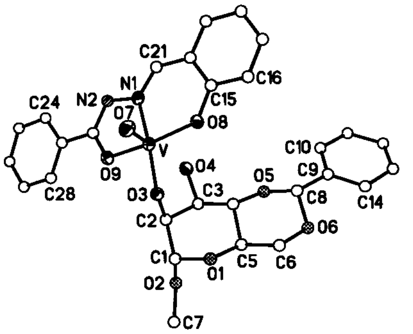


Figure 1. Perspective view and atom-labeling scheme of VO(α-D-HMeBMP)(bsal).

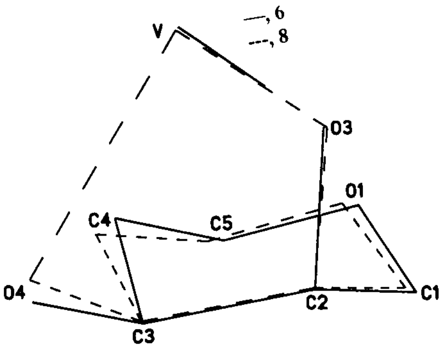
Table 1. Selected Bond Lengths (Å) and Angles (deg) for VO(α-D-HMeBMP)(bsal)

V–O3	1.795(4)	V–O7	1.592(5)
V–O8	1.839(4)	V–O9	1.918(4)
V–N1	2.084(6)		
O3–V–O7	102.8(2)	O7–V–O8	100.4(3)
O3–V–O8	104.3(2)	O7–V–O9	102.2(2)
O3–V–O9	89.1(2)	O8–V–O9	150.4(3)
O3–V–N1	156.3(2)	O7–V–N1	97.3(3)
O8–V–N1	84.0(2)	O9–V–N1	74.4(2)

contact, 2.514(5) Å, signifying the virtual absence of bonding. In effect, **6** is a square pyramidal complex.

Since the V=O length in **6** is normal, the state of the V···O(alcoholic) contact cannot be ascribed to any augmented trans influence. Its origin can be traced to changes in carbohydrate bond parameters as revealed by comparing **6** and **8**.[19] In **6** the benzylidine group is engaged in a cyclic diether as opposed to the most flexible acyclic situation in **8** incorporating two methyl groups. Angular changes at the C4 (and the C5) atom are thus induced, and this in turn affects the angles around C3 to which the alcoholic O4 atom is attached. This can be seen in the superposition diagram **9**, incorporating relevant parts of **6** and **8**: C4–C3–O4, 114.0(5)° in **6** and 108.6(8)° in **8**; C4–C3–C2, 107.0(5)° in **6** and 114.2(8)° in **8**. The net result is that the V···O4 contact is lengthened, vide **9**.

The V–O8, V–N1, and V–O9 distances within the V(bsal) fragment are similar to those observed elsewhere.[20,22] The atoms O3, O8, O9, and N1 constitute an excellent equatorial plane (mean deviation 0.02 Å) from which the metal atom is displaced by 0.35 Å toward the O7 atom. Significantly the displacement is larger than that (0.32 Å) observed in species[18−20,22−25] of type **1** in which the V–O(alcoholic) distance is 2.34 Å.



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The O4 atom is engaged in intermolecular hydrogen bonding with the oxo oxygen O7 (O4···O7, 2.918(10) Å) generating a helical pattern parallel to the *b* axis, Figure 2. This mode of hydrogen bonding is distinct from those observed in type **8** esters.[18,19] The OH hydrogen itself could not be directly located in difference Fourier maps of **6**, but its presence is unequivocally revealed by the IR and ^{1}H NMR results.

The vanadium site in **6** has no symmetry and is thus chiral. Viewing down the V=O axis and using the priority sequence O9 > O8 > O3 > N1 for the equatorial atoms, the observed configuration is *A* (anticlockwise).[26] There is no evidence that the diastereoisomer incorporating the *C* configuration exists either in the solid state or in solution (vide infra). Model building reveals the presence of serious steric interference between the pendent phenyl rings of the bsal^{2-} and α-D-HMeBMP^{-} ligands in the unobserved diastereoisomer.

NMR Spectra and Solution Structure. The spectrum of **6** (Figure 3 and Experimental Section) in CDCl$_3$ is consistent with gross retention of the solid state molecular structure in solution. It is unlikely that the weak hydrogen bonding observed in the solid state is retained in the polar CDCl$_3$ solution.

The presence of a single sharp ^{51}V NMR line for the complexes as well as of a single ^{1}H NMR feature for each type of proton corroborates the occurrence of only one chemical entity (absence of diastereoisomers) in solution.

The OH group gives rise to a relatively broad ^{1}H signal at 5.92 ppm which is no longer observed upon shaking the solution with D$_2$O. It is noteworthy that, in **8** and other related carbohydrate esters incorporating motif **1** having significant V–OH interaction, the OH signal is shifted downfield to ~7.2 ppm.[18,19] The H1 (i.e., the proton attached to C1) signal is a singlet because the small[27] equatorial–equatorial coupling with H2 is not resolved as is often the case.[18,19] On the other hand the alkoxidic H2 signal is a doublet (axial–equatorial coupling to H3) expectedly shifted[18−20,22−25] downfield by ~2 ppm from the free ligand value. The H3 atom coupled to H2, H4, and OH gives rise to a multiplet, and so does H5 coupled to CH$_2$ and H4. The H4 signal, a doublet of doublets, reveals axial–axial coupling to H3 and H5.

The ^{1}H spectrum of the carbohydrate segment of the ester **7** is grossly similar to that of **6**. The OH signal occurs at 5.98

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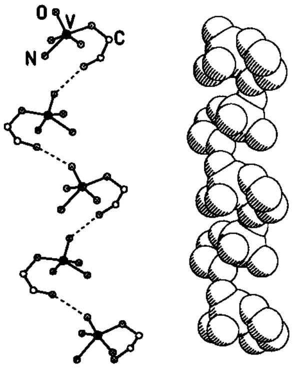

Figure 2. Hydrogen bonding in crystalline VO(α-D-HMeBMP)(bsal) in ball-and-stick and space-filling forms (selected atoms only).

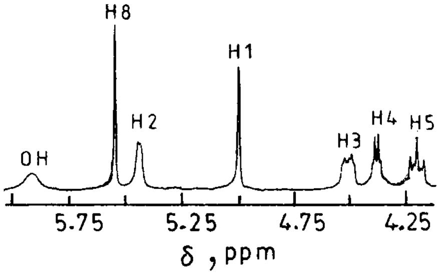

Figure 3. ^{1}H NMR spectrum of VO(α-D-HMeBMP)(bsal) in $CDCl_3$ in the region 4.2−6.0 ppm.

ppm, suggesting that here also the group is distanced from the metal as in **6**.

Concluding Remarks

The synthesis of the sugar vanadate VO(α-D-HMeBMP)(bsal), **6**, has been achieved in excellent yields. Distinctive structural features of the ester include (i) pronounced lengthening of the V···O(alcoholic) contact due to angular changes in the carbohydrate ligand resulting in effective pentacoordination, (ii) intermolecular hydrogen bonding between alcoholic and oxo oxygen atoms leading to a helical pattern, and (iii) exclusive *A* configuration of the vanadium site due to steric factors. Solution ^{51}V and ^{1}H NMR results have revealed that carbohydrate and coligand bindings are grossly similar to those in the solid state. The vanadate VO(α-D-HMeBMP)(gsal), **7**, has also been synthesized as an amorphous solid whose spectral features are similar to those of **6**.

Experimental Section

Materials. Methyl-α-D-mannopyranoside was purchased from Sigma Chemicals. The complex VO(bsal)(OMe)(OHMe)[20] and tetraethylammonium perchlorate (TEAP)[28] were prepared using reported methods. All other chemicals and solvents were of analytical grade and used as received.

Physical Measurements. ^{51}V NMR spectra were recorded in $CDCl_3$ on a Varian spectrometer (78.8 MHz, 298 K) with $VOCl_3$ as the external reference. Proton NMR spectra taken in $CDCl_3$ on a Bruker FT 300 MHz spectrometer are stated in this order: chemical shift in ppm (proton label, multiplicity, *J* value in Hz). IR and electronic spectra were taken respectively on a Perkin-Elmer 783 spectrometer and Hitachi 330 spectrophotometer. Electrochemistry was done using a PAR model 370-4 system as previously.[29] A Perkin-Elmer elemental analyzer was used to perform C, H, N microanalysis.

Table 2. Crystallographic Data for VO(α-D-HMeBMP)(bsal)

	VO(α-D-HMeBMP)(bsal)
chem formula	$C_{28}H_{27}N_2O_9V$
fw	586.46
cryst syst	monoclinic
space group	$P2_1$
a, Å	11.357(7)
b, Å	9.613(5)
c, Å	12.326(7)
β, deg	97.66(5)
V, Å^3	1334(1)
Z	2
T, °C	22
λ, Å	0.710 73
D_c, g cm^{-3}	1.460
μ(Mo Kα), cm^{-1}	4.30
F(000)	608
$R1$,[a] wR2[b] [$I > 2\sigma(I)$]	0.0536, 0.1012
goodness of fit on F^2	1.036

[a] R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. [b] wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o2)^2]^{1/2}$.

Synthesis of Sugar Ligand, α-D−H$_2$MeBMP, 2. This was prepared by extending a procedure available for other sugars.[30] A 5.00 g (25.74 mmol) portion of methyl α-D-mannopyranoside was dissolved in 30 mL of dry *N,N*-dimethylformamide. To this solution were added benzaldehyde dimethylacetal (5.88 g, 38.61 mmol) and a pinch of *p*-toluenesulfonic acid. The mixture was stirred for 18 h, neutralized with triethylamine, and finally evaporated to dryness under reduced pressure. The solid thus obtained was chromatographed on a silica gel column (80 g, 60−120 mesh) using ethyl acetate−toluene (1:4) as eluant. Removal of solvent under reduced pressure afforded **2** as a white solid. Yield: 5.08 g (70%). Mp 141 °C. Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.57; H, 6.38. Found: C, 59.48; H, 6.45. ^{1}H NMR: 4.76 (H1, s); 4.30 (H4, dd, 3.6,8.1); 4.04 (H3, m); 3.92 (H5, m); 3.84 (H6, dd, 4.8,9.3); 5.50 (H8, s); 3.41 (O*Me*, s); 7.38−7.52 (arom).

Preparation of VO(α-D-HMeBMP)(bsal), 6. To a methanolic solution (10 mL) of VO(bsal)(OMe)(OHMe) (0.10 g, 0.27 mmol) was added **2** (0.10 g, 0.35 mmol), and the dark red solution thus formed was left to evaporate to nearly 5 mL in air, affording **6** as a deep-brown crystalline solid. Yield: 0.13 g (82%). Anal. Calcd for $C_{28}H_{27}N_2O_9V$: C, 57.33; H, 4.60; N, 4.78. Found: C, 57.38; H, 4.69; N, 4.71. ^{1}H NMR: 5.00 (H1, s); 5.45 (H2, d, 3.2); 4.51 (H3, m); 4.37 (H4, dd, 5.1,7.8); 4.20 (H5, m); 3.95 (H6, dd, 3.9,8.4); 5.55 (H8, s); 5.92 (O*H*, br); 3.51 (O*Me*, s); 8.48 (H21, s); 6.60−7.79 (arom). ^{51}V NMR: −539 ppm.

Preparation of VO(α-D-HMeBMP)(gsal), 7. The complex was prepared using the same procedure as above. Here VO(gsal)(OMe)(OHMe) is used instead of VO(bsal)(OMe)(OHMe). Yield: 80%. Anal. Calcd for $C_{23}H_{24}NO_{10}V$: C, 52.57; H, 4.57; N, 2.66. Found: C, 52.66; H, 4.53; N, 2.61. UV−vis (CH_2Cl_2, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 550 (650), 325 (4230). IR (KBr, cm^{-1}): ν(V═O) 988; ν(CO_2), 1300(sym), 1615(asym), 1700(asym); ν(OH) 3120. ^{1}H NMR: 4.79 (H1, s); 5.42 (H2, m); 4.26 (H3, m); 4.01 (H4, m); 3.80 (H5, H6, m); 5.31 (H8, s); 3.45 (O*Me*, s); 5.98 (O*H*, br); 8.17 (C*H*═N, s); 4.74, 4.26 (C*H*$_2$, d, 18.3,19.1); 6.78−7.62 (arom). ^{51}V NMR: −550 ppm. $E_{1/2}$ ($VO^{3+}-VO^{2+}$ couple) in CH_2Cl_2: −0.18 V (irr).

X-ray Structure Determination. Crystals of VO(α-D-HMeBMP)(bsal) (0.3 × 0.4 × 0.3 mm) were grown by slow evaporation from a methanolic solution. Cell parameters were determined by 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 = 0.71073 Å). Two check reflections were measured after every 98 reflections showed no intensity reduction. All calculation and solutions were done using SHELXTL version 5.03.[31] The

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structure was solved by direct methods and was refined by full-matrix least squares on F^2. Data were corrected for Lorentz and polarization effects and for absorption.[32] Of the 2839 reflections collected, 2524 were unique, 1965 satisfying $I > 2\sigma(I)$. The available observed data did not permit full anisotropic refinement, and the C9−C14 and C23−C28 atoms were left isotropic. All hydrogen atoms were included in calculated positions. Significant crystal data are listed in Table 2.

Acknowledgment. Financial support received from the Indian National Science Academy, the Department of Science and Technology, and the Council of Scientific and Industrial Research, New Delhi, is acknowledged. Affiliation to the Jawaharlal Nehru Centre for Advance Scientific Research, Bangalore, is acknowledged.

Supporting Information Available: For VO(α-D-HMeBMP)(bsal), tables of crystal data, complete atomic coordinates and thermal parameters, bond distances and angles, anisotropic thermal parameters, and hydrogen atom positional and thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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