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Carbohydrate Research 329 (2000) 41–47

CARBOHYDRATE
RESEARCH

Characterization of new oxovanadium(IV) complexes of saccharides

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Received 9 November 1999; accepted 11 May 2000

Abstract

Oxovanadium(IV) complexes of the monosaccharides D- and L-arabinose, D-galactose, D-mannose, D-lyxose, D-xylose and the disaccharide maltose were obtained in aqueous solutions at pH 13. Their sodium salts were precipitated with absolute ethanol and characterized by UV–vis spectroscopy (absorption and reflectance), thermoanalytical (TG and DTA) data, magnetic susceptibility measurements and IR-spectroscopy. All the complexes were found to be mononuclear, possessing the VO^{2+} moiety. The IR spectra were analyzed and discussed in detail allowing one to determine the characteristics of the metal-to-ligand interactions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: VO^{2+} complexes; Saccharide complexes; Electronic spectra; Infrared spectra

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1. Introduction

The interaction of vanadates with carbohydrates and the subsequent stabilization of the reduced VO^{2+} species are of central interest in relation to vanadium metabolism [1,2]. Different oxovanadium(IV) complexes with a variety of saccharides have been synthesized and characterized in the past few years [3–9] in order to attain a wider insight into the VO^{2+}–saccharide interactions.

As a continuation of our own studies in this field of vanadium biochemistry, we have now characterized a new group of simple saccharide complexes of oxovanadium(IV).

2. Materials and methods

D- and L-arabinose, D-galactose, D-mannose, D-lyxose, D-xylose and maltose were purchased from Sigma Chemical Co. and used as supplied. $VOCl_2$ (50% solution) was obtained from Carlo Erba.

UV–vis absorption spectra were measured on a Hewlett–Packard 8453 diode-array spectrophotometer, using 1-cm quartz cells. IR spectra were recorded on a Perkin–Elmer 580 B spectrophotometer using the KBr pellet technique.

Diffuse reflectance spectra were obtained with a Shimadzu UV-300 instrument, using MgO as an internal standard. The thermal behavior was investigated with a Shimadzu thermoanalytical system (TG-50 and DTA-50 models), with compounds in platinum crucibles under a constant oxygen flow of 60 mL/min. The heating rate was 10 °C/min, and Al_2O_3 was used as a DTA standard.

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PII: S0008-6215(00)00171-3

Room temperature magnetic susceptibilities were measured with a Cahn 2000 balance calibrated with $Hg[Co(SCN)_4]$ and using a field strength of 6 kG. C and H elemental analysis were carried out on a Carlo Erba 1108 elemental analyzer, and sodium was determined by flame photometry.

3. Experimental

The complexes were synthesized and characterized as previously described [6]. Briefly, the saccharide (4 mmol) was dissolved in doubly distilled water (10 mL), and $VOCl_2$ (2 mmol) was added with constant stirring. The pH of the mixture was raised to 13 by successive additions of small amounts of solid NaOH. The solid complexes were obtained from the green solutions by successive additions of absolute EtOH and discarding the supernatant until a microcrystalline solid was formed. The hygroscopic green sodium salts were kept in an oven at 60 °C. The results of elemental analyses are given in Table 1. The water content of the complexes was additionally confirmed by thermogravimetric measurements.

Unfortunately, it was impossible to obtain crystalline material adequate for crystallographic structural analyses, as is usual in similar systems [2].

4. Results and discussion

The elemental analyses are consistent with the following formulations for the solid sodium salts: $Na_4[VO(\text{D-Man})_2]\cdot 8H_2O$ (**1**); $Na_4[VO(\text{D-Gal})_2]\cdot 5H_2O$ (**2**); $Na_5[VO(\text{Mal})_2OH]\cdot 10H_2O$ (**3**); $Na_4[VO(\text{D-Ara})_2]\cdot 5H_2O$ (**4**); $Na_4[VO(\text{L-Ara})_2]\cdot 5H_2O$ (**5**); $Na_4[VO(\text{D-Xyl})_2]\cdot 5H_2O$ (**6**); and $Na_5[VO(\text{D-Lyx})_2OH]\cdot 6H_2O$ (**7**).

Other oxovanadium(IV) complexes with the same saccharides, but showing different stoichiometries, and prepared at somewhat lower pH values with a different synthesis procedure, were recently reported [7,8].

Thermal analysis.—The analysis of the thermoanalytical data of the complexes is presented in Table 2. As can be seen, the thermogravimetric data clearly confirm the water content inferred from the chemical analysis. In all cases the water loss begins at relatively low temperatures, and the total release of water involves three or four steps. These steps are related to weak and relatively broad endothermic DTA signals. After dehydration, the anhydrous compounds degrade rapidly, and in all cases a strong DTA signal, located around 330 °C, accompanies the beginning of this process.

Electronic spectra.—Absorption spectra of the green solution at pH 13 (Table 3) show the

Table 1
Elemental analysis (%) and room temperature magnetic moments for VO^{2+}–saccharide complexes **1**–**7** [a]

Compound	Molecular formula	Analyses			μ_{eff} (BM)
		C	H	Na	
1	$C_{12}H_{34}O_{21}Na_4V$	22.00	5.22	14.10	1.90
		(21.92)	(5.17)	(14.00)	
2	$C_{12}H_{28}O_{18}Na_4V$	23.40	4.58	15.10	1.68
		(23.88)	(4.69)	(15.25)	
3	$C_{24}H_{51}O_{34}Na_5V$	27.30	5.00	11.10	1.65
		(27.24)	(4.82)	(10.88)	
4	$C_{10}H_{24}O_{16}Na_4V$	21.80	4.15	17.16	1.81
		(22.10)	(4.41)	(16.94)	
5	$C_{10}H_{24}O_{16}Na_4V$	21.78	4.05	17.05	1.78
		(22.10)	(4.41)	(16.94)	
6	$C_{10}H_{24}O_{16}Na_4V$	22.20	3.98	17.10	1.85
		(22.10)	(4.41)	(16.94)	
	$C_{10}H_{27}O_{18}Na_5V$	19.80	4.73	19.20	1.72
7		(19.97)	(4.49)	(19.13)	

[a] Calculated values in parentheses.

Table 2
Analysis of the thermoanalytical data [a]

Complex	Data	1st step	2nd step	3rd step	4th step	Decomp.
1	Mols H_2O	1	1	2	4	
	T-range	20–60	60–99	99–148	148–215	
	DTA	45-*endo*	?	124-*endo*	197-*endo*	332-*exo*
2	Mols H_2O	1	1	2	1	
	T-range	22–105	105–140	140–183	183–210	
	DTA	73-*endo*	124-*endo*	?	190-*endo*	323-*exo*
3	Mols H_2O	2	2	4	2	
	T-range	20–90	90–135	135–166	166–181	
	DTA	?	112-*endo*	142-*endo*	175-*endo*	326-*exo*
4	Mols H_2O	2	2	1		
	T-range	24–162	162–240	240–281		
	DTA	126-*endo*	?	257-*endo*		323-*exo*
5	Mols H_2O	1	2	2		
	T-range	21–96	96–174	174–244		
	DTA	40-*endo*	125-*endo*	197-*endo*		325-*exo*
6	Mols H_2O	2	2	1		
	T-range	26–158	158–222	222–250		
	DTA	132-*endo*	?	243-*endo*		346-*exo*
7	Mols H_2O	1	2	3		
	T-range	232–110	110–178	178–270		
	DTA	45-*endo*	132-*endo*	240-*endo*		335-*exo*

[a] In °C.

three-band pattern characteristic of the coordination of saccharides with the VO^{2+} cation [3,6,10,11]. The diffuse reflectance spectra show the same patterns (Table 3). In the case of complex **3** the $b_2 \rightarrow b_1$ transition was difficult to measure. These results, together with those of the elemental analyses and the IR spectra (see below), show that the coordination of the VO^{2+} cation takes place through four deprotonated OH groups belonging to two different saccharide moieties.

Complexes prepared at lower pH values showed only two absorption bands, with the absence of the $b_2 \rightarrow a_1$ transition [7,8]. This different behavior is related to the different deprotonation grade of the saccharide ligands, at different pH values.

Magnetic susceptibilities.—The seven prepared complexes (**1**–**7**) present magnetic moments ranging between 1.65 and 1.90 BM at room temperature (Table 1). These values are close to those expected for the spin-only d^1 configuration and lie in the ranges usually found in VO^{2+} complexes [12]. These results support the generation of mononuclear complex species, with isolated VO^{2+} units.

Table 3
Electronic spectra of the VO^{2+}–saccharide complexes **1**–**7** [a]

Compound	λ_1 $b_2 \rightarrow a_1$	λ_2 $b_2 \rightarrow b_1$	λ_3 $b_2 \rightarrow e$
1	414 (32.8)	504 (14.7)	708 (28.0)
	420	*500*	*675*
2	422 (28.7)	504 (12.5)	708 (27.6)
	420	*500*	*675*
3	432 (35.8)	506 (15.0)	722 (29.7)
	440	*550?*	*700*
4	414 (29.2)	504 (12.8)	698 (27.0)
	420	*500*	*680*
5	414 (33.0)	504 (14.6)	698 (31.1)
	420	*510*	*670*
6	422 (39.5)	504 (15.8)	692 (30.2)
	420	*510*	*660*
7	416 (31.4)	504 (14.2)	708 (28.3)
	435	*510*	*675*

[a] Wavelength: nm. Parentheses: molar extinction coefficient, M^{-1} cm^{-1}. Italics: diffuse reflectance bands, nm.

Table 4
Band positions and tentative assignment for the VO^{2+}–saccharide complexes **1**–**3** [a]

Manose	Manose/VO	Galactose	Galactose/VO	Maltose	Maltose/VO	Assignments
1451 m	1464 m	1454 m	1446 m	1458 m	1450 m	δ CH_2
1424 m	1424 m	1419 m	1431 m	1435 m	1423 m	
1390 sh		1392 w		1395 sh		δ C-2–H
1370 m	1370 m		1372 w	1376 m	1376 m	ω CH_2
1360 sh	1360 sh	1356 m	1352 w	1356 m	1348 m	δ COH, τ C-1–HOH
1327 w	1311 sh	1325 m	1321 w	1321 w	1317 m	δ CH_2
				1309 w		
1273 m		1297 m		1274 m		δ COH (C-6–H_2OH)
1253 sh	1257 w				1258 w	δ CH_2, δ COH, δ C-1–H
1245 sh		1246 m	1243 vw	1246 w	1235 w	
1203 m				1203 w	1203 w	δ CH_2
	1164 m	1152 s	1148 sh	1135 s	1149 m	ν CO, p
1129 sh, 1109 s	1113 sh	1101 s	1117 sh	1105 vs	1100 sh	ν CO_{endo}
1067 vs	1070 vs	1066 vs	1070 vs	1074 vs	1074 sh	ν CO_{exo}, δ C-1–H, δ COH
1039 vs	1051 vs	1043 vs	1046 vs	1037 vs	1043 sh	δ C-1–H
1016 vs			1023 sh	1025 vs	1025 vs	δ COH
	1000 m	995 w		991 s	991 (sh,w)	
962 m		972 w				
		956 s				
	930 s		925 vs		925 m	ν V=O
				906 m		δ COH, β
907 m						δ C-1–H
876 m	895 sh			870 w	882 sh	see text
	861 w					
				850 m	856 vw	glycosidic linkage, α
826 m		835 s				δ C-1–H, α
	810 m		819 w			δ C-1–H, α
798 m	800 m		799 w			
775 m		771 w		776 m	760 w	ν_s COC
	752 m	760 s	741 w			ν_s COC
				752 m	748 w	1 → 4 type 3 linkage, α
705 m		705 w		717 m	702 w	

[a] In cm^{-1}; vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder intensities.

IR spectra.—The homomorphic sugars have the same configuration in each asymmetrically substituted carbon atom of the pyranose ring. They differ in the type of substituent bond to one of the carbon atoms. The following pairs D-xylose/D-glucose, L-arabinose/D-galactose and D-lyxose/D-mannose, differ from each other in the exocyclic –CH_2OH group bound to C-5. On the other hand, in the first two pairs the β form is favored, and in the latter pair the α form predominates.

The IR spectra of each homomorphic pair are similar in the fingerprint region (950–1200 cm^{-1}). Differences are found in the 1200–1500 cm^{-1} range, where –CH_2OH exocyclic groups contribute significantly to the normal vibrational modes. It can be seen from Tables 4 and 5 that in the 1250–1300 cm^{-1} range the bands corresponding to δ CH_2 of C-6 are absent in the IR spectra of pentapyranoses. Moreover, the disappearance of another δ CH_2 band, located at 1203 cm^{-1}, can also be observed.

On the other hand, the members of each pair of epimeric sugars differ in the orientation of one substituent in the pyranose ring. The epimeric pairs of sugars show different IR spectral patterns. Glucose and galactose differ at C-4. The most important differences in the IR spectra are observed in the 1500–1200 cm^{-1} region. While glucose shows a medium intensity band at 1341 cm^{-1} and a weak one at 1224 cm^{-1}, in galactose these bands are shifted to 1356 (m) and 1246 (m) cm^{-1}, respectively [6,13].

For the glucose/mannose pair, which differ at C-2, the vibrations in this region are 1377 (m) cm^{-1} and 1224 (w) cm^{-1} for glucose. These vibrations shift to 1370 (sh), 1360 (sh) cm^{-1} and 1253 (sh), 1245 (sh) cm^{-1}, respectively, in mannose. Two doublets are observed in a similar way as in the Raman optical activity spectra [14].

D-xylose/L-arabinose differ at C-4. The main differences are seen in the fingerprint region. Besides, in the high-frequency range a band at 1250 cm^{-1} can be observed in the arabinose spectrum, which is absent in the xylose spectrum. Moreover, other shifts are also observed in this region.

D-lyxose/D-xylose differ at C-2. The IR spectra are quite different. In the 1500–1200 cm^{-1} range, two new and weak bands appear for lyxose at 1274 (sh) and 1254 (w) cm^{-1}. For the pair D-lyxose/D-arabinose, which differ at C-3, the IR spectra are very similar.

VO^{2+}–mannose complex (**1**).—The ligand is found to be in the α form, because of the δ H-1 bands located at 907, 876, 826 and 798 cm^{-1}. The first band also indicates that mannose is in the pyranose form. The second band is related to a D-mannopyranose vibration with δ CH in the equatorial position (cf. Table 4). α-Mannose coordinates to the metal cation through the deprotonated 1- and 3-OH groups, which are in the *cis* position. The band at 1327 cm^{-1} is shifted to 1311 cm^{-1} in the complex. This band is sensitive to complexation, deuteration or deprotonation [6,15].

Table 5
Band positions and tentative assignment for the VO^{2+}–saccharide complexes **4**–**7** [a]

Arabinose	Arabinose/VO	Xylose	Xylose/VO	Lyxose	Lyxose/VO	Assignments
	1450 m	1450 m	1458 m	1458 m	1454 m	δ CH$_2$
1423 w	1425 sh		1435 m	1423 m	1439 sh	
1403 w	1410 sh	1395 m		1399 sh		δ C-2–H
1372 m	1384 m	1372 m	1376 m		1379 sh	ω CH$_2$
1356 m	1348 m	1337 m	1352 m	1364 m	1355 sh	COH, τ C-1–HOH
				1341 m	1339 sh	
1317 m		1305 m	1305 sh	1317 m	1315 sh	δ CH$_2$
1250 m	1254 w		1258 w	1254 w		δ CH$_2$, δ COH, δ C-1–H
1235 m		1239 w	1219 w	1227 m	1231 w	
		1192 m				
1133 vs	1137 s	1144 s	1148 sh	1164 s	1188 sh	ν CO, p
				1129 m		
1090 s	1109 s	1125 s	1121 s	1101 s	1097 sh	ν CO$_{endo}$
1062 sh	1078 sh	1070 sh	1066 sh	1066 vs	1066 vs	ν CO$_{exo}$, δ C-1–H, δ COH
1050 vs	1058 vs	1039 vs	1039 sh	1043 vs	1026 sh	δ C-1–H
		1015 sh	1015 sh			δ COH
995 vs	999 s			999 vs	1005 sh	
	965 sh				972 m	
941 m			949 sh,br	952 m		
	929 s	929 s	929 sh,br		921 s	ν V=O
		901 s	901 sh,br			
890 m						
876 m	878 m		874 sh	878 m	882 m	
	855 sh		850 sh	835 m	856 vw	
839 m						δ C-1–H, β
	823 sh		819 w		811 m	
784 s	803 m				803 w	ν_s COC
	748 sh		788 w	752 vs	772 sh	ν_s COC
		756 m				α-D-xylo
			737 w			
713 m	709 sh				713 sh	

[a] In cm^{-1}; vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh,shoulder intensities; br, broad.

The band at 1273 cm^{-1} belonging to a C-6–OH deformation disappears upon complexation, and a new band is observed at 1000 cm^{-1}. This last band is associated with the deprotonation of the COH group. The characteristic V=O stretching band is seen at 930 cm^{-1}.

VO^{2+}–galactose complex (**1**).—Ligand bands located at 835(s) and 760 (s) cm^{-1} indicate the presence of the α anomer [16]. It coordinates to oxovanadium(IV) through the 1 and 2-OH groups. The involvement of the 1-OH is supported by the intensity modification of the 1246 cm^{-1} band and the disappearance of the 835 cm^{-1} band, after complexation (cf. Table 4). The C-2–H band at 1392 cm^{-1} is also absent in the complex. Another important change observed upon coordination is the absence of the δ C–OH band at 1297 cm^{-1}, due to the deprotonation of the OH group. Finally, the ν(V=O) band is found at 925 cm^{-1}.

VO^{2+}–maltose complex (**1**).—Table 4 shows the assignment of the maltose vibrations. The band at 846 cm^{-1} is indicative of the presence of the α-glycosidic linkage characteristic of maltose. The bands located at 870 and 897 cm^{-1} confirm the presence of the β anomer in C-1 of maltose (B-residue) [14,17–19]. As it can be seen from Table 4, the bands corresponding to the CH_2 vibrations located at 1458, 1321 and 1203 cm^{-1} remain intact upon coordination. The deformations of the COH groups at 1356, 1074 and 1025 cm^{-1} show modifications, but they do not disappear because they are coupled with other vibrational modes. The band at 906 cm^{-1} disappears or becomes very weak as a consequence of deprotonation. The H-2 stretching located at 1395 cm^{-1} in the free ligand is absent in the complex. The intensities and band positions related to ligand H-1 modes (1356, 1246, 1074, 1037, 906 and 846 cm^{-1}) are somewhat modified in the complex. The ν(V=O) stretching is located at 925 cm^{-1}. Due to the complexity of these spectra and the different coordination possibilities offered by this ligand, it is very difficult to propose an unique and definite interaction scheme.

VO^{2+}–arabinose complexes (**4** *and* **5**).—The IR spectra of D- and L-arabinose show identical features. The bands corresponding to δ CH_2 (1454 cm^{-1}) and to δ COH of 6-OH (1297 cm^{-1}) of galactose are absent in arabinose. The medium intensity band at 939 cm^{-1} shows that arabinose is present as the β anomer (cf. Table 5). Also the IR spectra of both oxovanadium(IV) complexes **4** and **5** are identical. The deformation vibrations δ H-2 and δ H-1 at 1400 and 1050 cm^{-1}, respectively, show no important modification after complexation, indicating that the 1- and 2-OH groups are not involved in coordination. On the other hand, the changes observed in the δ COH vibrations after coordination, indicate that metal-to-ligand interaction occurs through the OH groups of C-3 and C-4, which are in the *cis* position. The V=O stretching vibration appears at 929 cm^{-1} in these two complexes.

VO^{2+}–xylose complex (**6**).—As stated above, the IR spectrum of xylose differs from that of its homomorphic sugar (glucose) in the 1500–1200 cm^{-1} region due to the absence of the CH_2OH substituent at C-5 [14]. The δ CH_2 vibration at 1460 cm^{-1}, strong in the spectrum of glucose, appears with medium intensity at 1450 cm^{-1} in the spectrum of xylose. Another δ CH_2 vibration located at 1320 cm^{-1} in galactose, mannose and maltose is absent in the spectrum of xylose. On the other hand, the complex vibration at 1246 cm^{-1} in glucose, originated by a mixing of the (δ CH + δ COH + δ C-1–H) deformational modes, shifts to 1239 cm^{-1} and weakens its intensity in the xylose spectrum (cf. Tables 4 and 5). The medium intensity band at 756 cm^{-1} shows the presence of the α-D-xylose form [19]. In the complex the band at 1395 cm^{-1} and corresponding to δ C-2–H disappears, whereas that located at 1337 cm^{-1} (assigned to τ C-1–HOH + δ COH) shift to 1352 cm^{-1} after coordination (cf. Table 5). These results imply the involvement of 1- and 2-OH groups in coordination with the metal center. The weak 1258 and 1219 cm^{-1} bands of the complex originate in a splitting of the weak 1239 cm^{-1} band of the free sugar, corresponding to the mixed vibration δ CH_2 + δ COH + δ C-1–H. The strong ligand bands observed at 929 and 901 cm^{-1} changed into a broad band due to the presence of the ν(V=O)

stretching which appears in this same region. This broad band is centered at 929 cm^{-1} and shows two strong shoulders at 949 and 901 cm^{-1}.

VO^{2+}–lyxose complex (**7**).—The medium intensity 1370 cm^{-1} band of mannose corresponding to a CH_2 wagging is not observed in the homomorphic lyxose. Besides, the two δ CH_2 bands found at 1327 and 1203 cm^{-1} in mannose are absent in lyxose. Finally, the band at 1066 cm^{-1} can be related to the anomeric C–O stretching of the β form [20]. After coordination to VO^{2+} the shoulder at 1399 cm^{-1} corresponding to δ C-2–H of the sugar, disappears. Besides, the lyxose band of medium intensity at 1364 cm^{-1}, corresponding to δ COH + τ C-1–HOH, splits into two shoulders located at 1379 and 1355 cm^{-1} in the complex. The weak lyxose band at 1254 cm^{-1} (δ CH_2 + δ COH + δ C-1–H) is also absent in the complex. The V=O stretching vibration is observed at 921 cm^{-1}. On the basis of the commented results, it is possible to speculate that the metal-to-ligand interaction probably occurs through the deprotonated OH groups on the C-2 and C-3 atoms that constitute a *cis* pair of donors adequate for this interaction.

To conclude, the infrared spectroscopic data discussed in detail in this last section, allow a good insight into the bonding characteristics of the new complexes reported in this paper and generated by interaction of the VO^{2+} cation with different sugars, in a highly alkaline medium.

Acknowledgements

This work has been supported by CONICET, CIC-Provincia de Buenos Aires and the Agencia Nacional de Promoción Científica y Tecnológica (PICT 00119). S.B.E. and E.J.B. are members of the Research Career from CONICET. P.A.M.W. is a member of the Research Career from CIC-PBA.

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