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Synthesis and characterization of oxovanadium(IV) complexes with saccharides

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Abstract

Oxovanadium(IV) complexes of the monosaccharides D-glucose and D- fructose, and the disaccharides sucrose and turanose, were obtained in aqueous solution at pH 12. Their solid sodium salts were precipitated with absolute ethanol and characterized by UV–VIS, IR, and diffuse reflectance spectroscopies. Magnetic susceptibilities at room temperature were also determined. The L:M stoichiometry, as derived from spectrophotometric titrations, was 2:1 for all saccharides except for the D-fructose complex, which was 3:1. The analytical and magnetic data also show that in the solid state the complex of this ligand shows a different behavior, generating a dinuclear species bridged by a sugar molecule, whereas all the other complexes are mononuclear. © 1997 Elsevier Science Ltd.

Keywords: VO^{2+} complexes; Monosaccharide complexes; Disaccharide complexes; Electronic spectra; Vibrational spectra

1. Introduction

Vanadium is a micronutrient element which has been shown to produce several important biological effects in living organisms [1–5]. Its deficiency causes growth retardation and skeletal deformations in animals. It has also been suggested that vanadium may play a role in the regulation of (Na,K)-ATPases, phosphoryl transferases, adenylate cyclase, and protein kinases, and its possible participation in hormone, bone, glucose, and lipid metabolism has also been discussed [1,4–6]. A number of simple and complex vanadium(IV) and vanadium(V) compounds have shown insulin-mimetic actions in animals and in different types of cultured cells [3–8]. Despite the relevance of the bioactivity of vanadium derivatives, the involved mechanisms of action are poorly understood.

In past years we have reported a number of studies that have identified and characterized complexes formed by active vanadium species with different important biomolecules. Since carbohydrates are the most abundant compounds in nature and are directly involved in several important functions like the regulation of metal flow through cell walls [9], we have recently initiated studies to examine the interaction of biologically relevant vanadium species with simple carbohydrates [10–14].

Although there are many articles dealing with the interactions of saccharides with non-transition metals, information about the interaction of carbohydrates with transition metal ions is scarce [9]. This may be

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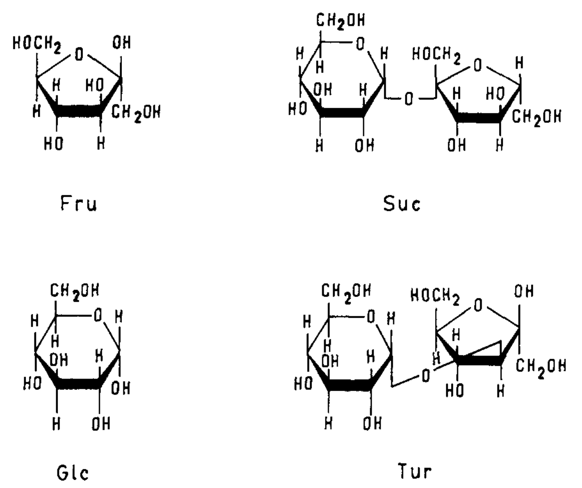

Fig. 1. Schematic structures of saccharides: Fru = β-D-fructofuranose; Glc = α-D-glucopyranose; Suc = sucrose; Tur = α-D-glucopyranosyl-(1 → 3)-β-D-fructofuranose.

explained by the low reactivity of the hydroxyl groups of sugars at acidic or neutral pH values. Complexation of the VO^{2+} cation with sugars is facilitated by the presence of carboxylate groups in addition to hydroxyl moieties, as found in acidic carbohydrates [11,13]. In the case of neutral sugars, complexation is favored by basic media and takes place only with molecules possessing adjacent *cis*-hydroxyl groups [15,16].

The aim of the present work was the synthesis and characterization of complexes of the oxovanadium(IV) cation with the neutral sugars D-fructose, D-glucose, sucrose, and turanose (Fig. 1), both in aqueous solution and in the solid state.

2. Materials and methods

D(+)-Glucose, D(−)-fructose, sucrose (β-D-fructofuranosyl α-D-glucopyranoside), and D(+)-turanose (α-D-glucopyranosyl-(1 → 3)-D-fructose) were purchased from Sigma 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. 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 analyses were done on a Carlo Erba 1108 elemental analyzer; vanadium was determined by the tungstophosphovanadic method and sodium by flame photometry.

3. Experimental

All the compounds were prepared by the following procedure: 2 mmol of the saccharide were dissolved in distilled water (10 mL). Small amounts of solid NaOH were added until a final pH of 12 was reached. One mmol of $VOCl_2$ was added to each alkaline sugar solution under constant stirring, maintaining the pH of the solution at 12 during the process.

Although the resulting solutions were green, the sucrose–vanadyl solution became brownish in a short time, suggesting rapid decomposition. Therefore, it is essential to measure the electronic spectra and to precipitate the solid complexes immediately.

The solid complexes were obtained from the green solutions by successive additions of absolute ethanol, discarding the supernatant until a microcrystalline solid was formed. The hygroscopic sodium salts were

Table 1
Elemental analysis (%) for VO^{2+}-saccharide complexes **1**–**4**

Complex	Formula		C	H	V	Na
1	$C_{30}H_{50}O_{32}V_2Na_6 \cdot 4H_2O$	Calcd	29.17	4.70	8.26	11.18
		Found	28.57	4.74	8.66	11.20
2	$C_{12}H_{21}O_{14}VNa_3 \cdot 5H_2O$		24.04	5.17	8.51	11.52
			24.84	4.79	8.34	11.88
3	$C_{24}H_{41}O_{24}VNa_3 \cdot H_2O$		33.82	5.05	5.99	8.10
			33.12	5.41	5.70	8.64
4	$C_{24}H_{41}O_{24}VNa_3 \cdot 3H_2O$		32.44	5.29	5.74	7.79
			32.95	5.47	5.45	7.33

kept in an oven at 60 °C. The results of elemental analyses are given in Table 1.

4. Results and discussion

The elemental analyses are consistent with the following formulations for the solid sodium salts: $Na_6[(VO)_2(Fru)_5] \cdot 4H_2O$ (**1**), $Na_3[VO(Glc)_2OH] \cdot 5H_2O$ (**2**), $Na_3[VO(Suc)_2OH] \cdot H_2O$ (**3**), and $Na_3[VO(Tur)_2OH] \cdot 3H_2O$ (**4**).

Electronic spectra.—Complexes **1** and **2** show the well-known three-band pattern (Table 2) characteristic of the coordination of the VO^{2+} cation through four deprotonated OH groups of two sugar ligands [10,13,15–17].

Complex **4** shows an electronic spectrum similar to those of **1** and **2**, but the UV absorption overlaps with the band centered at ~ 400 nm causing a small increase in its intensity (Table 2). On the other hand, complex **3**, with a non-reducing sugar acting as a ligand, shows a greater overlapping with the UV absorption than **4**, it being difficult to get the exact position of the band placed at ~ 420 nm.

It is interesting to point out that our results differ from those obtained by Sreedhara et al. [18] and Rao and Kaiwar [19] for the VO^{2+} complexes with glucose and fructose. The main difference is the lack of the $b_2 \rightarrow a_1$ transition in their electronic absorption spectra as well as in the diffuse reflectance spectra. They postulate a pentacoordinated vanadyl(IV) cation in the solid state. On the other hand, their aqueous solution spectra were obtained at a pH < 12. Nevertheless, the reported data for other related systems [9,10,13] show that the sugar coordination to the VO^{2+} cation is strongly pH dependent. All these reports agree with the fact that ,at pH > 11, the coordination sphere consists of two saccharides with two deprotonated OH groups per sugar. Under these conditions the spectra of solutions and solids (in cases where they were measured) exhibit the well-known three-band pattern.

Spectrophotometric titrations.—These titrations were carried out at pH 12 with 0.02 M solutions of the sugars and ligand to metal ratios varying from 10:1 to 1:1. The results show that the stoichiometry of the complexes is 2:1 (L:M) in all cases except for the fructose complex, which was 3:1. The different coordination behavior of fructose with VO^{2+} has also been observed in the solid state. In this case there is one fructose molecule bridging two metal centers, with each metal center also coordinated to two other fructose moieties.

Diffuse reflectance spectra.—It can be seen from Table 2 that the four solid complexes also exhibit the three-band pattern, as expected. The interaction between sucrose and the vanadyl(IV) cation in the solid complex also produces a displacement of the $b_2 \rightarrow e$ band to the red, as observed in solution.

Magnetic susceptibilities.—The magnetic behavior of complexes **2**, **3**, and **4** is simple and the μ_{eff} values are close to that expected for the 'free' VO^{2+} (d^1) cation (1.73 M.B.) (Table 2). On the other hand, the room temperature magnetic moment of complex **1** indicates extensive quenching of the VO^{2+} spin moment. Elemental analysis of this complex suggests that the coupling between the vanadyl cations occurs

Table 2
Electronic absorption spectra and effective magnetic moments (μ_{eff}) of the VO^{2+}-saccharide complexes in aqueous solution [a]

Complex	λ (nm) (ε, $M^{-1}cm^{-1}$)			μ_{eff} (M.B.)
	$b_2 \rightarrow a_1$	$b_2 \rightarrow b_1$	$b_2 \rightarrow e$	
1	424 (29.8) 420	518 (13) 520	686 (36.2) 672	1.26
2	418 (24.7) 420	508 (11) 518	700 (22.5) 687	1.75
3	420? (45) 420	520 (16) 525	748 (15.7) 785	1.70
4	424 (21) 420	510 (14) 515	698 (27.7) 678	1.73

[a] Underlined values are from diffuse reflectance spectra of the solids.

through a fructose ligand. According to the experimental μ_{eff} value (Table 2), the distance between the two metallic centers should be short, suggesting that the bridging ligand may use two adjacent deprotonated OH groups for coordination. However, in the case of the electronic solution spectra, the observed bands could be due to a monomeric (3:1) species resulting from the partial rupture of the bridged dimer in solution.

Infrared spectra.—The IR spectra of the obtained solids were recorded down to 200 cm^{-1} and compared with those of the free ligands. Tentative assignments for the sugar ligands according to the literature [20–27], and some characteristic changes in the complex bands, are shown in Tables 3 and 4 for the mono- and di-saccharides, respectively.

All of the free ligands exhibit intermolecular hydrogen bonds between 3400 and 3200 cm^{-1}. Upon complexation, there is a breakage of the H-bonds and the sharp and well-resolved bands of the free ligands are lost. Our spectra agree with those previously reported for saccharides coordinated to transition metals [19,28,29]. All of them show a broad band centered around 3400 cm^{-1} and a shoulder at ~ 2900 cm^{-1}. The other regions are discussed separately for each ligand and its vanadyl(IV) complex.

Fructose / VO^{2+} complex.—The IR bands of fructose (Fig. 2), located at 922, 870, and 783 cm^{-1},

Table 3
Band positions [a] and tentative assignment of the IR spectra of the monosaccharide ligands and monosaccharide/VO^{2+} complexes

Fructose	Fructose/VO^{2+}	Glucose	Glucose/VO^{2+}	Assignment
1469 sh, w		1460 s	1458 m	$\delta(\mathrm{CH_2})$
1449 sh, w	1453 m	1441 sh		
1429 m	1410 m	1423 sh		
		1408 sh	1415 m	$\delta[\mathrm{C(2)H}]$
1399 m				
1377 w	1377 m	1377 m	1376 m	$\omega(\mathrm{CH_2})$
1338 s	1338 sh	1341 m	1338 w	$\delta(\mathrm{COH}) + \tau[\mathrm{C(1)H_2OH}]$
1299 w		1293 w		
1267 m		1277 w	1273 w	$\tau(\mathrm{CH_2})$
1250 sh	1256 w		1258 vw	
1232 sh		1224 w		$\delta(\mathrm{CH_2} + \mathrm{COH})$
		1202 w	1203 w	
1176 m	1177 w			$\nu(\mathrm{CO})$, f
1150 s	1156 w	1149 m	1137 m	$\nu(\mathrm{CO})$, p
1130 sh				
1093 sh	1096 sh	1111 m	1113 m	$\nu(\mathrm{CO})$endo
1078 s		1078 m	1066 s	$\nu(\mathrm{CO})$exo
1054 s	1051 s	1050 s	1046 s	
1028 sh		1023 vs	1027 vs	
		995 vs	1003 vs	see text
976 s	970 w			$\delta(\mathrm{CCH})$, p
	925 s		925 vs	$\nu(\mathrm{V{=}O})$
922 m				$\delta(\mathrm{CCH})$, f
		913 m		$\delta[\mathrm{C(1)H}]$, p
870 m			858 w	
	844 w			
		836 m		$\delta[\mathrm{C(1)H}]$, α
818 m				$\nu(\mathrm{CC})$, p
783 s	786 vw	774 m	791 m	$\nu_s(\mathrm{COC})$
	741 w	729 w	737 sh	
685 m, b	709 sh		693 sh	
627 m	664 sh	646 m		
594 sh	613 sh	621 m	603 m	
570 m	561 m	579 w		
544 m		555 w	548 m	
523 sh	523 m	538 w		

[a] In cm^{-1}; vs, very strong; s, strong; m, medium; w, weak; vw, very weak; b, broad; sh, shoulder; p, pyranose; f, furanose.

support the β-configuration of the ligand [20,24,25]. Because of the presence of furanose and pyranose characteristic conformational bands, we can conclude that the solid ligand is a mixture of both conformers: bands at 1250, 1176, 922, 870, and 685 cm^{-1}, and bands at 1150, 976, 818, and 523 cm^{-1}, correspond to furanose and pyranose rings, respectively. Table 3 shows the band assignments for the free ligand and its vanadyl(IV) complex.

As previously reported [28], in the interaction of transition metals with saccharides, a broadening of the bands corresponding to the four complexes is observed. However, the following spectral modifications can be observed:

(i) The ligand band at 1338 cm^{-1}, corresponding to $\delta(COH) + \tau C(1)H_2OH$ [20,30], is sensitive to deuteration, which causes a decrease in its intensity [20]. It shows a similar behavior after complexation.

(ii) The furanose band at 1250 cm^{-1} appears at 1256 cm^{-1} in the complex. The pyranose bands (1150 [$\nu(CO)$], 1078 [$\nu(CO_{exo})$], and 818 [$\nu(CC)$] cm^{-1}) disappear after coordination.

Table 4
Band positions [a] and tentative assignment of the IR spectra of the disaccharide ligands and disaccharide/VO^{2+} complexes

Sucrose	Sucrose/VO^{2+}	Turanose	Turanose/VO^{2+}	Assignment
1465 m				F, $\delta(CH_2)$
1456 m	1454 m	1453 m	1452 sh	$\delta(CH_2)_{suc}$
1433 s	1433 sh	1433 m	1433 sh	F, G
		1409 m	1417 m	F, G
1374 w	1381 m	1385 m	1372 m	F, G, $\omega(CH_2)$
		1354 m		$\rho(CH_2)$
1346 m	1334 sh	1335 m	1333 sh	F, G $\rho(CH_2)_{suc}$
1322 w		1301 w		F
1279 w	1287 w	1288 w		
		1278 m	1262 w	
	1250 vw	1246 m	1247 w	F, f
1238 m	1240 vw	1234 sh		$\delta(CH_2 + COH)$
1208 w	1208 vw	1201 m	1201 w	
1165 sh	1158 sh			
	1139 m	1143 s	1146 m	$\nu(CO)$, p
1126 s	1120 sh	1127 sh		F, G, $\delta(COH)_{suc}$
1113 s		1107 s	1103 sh	G, $\nu(CO)$endo
1067 s		1082 sh	1079 sh	F, G, $\nu(CO)$exo
		1057 s	1051 s	F, G
1048 s	1049 s	1042 sh	1034 s	G
1007 sh		1018 w		F, G
994 s	991 m			G
		968 m	967 w	F, $\delta(CCH)$, p
942 sh	946 sh			
		932 w		$\delta(CCH)$, f
	931 s		924 s	$\nu(V{=}O)$
920 sh				β-F, f
912 s	880 w	914 sh		α-G, p
		896 m		
860 m	856 w	862 m		β-F, f
846 sh		838 m	840 w	α-G
		804 w	773 sh	see text
		746 m	750 sh	
728 w	702 sh	727 sh	735 sh	G
		710 m	704 sh	
685 m			698 sh	see text
	661 sh	650 m	663 sh	G
642 w	642 sh			
585 m	599 m	606 m	571 sh	
561 m	590 m	561 w		G
531 sh	526 m	533 m	528 m	G, $\delta(CCO)$, p

[a] In cm^{-1}; vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; F, fructose; G, glucose; p, pyranose; f, furanose.

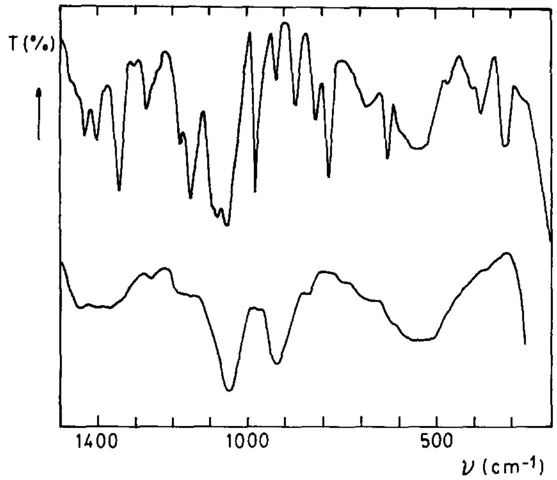

Fig. 2. IR spectra of fructose (above) and of $Na_6[(VO)_2(Fru)_5]\cdot 4H_2O$ (below) (1500–200 cm^{-1} region).

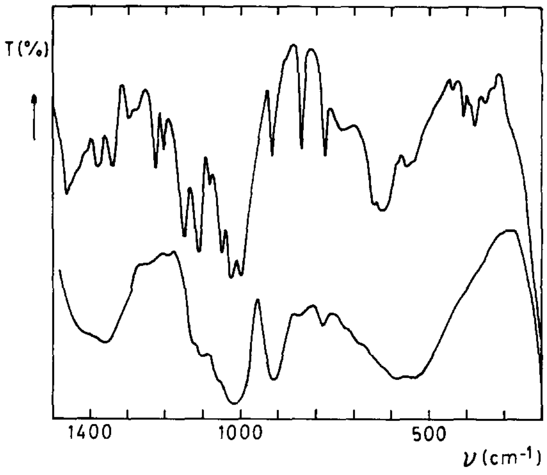

Fig. 3. IR spectra of glucose (above) and $Na_3[VO(Glc)_2OH]\cdot 5H_2O$ (below) (1500–200 cm^{-1} region).

(iii) Another characteristic feature of the spectrum of this complex is the strong band at 925 cm^{-1}, corresponding to the $\nu(V{=}O)$ stretching [11].

The fact that the primary OH is the most reactive hydroxyl sugar group [20] together with the above observations allow the conclusion that the coordination takes place through the deprotonated OH groups (pH 12) of $C(1)H_2OH$ and the anomeric C(2)OH. The spectrum also shows that the fructose moieties are present as β-anomers in furanose form.

Glucose / VO^{2+} complex.—According to the previously reported IR spectrum [24], we conclude that the free ligand (D-glucose) is the α-anomer (836 cm^{-1}) in the pyranose form (913 cm^{-1}) (Table 3). Its coordination to VO^{2+} at pH 12 produces the following changes (Fig. 3):

(i) The band at 1341 cm^{-1} decreases in intensity in a similar way to that observed for the fructose/VO^{2+} complex.

(ii) The weak band of the free ligand at 1078 cm^{-1}, assigned to $\delta[C(1)H]$ [21], shifts to 1066 cm^{-1} and increases in intensity.

(iii) A new band at 1003 cm^{-1} related, to deprotonated COH groups [13], is observed.

(iv) The $\nu(V{=}O)$ stretching appears at 925 cm^{-1} as a very strong band

These observations suggest that the cation is chelated by D-glucose through the anomeric O-1 and O-2 atoms, which are *cis* in the α-anomer.

Our IR, UV/VIS, and diffuse reflectance spectra indicate that the OH group at C-2 is deprotonated, in contrast to previous results [19]. As stated above, this difference may be due to the fact that our complexes were prepared at pH 12.

Sucrose / VO^{2+} complex.—Spectra of the free sugar and its vanadyl(IV) complex are shown in Fig. 4. Table 4 shows the assignment of the observed IR bands of sucrose. Typical bands of α-D-glucose (912, 846 cm^{-1}) in the pyranose form, and β-D-fructose (920, 860 cm^{-1}) in the furanose form, as well as some vibrations characteristic of sucrose, can be seen [26]. We conclude that the fructose residue is in the furanose form because of the presence of the 685 cm^{-1} band, which is characteristic of disaccharides with this kind of residue [24].

Upon formation of the complex, the following modifications are observed:

(i) The behavior of the band at 1346 cm^{-1} (assigned to $\rho(CH_2)$ in sucrose) is the same as that found for the constituent monosaccharides.

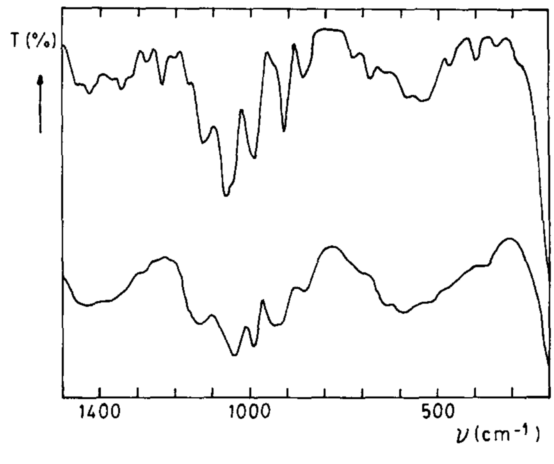

Fig. 4. IR spectra of sucrose (above) and $Na_3[VO(Suc)_2OH]\cdot H_2O$ (below) (1500–200 cm^{-1} region).

(ii) The medium intensity band at 1238 cm^{-1} [$\delta(CH_2) + \delta(COH)$], characteristic of sucrose, drastically decreases in intensity after coordination. The weak band of free sucrose located at 1208 cm^{-1} (corresponding to the 1202 cm^{-1} band of α-D-glucose) does not change upon coordination, in contrast that observed in the glucose/VO^{2+} complex.

(iii) The band at 1067 cm^{-1} [$\nu(CO_{exo})$] behaves in a similar manner as in the fructose complex, suggesting coordination of the cation through the fructose residue of the sugar.

(iv) The band at 931 cm^{-1} can be assigned to the $\nu(V{=}O)$ vibration, and probably overlaps with the anomeric bands at 920 (fructose) and 912 cm^{-1} (glucose).

From the above observations we conclude that in the complex $Na_3[VO(Suc)_2OH] \cdot H_2O$, the vanadyl(IV) cation coordinates with the fructose moiety of sucrose. Since sucrose is a non-reducing disaccharide, the anomeric carbons of the monosaccharides are involved in the glycosidic linkage. The high instability of the complex in aqueous solution, which requires its immediate precipitation after mixing the reagents in order to avoid vanadyl hydrolysis, suggests that, in this case, a seven-membered chelate ring is formed, involving either O-1 and O-4, or O-3 and O-6 of the fructose moiety. The coordination sphere is completed with an hydroxyl group.

Turanose / VO^{2+} complex.—Spectra of the free ligand and of its vanadyl(IV) complex are shown in Fig. 5. The IR spectrum of turanose has not been reported previously. The band assignments were made by comparison with the spectra of glucose, fructose, and sucrose (Table 4).

Turanose, like sucrose, shows bands which are characteristic of pyranose and furanose forms. The band at 698 cm^{-1} is typical of disaccharides with a fructose residue [24].

The anomeric region (900–750 cm^{-1}) shows the glucose residue in the α-form, while the fructose moiety is found in the β-anomeric form. As observed in the sucrose spectrum, the bands at 778 (α-glucose) and 784 cm^{-1} (β-fructose) are absent. Moreover, the band at 804 cm^{-1} is the only indication of the glycosidic 1 → 3 linkage present in turanose. This band is also observed in (1 → 3) α-dextran and it is not present in the spectrum of (1 → 4) α-dextran [24].

The major features of the IR spectrum of the turanose/VO^{2+} complex are:

(i) The band at 1354 cm^{-1} drastically decreases in intensity after complexation, as expected.

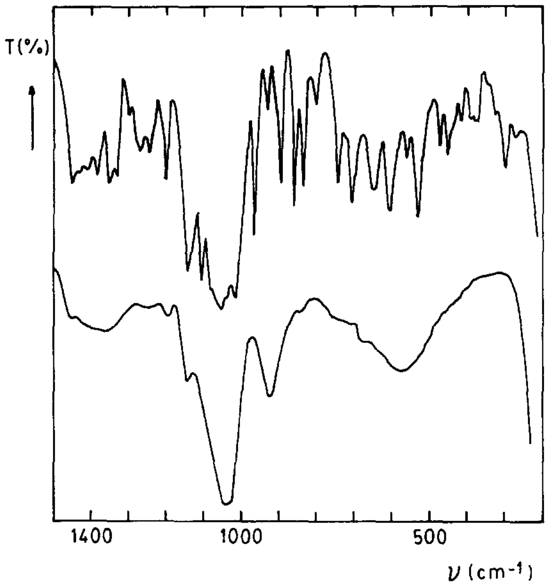

Fig. 5. IR spectra of turanose (above) and $Na_3[VO(Tur)_2OH] \cdot 3H_2O$ (below) (1500–200 cm^{-1} region).

(ii) The bands in the 1300–1200 cm^{-1} region [$\delta(CH_2) + \delta(COH)$], in particular those that indicate the furanose form, become weaker after complexation.

(iii) The band at 1201 cm^{-1}, present in the spectrum of free α-D-glucose, remains unchanged in the turanose complex (contrary to what is observed in the glucose/VO^{2+} complex).

(iv) The strong band at 924 cm^{-1}, assignable to the $\nu(V{=}O)$ mode, masks the ligand bands in this region.

All of these observations suggest that the VO^{2+} cation coordinates with turanose through the fructofuranose residue. The chelate formation probably occurs through the deprotonated OH groups at C-2 (anomeric) and C-1, which are the two most reactive groups.

5. Conclusions

As indicated by spectrophotometric titration, all of the investigated complexes, except that of fructose, respond to a 2:1 (L:M) stoichiometry in solution. The fructose complex appears as a 3:1 species. These differences remain also in the solid compounds because, whereas the fructose complex is a dimer formed by two $(Fru)_2VO$ moieties linked by a fructose bridge (stoichiometry 5:2), all of the other species are monomeric.

Previous structural studies on vanadate(V) complexes with ribose derivatives have established a distorted trigonal bipyramidal coordination sphere around the metal center, which is a typical geometry in the transition state in hydrolytic enzymatic reactions (see ref. [31] and references therein). On the other hand, oxovanadium(IV) complexes usually exhibit a square pyramidal coordination with the oxygen bonded to vanadium in the axial position, although, in aqueous solution, the coordination is normally a distorted octahedron because of the weak bonding of a water molecule in the sixth position.

All of the vanadium(IV)/sugar complexes characterized in the present study are hexacoordinated. This conclusion is not only supported by the established stoichiometries but also by the spectroscopic behavior of the complexes.

The values found for the characteristic ν(V=O) vibration are similar to those previously found in the vanadyl(IV) complexes of chondroitin sulfate A [11] and D-glucuronic acid [13], which also show the ν(V=O) stretching at ~ 930 cm^{-1} (both in aqueous solution and in the solid state). The agreement between the frequencies in the two states suggests, according to Micera et al. [15], that the coordination sphere of the VO^{2+} cation consists of four deprotonated sugar oxygen atoms with the possible presence of another OH group (complexes **2**, **3**, and **4**) or a ligand molecule (complex **1**) in the sixth coordination position.

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