Coordination study of D-xylo 5-hexulosonic acid with borate, molybdate and tungstate in aqueous solution by nuclear magnetic resonance spectroscopy

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Abstract

The interaction behaviour of borate, molybdate and tungstate ions with D-xylo 5-hexulosonic acid is compared using multinuclear NMR. Borate binds exclusively with the β-furanose form through the two *cis*-diol groups, even at low pH values where the keto isomer could be suitable for the formation of borate esters by carboxylic and α-hydroxyl groups. One 1:1 borate ester and two 1:2(borate:ligand) diastereoisomers are formed. Molybdate and tungstate bind with all three forms of the acid (the keto form and the α- and β-anomers). Depending on pH and relative concentration, a 1:1 complex and two diastereoisomeric 1:2 (metal:ligand) complexes are formed. In addition, for solutions of high metal content, evidence is found for the formation of polynuclear species, namely a 7:3 complex involving $Mo_7O_{24}^{6-}$. With W(VI), two further complexes form, involving the furanose forms.

Key words: NMR spectroscopy; Borate complexes; Molybdate complexes; Tungstate complexes; Carbohydrate complexes

Introduction

Borate and molybdate are inorganic anions that have been recognized as relevant in the carbohydrate field. For example, aldoses are converted to ketoses in aqueous alkaline borate solutions [1]; borate esters enhance the selectivity of the hydrogenation of fructose [2], and it has been suggested that borate ester formation may lead to an increase of the selectivity of the hydrogenation of D-xylo 5-hexulosonic acid [3–5]. The catalytic activity of molybdate in the epimerization of aldoses has been known for some time [6], and the presence of molybdate complexes in the catalytic step of the reaction has been described [7–10]. For a review of the coordination chemistry of sugars and their derivatives with various metals see ref. 11.

Coordination between the borate anion and polyols, polyhydroxycarboxylic acids and carbohydrates is quite well documented [12, 13]. Recently, a borate complexation study with potassium D-xylo 5-hexulosonate oxime (a derivative of D-xylo 5-hexulosonic acid) was published [14].

We have recently observed that, in contrast to previous suggestions in the literature, addition of Ca(II), La(II), borate, molybdate and tungstate has no influence on the selectivity of the hydrogenation of D-xylo 5-hexulosonic acid to D-gluconic acid and L-idonic acid [3].

In this paper we report a multinuclear magnetic resonance study of the interaction of the borate, molybdate and tungstate ions with D-xylo 5-hexulosonic acid, in aqueous solution. Due to relatively slow exchange phenomena in the NMR time scale, distinct spectra are obtained for the different species in solution.

Experimental

D-Xylo 5-hexulosonic acid was supplied as the calcium salt by AKZO Research B.V.(Arnhem, Netherlands). The acid was obtained by passing the calcium salt through a strongly acidic Dowex colum. Freeze-drying of the solution obtained afforded the acid. Analytical

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grade sodium salts of molybdate, tungstate and borate were used.

The acid was lyophilized from deuterium oxide solution and the molybdate and tungstate were dried at 120 °C in order to reduce the intensity of HDO NMR signal.

The pH was adjusted by addition of DCl and NaOD solutions. The pH values are the direct pH-meter readings, at room temperature, after standardization with aqueous buffers.

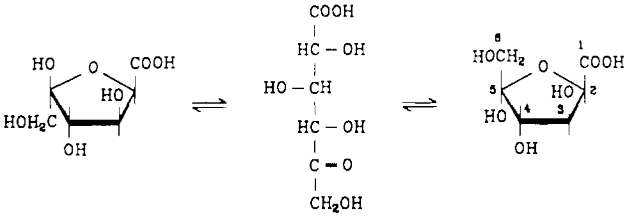
T_1 relaxation times (^{13}C) were measured on a D_2O solution (pH = 5) of sodium molybdate (1.5 M) and D-xylo 5-hexulosonic acid (0.5 M), using the 180°–τ–90° inversion recovery pulse sequence.

^{11}B NMR spectra were recorded on a Nicolet NT-200 WB spectrometer at 64.19 MHz. ^{95}Mo and ^{17}O spectra were obtained on a Varian VXR-400 S using D_2O solutions of Na_2MoO_4 at pH = 9 and pure H_2O as external references, respectively. The ^1H and ^{13}C spectra were measured on Varian XL-200 and Varian VXR-400 S spectrometers. The spectra were recorded at temperatures in the range 20–30 °C. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate ($\delta = 0$) and the methyl signal of t-butyl alcohol ($\delta = 31.2$) were used as internal reference for ^1H and ^{13}C chemical shifts, respectively. Boric acid 0.1 M in D_2O was used as external reference for ^{11}B NMR spectra.

Results and discussion

Borate esters analysed by ^1H, ^{11}B and ^{13}C NMR

The D-xylo 5-hexulosonic acid exists in aqueous solution as an equilibrium of three tautomers (Scheme 1), the β-furanose form being the major one. The corresponding ^{13}C and ^1H NMR data have been reported [15, 16].


1-α 1-keto 1-β

Scheme 1.

The formation of borate esters of the acid was followed along the pH by ^{11}B NMR. Besides a ^{11}B signal corresponding to the equilibrium between boric acid and borate (fast exchange on the ^{11}B NMR time scale), two other peaks are present. The complexation begins at pH = 1. Only one borate ester signal is visible till pH = 5. For higher pH values a second one emerges, its relative intensity increasing till pH = 8. The extent of complexation decreases beyond this value. Above pH = 13 no complexes are present. The relative concentration of the two species depends also on the borate:ligand molar ratio. ^{13}C and ^1H NMR spectra confirmed the presence of two borate ester species.

Usually, for polyhydroxycarboxylic systems, bidentate mono- and diesters are formed with borate involving, 1,2-diol or 1,3-diol hydroxyl functions at pH greater than 9, and involving the carboxylic and the neighbouring hydroxyl group at low pH values. In our system, ^{13}C data show that the carboxylic group is never involved in complexation.

The ^{11}B chemical shifts (δ) of 1:1 borate esters (BL) of the 1,2-diol type usually lie between −7.7 and −11.9 ppm relative to an external boric acid reference [17–20]

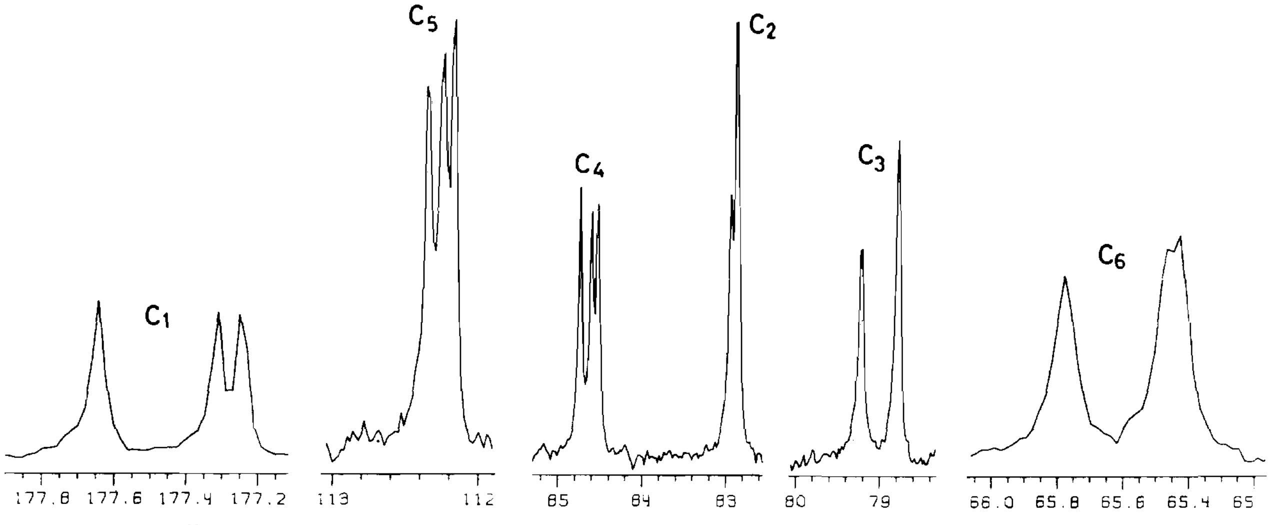


Fig. 1. 50.3 MHz ^{13}C spectrum of a solution of borate(0.4 M) and D-xylo 5-hexulosonic acid (0.4 M) in D_2O, pH = 7.8, temperature 30 °C (see also 'Experimental'). For the numbering of carbon atoms see Scheme 1.

whereas for the 1:2 esters (BL_2) they lie between -12.6 and -14.9 ppm. We found that the δ (^{11}B) values for the two borate species are -8.80 and -13.10 ppm whatever the pH. Therefore, it can be concluded that those species are the BL and BL_2 esters of the 1,2-diol type. This is confirmed by the line widths which are 66.6 and 34.5 Hz, respectively (at 30 °C). Since ^{11}B linewidths are dominated by quadrupolar relaxation [21] a BL_2 borate species is expected to give a broader ^{11}B signal than a BL one. This is because the boron atom in the former species can be more distorted from tetrahedral symmetry [12, 17] which gives rise to an increase of the quadrupolar relaxation. In addition, its correlation time will be longer, which also contributes to larger linewidths.

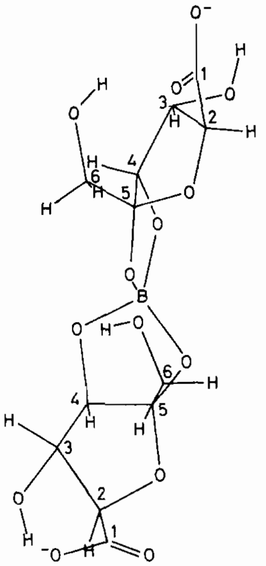
The difference in δ (^{11}B) for a threo and an erythro diol configuration is usually small. The smallest difference is found to be 0.2 ppm [12]. As the exact values are specific for each system, it is impossible to distinguish between a threo and an erythro diol configuration in this system by the ^{11}B chemical shifts.

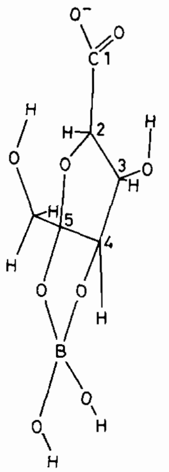
Due to the presence of a chiral boron centre in borate diesters, two diastereoisomeric BL_2 species are possible. However, ^{11}B NMR does not usually allow the distinction between different diastereoisomeric borate diesters, probably because their ^{11}B chemical shift difference is smaller than the linewidths [12]. However, at pH greater than 5, ^{13}C and ^{1}H NMR spectra show three sets of signals besides the free ligand (when in excess) (Fig. 1), which can be assigned to BL species and to the two diastereoisomer forms of the BL_2 species.

Comparison of the ^{11}B with the ^{13}C and ^{1}H spectra as well as consideration of the relative intensities as a function of the B:L ratio, for difference pH values, allowed the assignment of the spectra of the two esters. The carbon signals C(2), C(3) C(4) and C(6) of the esters were assigned by CH correlation experiments (HETCOR). Table 1 summarizes the results.

In principle, the three forms of D-xylo 5-hexulosonic acid (α, keto and β) could interact with borate. But the ^{13}C data on C(5) show that the keto form is not involved whatever the pH. It has been suggested [22] that the stability of the borate esters of closed forms as compared with open chains in carbohydrate systems is entropically favoured.

From previous studies with *cis*-1,2,cyclopentanediol and D-fructose [23] it has been concluded that two vicinal *cis*-hydroxyl groups in a furanose ring have a favourable geometry for borate ester formation. In the present case, the β-furanose form has OH(4) and OH(5) in such a configuration. The large high frequency shifts on C(4) and C(5) (7–8 ppm) upon borate ester formation clearly show that those sites are involved in the five-membered borate ester ring. Those values are in agreement with those reported for D-fructose esters [23]. It can thus be concluded that BL_2 and BL have structures I and II, respectively.





The ^{1}H chemical shifts hardly change upon borate ester formation. However, the coupling constant $^{3}J_{H(3)H(4)}$ changes from 4.2 to 0 Hz. Some contribution for this decrease might come from the substituent effect on the gauche $^{3}J_{HH}$ [24]. Upon esterification, the electronegativity of O(4) (in a gauche position in relation to H(3)) becomes smaller and this causes a decrease on the gauche $^{3}J_{H(3)H(4)}$ value, but it cannot alone be responsible for the 4.2 Hz difference. There must be a significant conformational change of the ligand, in both esters, near the coordination sites. From the coupling constant it can be estimated that the dihedral angle H(4) C(4) C(3) H(3) is about 90° in the bound β-anomer.

Figure 2 shows the distribution of the borate species as a function of pH in a solution of 1:1 borate:ligand molar ratio. It is quite remarkable that the BL_2 species already occurs at pH 1. Usually these species are only observed at pH greater than 5. Curves of the ^{13}C chemical shifts of BL_2 as a function of pH show a jump between pH 2 and 4. From the shape of these curves the pK_a values of the carboxylic acid groups in the borate diester are estimated to be about 3.8, which is about the same as in the free ligand. Figure 2 shows that for higher pH the concentration of BL_2 decreases, while BL is being formed. Apparently, the negative charge of the carboxylate groups destabilises the BL_2 ester. The maximum of the BL_2 concentration at pH 10 (see Fig. 2) can be attributed to a steep increase of the $B(OH)_4^-$ concentration above the pK_a of boric acid (9.1), which causes a shift of the concerning equilibria to the side of the borate diester.

If the overall stability constant β is defined by

$$\beta = [BL_2]/[B][L]^2 \qquad (1)$$

TABLE 1. Chemical shifts (ppm) of ^1H and ^{13}C and proton–proton coupling constants (Hz) of free ligand and its borate esters at pH = 8, temperature = 25 °C

		Free Ligand			BL[a]	BL$_2$[b]	
		α	keto	β			
$\delta(^{13}C)$	C(1)	177.77	179.76	177.34	177.64	177.24	177.30
	C(2)	84.57	73.74	80.72	82.84	82.91	82.84
	C(3)	78.26	74.54	77.82	79.20	78.77	
	C(4)	81.05	77.58	77.65	84.50	84.58	84.71
	C(5)	108.29	214.12	104.53	112.23	112.15	112.33
	C(6)	63.91	67.62	65.15	65.77	65.42	65.45
$\delta(^1H)$	H(2)	4.68		4.62	4.71	4.63	4.65
	H(3)	4.38		4.43	4.20	4.21	4.25
	H(4)	4.17		4.11	4.16	4.16	4.17
	H(6)	3.67		3.66	3.67	3.67	3.66
	H(6′)	3.76		3.66	3.72	3.73	3.68
^3J	H(2),H(3)	4.9		5.8	2.8	3.2	2.8
	H(3),H(4)	1.6		4.2	0	0	0
$\lvert ^2J \rvert$	H(6),H(6′)	11.8		12.1	12.0	12.0	12.0

[a] 0.4 M:0.4 M borate: D-xylo 5-hexulosonic acid solution. [b] 0.1 M:0.4 M borate: D-xylo 5-hexulosonic acid solution.

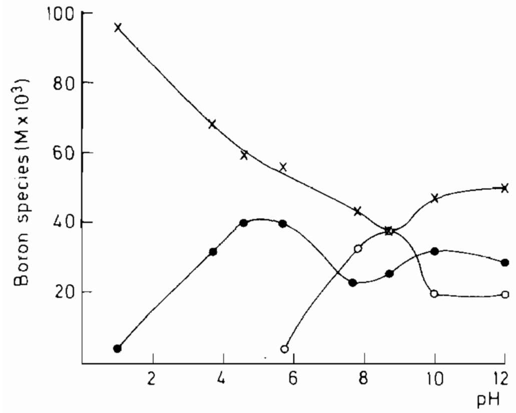


Fig. 2. Concentration (M) of boron species as a function of pH for a 0.1 M:01 M borate:ligand solution, obtained by ^{11}B NMR at 30 °C: x, free boric/borate; ●, 1:2 esters; ○, 1:1 ester.

then β values at low and high pH can be estimated from the pK_a values of boric acid, [L] and [BL$_2$], the ratio of the various anomers of L and mass balances. For pH well below the pK_a value of BL$_2$ the value of β is about 10^9, whereas above it is about 2×10^4.

The high stability of BL$_2$ at low pH, as compared to the corresponding species of fructose ($\beta\sim10^5$), for example, can be ascribed to the high degree of preorganisation in the free ligand and to the sterically favourable geometry of the BL$_2$ ester in the present case.

Molybdate and tungstate complexes analysed by ^1H, ^{13}C, ^{17}O and ^{95}Mo NMR

^{13}C NMR spectra of aqueous solutions of variable metal:D-xylo 5-hexulosonic acid ratios (3:1 to 1:3) and pH values (3.5–9 for Mo(VI), 2–9 for W(VI)) show various complexes and free ligand whenever in excess (Fig. 3). Due to the higher Mo(VI) reduction potential, pH values smaller than 3.5 make the solution unsuitable for NMR studies.

Four main species were observed with Mo(VI) (**a**, **b**, **c**, **d**) in the following conditions:

Mo(VI)/ligand ratio	pH	
	3.5–7	7–8.5
>1	**a**	
<1	**b**, **c**	**d**

Table 2 shows the ^{13}C data. The presence of minor species is also revealed but no further analysis was possible.

With W(VI) six main species were found (**b′**, **c′**, **d′**, **e**, **f**, **g**) as follows:

W(VI)/ligand ratio	pH	
	2–4	4–9
>1	**b′**, **c′**	**g**
=1	**b′**, **c′**	**e**, **f**, **g**
<1	**b′**, **c′**	**d′**

Table 3 shows the corresponding ^{13}C chemical shifts.

According to the literature for similar compounds, all the three forms of the acid can coordinate to Mo(VI) or W(VI). The open form is a derivative of a poly-

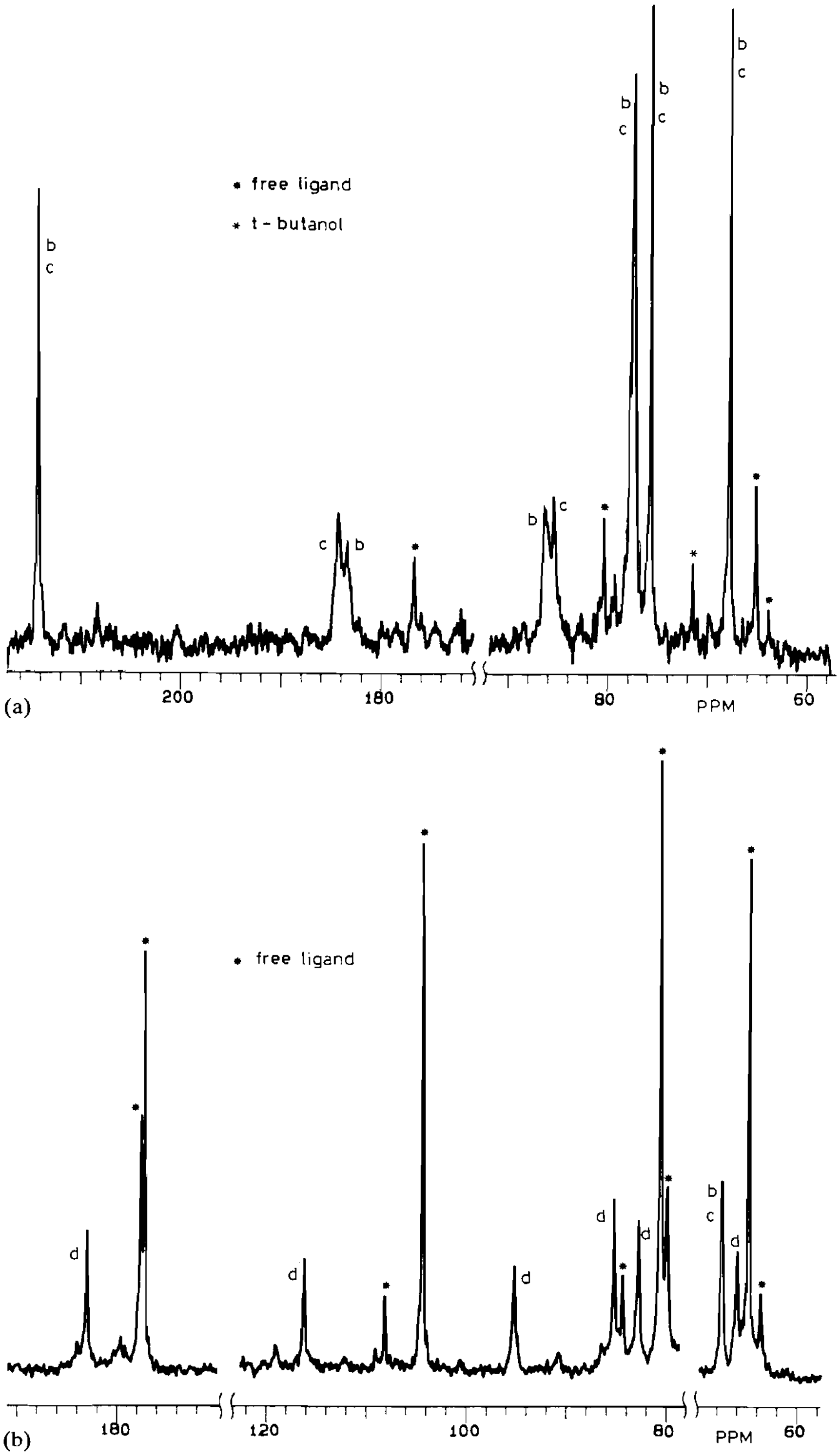


Fig. 3. (a) 50.3 MHz ^{13}C spectrum of a solution of molybdate (0.17 M) and D-xylo 5-hexulosonic acid (0.5 M) in D_2O, pH = 3.5, temperature = 20 °C (see 'Experimental'). The signals b and c refer to two 1:2 complexes of basic structure III. (b) 50.3 MHz ^{13}C spectrum of a solution of molybdate (0.17 M) and D-xylo 5-hexulosonic acid (0.5 M) in D_2O, pH = 7.0, temperature = 20 °C (see 'Experimental'). The signals d are assigned to a 1:1 complex involving the α-anomer.

hydroxycarboxylic acid and Mo(VI) and W(VI) coordination with polyhydroxycarboxylic acids has been extensively studied [25, 26]. Also open aldoses have been proposed to complex with Mo(VI) [27–29]. The furanose form of the monosaccharide D-lyxose is the one found in the crystal structure of a 2:1 Mo(VI):ligand compound

TABLE 2. ^{13}C NMR chemical shifts (ppm) of Mo(VI)/D-xylo 5-hexulosonic acid, temperature = 25 °C

pH	Species	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
5	1-Keto	179.72	73.72	74.54	77.58	214.11	67.62
	1-α	177.73	84.54	81.05	78.26	108.30	63.91
	1-β	177.32	80.71	77.82	77.64	104.53	65.15
	Complex **a**^{a}	183.62	83.34	86.32	87.58	109.31	71.74
3.5	1-Keto	178.90	73.20	74.50	77.30	213.40	67.62
	1-α	177.00	84.30	80.95	78.20	108.30	63.90
	1-β	176.70	80.29	77.80	77.60	104.53	65.10
	Complex **b**^{b}	183.35	86.20^{d}	75.34	77.10	214.12	67.48
	Complex **c**^{b}	184.20	85.35^{d}	75.34	77.10	214.12	67.48
7	1-Keto	179.76	73.74	74.54	77.58	214.11	67.62
	1-α	177.77	84.57	81.05	78.26	108.29	63.91
	1-β	177.34	80.72	77.82	77.65	104.53	65.15
	Complex **d**^{c}	182.98	85.16	95.20	82.74	116.15	65.96

[a] 1.50 M:0.50 M metal:ligand solution. [b] 0.17 M:0.50 M metal:ligand solution. [c] 0.17 M:0.50 M metal:ligand solution. [d] Could be interchanged.

TABLE 3. ^{13}C NMR chemical shifts (ppm) for W(VI)/D-xylo 5-hexulosonic acid, temperature = 25 °C

pH	Species	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
3	1-Keto	178.53	73.01	74.36	77.24	213.89	67.65
	1-α	176.58	83.69	80.84	78.20	108.52	63.87
	1-β	176.33	80.12	77.73	77.52	104.75	65.12
	Complex **b**′^{a}	185.12	84.70	75.92	77.07	214.46	67.94
	Complex **c**′^{a}	183.96	85.76	75.92	77.36	214.46	67.94
5	1-Keto	179.72	73.72	74.54	77.58	214.11	67.62
	1-α	177.73	84.54	81.05	78.26	108.30	63.91
	1-β	177.32	80.71	77.82	77.64	104.53	65.15
	Complex **d**′^{b}	184.34	85.04	95.15	83.14	116.58	66.56
	Complex **e**^{c}	177.48				111.41	
7	1-Keto	179.76	73.74	74.54	77.58	214.11	67.62
	1-α	177.77	84.57	81.05	78.26	108.29	63.91
	1-β	177.34	80.72	77.82	77.65	104.53	65.15
	Complex **f**^{d}	177.92				120.09	
	Complex **g**^{e}	186.82	84.86	85.84	88.25	219.04	68.37

[a] 0.17 M:0.50 M metal:ligand solution. [b] 0.17 M:0.50 M metal:ligand solution. [c] 0.50 M:0.50 M metal:ligand solution. [d] 0.50 M:0.50 M metal:ligand solution. [e] 1.50 M:0.50 M metal:ligand solution.

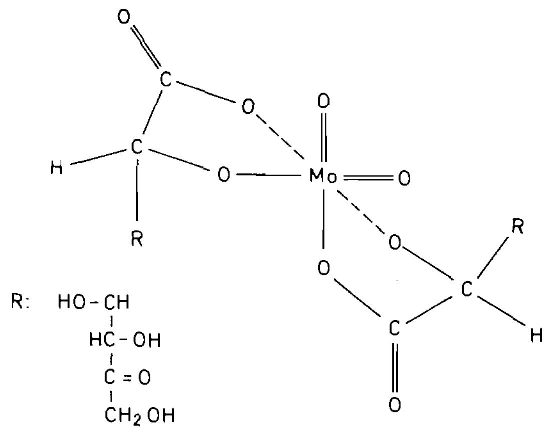
[30]. A furanose ring is also involved in the crystal structure of other 2:1 Mo(VI) compounds [31]. The α- and β-furanose forms of D-xylo 5-hexulosonic acid, having a carboxylic group, show a better capability to form stable coordination compounds with Mo(VI) or W(VI).

The ^{13}C spectrum, particularly the C(5) chemical shift which is very different for the open and the closed forms, is a direct means to infer if the metal ion binds the keto or the furanose forms.

Complexes with the keto form

From the C(5) shifts (Tables 2 and 3) for the Mo(VI) **b**, **c** complexes, and for the W(VI) **b**′, **c**′, **g** complexes, it can be concluded that they all involve the keto tautomer.

For the **b**, **c** and **b**′, **c**′ species, the signal of the ligand carboxylic group (C1) is shifted by 4–5 ppm to high frequency upon complexation and the C(2) signals show a 10–12 ppm high frequency shift. These values are typical of the involvement of the carboxylic group and of the adjacent OH group in binding to the metal ion [25, 26]. By analogy with the complexes formed with hydroxycarboxylic acids, those four compounds could have a 1:2 stoichiometry [25, 26]. In accordance, their relative abundance is constant for different metal:ligand ratios. A^{95}Mo signal at 96 ppm is consistent with this proposal [26]. One of the possible isomers is III.



The proton–proton vicinal coupling constants (Table 4) are characteristic of an essentially gauche arrangement of the H(2)/H(3) and H(3)/H(4) nuclei.

In complex **g**, the keto form binds by the carboxylic group and the hydroxyl groups at C(2), C(3) and C(4) according to the shifts showed upon complexation: 7 ppm for COOH and 8–14 ppm for the CHOH groups (Table 3). The carbon signal of the CO group is shifted by 5 ppm to high frequency which seems to indicate, in addition, the involvement of the keto group in complexation. All the data point to a polynuclear compound, probably a 2:1 complex. This complex has no equivalent in the molybdate system. However, with glucaric acid, the formation of a complex, at high pH, with the four central OH groups bound to Mo(VI) was reported [26]. Also, compounds of this kind are referred for Mo(VI) with alditols and aldoses of the xylose homomorphous series [27, 28, 32].

Complexes with the furanose forms

The other species **d**′, **e**, **f** for W(VI) and **a**, **d** for Mo(VI) are formed with the furanose forms as shown by the C(5) chemical shifts values.

Complex **a** is well characterised and no similar species for tungstate was detected. The C(1), C(3), C(4), C(6) signals have a considerable high frequency shift with respect to the free ligand and this is true irrespective of the furanose form assumed to be involved (Table 2). Between the two hypothesis, we choose the β form as involved in this complex, on the following grounds. A negative shift (-1.2 ppm) of the C(2) signal for the α form would be difficult to explain; also, the non-involvement of the OH group in position 5 as shown by a small carbon shift (1.0 ppm) would be difficult to accept in view of its orientation relative to COOH and to COH(3) which are definitely bound to the metal. In addition, we have determined the C(5) longitudinal relaxation time in the free ligand and in complex **a**; the observed decrease from 8 to 2 s upon complexation supports the view that COH (5) is bound to the metal. Complex **a**, being the dominant species in solutions having a high metal:ligand ratio, is, thus, probably a *n*:1(*n* greater than 1) species involving the carboxylic and all the OH groups of the β-furanose form. Species with metal:ligand ratio greater than 1 are known for systems of Mo(VI) + sugars. In particular, a 2:1 Mo(VI) complex formed with the furanose form of xylose, via the hydroxyl groups at C(1), C(2), C(3) and C(5), is known from an X-ray study of the crystal [30].

A conformational change must occur on complexation as is shown by the decrease of $^{3}J_{H(3)H(4)}$ (Table 5) from 4.2 to 0 Hz: the H(3)CCH(4) dihedral angle becomes close to 90°.

The ^{17}O NMR spectrum of a solution where complex **a** is dominant, as shown by ^{13}C NMR (1.5 M:0.5 M solution, pH = 5) is almost identical to the ^{17}O NMR spectrum of $Mo_7O_{24}{}^{6-}$ except that the signal at $\delta = 820$ ppm, assigned to the peripheric oxygen atoms [33], becomes broader. It can be suggested that in complex **a** it is the oxyanion $Mo_7O_{24}{}^{6-}$ that binds to the ligand by its terminal oxygens, probably in a 7:3 metal:ligand ratio. The ^{95}Mo spectrum of complex **a** supports this hypothesis as the major ^{95}Mo signals are in the same region as for the heptamolybdate ion.

In spite of the limited data obtained for species **e** and **f** for the tungstate system (only C(1) and C(5) signals are unambiguously assigned), it is clear that they involve furanose forms as ligands, presumably the β form ($\Delta\delta(C(5)) = 12$ ppm) for **e** and the α form ($\Delta\delta(C(5)) = 7$ ppm) for **f**. It is found that the carboxylic group is not bound to the metal in these complexes. We note that stable compounds are known to exist between W(VI) and Mo(VI) with monosaccharides like D-lyxose, D-mannose and D-ribose coordinated through three consecutive *cis*-hydroxyl groups of the pyranose form [34].

Similarities between the two systems are shown by complexes **d**′ of W(VI) and **d** of Mo(VI). Tables 2 and 3 show very close ^{13}C chemical shifts for these two species. The furanose form involved will be the same

TABLE 4. ^{1}H chemical shifts (ppm) and coupling constants (Hz) for **b**′, **c**′ complexes in a solution of tungstate (0.2 M) and D-xylo 5-hexulosonic acid (0.2 M) at pH 3, temperature = 20 °C

Species	H_2	H_3	H_4	H_6 $H_{6'}$	$^{3}J_{H(2)H(3)}$	$^{3}J_{H(3)H(4)}$	$\lvert ^{2}J_{H(6)H(6')} \rvert$
Complex **b**′	4.99	4.30	4.59	4.75	4.0	3.8	19.0
Complex **c**′	5.28	4.27	4.64	4.71	3.5	4.0	19.0

TABLE 5. ^1H chemical shifts (ppm) and coupling constants (Hz) for complex **a** in a solution of Mo(VI) (0.3 M) and D-xylo 5-hexulosonic acid (0.1 M), pH = 5.0, temperature = 14 °C

Species	H_2	H_3	H_4	H_6	$H_{6'}$	$^3J_{H(2)H(3)}$	$^3J_{H(3)H(4)}$	$^3J_{H(4)H(6)}$	$\|^2J_{H(6)H(6')}\|$
1-β	4.62	4.43	4.11	3.66		5.8	4.2	0	12.0
Complex **a**	4.74	4.94	4.64	3.73	4.12	6.6	0	2.3	9.2

in both. If it is the β-anomer, the carbon shifts would point to involvement of COOH, and COH(3), COH(4) and COH(5), but not of COH(6). This, in turn, would mean a weak 2:1 complex. On the other hand, if the α-anomer is preferred, then the carbon shifts suggest the involvement of COOH, COH(3) and COH(5) but not of COH(4) and COH(6). This would be consistent with stronger 1:1 complexes. The fact that **d** and **d'** occur predominantly for metal:ligand ratios equal or smaller than 1 favours the latter hypothesis. The **d** complex gives a ^{95}Mo signal at 145 ppm.

Regarding the stability of the complexes with Mo(VI) or W(VI), contrary to what was possible for the borate esters of D-xylo 5-hexulosonic acid, no estimation of the formation constants was possible. This is due to large uncertainties in the intensities of the observed broad signals. There is, however, evidence that the borate esters are more stable than Mo(VI) or W(VI) complexes. For example, when borate and molybdate or tungstate are both mixed with D-xylo 5-hexulosonic acid, the dominant species are the borate esters. The fact that no mixed boron–metal species are detected does not come as a surprise as the binding possibilities left available in a borate moiety(involving the β-anomer, see II) are not appropriate to a stable metal complex.

Conclusions

The multinuclear NMR data obtained for solutions of borate, molybdate and tungstate with D-xylo 5-hexulosonic acid can be interpreted in terms of the formation of the following species.

1. Three borate species, namely a BL ester (II) and two diastereoisomeric BL_2 diesters (I). The BL_2 species occurs in the whole pH range studied (1–12) and the BL one emerges at pH 6. The former have their highest concentration at pH 5 and the latter at pH 9. In all the species borate binds the two *cis*-diol groups of the β-anomer of the D-xylo 5-hexulusonic acid.

2. Four molybdate species, namely two diastereoisomeric 1:2 metal to ligand complexes (III) at pH smaller than 7, one 1:1 complex at pH greater than 7 and a polymeric complex for metal to ligand ratios larger than 1. The 1:2 species are formed with the open anomer bound by the carboxylic group and the adjacent hydroxyl group. The 1:1 species is formed with the α-anomer bound by COOH, COH(3) and COH(5). The polynuclear complex involves $Mo_7O_{24}^{6-}$ and the β-anomer with a 7:3 metal to ligand composition, the ligand being coordinated by the hydroxyl groups at C(1), C(3), C(4), C(5) and C(6).

3. Six tungstate complexes, three being similar to the molybdate system, namely, two 1:2 diastereoisomeric complexes and a 1:1 species which are dominant at pH smaller than 4 and pH greater than 4, respectively. For metal to ligand ratios larger than 1 a polynuclear 2:1 complex is formed, involving the keto form of the ligand bound by the carboxylic, the hydroxyl groups at C(2), C(3), C(4) and the carbonyl group at C(5) position. Two further complexes are detected with the furanose forms of the ligand.

The structures proposed for the boron and for the metal complexes are such that it is not surprising that no stable mixed complexes are formed.

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References

1 J.F. Mendicino, *J. Am. Chem. Soc.*, *82* (1960) 4975.
2 M. Makkee, A.P.G. Kieboom and H. van Bekkum, *Carbohydr. Res.*, *138* (1985) 237.
3 M.M. Caldeira, E. Wurtz, J.A. Peters and H. van Bekkum, *Recl. Trav. Chim. Pays-Bas*, *110* (1991) 111.
4 C.Y. Chen, H. Yamamoto and T. Kwan, *Chem. Pharm. Bull.*, *17* (1969) 2349.
5 C.Y. Chen, H. Yamamoto and T. Kwan, *Chem. Pharm. Bull.*, *18* (1970) 1305.
6 V. Bílik, *Chem. Zvesti*, *26* (1972) 183.
7 V. Bílik, L. Petrus and J. Zemek, *Chem. Zvesti*, *32* (1987) 242.
8 M.L. Hayes, N.J. Pennings, A.S. Serianni and R. Barker, *J. Am. Chem. Soc.*, *104* (1982) 6764.
9 B. Klaic, Z. Raza, M. Sankovic and V. Sunjic, *Helv. Chim. Acta*, *70* (1987) 59.
10 E.L. Clark Jr., M.L. Hayes and R. Barker, *Carbohydr. Res.*, *153* (1986) 263.
11 S. Yano, *Coord. Chem. Rev.*, *92* (1988) 113.
12 M. van Duin, J.A. Peters, A.P.G. Kiboom and H. van Bekkum, *Tetrahedron*, *41* (1985) 4311.

13 J.F. Verchere and J.P. Sauvage, *Bull. Soc. Chim. Fr., 2* (1988) 263.

14 J. van Haveren, M.H.B. van den Burg, J.A. Peters, J.G. Batelaan, A.P.G. Kibooom, and H. van Bekkum, *J. Chem. Soc., Perkin Trans. 2* (1991) 321.

15 M.M. Caldeira, H. van Bekkum and J.A. Peters, *J. Chem. Soc., Dalton Trans.,* (1990) 2707.

16 T.C. Crawford, G.C. Andrews, H. Faubl and G.N. Chmurny, *J. Am. Chem. Soc., 102* (1980) 2220.

17 W.G. Henderson, M.J. How, G.R. Kennedy and E.F. Mooney, *Carbohydr. Res., 28* (1973) 1.

18 M. van Duin, J.A. Peters, A.P.G. Kieboom and H. van Bekkum, *Tetrahedron, 40* (1984) 2901.

19 J.G. Dawber and S.I.E. Green, *J. Chem. Soc., Farady Trans. I, 82* (1986) 3407.

20 J.G. Dawber, *J. Chem. Soc., Farady Trans. I, 83* (1987) 771.

21 H. Noth and B. Wrackmeyer, *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*, Springer, Berlin, 1978.

22 R. Aruga, *J. Chem. Soc., Dalton Trans.*, (1987) 2791.

23 M. Makkee, A.P.G. Kieboom and H. van Bekkum, *Recl. Trav. Chim. Pays-Bas, 104* (1985) 230.

24 K.G.R. Pachler, *Tetrahedron, 27* (1971) 187.

25 V.M.S. Gil, *Appl. Chem., 61* (1989) 841.

26 M.L. Ramos, M.M. Caldeira and V.M.S. Gil, *Inorg. Chim. Acta, 180* (1991) 219.

27 V. Bílik and M. Matulová, *Chem. Pap., 44* (1990) 257.

28 M. Matulová and V. Bílik, *Chem. Pap., 44* (1990) 703.

29 M. Matulová and V. Bílik, *Chem. Pap., 44* (1990) 77.

30 G.E. Taylor and J.M. Waters, *Tetrahedron Lett., 22* (1981) 1277.

31 S. Liu and J. Zubieta, *Polyhedron, 8* (1989) 1213.

32 S. Chapelle, J.F. Verchere and J.P. Sauvage, *Polyhedron, 9* (1990) 1225.

33 M. Filowitz, R.K.C. HO, W.G. Klemperer and W. Shum, *Inorg. Chem., 18* (1979) 93.

34 C.F.G.C. Geraldes, M.M.C.A. Castro, M.E. Saraiva, M. Aureliano and B.A. Dias, *J. Coord. Chem., 1* (1988) 205, and refs. therein.