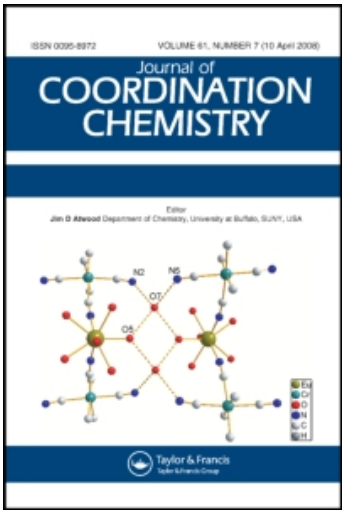

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INTERACTION OF MONOSACCHARIDES AND RELATED COMPOUNDS WIT OXOCATIONS OF MO(VI), W(VI) AND U(VI)STUDIED BY NMR SPECTROSCOPY

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INTERACTION OF MONOSACCHARIDES AND RELATED COMPOUNDS WITH OXOCATIONS OF Mo(VI), W(VI) AND U(VI) STUDIED BY NMR SPECTROSCOPY

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Proton, ^{13}C and ^{31}P nuclear magnetic resonance spectroscopy has been used to study the complexation of Mo(VI), W(VI) and U(VI) oxocations with various aldoses, cyclic polyols and ribose-5-phosphate in aqueous solution. The aldoses *D*-mannose, *D*-lyxose and *D*-ribose form tridentate complexes with Mo(VI) and W(VI) at pH $\simeq$ 5, *via* the 1,2,3-hydroxyl groups, which are *cis* to each other in these sugars. Other aldoses, like *D*-arabinose, *D*-glucose, *D*-xylose and *D*-galactose form weaker bidentate complexes with those ions because they can only use the 1 and 3-*cis* hydroxyl groups in metal binding. These bidentate interactions also take place in the binding of U(VI) to *D*-mannose and *D*-ribose, at pH $\simeq$ 10. However, sugars having 1,3,5-hydroxyl groups in the *cis* position do not form stable chelates with these oxocations, possibly due to steric crowding.

In the case of ribose-5-phosphate, the phosphate group is the exclusive binding site for the three oxocations, except for U(VI) at very basic pH (pH > 10), where the hydroxyl groups also interact with UO_2^{2+}.

Keywords: Molybdenum, tungsten, uranium, sugars, complexes

INTRODUCTION

The formation of complexes by interaction of carbohydrates with metal ions has long been used as an analytical tool in separation methods such as chromatography[1,2] and electrophoresis.[3] Recent increased interest in this field[4–8] results mainly from the possible role of root polysaccharides in the uptake of metal ions by plants.[9,10] In particular, it has been found that an extracellular apparatus, rich in polyuronates, allows plant roots to remove nutrient cations from soils.[11,12] Specific interactions, such as those found between polygalacturonic acid and metal ions, could have relevant functional and physiological implications.[13–15]

Specific interactions of the hydroxyl groups of various monosaccharides with borate and molybdate have been proposed to play a role in the negative catalysis of selective epimerization of aldoses displayed by those anions in aqueous solution.[16–18] Nuclear magnetic resonance (NMR) spectroscopy has been used to detect specific interactions of borate with *cis*-diol groups forming five or six membered rings. For example, *D*-glucose forms 1,2-furanose and 1,2-pyranose

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complexes,[19] in accordance with studies involving borate and model hydroxy compounds.[20,21] A particularly favourable arrangement for complexing cations, which is an axial, equatorial, axial sequence of oxygens on consecutive carbon atoms in a six-membered ring,[22] has been found by NMR to operate in the complexation of aldoses and cyclitols with Ca^{2+} and lanthanide (III) cations in water,[23,24] in the interaction of carbohydrate derivatives with Na^+ in acetone solution,[25] and in the formation of tridentate complexes of monosaccharides with periodate[26] and molybdate[27,28] in aqueous solution.

In this work specific interactions of various aldoses, cyclic polyols and aldose derivatives with oxocations of Mo(VI), W(VI) and U(VI), to give species with different stereochemistries of complexation, is studied using ^1H and ^{13}C NMR. The efficiency of binding of hydroxyl groups in the 1,2,- 1,3,- 1,2,3- and 1,3,5-positions, as well as the competition of polyhydroxy and phosphate group binding are investigated. The interaction of some aldoses with molybdate, previously investigated,[27,28] is reported in more detail. These interactions may be used as models for binding to polysaccharides with respect to modes of metal ion uptake by plant roots.

EXPERIMENTAL

The aldoses *D*-mannose, *D*-ribose, *D*-lyxose, *D*-glucose, *D*-galactose, *D*-xylose, *D*-arabinose, 2-deoxy-*D*-glucose and 2-deoxy-*D*-galactose were obtained from BDH. The cyclic polyols all-*cis*-cyclohexane-1,3,5-triol (CHT) and *myo*-inositol were kindly supplied by Dr. J. Peters, Delft. Ribose-5-phosphate(disodium salt) was obtained from the Sigma Chemical Company. Sodium molybdate and sodium tungstate (Merck) were dried under vacuum at 120°C, and uranyl nitrate hexahydrate (BDH) was transformed into the monohydrate by the same process. Solutions were prepared in 99.8% D_2O (Stohler Isotope Chemicals) for ^1H NMR and in H_2O containing 10% D_2O for ^{13}C spectra. The solution pH, adjusted with DCl and NaOD (Sigma), was measured on a Metrohm E520 pH meter, and was not corrected for the deuterium isotope effect. NMR spectra were obtained using a Varian XL-200 or a Bruker CXP-300 FT spectrometer. ^{13}C spectra were obtained with broadband proton decoupling. TSS and *t*-butanol were used as internal references for ^1H and ^{13}C chemical shifts, respectively. ^{13}C shifts were recalculated relative to TMS.

RESULTS AND DISCUSSION

Interaction with Mo(VI) and W(VI).

The proton NMR spectra of the aldoses studied are very congested and of second order in the chemical shift region from 3 to 4 ppm, whereas the anomeric protons appear at higher frequencies (4.5 to 5.2 ppm). These spectra have been assigned according to the literature.[29–31]

The effect of the addition of molybdate and tungstate, at pH 5–6, on the proton NMR spectra of the aldoses depends dramatically on their structure.[27] The clearest evidence for complex formation arises in the case of the homeomorphous aldoses *D*-lyxose and *D*-mannose and for *D*-ribose, where the spectra of 1 : 1 solutions of aldoses and molybdate or tungstate contain new signals at higher frequency arising from the complexed species formed (Fig. 1). The observation of separate resonances

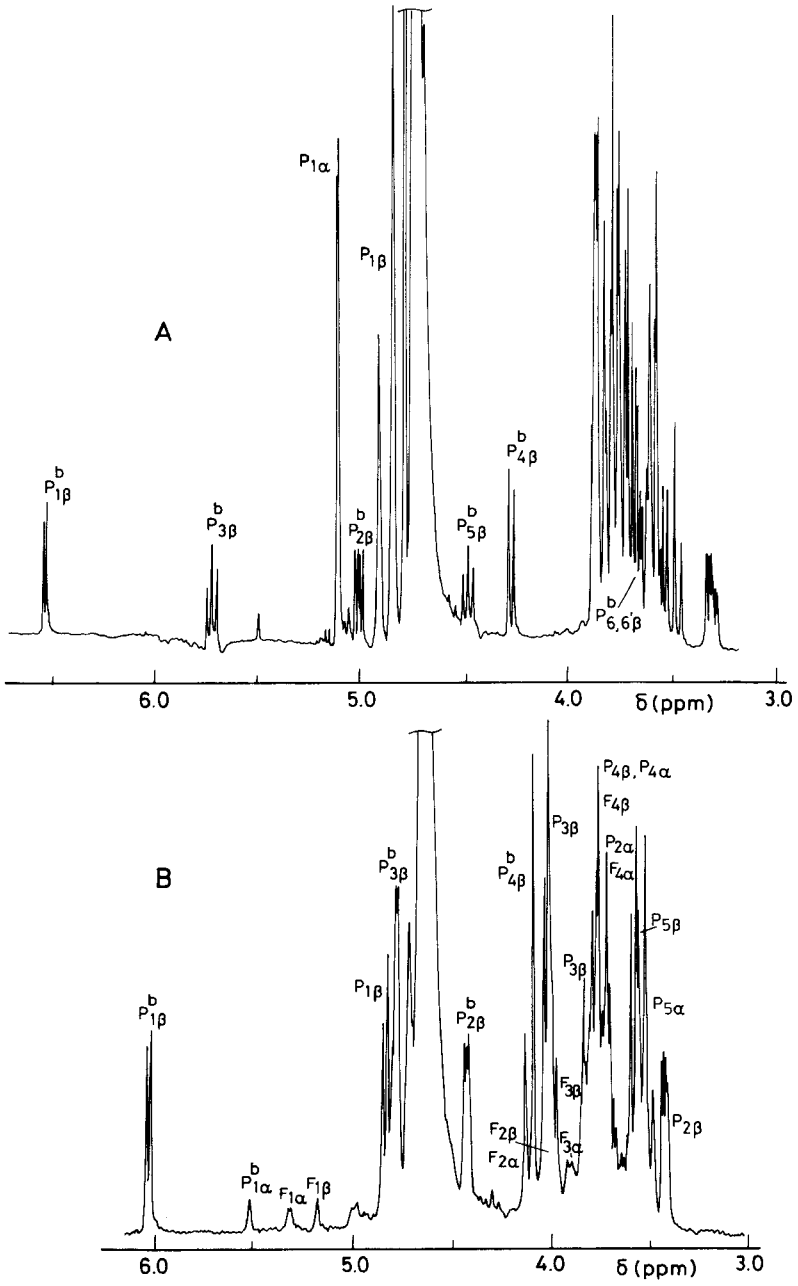

FIGURE 1 300 MHz proton NMR spectra of A): *D*-mannose/W(VI), 0.1M (1 : 1), pH = 5.5; B): *D*-ribose/Mo(VI), 0.1M (1 : 10), pH = 5.5.

from the free and bound forms of the aldoses indicates that there is slow exchange on the NMR time scale between these different species. The fact that the signals of the free form do not disappear at 1 : 1 stoichiometry results from the competition between extensive polymerization of MoO_4^{2-} and WO_4^{2-} in solution[32] and weak complexation of these ions by the aldoses.

The proton (Fig. 1A) and ^{13}C (Fig. 3A) NMR spectra of equimolar solutions of *D*-lyxose or *D*-mannose with molybdate or tungstate reveal the presence of the α and β anomers of the pyranose species as well as of a complex formed by the β anomer of the aldose with Mo(VI) or W(VI).[27] Assignment of the signals from the complexes was accomplished using literature data[27,28] and homonuclear spin decoupling. Integration of the H_1, signals from the free and bound forms in solutions with metal-to-ligand ratio of 1 : 10 up to 10 : 1 yielded Job plots with maxima at the 1 : 1 proportion (Fig. 2), which defines the stoichiometry of the complexes formed.[33]

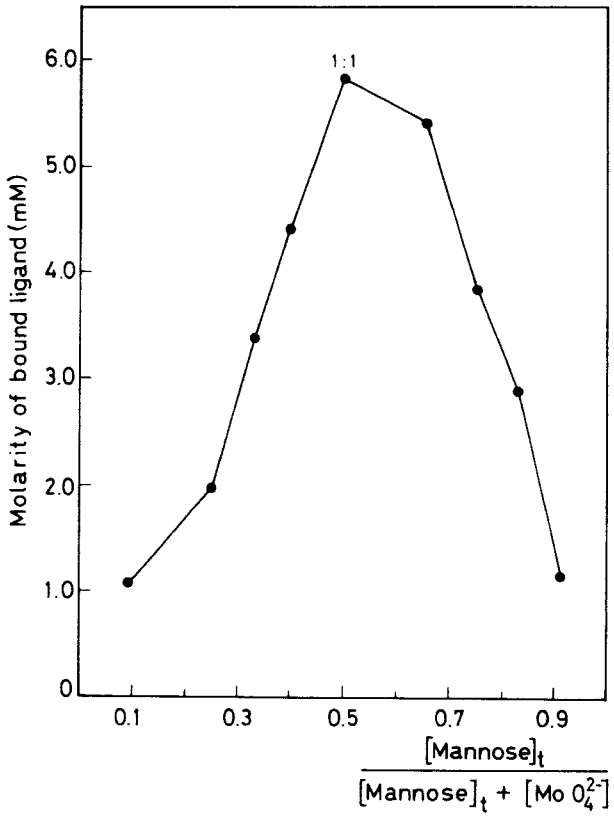

FIGURE 2 Job plot for *D*-mannose Mo(VI); C_t = [*D*-mannose] + [Mo(VI)] = 0.1 M, pH = 5.5.

The complexation shifts, Δδ, of the proton (Table I) and ^{13}C (Table II) nuclei are all positive and result from coordination of the molybdate or tungstate *cis*-dioxo-cations, MoO_2^{2+} or WO_2^{2+}, by the hydroxyl groups of the β anomers of the aldoses *D*-lyxose and *D*-mannose at C_1, C_2 and C_3.[27,28] The *cis-cis* arrangement of these hydroxyl groups allows these forms to function as terdentate donors and form one

face of the coordination octahedron of the Mo(VI) or W(VI) atom.[27] Analysis of proton vicinal coupling constants (Table III) shows that the two aldoses are distorted by complexation from a boat $^1C_4$ to a skew $^1S_5$ conformation.[27]

TABLE I

Complexation shifts, Δδ(ppm), for proton resonances of complexes between various *D*-aldoses and Mo(VI) or W(VI) in D_2O, pH = 5–6.

Species	H_1	H_2	H_3	H_4	H_{5e}	H_{5a}	H_6	$H_{6'}$
β-*D*-lyxose/Mo	+1.33	+1.04	+1.71	+0.56	+0.08	+1.02		
β-*D*-lyxose/W	+1.77	+1.13	+2.17	+0.62	+0.30	+1.15		
β-*D*-mannose/Mo	+1.28	+0.98	+1.71	+0.74		+1.07	a	a
β-*D*-mannose/W	+1.69	+1.09	+2.13	+0.79		+1.19	a	0.00
β-*D*-ribose/Mo	+1.18	+1.00	+0.77	+0.26	a	a		
α-*D*-ribose/Mo	+0.79	a	a	a	a	a		
β-*D*-ribose/W	+1.44	+1.02	+0.73	+0.20	a	a		
α-*D*-ribose/W	+1.09	a	a	a	a	a		

[a] Not determined.

TABLE II

Complexation shifts, Δδ(ppm), for the ^{13}C resonances of complexes of various *D*-aldoses and *D*-ribose-5-phosphate with Mo(VI) or W(VI) in D_2O, pH = 5–6.

Species	C_1	C_2	C_3	C_4	C_5	C_6
β-*D*-lyxose/Mo	+17.1	+16.6	+11.4	+14.7	+3.1	
β-*D*-lyxose/W	+17.3	+16.4	+9.1	+12.9	+3.3	
β-*D*-mannose/Mo	+17.6	+16.2	+10.3	+11.9	+2.8	+3.1
β-*D*-mannose/W	+17.2	+16.5	+9.7	+11.8	+2.0	+3.0
β-*D*-ribose/Mo	+7.6	+8.5	+16.5	+7.5	+2.1	
β-*D*-ribose/W	+6.8	+9.0	+15.5	+7.5	+2.1	
α-*D*-ribose-5-phosphate/Mo	0.00	+0.06	+0.12	+0.25	+0.53	
β-*D*-ribose-5-phosphate/Mo	+0.10	+0.12	+0.22	+0.22	+0.59	
β-*D*-mannose/U	+13.1	+20.1	+13.6	+11.2	+6.5	+0.8
β-*D*-ribose/U	+12.4	+21.7	+17.5	+6.1	+3.1	

TABLE III

Proton coupling constants, J(Hz), for the complexes of various *D*-aldoses with Mo(VI) and W(VI), in D_2O, pH = 5–6.

Species	J_{12}	J_{23}	J_{34}	J_{45e}	J_{45a}	J_{5e5a}	J_{56}	$J_{56'}$	$J_{66'}$
β-*D*-lyxose/Mo	4.4	6.8	7.8	2.9	0.0	−12.7			
β-*D*-lyxose/W	4.4	6.8	7.8	2.9	0.0	−13.2			
β-*D*-mannose/Mo	4.4	6.8	7.3		0.0		7.1	7.1	a
β-*D*-mannose/W	4.4	6.8	7.8		0.0		7.3	7.3	a
β-*D*-ribose/Mo	6.5	a	a	a	a	a			
α-*D*-ribose/Mo	2.1	a	a	a	a	a			

[a] Not determined.

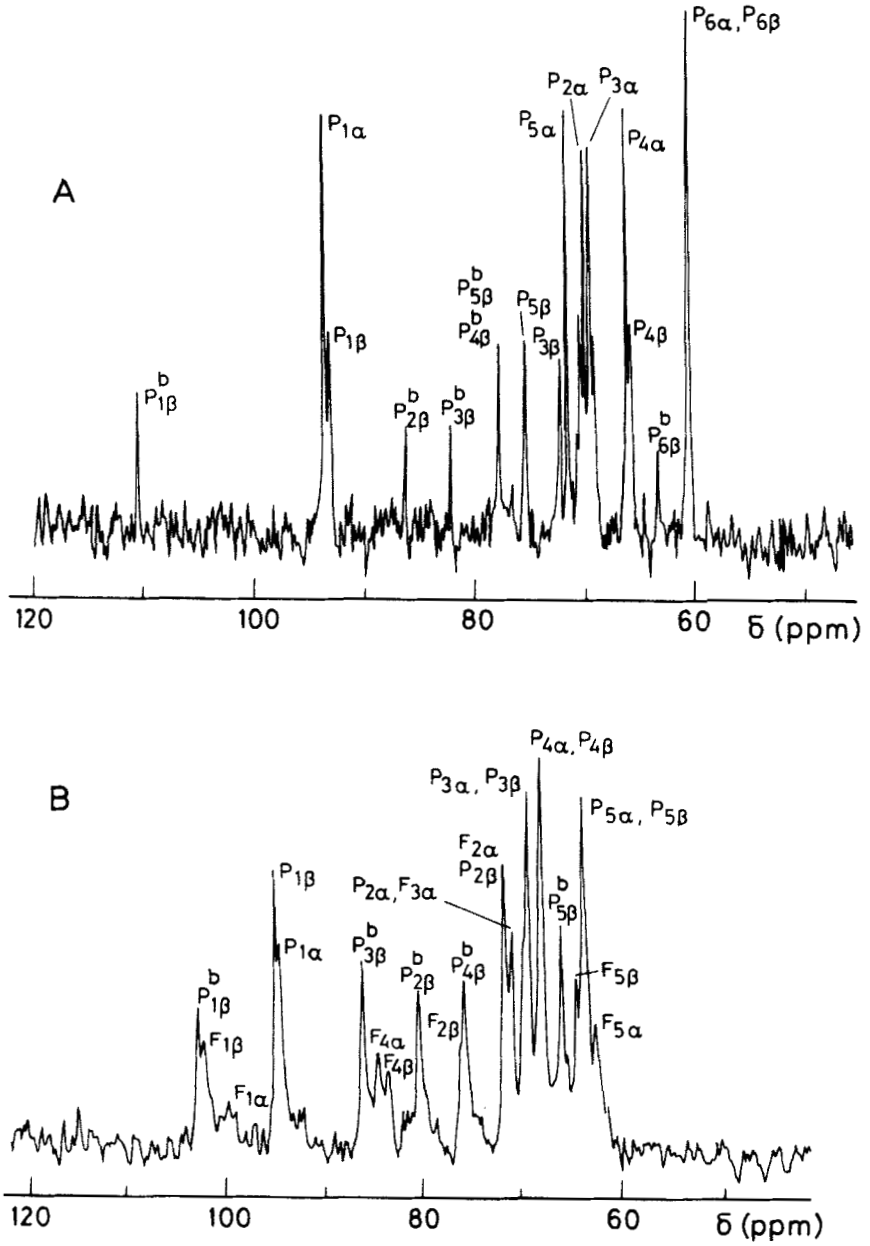

FIGURE 3 ^{13}C NMR spectra (at 53.3 MHz) of A): *D*-mannose/W(VI), 0.1 M (2 : 1), pH = 5.5; B): *D*-ribose Mo(VI), 0.2 M (1 : 5), pH = 5.5.

The proton spectrum of *D*-ribose in D_2O shows signals from four species, the α and β anomers of the pyranose (Pα and Pβ) and furanose (Fα and Fβ) forms.[29] The four anomeric H_1 protons are well defined, with coupling constants J_{12} of 2.1 Hz (Pα), 6.5 Hz (Pβ), 3.9 Hz (Fα) and 1.9 Hz (Fβ).[34] When anomeric equilibrium is

attained, the relative intensities of these signals give their relative populations, 20% (Pα), 56% (Pβ), 6% (Fα) and 18% (Fβ).[29] Addition of a tenfold excess of sodium molybdate to *D*-ribose causes new signals to appear in its proton spectrum (Fig. 1B), shifted to high frequency. Only two new anomeric proton signals are detected, corresponding to the complexed pyranose forms Pα and Pβ, with relative intensities of 1 : 10 and J_{12} couplings unchanged relative to the free forms. Therefore, both anomers of the pyranose form are complexed by molybdate (but not the furanose anomers) without change of their conformation about the C_1 carbon, which indicates that the complexation of Mo(VI) occurs through the hydroxyl groups at C_2, C_3 and C_4 and not at C_1, C_2 and C_3.[27] The positive proton complexation shifts, obtained after assignment of the signals of the complexed forms using spin decoupling, are given in Table I. The largest shift at H_1 of Pβ is due to electric and magnetic through-space effects from the MoO_2^{2+} centre. The increase from 1 : 3 to 1 : 10 of the population ratio of the Pα and Pβ forms upon complexation indicates that the uncoordinated C_1 hydroxyl group in the complex is preferentially oriented *trans* relative to the C_2 hydroxyl group and the metal centre, possibly to minimize electrostatic and steric repulsions.

The ^{13}C spectrum of *D*-ribose,[34,35] which again contains the four different species referred to above, is also changed in the presence of a fivefold excess of molybdate (Fig. 3B). New signals, corresponding to the pyranose forms complexed with Mo(VI), are detected. The complexation shifts of the Pβ form (Table II) are quite different from the values obtained with β-lyxose and β-mannose, and confirm that the complexation occurs through the C_2, C_3 and C_4 hydroxyl groups.[28] Some extra ^{13}C signals are seen, which correspond to the Pα complex, but these were not assigned. The furanose forms do not significantly interact with Mo(VI) because the orientation of their hydroxyl groups does not allow them to act adequately as terdentate ligands. Therefore, *D*-ribose complexes molybdate preferentially in the β-pyranose form as a terdentate ligand using the C_2, C_3 and C_4 hydroxyl groups. Consequently, it is distorted from a boat $^1C_4$ to a skew $^1S_3$ conformation, with a 2-*quasi*-3-equatorial-4-axial orientation of the three hydroxyl groups.[28]

The complexation shifts for the ^1H and ^{13}C nuclei of *D*-ribose in the presence of tungstate (Tables I and II) show that its interaction with W(VI) is very similar to that described for Mo(VI).

TABLE IV

Conformational comparison of free[29-31] and Mo(VI)-bound[27,28,36,37] and U(VI)-bound aldoses in solution.

Compound	Preferred Conformation of free ligand	Preferred Conformation of Mo(VI) bound ligand	Preferred Conformation of U(VI) bound ligand
D-mannose	α^4C_1	β^1S_5	β^1C_4
D-lyxose	$\alpha^1C_4 \rightleftarrows \alpha^4C_1$	β^1S_5	a
D-ribose	$\beta^1C_4 \rightleftarrows \beta^4C_1$	$\beta^1S_3 \rightleftarrows \alpha^1S_3$	α^4C_1
D-arabinose	α^4C_1	α^4C_1	a
D-galactose	β^4C_1	β^1C_4	a
D-xylose	β^4C_1	β^1C_4	a
D-glucose	β^4C_1	β^1C_4	a

[a] Not studied.

The aldoses *D*-mannose, *D*-lyxose and *D*-ribose act as terdentate ligands by using three consecutive hydroxyl groups of the pyranose forms in the binding of Mo(VI) and W(VI) oxocations. It has previously been shown that these strong complexation properties make these sugars very mobile during electrophoresis.[1] Solutions containing these sugars and molybdate or tungstate also have circular dicroism spectra with very well defined Cotton Effects.[36,37] The pyranoses with *cis* axial hydroxyl groups at positions C_1 and C_3 (or C_2 and C_4), but with a *trans* intermediate C_2 (or C_3) hydroxyl group, can form weaker bidentate complexes with Mo(VI) or W(VI) containing a six-membered chelate ring. The compounds *D*-arabinose, *D*-galactose, *D*-xylose and *D*-glucose all have conformations and anomers obeying this condition (Table IV), therefore weakly complexing Mo(VI) and W(VI). This weak complexation provides the aldose solutions with only very weak electrophoretic mobility[1] and circular dicroism spectra with poorly defined Cotton Effects.[36,37] The proton NMR spectra of solutions of these aldoses containing a tenfold excess of molybdate at pH = 5.8 gives new signals for the complexed forms, in slow exchange with the free forms, which are very weak for *D*-glucose and *D*-xylose and somewhat stronger for *D*-arabinose and specially for *D*-galactose. Under the same conditions, only *D*-galactose showed new signals with tungstate. Due to their low intensity, these new signals could not be fully assigned, but the measured proton complexation shifts are generally upfield and comparable to those obtained for the previously discussed complexes (Table I). For example, the Mo(VI) complexation shift for the β-D-xylose H_1 resonance is +0.86 ppm. The fact that the proton spectra of 2-deoxy-*D*-galactose and 2-deoxy-*D*-glucose in the presence of a tenfold excess of molybdate also show very weak signals from bidentate complexed forms indicates that bidentate binding in the aldoses *D*-xylose and *D*-glucose does not involve the axial C_2 and C_4 hydroxyl groups in the $^1C_4$ conformation, but rather the axial C_1 and C_3 groups of the β anomer in that conformation. This is confirmed by a change of specific rotation of these aldose solutions upon complexation with Mo(VI).[36]

The 1,3-*cis* diol binding efficiency was tested by studying the interaction of a fivefold excess Mo(VI) and W(VI) with the cyclic polyols all-*cis*-cyclohexane-1,3,5-triol (CHT) and *myo*-inositol. There was no detectable complex formation of the Mo(VI) or W(VI) oxocations with CHT in the pH range of 2.0 to 6.0. As a terdentate C_1, C_3, C_5 triaxial hydroxyl binding to Mo(VI) or W(VI) is sterically impossible, we conclude that bidentate C_1, C_3 binding is not strong enough to cause a conformational change of CHT from a stable chair triequatorial to a sterically crowded triaxial form, as required for complexation. In the case of *myo*-inositol, whose stable chair conformation has five equatorial and one axial hydroxyl groups, a conformational change to the other chair conformation is also required for complexation. This conformation has three axial groups at C_1, C_3, C_5 on one side of the ring and two axial groups at C_2, C_6 on the other. Only very weak new signals were observed for the Mo(VI) *myo*-inositol system, and none for W(VI), indicating that this complexation process is highly unfavourable due to steric crowding.

The interaction of *D*-ribose-5-phosphate with molybdate was studied using ^{31}P, ^1H and ^{13}C NMR. This *D*-ribose derivative, which has a furanose structure in solution, is found as part of 5′-mononucleotides. A single complex is formed in solution in the pH range from 2.0 to 5.0. The ^{31}P Mo(VI) complexation shift is +1.20 ppm, very similar to values found in complexes with phosphate and 5′-mononucleotides,[38] and implying direct coordination of Mo(VI) by the phosphate group. The proton spectrum of *D*-ribose-5-phosphate in D_2O (Fig. 4A) has signals from the α and β H_1 anomeric furanose protons well resolved from the others. $H_{1\alpha}$ has the largest J_{12}

coupling constant, shifted by +0.15 ppm relative to $H_{1\beta}$.[39] The effect on the proton spectrum of adding a tenfold excess of molybdate (Fig. 4B) was not analyzed in detail due to difficulties in obtaining assignments by spin decoupling. However, it is clear that both anomeric forms are fully complexed by Mo(VI), with positive complexation shifts for all protons, increasing from very small values for H_1 up to relatively high (about +0.5 ppm) values for H_4, H_5 and $H_{5'}$, near the phosphate group. These values agree with exclusive complexation of Mo(VI) by the phosphate group.

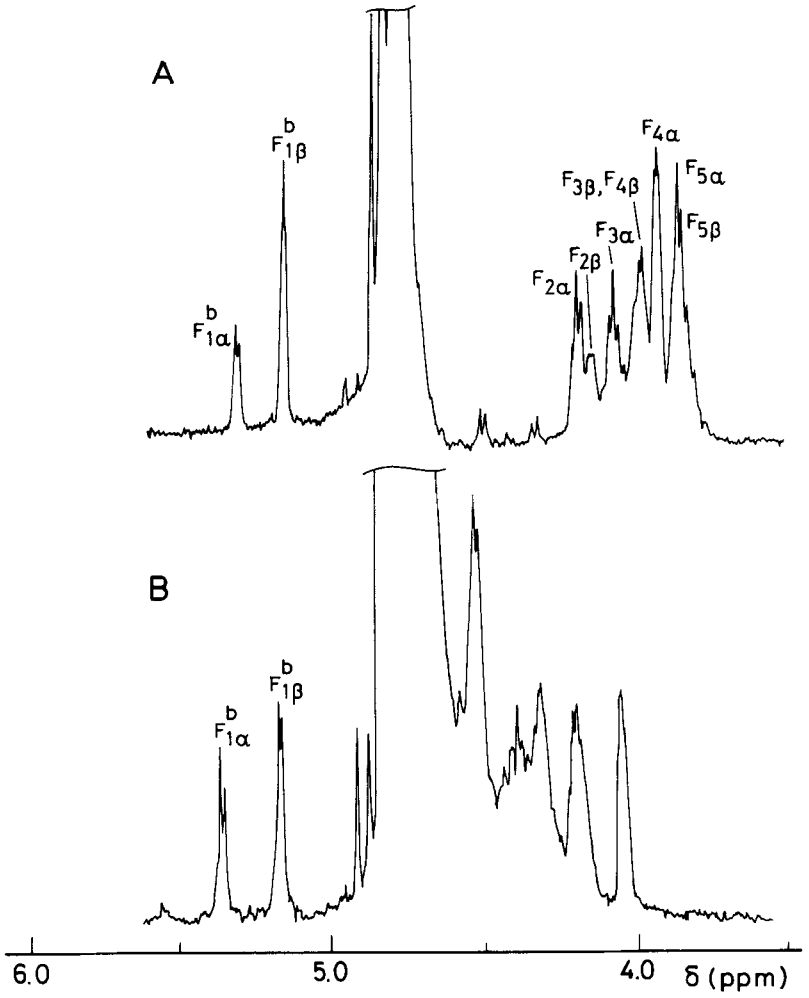

FIGURE 4 200 MHz proton NMR spectra of 0.03 M *D*-ribose-5-phosphate, pH = 4.2, A): In D_2O; B): In the presence of 0.3 M Na_2MoO_4.

The proton decoupled ^{13}C spectrum of *D*-ribose-5-phosphate (Fig. 5A), assigned in the literature,[40] has signals from the α and β furanose forms. The C_4 and C_5 signals display splittings from ^{13}C–^{31}P couplings. The addition of molybdate at a 1:1 mole ratio (Fig. 5B) causes a doubling of the signals of both anomers, with very

small complexation shifts (Table II). These are much smaller than those observed for the *D*-ribose pyranose form, thus showing that Mo(VI) does not interact with the hydroxyl groups. Their regular decrease from C_5 to C_1 shows that Mo(VI) interacts exclusively with the phosphate group, in accordance with a proposed[41] structure for the complex, with a metal-to-ligand stoichiometry of 2 : 5 containing an Mo_2P_5 cluster involving the phosphate groups of the sugar phosphate ester.

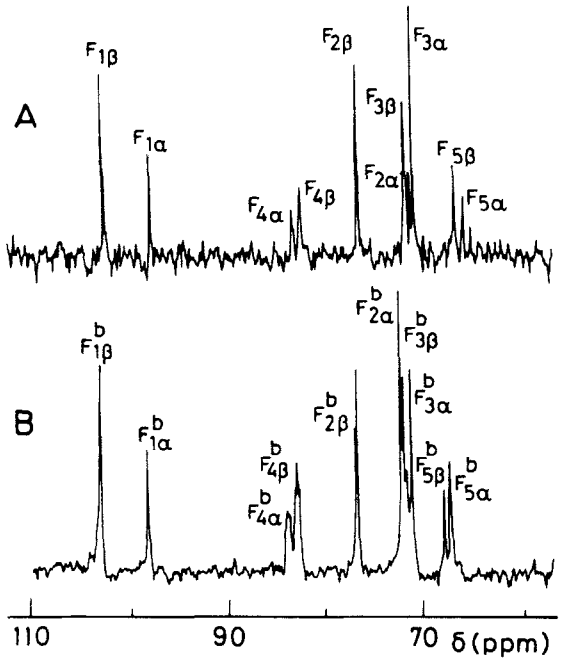

FIGURE 5 ^{13}C NMR spectra (at 53.3 MHz) of 0.1 M *D*-ribose-5-phosphate, pH = 4.2, A): In D_2O; B): In the presence of 0.1 M Na_2MoO_4.

Interaction with U(VI).

As opposed to the angular Mo(VI) and W(VI) MO_2^{2+} oxocations, which have an octahedral stereochemistry, the linear uranyl oxocation, UO_2^{2+}, has a preferred bipyramidal stereochemistry, with an equatorial coordination number of three to five.[42]

The interaction of uranyl ion with some aldoses and related compounds was studied in the pH range from 2.0 to 12.5, using proton and ^{13}C NMR. Below pH 4.0 no complexes are formed, and between pH 4.0 and about 10.0 a yellow precipitate of diuranate is formed. Above this pH range, the precipitate dissolves when complexation occurs.

The interaction of UO_2^{2+} with the aldoses *D*-mannose and *D*-ribose was studied in some detail (see Figs. 6 and 7 for typical proton and ^{13}C spectra obtained). Solutions containing *D*-mannose/U(VI) give proton spectra indicating formation of various complexes, with predominant 1 : 1 stoichiometry (FIg. 6A). The ^{13}C spectrum of a 2 : 1 solution (Fig. 7A) shows signals from the free ligand and the predominant

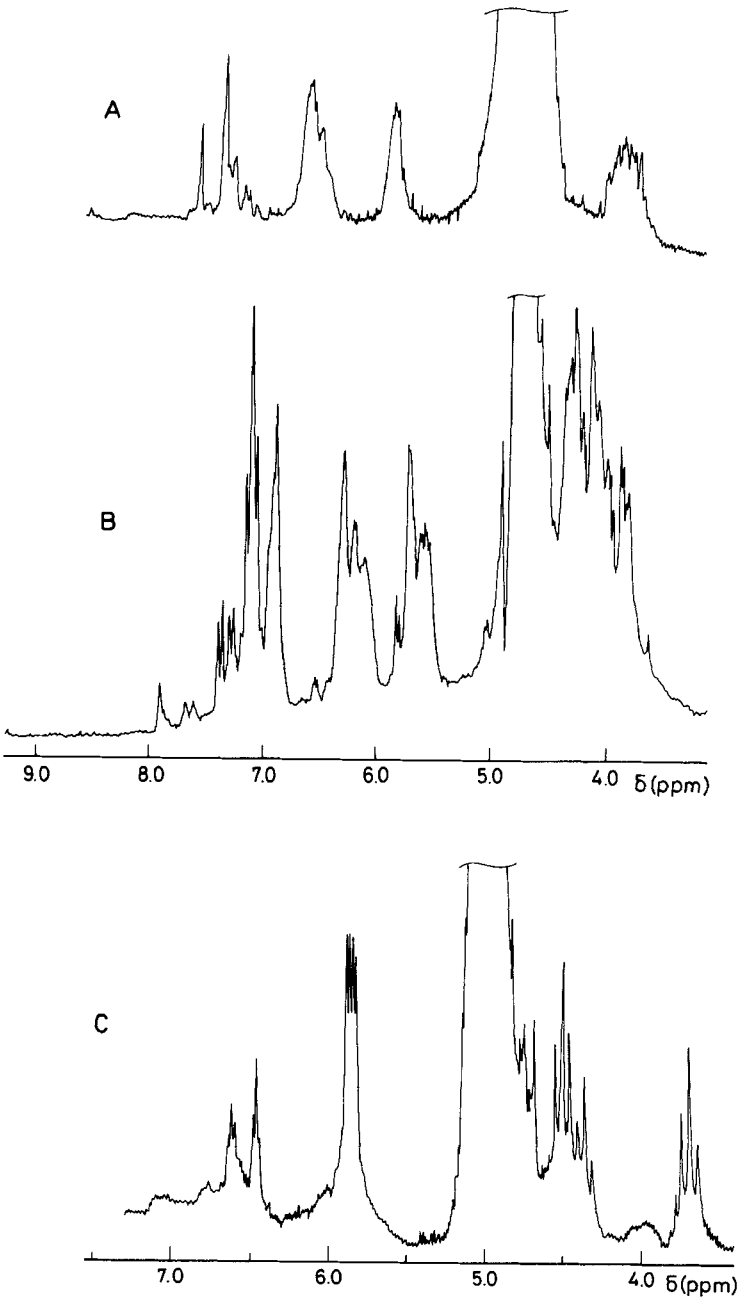

FIGURE 6 200 MHz Proton NMR spectra of A): *D*-mannose/U(VI), 0.1 M (1 : 1), pH = 12.6; B): *D*-ribose/U(VI), 0.1 M (1 : 2), pH = 12.2; C): *Myo*-inositol 0.1 M (1 : 2), pH = 12.6.

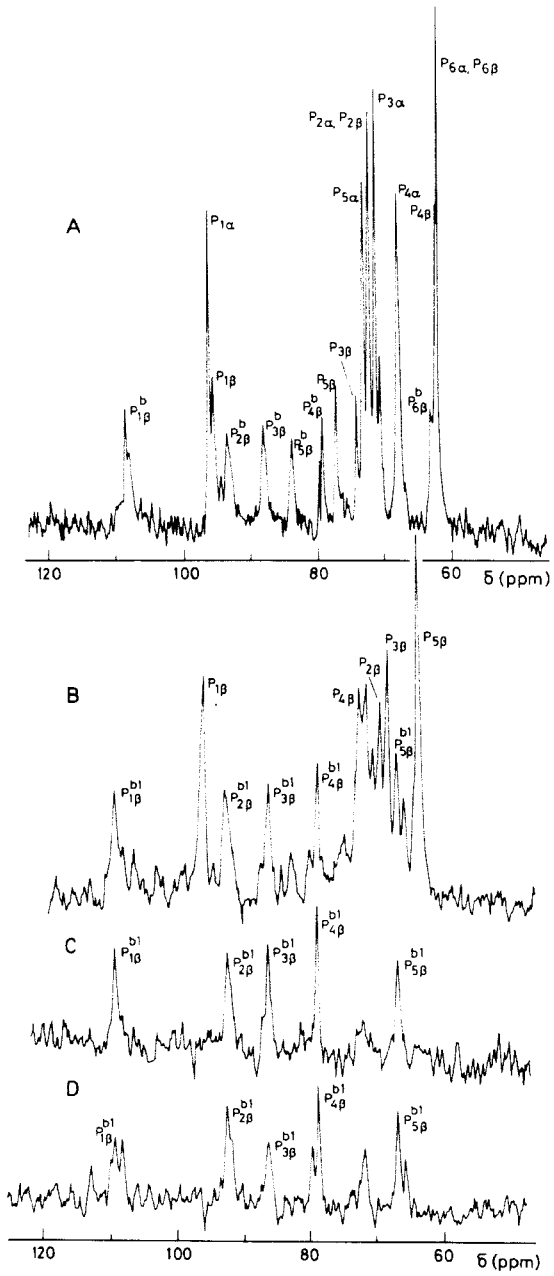

FIGURE 7 ^{13}C NMR spectra (at 53.3 MHz) of A): *D*-mannose/U(VI), 0.2 M (2 : 1), pH = 12.6; *D*-ribose U(VI), 0.2 M, pH 11.0: B): 2 : 1; C): 1 : 1 D): 1 : 2.

complex. The measured positive complexation shifts (Table II) are very similar to those found for the β-*D*-mannose/Mo(VI) complex, indicating that the structures of the two complexes are very similar. We therefore propose complexation of UO_2^{2+} by the pyranose β anomer of *D*-mannose in the $^1C_4$ conformation, using a 1,3-*cis* diaxial chelation. The proton spectra are difficult to assign, due to extensive broadening, but generally show large positive complexation shifts.[43,44] Another possible coordination mode of UO_2^{2+} by both *D*-mannose anomers is 2,4-*cis* diaxial chelation, which may contribute to the weaker signals found in the proton spectrum.

The ^{13}C spectra of *D*-ribose/U(VI) (Fig. 7B to D) depend on the ligand-to-metal ratio, giving two predominant complexes of 1 : 1 and 1 : 2 stoichiometries (see Table II for the complexation shifts of the 1 : 1 complex). The proton spectrum (Fig. 6B) has new resonances with large positive complexation shifts[43,44] and shows that, besides the two complexes formed by the pyranose (P) forms, the α and β furanose (F) forms also complex U(VI). In fact, Fβ can form a five membered 2,3-*cis* diol chelate whereas Fα can form two of these chelates, a 1,2-*cis* diol and a 2,3-*cis* diol. The pyranose Pα in the conformation $^4C_1$ can form a 1,3-*cis* diol chelate, whereas the $^1C_4$ conformation of both Pα and Pβ can form a 2,4-*cis* diol chelate. Although the actual chelation mode is difficult to define, the similarity of the ^{13}C complexation shifts of *D*-ribose/U(VI) and β-*D*-mannose/Mo(VI) points to a 1,3-*cis* diol complexation by the $^4C_1$ conformation of the Pα form.

The CHT cyclitol was not found to complex UO_2^{2+}, possibly due to steric crowding of the axial hydroxyl groups. *Myo*-inositol (Fig. 6C) forms one predominant complex with 1 : 2 stoichiometry, possibly involving a 1,3-*cis* diol interaction in the less stable ligand conformation.

Although the interaction of *D*-ribose-5-phosphate with UO_2^{2+} was not studied in this work, similar studies with 5′-AMP[43,44] indicate formation of various complexes with pH dependent structures. Above pH 10.9, polynuclear sandwich-type 2 : 2 and 2 : 4 complexes are formed involving chelation of olated uranyl both by the ribofuranose hydroxyl groups and the phosphate group. Between pH 9.9 and 7.5 non-sandwich-type complexes are formed by exclusive interaction with the phosphate group. These results should be applicable to the related *D*-ribose-5-phosphate compound.

Conclusions

The present NMR study allows some general conclusions to be made about the strength of various specific interactions between metal ions of different preferred stereochemistries and the substitutent groups of various aldoses and related compounds. The borate ion, possibly due to its tetrahedral geometry, can form strong 1,2-*cis* diol interactions with pyranoses and furanoses, giving five-membered chelate rings.[19] However, this does not occur with MoO_2^{2+} and WO_2^{2+} oxocations and is only found with UO_2^{2+} and furanose rings at pH values above 10.5. The interaction involving the 1,2,3-*cis* hydroxyl groups takes place for octahedral MoO_2^+ and WO_2^+ with aldoses like *D*-mannose, *D*-lyxose and *D*-ribose.[27,28] In cases where this is not possible, as in *D*-arabinose with MoO_2^{2+}, or generally with UO_2^{2+} and the aldoses or *myo*-inositol, 1,3-*cis* diol interactions, giving six-membered chelate rings, although weaker, can still form in some cases. However, the present studies with *myo*-inositol and molybdate show that steric interactions can easily overcome this weaker interaction. The interactions using the 1,3,5-hydroxyl groups in *cis* positions

are not possible for the present cations, but might be important in the complexation of other types of cations, such as Ca^{2+} and the lanthanides.[23,24]

When the hydroxyl groups coexist in a sugar derivative with a more basic group, like a phosphate, this latter donor naturally becomes the primary binding site (for example for Mo(VI) and W(VI) (pH 4–6) and U(VI) (pH 7.5–10) with *D*-ribose-5-phosphate). However, in the case of U(VI) at pH above 10, the hydroxyl groups compete with the phosphate group for binding. Similar situations could occur with the carboxylate groups of polygalacturonates.[13–15]

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