^{183}W NMR Studies of Tungstate Complexes of Carbohydrates. 2. Competitive Formation of *erythro* and *threo* Complexes of Alditols. Characterization of a Novel Bis-Dinuclear Complex Formed with Perseitol†

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Received June 22, 1993•

Tungstate complexes of alditols have been studied in aqueous solution by ^{183}W and ^{13}C NMR spectroscopies. The ligands used in this work may chelate a ditungstate group through several different sites having *erythro* or *threo* configurations and therefore yield mixtures of complexes. The structural type of each complex was defined by the characteristic pattern of its ^{183}W NMR spectrum, and the sites of chelation were identified by ^{13}C NMR spectroscopy. Alditols which possess an asymmetrical site of *erythro* configuration (D-arabinitol, D-mannitol, D-glucitol) form two isomeric complexes, as this tetradentate site can be occupied in two reversed orientations. Ribitol forms a single complex of the same type. A single additional complex is formed when another tridentate site of chelation of *threo* configuration is available (D-arabinitol, D-glucitol). Perseitol (D-*glycero*-D-*galacto*-heptitol) affords a pair of *erythro* complexes involving the tetradentate HO-2,3,4,5 *galacto* site, together with a third complex of a novel "mixed" bis-dinuclear type. For the latter species, four sharp signals in the ^{183}W NMR spectrum characterized two ditungstate groups bound respectively to an *erythro* site (δ -74.2 and -81.4) and a *threo* site (δ -55.4 and -117.6). These sites were assigned from the ^{13}C NMR spectrum respectively to the HO-4,5,6,7 and the HO-1,2,3 systems, indicating that the ligand was heptadentate.

Introduction

Like molybdate ions, tungstate ions react with alditols (L) in acidic solution to form anionic dinuclear complexes.[1-4] At pH > 5, the complex-forming reaction is[5]

$$2WO_4^{2-} + L + 2H^+ \rightleftarrows (2,1,2)^{2-} + H_2O$$

and the corresponding equilibrium constant is the formation constant K_{212}. The tungstate species are stronger than their molybdate homologues, which allows the acidimetric titration of tungstate after complexation by alditols like D-glucitol.[5] Moreover, because the stabilities of the complexes strongly depend on the configurations of the ligands, carbohydrates may be separated by chromatography on cellulose impregnated with tungstate.[6] A better knowledge of the relationship between the structures and the stabilities of the complexes involved in this process would help to improve the separation efficiency. It was also believed that, like most ligands, carbohydrates formed homologous complexes with molybdate and tungstate, providing the basis for studies of the tungstate compounds as "models" for the molybdate species that catalyze the C-2 epimerization of aldoses.[7]

Up to now, structural data on carbohydrate complexes in solution were generally obtained by ^{13}C NMR. Attempts made to study the assumed homologous molybdate complexes with ^{95}Mo NMR gave poor results[8,9] because only broad, unresolved signals could be observed. On the contrary, we have recently[10] shown that the greater resolution in the ^{183}W NMR spectrum provided much more information than was obtained from the corresponding ^{95}Mo NMR spectrum. Complementary ^{13}C NMR data[10] revealed that tungstate and molybdate complexes are homologous only if the site of chelation has the *erythro* configuration. On the contrary, alditols that possess a *threo* site form two separate series of complexes in which the ligand is tetradentate (with molybdate) or tridentate (with tungstate). For the sake of simplicity, previous work[10] had been limited to alditols that formed single *erythro* or *threo* tungstate complexes, but we have now extended our investigations to alditols that possess several possible sites of chelation and thus may afford mixtures of isomeric complexes. Such compounds include D-arabinitol, ribitol, D-mannitol, D-glucitol, and maltitol (4-*O*-α-D-glucopyranosyl-D-glucitol) (Chart 1).

Perseitol (D-*glycero*-D-*galacto*-heptitol) belongs to a group of naturally-occuring seven-carbon carbohydrates that are involved in the metabolism of plants (it is found in avocado fruit).[11] Interestingly, this alditol possesses several possible *erythro* and *threo* sites of chelation, which makes it possible to compare the stabilities of the complexes with respect to the configuration of the site of chelation. The first studies of the molybdate complexes[8,12] of perseitol detected two tetradentate species that were believed to involve the *galacto* (HO-2,3,4,5) and the *manno* (HO-3,4,5,6) sites. A subsequent ^{13}C NMR study of the complexes of perseitol and D-mannitol[13] showed that molybdate and tungstate formed homologous complexes and demonstrated conclusively that no chelation occured at the *manno* sites of the ligands and that the complexes of perseitol were a pair of isomers involving the *galacto* site occupied in reversed orientations. A third minor (<10%) tungstate complex of perseitol was detected

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• Abstract published in *Advance ACS Abstracts*, March 15, 1994.

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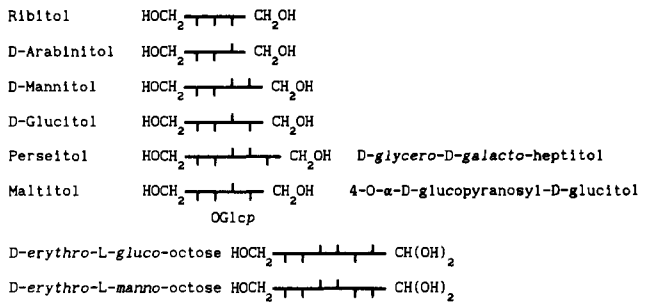
0020-1669/94/1333-1966$04.50/0

Chart 1. Fischer's Formulas of Carbohydrates Cited in the Paper[a]



[a] Following the rules adopted for carbohydrate chemistry, carbon atoms are numbered starting from the right-hand side. The aldoses are represented in acyclic hydrated form.

but could not be identified at the time. We have now succeeded in obtaining a larger proportion of this compound and characterizing it as a novel "mixed" *erythro–threo* complex involving the heptadentate ligand.

Experimental Section

All chemicals were of the purest available reagent grade and were not further purified. The solutions of complexes were prepared as before.[10,13] In some occasions, the hydrochloric acid was added stepwise to the mixture of carbohydrate and disodium tungstate, in order to modify the relative proportions of the complexes. The determination of the formation constant of the tungstate–maltitol complex was performed by a published procedure.[5]

All NMR experiments were performed at 298 K on a multinuclear Bruker AM 400 spectrometer equipped with 5- and 10-mm VSP probes. For ^{183}W NMR experiments, sample concentrations were 1 M (polyol), 2.5 M (tungstate), and 1.25 M (HCl). For ^{1}H and ^{13}C NMR experiments, the concentrations were four times lower. The chemical shifts were determined by the substitution method,[14] with reference to aqueous sodium 2,2,3,3-tetradeutero-3-trimethylsilylpropionate (TMSP) for ^{13}C and aqueous alkaline Na_2WO_4 (2 M) for ^{183}W. Experimental details for the recording of ^{13}C spectra have been described before.[10] 2D NMR ^{13}C–^{1}H heteronuclear correlation shift experiments were made using polarization transfer from ^{1}H to ^{13}C through $^{1}J_{C,H}$ coupling constants.[15] The necessary ^{1}H assignment was obtained previously through a 2D homonuclear proton–proton correlation experiment[16] including an additional sequence for water-peak attenuation by spin–spin relaxation (CPMG sequence[17]). 1D ^{183}W NMR spectroscopy was performed with a pulse width of 25 μs, corresponding to a 60-deg tip angle, a sweeping range of 8000 Hz, an acquisition time of 2 s, a relaxation delay of 3 s, and a digital resolution of 0.5 Hz/pt. To reduce the effects of probe acoustic ringing on the baseline, several left shifts were applied to the free induction decay prior to Fourier transform. A satisfying signal-to-noise ratio was typically obtained after 2 h.

2D ^{1}H–^{183}W correlation shift experiments were made via heteronuclear zero and double quantum coherence using the indirect mode.[18] Typical 90-deg pulse durations were 9 μs for ^{1}H and 39 μs for ^{183}W. The experiments were optimized for long-range $^{3}J_{W,H}$ coupling constants of magnitude 8–10 Hz. No decoupling was made during acquisition. The number of experiments was 128 × 1K.

Results

Previous ^{13}C NMR studies[9,10,13] of molybdate and tungstate complexes of carbohydrates have established that the signals of the carbon atoms involved in the site of chelation exhibit very characteristic deshielding patterns, depending on the configuration of the coordinating oxygen atoms. The identification of such patterns is helpful for the classification of complexes to the E type (*erythro* site) or to the T type (*threo* site). Hereafter, this phenomenon is referred to as the CIS (coordination induced shift), by analogy with the well-known LIS of lanthanides. The molybdate or tungstate complexes of type E exhibit similar CIS patterns for the tetradentate site (10-10-20-10 ppm). On the contrary, *threo* alditols show different CIS patterns in their tungstate complexes (tridentate site, 10-14-10 ppm) and in their molybdate complexes (tetradentate site, 13-10-10-13 ppm).

In the same way, the ^{183}W NMR spectra of the dinuclear tungstate complexes of alditols were reported[10] to display two signals (possibly doublets if coupling to a proton exists). The magnitude of the gap $\Delta\delta_{W\text{-}1,2}$ between the signals for W-1 and W-2 appears to be a reliable indicator of the structure of the site of chelation, since characteristic values are below 15 ppm for type E or near 60 ppm for type T.

The assignment of the protons coupled to each tungsten atom was previously[10] made through direct 2D heteronuclear correlation ^{183}W–^{1}H experiments. In this study, we have used the same correlation, but in the indirect mode,[19,20] which is much more sensitive. The detection of the tungsten signal is made *via* the coupled protons which possess signals of much higher intensities. Because of their coupling to a tungsten atom (natural abundance 14.4%), these protons give rise to satellite signals (intensity 14.4% of the uncoupled main proton signal). The interest of working in the indirect mode is shown by the inherent enhancement of the signal-to-noise ratio with respect to the direct mode: $(\gamma_H/\gamma_W)^{5/2} = 2827$ *vs* $(\gamma_H/\gamma_W)^{3/2} = 118$, where γ_N is the gyromagnetic ratio of the nucleus N. It allows one to reduce up to five times the duration of the experiments.

D-Mannitol. Previous X-ray structural characterization of molybdate complexes of D-mannitol[21,22] has shown conclusively that the *arabino* HO-3,4,5,6 system is the single site of chelation. Subsequent ^{13}C NMR studies[9,13] demonstrated that molybdate and tungstate species were homologous, and that the unsymmetrical site was occupied in two reversed orientations (defined as HO-3,4,5,6 and HO-6,5,4,3). It allows the formation of a pair of isomeric complexes M_1 (major) and M_2 (minor) of type E, characterized by their reversed CIS patterns.

In the ^{183}W NMR spectrum, four coupled signals (doublets) were found in the –80 ppm region and were attributed, according to their unequal intensities, to the M_1–M_2 pair of complexes that gave two doublets each (Table 1). The small gaps between the chemical shifts of the signals in each complex ($\Delta\delta_{W\text{-}1,2}$ 7.2 and 10.0 ppm) are in agreement with typical values for type E complexes: $\Delta\delta_{W\text{-}1,2}$ 3.4 for erythritol and 6.5 for galactitol.[10]

The observation that the tungsten atoms were coupled to some protons of mannitol allowed to perform complementary investigations through 2D indirect heteronuclear ^{1}H–^{183}W NMR, in order to precise the sites of chelation of each tungsten atom. For complex M_1, correlations were observed between W-1 and H-5 (strong) and H-4 (weak), whereas W-2 gave three weak correlations with H-3, H-4, and H-6. It indicated that in M_1, the chelating oxygen atoms were O-4,5,6 for W-1 and O-3,4,6 for W-2 (Figure 1). For complex M_2, a strong correlation was found between W-1 and H-4, and a weak correlation between W-2 and H-6, in agreement with M_1 and M_2 forming at the same site of chelation. In M_2, W-1 is bound to O-3,4,5 and W-2 is bound to O-3,5,6.

Ribitol. All the hydroxyl groups of ribitol are in *erythro* configuration; hence, only complexes of type E can be expected, involving the unsymmetrical tetradentate HO-1,2,3,4 site. However, the formation of a single molybdate complex was reported.[9] We also observed a single tungstate complex, as the ^{183}W NMR spectrum showed two signals only (Table 1). The value of

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Table 1. 16.65-MHz ^{183}W NMR Chemical Shifts δ and $^3J_{W,H}$ Coupling Constants of Tungstate Complexes of Alditols[a]

alditol	param	W-1	W-2	Δδ	type
galactitol	δ (ppm)	−79.3	−85.8	6.5	E
	$^3J_{W,H}$ (Hz)	8.3[b] (H-4)	8.3[b] (H-2)		
DL-threitol	δ (ppm)	−59.3	−118.3	59.0	T
ribitol	δ (ppm)	−72.1	−83.9	11.8	E
	$^3J_{W,H}$ (Hz)	unresolved	10.3 (H-2)		
D-mannitol M_1	δ (ppm)	−74.4	−81.6	7.2	E
	$^3J_{W,H}$ (Hz)	9.2[b] (H-5)	8.6[b] (H-3)		
D-mannitol M_2	δ (ppm)	−73.1	−83.1	10.0	E
	$^3J_{W,H}$ (Hz)	10.0 (H-4)	8.9[b] (H-6)		
D-arabinitol A_1	δ (ppm)	−75.3	−82.4	7.1	E
	$^3J_{W,H}$ (Hz)	9.2 (H-4)	5.5 (H-2)		
D-arabinitol A_2	δ (ppm)	−78.1	−82.1	4.0	E
	$^3J_{W,H}$ (Hz)	9.6 (H-3)	5.2 (H-5)		
D-arabinitol A_3	δ (ppm)	−55.5	−120.0	64.5	T
D-glucitol G_1	δ (ppm)	−57.7	−121.6	63.9	T
	$^3J_{W,H}$ (Hz)	8.6 (H-3)	unresolved		
D-glucitol G_2	δ (ppm)	−73.7	−79.2	5.5	E
	$^3J_{W,H}$ (Hz)	9.2 (H-5)	7.75 (H-3)		
D-glucitol G_3	δ (ppm)	−76.2	−78.7	2.5	E
	$^3J_{W,H}$ (Hz)	9.5 (H-4)	7.75		
maltitol	δ (ppm)	−62.8	−118.3	55.4	T
perseitol P_1	δ (ppm)	−77.0	−83.7	6.7	E
	$^3J_{W,H}$ (Hz)	9.35 (H-3)	8.4 (H-5)		
perseitol P_2	δ (ppm)	−72.85	−85.65	12.8	E
	$^3J_{W,H}$ (Hz)	8.9 (H-4)	8.4 (H-3)		
perseitol P_3[c]					
erythro site	δ (ppm)	−74.2	−81.4	7.2	E
	$^3J_{W,H}$ (Hz)	10.8 (H-5)	ND		
threo site	δ (ppm)	−55.4	−117.6	62.2	T

[a] Reference: Na_2WO_4 in alkaline D_2O (by the substitution method[14]). Accuracy: δ ± 0.1 ppm; $^3J_{W,H}$ ± 0.1 Hz. [b] Small additional coupling ($^3J_{W,H} \simeq 2$ Hz). ND: not determined. The types E (*erythro*) and T (*threo*) are defined in the text. [c] Heptadentate ligand with two sites of chelation.

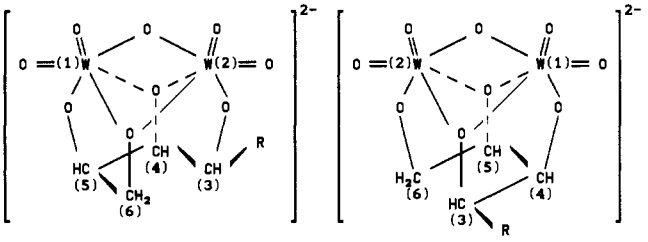

Figure 1. Structures of the ditungstate complexes (type E) of D-mannitol (M_1–M_2) and D-glucitol (G_2–G_3), showing the HO-3,4,5,6 site occupied in two different orientations. R = $CHOHCH_2OH$. The D-mannitol compounds are similar to the molybdate complexes.[21,22]

$\Delta\delta_{W\text{-}1,2}$ (11.8) characterized a species of type E. The signal for W-1 was unresolved, whereas W-2 presented a clear coupling to H-2.

The ^{13}C NMR spectrum (Table 2) was in agreement with a single complex (five peaks). The primary HO-5 group was not involved in the site of chelation (HO-1,2,3,4). The CIS pattern (7-17-8-13) was reminiscent of that for type E and analogous to that found for the molybdate complex.[9]

Among alditols that form complexes of type E, ribitol has a peculiar behavior because it forms a single complex. Moreover, the available data show that the more deshielded atom (therefore W-1) is weakly coupled, whereas W-2 is coupled to H-2. For comparison, both W-1 and W-2 are clearly coupled to a proton of the ligand in other complexes of type E (Table 1). A possible structure for the ribitol species is represented in Figure 2. A comparison with the tungstate complexes of D-mannitol (Figure 1) shows how the reversed orientation of the side chain borne at C-4 creates a steric strain at the site of chelation, forbidding the formation of one of both possible isomers. Evidence for this strain is also provided by the absence of coupling between W-1 and H-4, showing that the corresponding dihedral angle has been modified.

Table 2. 100.62-MHz ^{13}C NMR Chemical Shifts δ and $^1J_{C,H}$ Direct Coupling Constants of Alditols and of Their Tungstate Complexes

	carbon position					
param	1	2	3	4	5	6
			Ribitol			
u, δ (ppm)[a]	63.9	73.4	73.7	73.4	63.9	
c, δ (ppm)[a]	*71.0*	*90.1*	*82.0*	*86.1*	63.7	
c, $^1J_{C,H}$ (Hz)	*146*	*150*	*149*	*150*	143	
Δδ (ppm)	*7.1*	*16.7*	*8.3*	*12.7*	−0.2	
			D-Arabinitol			
u, δ (ppm)[a]	65.3	72.4	72.6	73.1	65.1	
A_1, δ (ppm)	64.9	*82.8*	*83.0*	*92.3*	*71.0*	
$^1J_{C,H}$ (Hz)	143	*148.5*	*147*	*150*	*145*	
Δδ (ppm)	−0.6	*10.4*	*10.4*	*19.2*	*5.9*	
A_2, δ (ppm)	64.7	*79.4*	*91.8*	*83.3*	*73.0*	
$^1J_{C,H}$ (Hz)	142	*149*	*150*	*147*	*145*	
Δδ (ppm)	−0.4	*7.0*	*19.2*	*10.2*	*7.9*	
A_3, δ (ppm)	**74.4**	**86.3**	**83.0**	74.2	65.3	
$^1J_{C,H}$ (Hz)	**145**	**150**	**147**	141	142	
Δδ (ppm)	**9.1**	**13.9**	**10.4**	1.1	0.2	
			D-Glucitol			
u, δ (ppm)[a]	64.7	75.0	71.7	73.2	73.2	65.0
G_1, δ (ppm)	67.0	**83.8**	**86.0**	**83.3**	74.3	66.0
$^1J_{C,H}$ (Hz)	143	**148**	**148**	**148**	143	143
Δδ (ppm)	2.3	**8.8**	**14.3**	**10.1**	1.1	1.0
G_2, δ (ppm)	65.1	75.8	*83.2*	*83.0*	*92.7*	*71.0*
$^1J_{C,H}$ (Hz)	142	144	*148*	*148*	*150*	*146*
Δδ (ppm)	0.4	0.8	*11.5*	*9.8*	*19.5*	*6.0*
G_3, δ (ppm)	64.7	75.6	*80.2*	*92.0*	*85.0*	*73.1*
$^1J_{C,H}$ (Hz)	142	144	*147*	*150*	*148*	*146*
Δδ (ppm)	0.0	0.6	*8.5*	*18.8*	*11.8*	*8.1*
			Maltitol			
u, δ (ppm)[b,c]	63.6	72.3	71.2	82.5	73.4	63.1
c, δ (ppm)	**73.2**	**86.0**	**82.2**	84.1	74.3	63.5
$^1J_{C,H}$ (Hz)	**145**	**151**	**147**	144	143	143
Δδ (ppm)	**9.6**	**13.2**	**11.0**	1.6	0.9	0.4

[a] $^1J_{C,H}$ = 141 Hz for all carbons. δ assigned from literature.[23] u: uncomplexed, c: complexed. Accuracy: δ ± 0.1 ppm; $^1J_{C,H}$ ± 1 Hz. Carbons that bear the chelating oxygen atoms are indicated in bold (T type) or in italics (E type). [b] For the glucitol moiety of maltitol. The carbon atoms of the glucopyranose moiety are not shifted after chelation (Δδ <0.2 ppm). [c] δ assigned from the literature.[24]

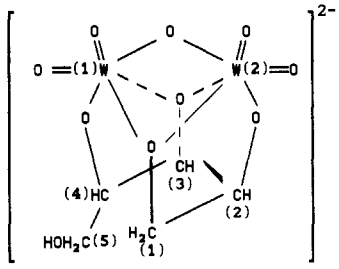

Figure 2. Proposed structure for the single tetradenate ditungstate–ribitol complex (type E) showing the HO-1,2,3,4 site of chelation.

D-Arabinitol. The main signals in the ^{183}W NMR spectrum (Table 1) are two doublets of unequal intensities at δ −75.3 and −78.1 and a multiplet at $\delta \simeq -82$ ppm. The intensity of the multiplet is almost equal to the sum of the intensities of the doublets. It is in agreement with the main species being a pair of type E isomers, A_1 and A_2, for which four doublets may be expected. The site of chelation, assigned from the ^{13}C NMR spectrum is the same as that in the known homologous molybdate complexes, *i.e.* HO-2,3,4,5. In addition, smaller signals are observed at −55.5 and −120 ppm. They are due to a minor species of type T, A_3, which is characterized below from ^{13}C NMR data. Although the W-1 signal (δ −55.5) appeared to be coupled to protons, the small $^3J_{W,H}$ coupling constants could not be determined.

In complex A_1, W-1 gave three correlations with H-4 (strong), H-3, and one of the H-5 atoms (weak). Weak correlations of

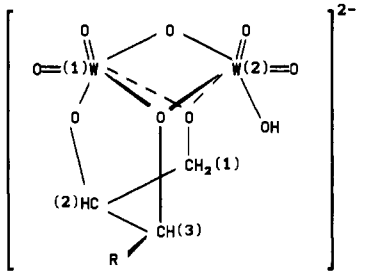

Figure 3. Proposed structures for ditungstate complexex of type T involving tridentate ligands. D-Arabinitol (complex A_3): R = $CHOHCH_2OH$. Maltitol: R = CH(OGlc*p*)$CHOHCH_2OH$.

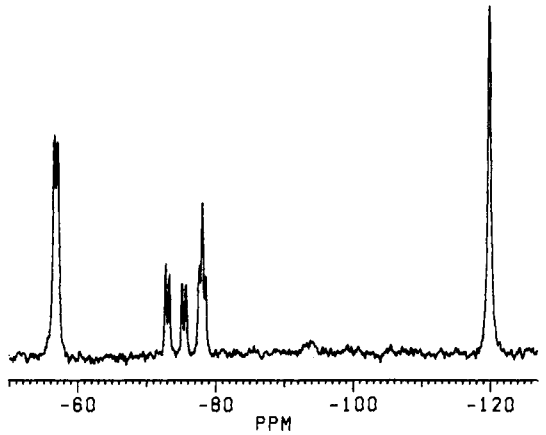

Figure 4. 16.65-MHz ^{183}W NMR spectrum of the mixture of 2:1 tungstate complexes of D-glucitol (4500 scans, 6 h). The multiplets at $\delta \simeq -75$ ppm are due to the pair of G_2–G_3 complexes (type E). The two signals at $\delta \simeq -60$ and -120 ppm are due to the type T complex G_1.

W-2 with H-2, H-3, and a single H-5 atom were also observed. It defined the chelating oxygen atoms as O-3,4,5 for W-1 and O-2,3,5 for W-2.

In complex A_2, two correlations with H-2 and H-3 were found for W-1, whereas W-2 was correlated with H-2, H-4, and H-5 (single). Considering the isomerism of complexes A_1 and A_2, the chelating oxygen atoms were assigned as O-2,3,4 for W-1 and O-2,4,5 for W-2.

^{13}C NMR. The addition of tungstate to an acidic solution of D-arabinitol results in the appearance of 15 new signals that were attributed (Table 2) to complexes A_1 (48%), A_2 (34%), and A_3 (18%). The CIS patterns of the A_1 and A_2 species characterized a pair of isomeric complexes of the *erythro* type. The spectrum of species A_3 was assigned to the complex of type T. Table 2 shows the characteristic CIS pattern of the *threo* HO-1,2,3 site of chelation: the central C-2 is more deshielded ($\Delta\delta$ 13.9) than the lateral C-1,3 ($\Delta\delta$ 9.1 and 10.4). A possible structure is illustrated in Figure 3.

D-Glucitol. From the appearance of six signals in the ^{183}W NMR spectrum (Figure 4), three complexes were identified (Table 1). Contrary to D-arabinitol, the spectrum of the major complex G_1 shows between the tungsten signals the large gap ($\Delta\delta_{W\text{-}1,2}$ 63.9 ppm) that characterizes type T. A single coupling of the more deshielded W-1 signal to H-3 was observed. It is the first measurement of a $^3J_{W,H}$ coupling constant for a complex of type T, giving the first direct experimental evidence that W-1 is bound to O-3. For comparison, the tungsten signals of the structurally analogous complexes of DL-threitol and xylitol appeared only as unresolved multiplets.

The four smaller doublets showed the characteristic gap ($\Delta\delta_{W\text{-}1,2}$ <15 ppm) of type E complexes and were attributed to the G_2–G_3 pair of isomers. Some tungsten–proton couplings were apparent in the 2D correlation spectra. For G_2, W-1 was correlated with H-5 (strong) and H-4 (weak), and W-2 gave a single correlation with H-3. For G_3, W-1 was correlated with H-4 and H-5, but W-2 did not show any correlation.

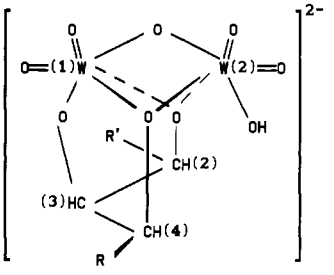

Figure 5. Proposed structure for the ditungstate complex G_1 of D-glucitol (tridentate ligand, type T). R = $CHOHCH_2OH$; R′ = CH_2OH. A related structure was proposed[10] for the xylitol complex, R = R′ = CH_2OH.

^{13}C NMR. The results parallel those obtained for D-arabinitol, as three complexes designed as G_1 (65%), G_2 (20%), and G_3 (15%) were identified from 18 new signals (Table 2). In the major complex G_1, the ligand possesses three deshielded carbon atoms that display the characteristic CIS pattern of type T ($\Delta\delta$ 9-14-10). The site of chelation was assigned to the tridentate *xylo* HO-2,3,4 system. In complexes of type T, W-1 and W-2 are bridged by two oxygen atoms (here O-2,4) of the ligand,[10] and W-1 is additionally bound to the central O-3 atom. Hence the W-1 atom is bound to O-2,3,4, whereas W-2 is bound to O-2,4. A possible structure for complex G_1 is shown in Figure 5.

The G_2 and G_3 species were characterized as a pair of E type complexes homologous to the mannitol species, involving the *arabino* HO-3,4,5,6 site of chelation (Figure 1). In complex G_2, W-1 is chelated by O-4,5,6 and W-2 by O-3,4,6. In complex G_3, W-1 is chelated through O-3,4,5 and W-2 through O-3,5,6.

Maltitol. This disaccharide, obtained by the reduction of maltose, possesses a D-glucitol moiety substituted by a α-D-glucopyranosyl residue at O-4. Šunjic *et al.* have recently obtained[25] circular dichroism data that indicate the formation of a tungstate complex of maltitol, without structure determination. Chelation was reported not to involve the cyclic glucose moiety. We expected that the chelation scheme of the glucitol moiety would be simplified with respect to that of glucitol, as no HO-4 group was available.

The formation constant of the maltitol complex was determined as in previous studies[5]: $\log K_{212} = 18.00 \pm 0.10$. This value lies between that found for DL-threitol (16.95) and those for xylitol (18.50) and D-glucitol (19.15).

^{183}W NMR. The spectrum shows only two signals (Table 1) characteristic for a single complex of type T ($\Delta\delta_{W\text{-}1,2}$ 55.4). As expected, this species is slightly different from the type T complex of D-glucitol (G_1, site of chelation HO-2,3,4, $\Delta\delta_{W\text{-}1,2}$ 63.9).

^{13}C NMR. The study of the spectrum confirms the existence of a single complex of type T (Table 2), as three vicinal carbon atoms (C-1,2,3) of the glucitol moiety are deshielded with the typical CIS pattern ($\Delta\delta$ 9.6–13.7–11.0). No deshielding effects are observed on the carbon atoms of the glucopyranose moiety. It was concluded that maltitol complex tungstate through its single available site of *threo* configuration at HO-1,2,3, in agreement with the analogy of this complex with the A_3 species of D-arabinitol (Figure 3).

Perseitol. The already known P_1-P_2 pair of type E complexes was immediately identified in the ^{183}W NMR spectrum, appearing as four doublets of high intensities in the –80 ppm region (Figure 6). The observation of $^3J_{W,H}$ coupling constants allowed us to perform tungsten–proton correlations. For P_1, W-1 was correlated to H-3 (strong) and H-4 (weak), and W-2 was weakly correlated with H-4 and H-5. For P_2, W-1 was correlated to H-4 (strong) and H-3 (weak), and W-2 showed a single correlation with H-3.

The presence of at least one more complex was revealed by additional signals. Two doublets of low intensities, overlapping

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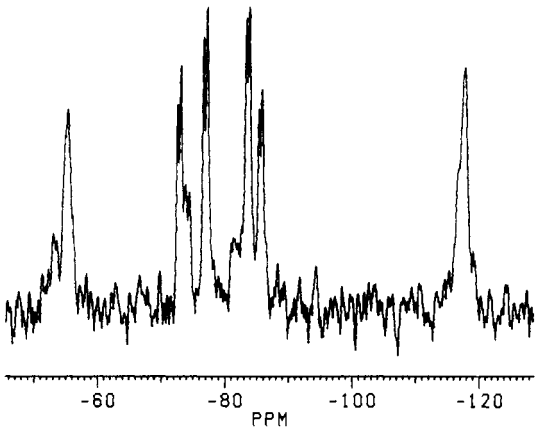

Figure 6. 16.65-MHz ^{183}W NMR spectrum of the mixture of tungstate complexes of perseitol (1539 scans, 2 h). The four major doublets at $\delta \simeq -80$ ppm are due to the pair of P_1–P_2 complexes of type E. The smaller signals in the same range are assigned to the tungsten atoms bound to the *erythro* site of the tetratungstate P_3 species. The signals at $\delta \simeq -60$ and -120 ppm are assigned to the tungsten atoms bound to the *threo* site of the P_3 complex.

Table 3. 100.62-MHz ^{13}C NMR Chemical Shifts δ and $^1J_{C,H}$ Direct Coupling Constants of Perseitol and of Its Tungstate Complexes

	carbon position						
param	1	2	3	4	5	6	7
u, δ (ppm)[a]	65.3	72.3	71.3	70.3	71.2	73.0	65.3
P_1, δ (ppm)	65.9	*79.5*	*92.0*	*83.2*	*82.9*	73.0	65.1
$^1J_{C,H}$ (Hz)	142	*146*	*150*	*152*	*148*	144	143
$\Delta\delta$ (ppm)	0.6	*7.2*	*20.7*	*12.9*	*11.7*	0.0	–0.2
P_2, δ (ppm)	65.2	*81.8*	*83.3*	*91.6*	*79.1*	73.8	65.0
$^1J_{C,H}$ (Hz)	143	*147*	*152*	*151*	*146*	144	143
$\Delta\delta$ (ppm)	–0.1	*9.5*	*12.0*	*21.3*	*7.9*	0.8	–0.3
P_3, δ (ppm)	**74.4**	**86.4**	**82.4**	*81.3*	*92.8*	*82.8*	*71.4*
$^1J_{C,H}$ (Hz)	**147**	**148**	**147**	*148*	*152*	*151*	*149*
$\Delta\delta$ (ppm)	**9.1**	**14.1**	**11.1**	*11*	*21.6*	*9.8*	*6.1*

[a] $^1J_{C,H}$ = 141 Hz for all carbons. δ assigned from literature.[12] u: uncomplexed. Accuracy: $\delta \pm 0.1$ ppm; $^1J_{C,H} \pm 1$ Hz. Carbons that bear the chelating oxygen atoms are indicated in bold (T type) or in italics (E type).

with those of P_1 and P_2, were observed in the region characteristic of type E. The W-1 signal (δ –74.2) was correlated to H-5, whereas two correlations to H-4 and H-7 were found for W-2 (δ –81.4). In addition, two signals of equal intensities were detected, that could not be resolved for the coupling constants, with chemical shifts typical for a complex of type T (W-1′, δ –55.4; W-2′, δ –177.6). The W-1′ signal (δ –55.4) was correlated to H-2. At first sight, these results suggested the formation of two minor complexes.

^{13}C NMR. The assignment of the spectra (14 signals) of the P_1–P_2 isomeric complexes of type E had been made previously[13] and is shown for comparison in Table 3. The site of chelation of these complexes is the tetradentate *galacto* (HO-2,3,4,5) system.

In addition, we expected 14 small signals due to the presence of the minor complexes, but only 7 such signals were observed (Table 3, complex P_3 in 30% yield). Moreover, it appeared that all carbons were deshielded, indicating that the ligand should be heptadentate and pointing to the formation of a single complex that possessed four tungsten atoms, since four signals were apparent in the ^{183}W NMR spectrum. Once assigned, C-4,5,6,7 displayed the typical CIS pattern of a type E site of chelation, whereas C-1,2,3 showed that of a type T site. It must be concluded that two different sites of perseitol chelate two ditungstate groups, forming an unusual bis-dinuclear complex. A possible structure is represented in Figure 7, taking into account that the *arabino* site (C-4,5,6,7) must adopt a *sickle* conformation and the *threo* site (C-1,2,3) a *zigzag* conformation. The sites of chelation have

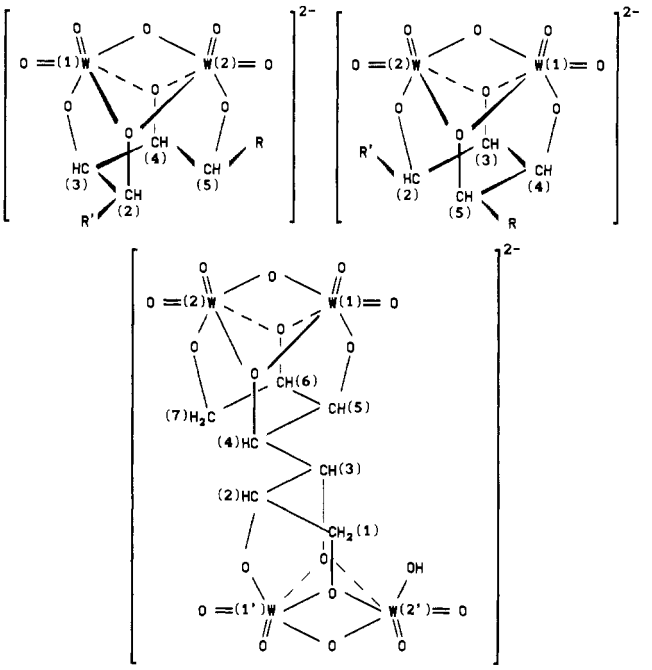

Figure 7. Proposed structures for the tungstate complexes of perseitol. Top: The pair of type E complexes P_1 and P_2 involving the *galacto* HO-2,3,4,5 site. R′ = CH_2OH; R = $CHOHCH_2OH$. Bottom: The tetratungstate complex P_3, involving the type E *arabino* HO-4,5,6,7 site and the type T *threo* HO-1,2,3 site. The torsional angle at O-3,C-3,C-4,O-4 was arbitrarily set at 180°, without experimental evidence.

been oriented *trans* rather arbitrarily. The torsion angle around the C-3,4 bond cannot be precised from available data.

Discussion

First, it should be emphasized that the study of the ^{183}W NMR spectrum of a tungstate–alditol solution allows the fast identification of the number and of the type of the complexes. The subsequent assignment by ^{13}C NMR of the carbon atoms bearing the oxygen atoms involved in the site of chelation is made easier. Additional 2 D heteronuclear correlation experiments allow the identification of some protons coupled to each tungsten atom and give complementary structural information. Previous studies of the molybdate complexes using ^{95}Mo NMR were not so successful,[8,9] since the signals are broad and preclude the measurement of coupling constants. The importance of obtaining independent data on molybdate and tungstate complexes appears more clearly now, because it has been shown that these elements do not always afford homologous species.[10]

Relative Stabilities of the Complexes. The proportions of both species of type E are not equal in a pair of isomeric complexes formed at an asymmetrical *erythro* site of chelation (D-arabinitol, D-glucitol, and perseitol). Previous studies have established that the major complex is always the one in which the more deshielded carbon (bound to W-1) is located on the side of the shortest side chain. This finding suggests that the W-1 atom, which is bound to three vicinal oxygen atoms, occupies the less hindered site. Ribitol, which gives a single complex, does not behave in the same way. A possible reason is the steric strain due to the uncomplexed CH_2OH group borne at C-4, which may decrease the stability of one of the isomeric complexes.

The differences between molybdate and tungstate complexes of alditols will be discussed now. Structures for the molybdate complexes of alditols with *erythro* sites of chelation have been obtained by X-ray crystallography, in the cases of D-mannitol[21,22] and D-erythritol.[26] It is not the case for molybdate *threo* compounds, which have been characterized only from NMR data.[9] However, the proposed structure agrees closely with that found

(26) Ma, L.; Liu, S.; Zubieta, J. *Polyhedron* **1989**, *8*, 1571.

by X-ray crystallography for the molybdate complex of 1,4-dithiothreitol.[27] No structures seem to have been determined for both types of tungstate complexes.

The analogy of the molybdate and tungstate complexes of D-mannitol is well documented[13] from ^{13}C NMR data, demonstrating that two isomeric complexes of type E were formed through the same *arabino* site (HO-3,4,5,6) and that no chelation took place at the *manno* system (HO-2,3,4,5). ^{183}W NMR data confirm that the structures assumed in solution for the tungstate complexes are in complete agreement with those of the known molybdate complexes.[21,22]

With D-arabinitol, molybdate and tungstate form a pair of complexes of type E, in which the *arabino* HO-2,3,4,5 site of chelation is analogous to the HO-3,4,5,6 site of D-mannitol. In the case of tungstate only, a third minor species of type T is found, involving the tridentate *threo* HO-1,2,3 site of chelation. No complex with a *threo* site was observed with molybdate, indicating the poor chelating ability of the HO-1,2,3,4 site of *lyxo* configuration. Since many stable molybdate complexes are known that involve *xylo* systems and a vicinal CH_2OH group,[9] it must be concluded that the molybdate complexes formed at tetradentate *threo* sites are less stable when a lateral coordinating oxygen atom is oriented *erythro*.

Molybdate forms four complexes with D-glucitol, two of type E (*arabino* site, HO-3,4,5,6) and two of type T (*xylo* site HO-1,2,3,4 and *gluco* site, HO-2,3,4,5). With tungstate, only three species are identified: the minor species are the pair of type E complexes similar to their molybdate homologues, whereas the major complex is of type T (*xylo* site, HO-2,3,4). It is interesting to note that, contrary to the tungstate-arabinitol species, the type T complex (which involves three oxygen atoms from secondary hydroxyl groups) is formed in higher proportion than the type E complexes. It may be related to the involvement of O-1 (from the primary CH_2OH group) in the site of chelation of D-arabinitol, which is known to be a destabilizing factor.[9]

In a previous study of perseitol,[13] we characterized only the P_1–P_2 pair of type E tungstate complexes homologous to the molybdate complexes, involving the *galacto* site (HO-2,3,4,5). The small proportion of complex P_3 (lower than 10%) precluded its identification, either from ^{13}C NMR data or during the potentiometric determination of its formation constant. The higher proportion (30%) obtained in the present work is likely due to the use of more acidic conditions. However, the addition of acid to the mixture of alditol and tungstate must be very slow in order to prevent any precipitation of tungsten trioxide. Since the major complexes of perseitol with molybdate and tungstate involve the same *galacto* site as galactitol, the closeness of the formation constants of the complexes of these alditols,[5,13] determined by the potentiometric method, seems a reasonable result. The complex P_3 is probably slightly less stable.

The absence of any molybdate *threo* complex of perseitol may be ascribed to the lack of available tetradentate sites of *threo*–*threo* configuration. On the contrary, in the case of tungstate that may be accommodated at tridentate *threo* sites, the existence of a complex of type T (at HO-1,2,3) was expected. Besides, the formation of other tungstate complexes of type E at the *arabino* site HO-4,5,6,7 was also anticipated, keeping in mind that such species, that involve a CH_2OH group, should be less stable than complexes P_1–P_2 and were not formed with molybdate. Thus the finding that P_3 was a novel tetratungstate species involving the heptadentate ligand with two sites of chelation was totally unexpected. However, while this work was in progress, it came to our attention that tetramolybdate complexes of the same type were recently identified[28] in the reaction of ammonium molybdate with two aldooctoses, D-*erythro*-L-*gluco*-octose and D-*erythro*-L-*manno*-octose. Both complexes are believed to involve acyclic hydrated sugars as octadentate ligands chelating two dimolybdate groups at two tetradentate sites (HO-1,2,3,4 and HO-5,6,7,8).

Structure of the Tetranuclear Perseitol Complex. Tetranuclear molybdate complexes are not uncommon and belong to several structural types. The compound of formula $[Mo_4O_{10}(O_4C_6H_2)_2]^{2-}$ obtained with 2,5-dihydroxybenzoquinone is a bis-dinuclear complex in which the dimolybdate groups are independent.[29] On the contrary, species $[Mo_4O_{11}(cit)_2]^{4-}$ and $[Mo_4O_{11}(mal)_2]^{2-}$, obtained with respectively citrate[30,31] and malate,[32] were structurally characterized as possessing two identical Mo_2O_5 groups linked via a lone oxygen atom, with additional bridging by the ligand anions. With tartrate, two types of tetramolybdate complexes were detected in a potentiometric study:[33] two dinuclear groups are involved in the minor 4:2 species, whereas the prominent 4:4 species presumably involve mononuclear molybdate groups.

Unlike such molybdate species, the corresponding tungstate complexes are not tetranuclear. The malate complexes are at most dinuclear.[34–36] All the tungstate–citrate complexes recently characterized by Cruywagen *et al.* in solution[37] are mono- or dinuclear, and the species $[W_2O_5(cit)_2]^{6-}$ isolated in the solid state[38] was dinuclear. Present evidence also favors the hypothesis that the tungstate complex of perseitol is probably a bis-dinuclear complex and not a tetranuclear species, because the ^{183}W NMR data are close to those for simple dinuclear complexes.

In addition to the three tungstate complexes of perseitol, other species might have been formed like complexes of pure type E (at the *arabino* site HO-4,5,6,7, identical to the arabinitol and mannitol sites) or of pure type T (at the *threo* site HO-1,2,3). The absence of such complexes points to their low stability with respect to that of the bis-dinuclear species P_3 and may indicate the existence of a synergetic effect that would favor the simultaneous complexation of both sites.

Conclusion

By associating ^{183}W and ^{13}C NMR spectroscopies, the study of tungstate complexes of alditols is made much more efficient, especially for compounds that form mixtures of complexes. The number and the nature of the species are rapidly obtained. The analysis of the $^3J_{W,H}$ coupling constants give some insight of the structures of the complexes in solution.

This work confirms that alditols possessing a site of chelation in *threo* configuration do not form homologous chelates with molybdate and tungstate. In this respect, they differ from alditols which possess sites of *erythro* configuration and form similar species with both elements. When two independent sites of chelation are available on the same ligand, as in the case of perseitol or aldooctoses, "mixed" complexes are formed in which a dinuclear metallic group is bound to each site. Such complexes appear to be stronger than species in which a single site of chelation would be involved.

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