^{183}W NMR Studies of Tungstate Complexes of Carbohydrates. 3. Species Formed with All-*threo* Alditols Acting as Tridentate, Tetradentate, or Pentadentate Ligands†

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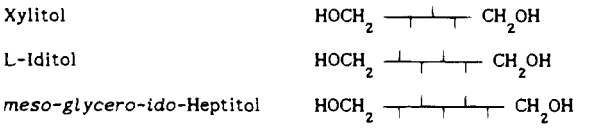
Tungstate complexes of all-*threo* alditols $HOCH_2(CHOH)_{n-2}CH_2OH$ (DL-threitol, xylitol, L-iditol, *meso-glycero-ido*-heptitol) have been studied by multinuclear ^{13}C and ^{183}W NMR. Contrary to the corresponding molybdate species in which the ligands are always tetradentate, the tungstate species exhibit structural variety, depending on the pH of formation. Only the tungstate complexes (type M) formed at pH 7 are homologous to the molybdate species. At pH 7−9, the ligands are tridentate and chelate a ditungstate group in an asymmetrical way (type T). The corresponding tungstate complex of glycerol is reported for the first time. At pH 9−12, dinuclear species of a previously unknown type P are slowly formed by the pentadentate xylitol and iditol. The heptitol affords two complexes of type P, in which the sites of chelation are HO-2,3,4,5,6 (major complex) and HO-1,2,3,4,5. A possible structure, in agreement with ^{13}C and ^{183}W NMR data, is proposed for complexes of type P in which the presence of two WO_6 octahedra linked by an edge is reminiscent of structures of ditungstate subunits of polytungstate ions.

Introduction

The formation of dinuclear molybdate complexes of carbohydrates in aqueous solution has recently received considerable attention[1,2] because of its relevance to catalytic species involved in the C-2 epimerization of aldoses.[3−5] With alditols (Scheme 1), which are derivatives of aldoses obtained by reduction of the aldehyde group and are often used as simple models, ^{13}C NMR spectroscopic data demonstrated the existence of two different series of molybdate complexes, depending on the configuration of the central hydroxyl groups of the tetradentate site of chelation (*threo*, type M, or *erythro*, type E).[6−8] For type E, X-ray structural determinations of solid complexes[9−11] showed a *sickle* conformation, in agreement with NMR data. In the case of type M, a structure involving the ligand in zigzag conformation was proposed from NMR data, in close agreement with that reported for the molybdate complex of dithiothreitol[12] in the solid state.

Tungstate complexes are not so well known, although they are useful for the separation[13] and analysis[14,15] of various carbohydrates. Tungstate and molybdate species are generally assumed to be isostructural.[16] Nevertheless, the formation of tungstate complexes of *erythro* alditols was reported to be slower than that of their *threo* isomers.[17] Moreover, in a chromatographic study on cellulose impregnated with tungstate,[14] the authors remarked that the "pseudo-stability constants" of the complexes of *erythro* alditols slightly decreased from pH 6 to 8, whereas they increased for *threo* alditols like L-threitol, xylitol, D-glucitol, and L-iditol. It might suggest the existence of new complexes at pH above 7 in the latter case.

Scheme 1. Fischer Formulas for Alditols Used (C-1 Is on the Right-Hand Side)



^{13}C NMR is an efficient technique for characterizing the structure of the complexed ligands. The carbon atoms that bear the chelating oxygen atoms exhibit a characteristic deshielding pattern, referred to as the coordination induced shift (CIS). Besides, the study of molybdate complexes by ^{95}Mo NMR in aqueous solution hardly affords information on the environment of the metal atoms[6,18,19] because this quadrupolar nucleus gives broad signals. On the contrary, ^{183}W NMR spectroscopy was recently shown to be a powerful tool for the study of tungstate complexes,[20,21] because this spin $^1/_2$ nucleus gives rise to sharp

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(1) Bílik, V.; Matulová, M. *Chem. Pap.* **1990**, *44*, 257.
(2) Geraldes, C. F. G. C.; Castro, M. M. C. A.; Saraiva, M. E.; Aureliano, M.; Dias, B. A. *J. Coord. Chem.* **1988**, *17*, 205.
(3) Bílik, V. *Chem. Zvesti* **1972**, *26*, 76.
(4) Hayes, M. L.; Pennings, N. J.; Serianni, A. S.; Barker, R. *J. Am. Chem. Soc.* **1982**, *104*, 6764.
(5) Clark, E. L., Jr.; Hayes, M. L.; Barker, R. *Carbohydr. Res.* **1986**, *153*, 263.
(6) Chapelle, S.; Verchère, J. F.; Sauvage, J. P. *Polyhedron* **1990**, *9*, 1225.
(7) Matulová, M.; Bílik, V.; Alföldi, J. *Chem. Pap.* **1989**, *43*, 403.
(8) Chapelle, S.; Verchère, J. F. *Carbohydr. Res.* **1991**, *211*, 279.
(9) Godfrey, J. E.; Waters, J. M. *Cryst. Struct. Commun.* **1975**, *4*, 5.
(10) Hedman, B. *Acta Crystallogr.* **1977**, *B 33*, 3077.
(11) Ma, L.; Liu, S.; Zubieta, J. *Polyhedron* **1989**, *8*, 1571.
(12) Burgmaier, S. J. N.; Stiefel, E. I. *Inorg. Chem.* **1988**, *27*, 2518.
(13) Angus, H. J. F.; Bourne, E. J.; Weigel, H. *J. Chem. Soc.* **1965**, 21.
(14) Angus, H. J. F.; Briggs, J.; Sufi, N. A.; Weigel, H. *Carbohydr. Res.* **1978**, *66*, 25.
(15) Briggs, J.; Chambers, I. R.; Finch, P.; Slaiding, I. R.; Weigel, H. *Carbohydr. Res.* **1980**, *78*, 365.
(16) Cotton, F. A.; Wilkinson, G. *Modern Inorganic Chemistry*, 5th ed; John Wiley: New York, 1988.
(17) Verchère, J. F.; Sauvage, J. P.; Rapaumbya, G. R. *Analyst* **1990**, *115*, 637.
(18) Verchère, J. F.; Chapelle, S. *Polyhedron* **1989**, *8*, 333.
(19) Matulová, M.; Bílik, V. *Chem. Pap.* **1990**, *44*, 703.
(20) Chapelle, S.; Verchère, J. F. *Inorg. Chem.* **1992**, *31*, 648.

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signals that are sometimes coupled to vicinal protons, allowing thorough investigation of structural details. Previous studies[6,18,20] of the complexes of alditols possessing a site of chelation with *threo* configuration (threitol, xylitol) revealed the formation of two different series. The ligands are tetradentate in the molybdate complexes (type M) and tridentate (type T) in the tungstate species.

This work reports a study of the tungstate complexes of the "all-*threo*" alditols, namely, in the order of increasing chain length: threitol, xylitol, iditol, and *meso-glycero-ido*-heptitol. Contrary to molybdate that forms only one complex (type M) with each ligand at pH < 10, tungstate affords mixtures of species up to pH 12, the nature and proportions of which depend on the acidity.

Experimental Section

All chemicals were commercially available, of the purest grade and were used as received. *meso-glycero-ido*-Heptitol was prepared according to the literature.[22]

Solutions of the complexes in water containing deuterium oxide (10 % v/v) were prepared by mixing in 2.5:1 ratio disodium molybdate (or tungstate) dihydrate and the alditol, followed by stepwise addition of concentrated HCl. The concentration of molybdate or tungstate was 2.5 M (1.0 M for the heptitol, available in small amount). The pH values were measured with a Radiometer MI-412 combined micro glass electrode (external diameter 2 mm) and a Metrohm 632 pH-meter. The electrode was calibrated with fresh solutions made from commercial buffers (pH 7.00 and 4.00). The samples were not protected form atmospheric carbon dioxide, but were kept in stoppered NMR tubes.

The NMR spectra were recorded at 297 K on two Bruker spectrometers, AM-360 and ARX-400, equipped with a multinuclear 5-mm probe (ARX-400), a multinuclear 10-mm probe (ARX-400 and AM 360), and a dual (^{13}C, ^{1}H) 5-mm probe (AM-360). The frequencies for nuclei ^{13}C and ^{183}W were respectively 90.56 and 14.99 MHz (AM-360) and 100.62 and 16.65 MHz (ARX-400). The reference for ^{183}W NMR was a 2 M solution of Na_2WO_4 in alkaline deuterium oxide. The reference for ^{13}C was an aqueous solution of sodium 2,2,3,3-tetradeutero-3-trimethyl-silylpropionate (TMSP). Experimental details for the recording of the ^{13}C NMR spectra were described in previous papers.[6,8,20] When the integration of peaks areas was needed, the experiments were made with particular conditions, i.e. the NOE was suppressed by gating off the decoupler during the relaxation delay (10 s).

1 D ^{183}W NMR spectra were obtained with a sweeping range of 8 kHz, an acquisition time of 1 s, a relaxation delay of 1 s and a digital resolution of 0.5 Hz/pt. Because the peaks were broad for the complexes of xylitol and iditol at pH 7, the relaxation delay was suppressed. The pulse width corresponds to a 90° tip angle (40 μs for the AM 360 and 45 μs for the ARX 400). Effects of probe acoustic ringing on the baseline were minimized by applying four to six left shifts to the free induction decay prior to Fourier transform.

The complexes were identified by the appearance of specific signals in the ^{13}C and ^{183}W NMR spectra. When necessary, the carbon atoms of the ligands were assigned by 2 D heteronuclear correlation experiments using polarization transfer from ^{1}H to ^{13}C through $^{1}J_{C,H}$ (CHCORR)[23] and $^{3}J_{C,H}$ (COLOC)[24] coupling constants. The sites of chelation were defined from the deshielding patterns of the carbon atoms of the ligands.

Results and Discussion

Molybdate–Iditol Complex. A ^{13}C NMR study showed that L-iditol formed a single molybdate complex at pH 5–10. Relevant data are given in Table 1. Three signals only are observed in 1:1:1 ratio, indicating that the symmetry of the ligand is retained in the complex. Since the signals for both CH_2OH groups are practically unshifted, contrary to those for the CHOH groups that are deshielded by 11–13 ppm, the site of chelation was assigned to the tetradentate *ido* system (HO-2,3,4,5). The ^{95}Mo NMR spectrum was reported to show a single, broad signal[19] (δ, 22 ppm) typical for a *threo* site of chelation (δ, 21 ppm in the case of xylitol[6,19]). Thus this iditol complex is homologous to the dinuclear complexes of tetradentate threitol and xylitol previously described.[6,7,19]

Table 1. 90.56-MHz ^{13}C NMR Data for Xylitol, L-Iditol, Their Tetradentate Molybdate and Tungstate Complexes (M), and Their Tridentate (T) and Pentadentate (P) Tungstate Complexes[a]

carbon		C-1	C-2	C-3	C-4	C-5	C-6
L-iditol	δ	64.4	73.3	72.6	72.6	73.3	64.4
	$^{1}J_{C,H}$	142	141	141	141	141	142
complex M (Mo)	δ	63.7	86.0	83.6	83.6	86.0	63.7
	$^{1}J_{C,H}$	145	146	149	149	146	145
	$\Delta\delta$	−0.7	*12.7*	*11.0*	*11.0*	*12.7*	−0.7
	ΔJ	3	5	8	8	5	3
complex M (W)	δ	63.5	84.8	83.7	83.7	84.8	63.5
	$^{1}J_{C,H}$	140.5	147	150	150	147	140.5
	$\Delta\delta$	−0.9	*11.5*	*11.1*	*11.1*	*11.5*	−0.9
	ΔJ	−1.5	6	9	9	6	−1.5
complex T	δ	65.7	82.6	85.3	82.4	75.2	63.7
	$^{1}J_{C,H}$	143	146	146	146	140	143
	$\Delta\delta$	1.3	*9.3*	*12.7*	*9.8*	1.9	−0.7
	ΔJ	1	5	5	5	−1	1
complex P	δ	78.4	83.7	86.0	83.2	88.0	65.3
	$^{1}J_{C,H}$	145	146	146	146	146	143
	$\Delta\delta$	*14.0*	*10.4*	*13.4*	*10.6*	*14.7*	0.9
	ΔJ	3	5	5	5	5	1
xylitol	δ	63.8	72.9	71.7	72.9	63.8	
	$^{1}J_{C,H}$	142.5	142	140.5	142	142.5	
complex M (Mo)[b]	δ	63.1	85.5	82.3	83.2	76.1	
	$^{1}J_{C,H}$	142	149	149	148	146	
	$\Delta\delta$	−0.7	*12.6*	*10.6*	*10.3*	*12.3*	
	ΔJ	−0.5	7	8.5	6	3.5	
complex M (W)[c]	δ	63.4	84.8	82.2	84.2	75.5	
	$\Delta\delta$	−0.4	*11.9*	*10.5*	*11.3*	*11.7*	
	$^{1}J_{C,H}$	139	ND	151	ND	152	
	ΔJ	−3.5	ND	10.5	ND	9.5	
complex T[d]	δ	65.3	81.9	85.0	81.9	65.3	
	$^{1}J_{C,H}$	140	145	146	145	140	
	$\Delta\delta$	1.5	*9.0*	*13.3*	*9.0*	1.5	
	ΔJ	−2.5	3	5.5	3	−2.5	
complex P	δ	78.1	81.9	84.9	81.9	78.1	
	$^{1}J_{C,H}$	145	146	146	146	145	
	$\Delta\delta$	*14.3*	*9.0*	*13.2*	*9.0*	*14.3*	
	ΔJ	2.5	4	5.5	4	2.5	

[a] δ assigned from the literature.[25] δ (± 0.1 ppm); $^{1}J_{C,H}$ (± 1 Hz); $\Delta\delta$ in ppm and ΔJ in Hz. ND: not determined. $\Delta\delta$ values for carbon atoms that bear chelating oxygen atoms are italic. [b] Reference 6. [c] Because of the broad signals, some of the coupling constants could not be determined. [d] Reference 20.

Tungstate Complexes of Alditols at Neutral pH. At pH ≤ 7, the ^{13}C NMR spectra of mixtures of alditols ($n \geq 4$) and disodium tungstate indicate the presence of one or two complexes. The major one exhibits quite broad signals, except in the case of threitol. The spectra are simplified for threitol (two peaks) and iditol (three peaks), indicating that the chelating ligands are symmetrical. The deshielding CIS patterns (Tables 1–3) are very similar ($\Delta\delta$, 12-11-11-12 ppm) and indicate that four vicinal hydroxyl groups are involved in the site of chelation. It may be concluded that the four alditols afford an homologous series of tungstate complexes, similar to the already reported series of molybdate complexes (type M), in which the ligands are tetradentate and adopt the *zigzag* conformation (Figure 1)

(21) Chapelle, S.; Sauvage, J. P.; Verchère, J. F. *Inorg. Chem.* **1994**, *33*, 1966.
(22) Onishi, H.; Perry, M. B. *Can. J. Microbiol.* **1972**, *18*, 925; Pratt, J. W.; Richtmyer, N. K.; Hudson, C. S. *J. Am. Chem. Soc.* **1952**, *74*, 2210.
(23) Bax, A.; Morris, G. *J. Magn. Reson.* **1981**, *42*, 501.
(24) Kessler, H.; Griesinger, C.; Zarbock, J.; Loosli, H. R. *J. Magn. Reson.* **1984**, *57*, 331.
(25) Bock, K.; Pedersen, C. *Adv. Carbohydr. Chem. Biochem.* **1983**, *41*, 27.

Table 2. 100.62-MHz ^{13}C NMR Data for *meso-glycero-ido*-Heptitol and Its Tetradentate (M) and Pentadentate (P) Tungstate Complexes[a]

carbon		C-1	C-2	C-3	C-4	C-5	C-6	C-7
heptitol[b]	δ	64.4	73.5	72.6	73.5	72.6	73.5	64.4
	$^1J_{C,H}$	140.5	140	138	140	138	140	140.5
complex M[c]	δ	64.7	85.2	84.2	85.3	84.2	74.0	64.7
	$\Delta\delta$	0.3	*11.7*	*11.6*	*11.8*	*11.6*	0.5	0.3
complex P_1[d]	δ	66.0	88.6	84.3	86.8	84.3	88.6	66.0
	$^1J_{C,H}$	143.5	145	145.5	143	145.5	145	143.5
	$\Delta\delta$	1.6	*15.1*	*11.7*	*13.3*	*11.7*	*15.1*	1.6
	ΔJ	3	5	7	3	7.5	5	2.5
complex P_2[d]	δ	79.1	83.7	86.4	84.0	88.1	75.8	64.5
	$^1J_{C,H}$	145.5	146	147	145.5	145	143.5	143.5
	$\Delta\delta$	*14.7*	*10.2*	*13.8*	*10.5*	*15.5*	2.3	0.1
	ΔJ	5	6	9	5.5	7	3.5	3.5

[a] δ ($\pm$ 0.1 ppm); $^1J_{C,H}$ ($\pm$ 1 Hz); $\Delta\delta$ in ppm and ΔJ in Hz. $\Delta\delta$ values for carbon atoms that bear chelating oxygen atoms are italic. [b] Because of different n.o.e., the intensities of CHOH signals were almost equal (not in the expected 3:2 ratio). The assignment of the spectrum was based on 2 D homo- and heteronuclear experiments.[c] pH 7.0, broad signals are obtained for complex M, that preclude the determination of the coupling constants $^1J_{C,H}$. [d] pH 9.2, after two months: free ligand 15%, P_1 75%, P_2 10%.

Table 3. ^{13}C NMR Data for Glycerol, Threitol, and Their Tungstate Complexes[a]

carbon		C-1	C-2	C-3	C-4
glycerol	δ (ppm)	63.7	73.2	63.7	
complex T	δ (ppm)	72.9	86.2	72.9	
	$\Delta\delta$ (ppm)	*9.2*	*13.0*	*9.2*	
threitol	δ (ppm)	64.8	73.6	73.6	64.8
	$^1J_{C,H}$ (Hz)	143	142.5	142.5	143
complex M (Mo)[b]	δ (ppm)	77.0	83.4	83.4	77.0
	$\Delta\delta$ (ppm)	*12.2*	*9.8*	*9.8*	*12.2*
	$^1J_{C,H}$ (Hz)	144	147	147	144
	ΔJ (Hz)	1	4.5	4.5	1
complex M (W)	δ (ppm)	75.3	82.8	82.8	75.3
	$\Delta\delta$ (ppm)	*10.5*	*9.2*	*9.2*	*10.5*
	$^1J_{C,H}$ (Hz)	148.5	142.5	142.5	148.5
	ΔJ (Hz)	5.5	0	0	5.5
complex T[c]	δ (ppm)	74.3	86.7	83.0	66.6
	$\Delta\delta$ (ppm)	*9.5*	*13.1*	*9.4*	1.8
	$^1J_{C,H}$	144	149	147	143
	ΔJ	1	6.5	4.5	0

[a] δ ($\pm$ 0.1 ppm); $^1J_{C,H}$ ($\pm$ 1 Hz); $\Delta\delta$ in ppm and ΔJ in Hz. $\Delta\delta$ values for carbon atoms that bear chelating oxygen atoms are italic. [b] Reference 6. [c] Reference 20.

deduced from NMR results[6,7,19] and characterized in the solid state for the dithio analog of threitol.[12]

^{183}W NMR spectra were obtained for the complexes of xylitol and iditol (Figure 2a), but not for the heptitol (used in low concentration only). They showed a single, but broad signal ($\Delta\nu_{1/2}$, 140 Hz for iditol, 35 Hz for xylitol) at $\delta \simeq -93$ ppm (Table 4). At this pH, uncomplexed tungstate is present as the heptatungstate ion[26] $[W_7O_{24}]^{6-}$, which gives three sharp resonances in 1:4:2 ratio at δ, +269, −92, and −180 ppm.[27,28] The large proportion of heptatungstate precluded the observation of the signal of the threitol complex (proportion 10%) that probably overlapped with the heptatungstate signal at −92 ppm. The dinuclear, symmetrical structure shown in Figure 1 predicts, for the iditol complex, two equivalent tungsten atoms that would appear as a single peak. Besides, two peaks are expected for the xylitol species. However, these two close signals may overlap in the observed broad signal. Finally, by analogy with complexes formed by alditols of *erythro* configuration (type E) that are always characterized by two signals at $\delta \simeq -75$ ppm,[20] with little variations around this value for the different alditols, the −93 ppm range will probably be a characteristic "fingerprint" for complexes of type M, although two examples only are presented in this paper.

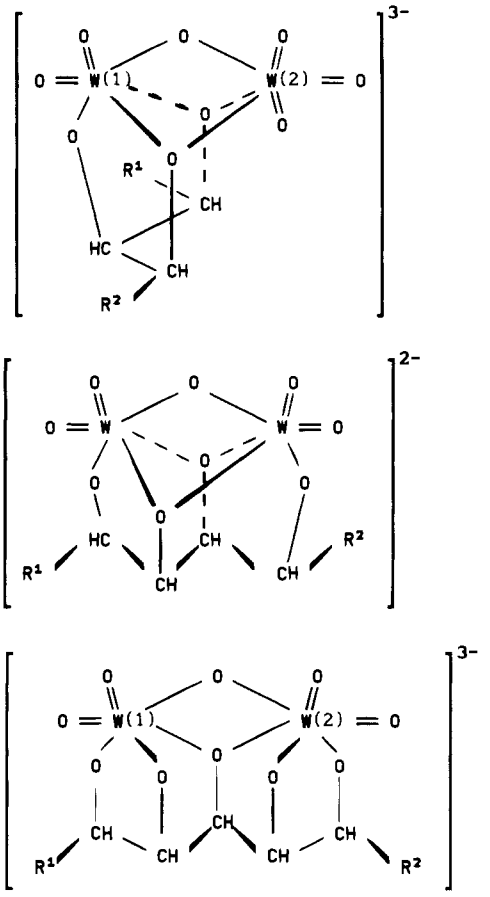

Figure 1. Proposed structures for the ditungstate complexes of all-*threo* alditols. For type T (top), the signal at *ca* −60 ppm is attributed to W-1, the signal at *ca* −120 ppm to W-2. Glycerol, $R^1 = R^2 = H$. Threitol, $R^1 = H$, $R^2 = CH_2OH$. Xylitol, $R^1 = R^2 = CH_2OH$. Iditol, $R^1 = CH_2OH$, $R^2 = CHOH\text{-}CH_2OH$. Type M (middle) is common to molybdenum and tungsten. Threitol, $R^1 = R^2 = H$. Xylitol, $R^1 = H$, $R^2 = CH_2OH$. Iditol, $R^1 = R^2 = CH_2OH$. Heptitol, $R^1 = CH_2OH$, $R^2 = CHOH\text{-}CH_2OH$. For type P (bottom), the signal at 93.4 ppm is attributed to W-1, the signal at 82.3 ppm to W-2 in the complex of iditol, $R^1 = H$, $R^2 = CH_2OH$. Xylitol, $R^1 = R^2 = H$. Heptitol: P_1, $R^1 = R^2 = CH_2OH$; P_2, $R^1 = H$, $R^2 = CHOH\text{-}CH_2OH$.

The relative stabilities of the tungstate species of type M were estimated from the percents of ligands occuring in complexed form in the ^{13}C NMR spectra recorded in similar conditions, at pH 7: heptitol 100%, iditol 60%, xylitol 30%, and threitol 10%. This apparent influence of the chain length is actually related to the general rule that chelation by CH_2OH groups is less favorable than chelation by internal CHOH groups, for entropic reasons.[6] The reproducibility of the proportions of complexes existing at a given pH and the reversibility of the equilibria when the pH was varied were carefully verified.

Tungstate Complexes of Alditols at pH 8−9. The ^{13}C NMR spectra of tungstate−iditol mixtures at pH $\simeq$ 8.5 indicate the presence of a major complex similar to those[20] reported for threitol and xylitol (type T), involving the tridentate (HO-2,3,4) *xylo* site of chelation (Tables 1 and 3). The ^{183}W NMR spectrum (Figure 2b) shows two signals, characteristic for two tungsten atoms bound respectively to three (δ, −61.5) and two

(26) Cruywagen, J. J.; van der Merwe, I. F. J. *J. Chem. Soc., Dalton Trans.* **1987**, 1701.
(27) Maksimovskaya, R. I.; Burtseva, K. G. *Polyhedron* **1985**, *4*, 1559.
(28) Hastings, J. J.; Howarth, O. W. *J. Chem. Soc., Dalton Trans.* **1992**, 209.

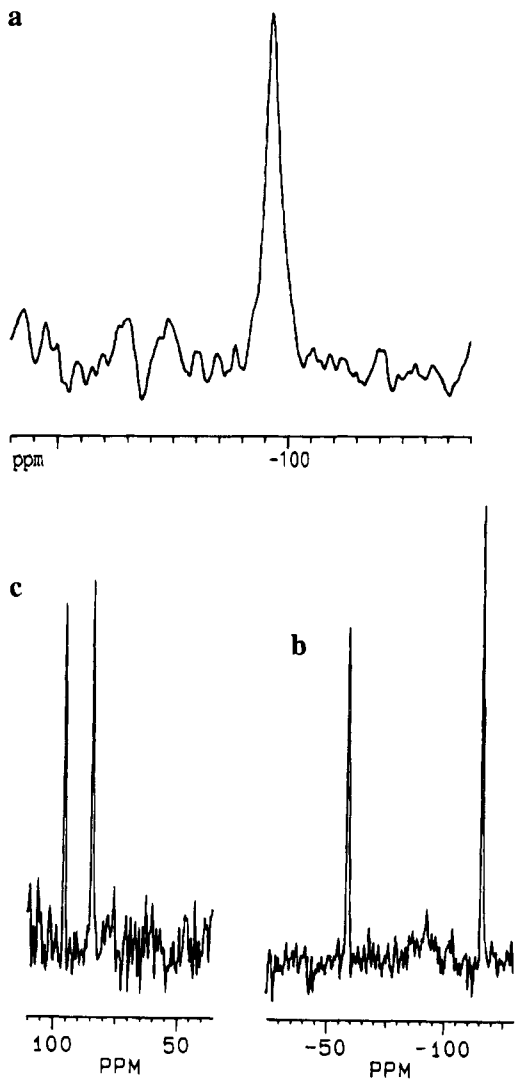

Figure 2. (a) 16.65-MHz ^{183}W NMR spectrum of the 2:1 tungstate complex of iditol (type M) at pH 7.0 (43970 scans, 12 h). (b) 14.99-MHz ^{183}W NMR spectrum of the 2:1 tungstate complex of iditol (type T) at pH 9.2 (4300 scans, 2.5 h). (c) 14.99-MHz ^{183}W NMR spectrum of the 2:1 tungstate complex of iditol (type P) at pH 10.2 (4200 scans, 2.5 h).

Table 4. ^{183}W NMR Chemical Shifts δ (in ppm) for Tungstate Complexes of All-*threo* Alditols[a]

alditol	complex M	complex T	complex P
DL-Threitol	ND	−59.3/−118.3[b]	NF
Xylitol	−92.0[c]	−61.7/−120.8[b]	93.3
L-Iditol	−93.8[c]	−61.5/−118.6	82.3/93.4

[a] ND: not determined. NF: complex not formed. Complexes of type M obtained at pH 7; type T, pH 7−9; type P, pH 9−12. [b] From ref. 20. [c] Broad signals: $\Delta\nu_{1/2}$, 35 Hz (xylitol), 140 Hz (iditol).

oxygen atoms (δ, −118.6 ppm) of the ligand. Vicinal coupling of these tungsten atoms to protons of the ligands was not detected for both signals, as is frequently the case for complexes of type T.[21] Unexpectedly, no complex of type T was formed by the heptitol, which gave only pentadentate complexes (discussed below) at pH ≥ 9.

The finding of complexes involving tridentate ligands suggested that glycerol (1,2,3-propanetriol) should also chelate tungstate. Thus we recorded the ^{13}C NMR spectrum of a glycerol-tungstate mixture at pH 9.0 (Table 3) and found three deshielded signals (CIS pattern: $\Delta\delta$, 9-13-9 ppm) corresponding to the expected complex. Its low proportion (10%) precluded the measurement of its ^{183}W NMR spectrum. Our result is contrary to the previous statement that glycerol does not react with tungstate.[13−15] On the other hand, glycerol was reported not to react with molybdate,[29] in agreement with the observation that all known molybdate complexes of alditols involve tetradentate ligands. We verified that no changes occured in the ^{13}C NMR spectrum of glycerol with addition of disodium molybdate in the pH range 4.5−7.8.

The order of stabilities in series T is, according to the proportions at equilibrium at pH ≃ 9: threitol 45%, xylitol 20% (in the presence of other complexes), iditol 15% (in the presence of other complexes), glycerol 10% and heptitol none. The low stability of the glycerol species can be accounted for by the chelation of two CH_2OH groups, together with the higher stability of the threitol complex (only one chelating CH_2OH group). Besides, the complexes of xylitol and iditol involve only CHOH groups and should present enhanced stabilities. This is not the case, probably because the formation of other complexes competes with that of the complex of type T. Accordingly, the heptitol, that gives two pentadentate species (see below) does not form any complex of type T at pH ≃ 9.

Tungstate Complexes of Alditols at pH 9−12. When alditols with n ≥ 5 react with tungstate at pH > 9, new species are detected in the ^{13}C and ^{183}W NMR spectra. With iditol, a single complex is formed in 25% yield at pH 10.2. It is a dinuclear species of an unprecedented type, as its ^{183}W NMR spectrum (Figure 2c) shows two signals of equal intensities with *positive* chemical shifts (δ 82.3 and 93.4 ppm). The assignment of the ^{13}C NMR spectrum (Table 1) indicates that the ligand is pentadentate (HO-1,2,3,4,5), as all carbon atoms but C-6 are deshielded by at least 10 ppm and have enhanced $^1J_{C,H}$ values. The site of chelation is almost symmetrical, as shown by its CIS deshielding pattern: $\Delta\delta$, 14-10-13-11-15 ppm.

A similar complex is formed with xylitol, always as a minor species in mixture with the complex of type T (Table 1). Only three ^{13}C NMR signals in 2:2:1 ratio are observed, indicating that the ligand is perfectly symmetrical and that all five hydroxyl groups are involved in chelation. The deshielding pattern is close to that for iditol: $\Delta\delta$, 14-9-13-9-14 ppm. The ^{183}W NMR spectrum shows a single signal at δ 93.3 ppm (Table 4), the shape and line width of which suggest a small coupling to protons (ca. 3−4 Hz) that could not be measured accurately. By comparison with the δ values for the complex of iditol, and considering the symmetry of the site of chelation, the presence of two equivalent tungsten atoms is very likely. The complexes of xylitol and iditol therefore belong to the same type which is referred to as type P.

Since heptitol does not form any complex of type T, the formation of species of type P begins at a lower pH. After 1 day at pH 9.2, two complexes P_1 (major) and P_2 in 4:1 ratio are identified, together with 50% uncomplexed ligand. Complex formation is slow, and the proportion of complexed ligand reaches 85% after 2 months (P_1, 75%). Such kinetic effects are common in the chemistry of tungstate complexes of alditols.[17,30]

Owing to the small available amount of heptitol (50 mg), 1 D ^{183}W NMR experiments could not be made (the nucleus is of low sensitivity, due to its low natural abundance and its small magnetogyric ratio). Moreover, 2 D ^{1}H−^{183}W experiments were unsuccessful, since the tungsten signals were probably not coupled to protons. The assignments of the ^{13}C NMR spectra of species P_1 and P_2 were made through 2 D ^{13}C−^{1}H hetero-

(29) Bourne, E. J.; Hutson, D. H.; Weigel, H. *J. Chem. Soc.* **1961**, 35.
(30) Cervilla, A.; Ramirez, J. A.; Beltrán-Porter, A. *Transition Met. Chem.* **1983**, *8*, 21.
(31) Searle, M. S.; Williams, D. H. *J. Am. Chem. Soc.* **1992**, *114*, 10690.

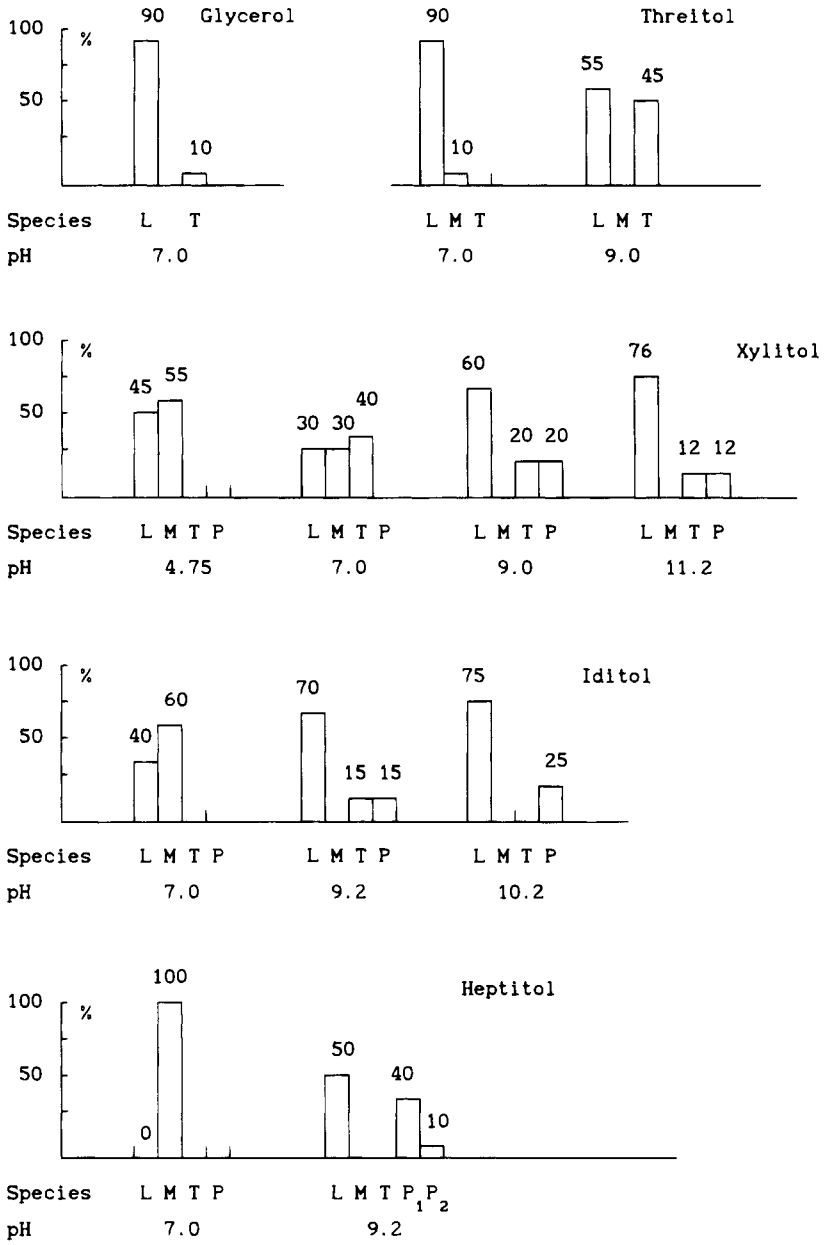

Figure 3. Percent of free and complexed alditols in the presence of disodium tungstate (WO_4^{2-}:L = 2.5), at several pH values, determined from ^{13}C NMR spectra obtained with suppression of n.o.e.. The proportions are accurate by ±5%. L = free ligand, M, T, and P refer to the corresponding types of tungstate complexes. The strength of complexation in the heptitol system should not directly be compared with the other systems since the ionic media are different, $[Na^+]$ = 2 and 5 M respectively.

nuclear correlation experiments[23,24] and are given in Table 2. The major species P_1 gave four signals in 2:2:2:1 ratio, indicating a symmetrical structure of the ligand due to the central location of the site of chelation (HO-2,3,4,5,6). The CIS pattern was $\Delta\delta$, 15-12-13-12-15 ppm. For P_2, the seven peaks found in the ^{13}C NMR spectrum (Table 2) indicate an asymmetrical ligand chelating through HO-1,2,3,4,5 with a CIS pattern (δ, 15-10-14-10-15 ppm) that characterizes a symmetrical site of chelation similar to that found in other complexes of type P. The slight variations in CIS patterns in the various complexes of type P are probably due to differences in the substitution of the site of chelation, in which both lateral carbon atoms bear identical groups in xylitol and P_1 but different groups (R,H and H,H) in iditol and P_2.

Structure of the Tungstate Complexes of Type P. For the new complexes of type P, the symmetry observed for the xylitol compound and complex P_1 of the heptitol allowed us to drawa possible structure (Figure 1) taking into account the presence of two tungsten atoms in the VI oxidation state, which generally occur as *cis*-dioxo groups bridged by μ-oxygen atoms. Alditols with hydroxyl groups in *threo* configurations must adopt a zigzag conformation[6,7,12,19] in order to have them pointing on the same side. The iditol complex only differs from the xylitol species by the CH_2OH substituent borne at C-5, which induces the non-equivalence of its tungsten atoms. W-1 bound to HO-1,2,3 possesses the same environment as the tungsten atoms of the xylitol complex, and thus was assigned the δ value 93 ppm. Therefore, the 82 ppm value was attributed to W-2 bound to HO-3,4,5.

The structure of the ditungstate complexes of type P is close to those of tungstate polyanions[16] since the ditungstate group is built up from two WO_6 octahedra sharing an edge. Besides, those of the complexes of types M and T are fundamentally different, as the tungsten octahedra share a face.[6,20,21] Such a

difference in the environment of tungsten atoms may justify the large difference between the ^{183}W NMR chemical shifts in species T and M ($\delta < 0$) and P ($\delta > 0$). It may be recalled that heptatungstate $[W_7O_{24}]^{6-}$ exhibits three NMR signals[27,28] at δ −92 and −180 ppm (crown octahedra) and +269 ppm (the "buried" octahedra that shares six edges), showing that small structural changes may cause important deviations in the ^{183}W NMR chemical shifts.

Considering now the ligands, the typical mean CIS patterns for the carbon atoms of the site of chelation (type P, $\Delta\delta$, 15-10-13-10-15 ppm; type T, $\Delta\delta$, 9-13-9 ppm; type M, $\Delta\delta$, 12-11-11-12 ppm) are in the same range for species of the three types, showing that no important difference exists between the geometry of the tri-, tetra- or pentadentate ligands in the various complexes. It may reflect the ligands being in *zigzag* conformation in all species.

pH Dependence of the Complexes. The data displayed in Figure 3 clearly indicate that the ratios [M]/[T] are pH-dependent, since T species are generally not observed at pH 7, whereas no M species exist near pH 9. It suggests that species of type T are obtained by proton abstraction from M, in contradiction with the previous claim[20] that complexes of both types M and T have the same stoichiometry $(2,1,2)^{2-}$. A re-examination of our earlier data showed that whereas the composition of species of type M was unambiguously established from titration curves (equivalence for 1 H^+/W), similar results cannot be attributed with certainty to type T species. On the contrary, the present study shows that in the conditions of the potentiometric study (pH *ca.* 7−8) the major complexes are generally not of type T, but of type M. It follows that species of type T should not be formulated $(2,1,2)^{2-}$, but $(2,1,1)^{3-}$. A possible structure is represented in Figure 1, together with that for type M reported in literature.[6,12,20,21] It differs from that proposed previously by the tungsten atom on the right-hand side bearing an ionized oxygen atom instead of an hydroxyl group. Accordingly, it is not unreasonable to postulate that the pK_a of an hydroxyl group bound to a tungsten atom would be close to 7.

The formation of the ditungstate complexes of type P only occurs in very alkaline medium, indicating proton abstraction from the $(2,1,2)^{2-}$ complexes of type M. Since it appears that the ratios [T]/[P] do not vary appreciably with acidity in the pH range 9−12 (Figure 3), both types T and P are probably in the same protonation state and possess the $(2,1,1)^{3-}$ stoichiometry. It agrees with the proposed structure for type P (Figure 1) that corresponds to a general formula $[(WO_2)_2O(H_{n-5}L)]^{3-}$. Thus the overall formation equilibria of the various complexes may be written:

type M: $2WO_4^{2-} + H_nL + 2H^+ \rightleftarrows [(WO_2)_2O(H_{n-4}L)]^{2-} + 3H_2O$

type T: $2WO_4^{2-} + H_nL + H^+ \rightleftarrows [(WO_2)_2O_2(H_{n-3}L)]^{3-} + 2H_2O$

type P: $2WO_4^{2-} + H_nL + H^+ \rightleftarrows [(WO_2)_2O(H_{n-5}L)]^{3-} + 3H_2O$

Below pH 4, the $(2,1,2)^{2-}$ molybdate complexes of alditols are known[6] to protonate to $(2,1,3)^-$ species, but the formation of analogous protonated tungstate species is not documented.[17] In this work, the tungstate solutions were acidified up to pH 4 without noticing the appearance of new complexes.

Relative Stabilities of the Tungstate Complexes. As a general rule, the stabilities of the complexes increase with the chain length, due to the stepwise replacement of two terminal CH_2OH groups by internal CHOH groups.[6] Our previous determinations of formation constants by potentiometry[17] have shown that the associated change in the logarithm of the formation constant is *ca.* 1 unit, corresponding to an energy gain of 2.5 kJ·mol^{-1}. This result agrees with a recent determination of the entropy cost of restricting a rotor within a hydrocarbon chain, between 1.6 to 3.6 kJ·mol^{-1}.[31] Consequently, the weaker complexes are those of glycerol (type T), threitol (type M), and xylitol (type P) in which two CH_2OH groups belong to the site of chelation. In contrast, complexes that involve only CHOH groups are very stable, as type T for xylitol, type M for iditol, and complex P_1 for heptitol. Complex P_2 is less stable than complex P_1 because its site of chelation involves one CH_2OH. It may also be noticed that the heptitol complex of type M is so stable at pH 7 that no free ligand could be detected.

Conclusion

This work reports the characterization of new tungstate complexes of *threo* alditols. Contrary to the molybdate species that all belong to the same type M, in which the ligands are tetradentate, different tungstate species are formed, depending on pH (type M, tetradentate ligand; type T, tridentate ligand; and type P, pentadentate ligand). A possible structure is proposed for species of type P in agreement with ^{13}C and ^{183}W NMR data. The ditungstate moiety in complexes of type P, made of two octahedra sharing an edge, is close to that of ditungstate subunits of polytungstate ions. On the contrary, types M and T contain ditungstate groups in which two octahedra share a face.

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