ELSEVIER

Carbohydrate Research 287 (1996) 37–48

CARBOHYDRATE RESEARCH

Furanose vs. acyclic forms of carbohydrate ligands. A multinuclear NMR spectroscopy study of the molybdate and tungstate complexes of D-*glycero*-L-*manno*-heptose

Maria Matulová [a], Jean-François Verchère [b], Stella Chapelle [c,*]

[a] *Institute of Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-842 38 Bratislava, Slovak Republic*

[b] *Université de Rouen, URA 500 du CNRS, Faculté des Sciences, F-76821 Mont-Saint-Aignan, France*

[c] *Université de Rouen, Laboratoire de RMN, URA 464 du CNRS, Faculté des Sciences, F-76821 Mont-Saint-Aignan, France*

Received 18 December 1995; accepted 4 March 1996

Abstract

The formation of dinuclear tungstate and molybdate complexes of D-*glycero*-L-*manno*-heptose was studied in aqueous solution by ^{13}C and ^{183}W NMR spectroscopy. The chelating aldose is always tetradentate and occurs exclusively in furanose or acyclic hydrated forms, the proportions of which depend on the pH and nature of the metal ion. In the tungstate species, two types of major complexes, noted M (O-2,3,5,6) and L (O-1,2,3,5) according to the site of chelation, involve the ligand in furanose form. In one of the minor tungstate complexes, chelation occurs at the *galacto* (O-3,4,5,6) site of the acyclic heptose. In the molybdate species, the complex of type M does not exist, and besides the complex of type L, the major species involve the acyclic ligand with either the *galacto* (O-3,4,5,6) or *arabino* (O-1,2,3,4) sites of chelation. Multinuclear NMR data are provided for the identification of the various types of complexes. Marked differences were noticed with respect to the complexes of D-mannose, in which species of type L prevailed with both molybdate and tungstate. © 1996 Elsevier Science Ltd.

Keywords: D-*glycero*-L-*manno*-Heptose; Tungstate complexes; Molybdate complexes; ^{13}C NMR; ^{183}W NMR, Furanose forms

* Corresponding author.

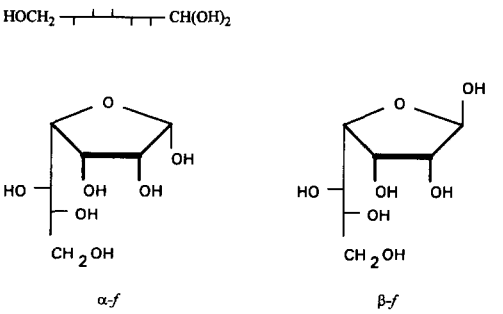
PII S0008-6215(96)00059-6

1. Introduction

In aqueous solution, sugars are generally found in pyranose form. The less common furanose and acyclic forms are only observed in the free state for carbohydrates of peculiar structures, like 2-ketoses which often afford a high amount of furanose form [1]. However, the formation of dinuclear molybdate chelates of sugars is known to stabilize the acyclic [2–9] or furanose forms [8,10,11]. An X-ray structure determination of the dimolybdate complex of D-lyxose showed that the sugar was in the *β-f* form, with the O-1,2,3,5 sites of chelation [12]. Since this report, many workers have used NMR spectroscopy of the ^{1}H, ^{13}C, [4,7–11] and ^{95}Mo [4,13–15] nuclei for the structural characterization of the molybdate complexes of carbohydrates. Such studies are relevant to the mechanistic study of the syntheses of rare sugars from available natural aldoses by epimerization at C-2 in acidic medium [16]. This reaction is catalyzed by molybdate, but not by tungstate ions, and its mechanism probably involves transient molybdate complexes in which a C-1/C-2 transposition occurs [17,18].

Because of the chemical similarity between molybdenum and tungsten [19], tungstate complexes are often studied as analogues of the molybdate species. For the study of complexes of alditols [20–23], we have recently developed the use of ^{183}W NMR spectroscopy, a more informative technique than ^{95}Mo NMR spectroscopy. Its interest lies in the existence of coupling constants between the tungsten atoms and protons of the ligand, which allow the unambiguous assignment of the sites of chelation of each tungsten atom through two-dimensional (2D) heteronuclear proton–tungsten experiments.

The stabilities of molybdate and tungstate complexes of aldoses and ketoses depend on the sugar configuration in the order: *lyxo* > *ribo* > *xylo* > *arabino*. A probable reason is that the major complexes involve the cyclic form of the sugars of *lyxo* and *ribo* configurations, but the acyclic form of those of *arabino* or *xylo* configurations. Nevertheless, small amounts of complexes of the acyclic hydrated aldoses also exist with *lyxo* and *ribo* sugars [6–8]. The main chelating species of *lyxo* aldoses were recently demonstrated to be the furanose form in which a tetradentate site of chelation [10] accommodated a dinuclear metallic core. A subsequent study [11] revealed that these furanoses formed two series of complexes. The first one, named series L (for



Scheme 1. Structure of D-*glycero*-L-*manno*-heptose, in acyclic hydrated form and in furanose forms.

lyxose), involves the O-1,2,3,5 site of the *β-f* form and is the more common. The second one, named series M (for mannose), involves the O-2,3,5,6 site of the *α-f* form and cannot be formed by pentoses. The occurrence of types L and M depends on the configuration of the anomeric hydroxyl group of the furanose entity. In aldoses, complexes of type L are obtained when HO-1,2,3 are *cis*, while complexes of type M are formed when HO-1 is *trans* to HO-2,3. One side-chain oxygen atom in type L and two in type M are involved in the site of chelation. Both types are interesting examples of complexes of ligands in which the four chelating hydroxyl groups are not vicinal, contrasting with the complexes of alditols.

In this work, the reactions of D-*glycero*-L-*manno*-heptose with disodium molybdate and tungstate in aqueous solution were examined by multinuclear NMR spectroscopy. Mixtures of complexes are formed that contain more species than in the systems of D-mannose and D-gulose. The factors that influence the cyclic or acyclic structure of the chelating ligand are discussed (Scheme 1).

2. Experimental

All chemicals were commercial products of analytical grade and were used as received. The heptose was prepared in the Slovak Academy of Sciences [24] and its purity was checked through its ^{1}H and ^{13}C NMR spectra.

The ^{1}H, ^{13}C, and ^{183}W NMR spectra were obtained at 298 K on a Bruker ARX 400 spectrometer equipped with a 5-mm multinuclear probe. Experimental details have been published elsewhere [20–23]. The complexes were prepared by mixing the heptose (0.5 mmol) and disodium tungstate (or molybdate) dihydrate (1 or 1.25 mmol) in deuterium hydroxide (1 cm^3) and adding concentrated HCl (0.5 mmol). The pH was measured in the NMR tube with a Radiometer MI-412 combined micro glass electrode (external diameter 2 mm) and a Metrohm 632 pH meter.

2D Heteronuclear $^{1}H\{^{183}W\}$ (HMQC) experiments were performed with optimization for coupling constants $^{3}J_{H,W} = 8$ or 5 Hz. The data size was 512 points in the t_2 time ^{1}H domain. The number of experiments was 128.

3. Results

The free heptose exists only in pyranose form in aqueous solution. The proportions of *α-p* (70%) and *β-p* (30%) anomers do not depend on the acidity. After reaction with molybdate or tungstate, the ^{13}C NMR spectrum shows several sets of new peaks that indicate the formation of various complexes, the proportions of which depend on the pH. The relative amounts of complexes (Table 1) were estimated from the relative intensities of the carbon signals, within 1 h after mixing the reagents. The pH ranges in which the complexes are formed are narrow, typically 2 pH units for both metals. The complexes were characterized after complete assignment of the carbon signals by 2D ^{1}H homonuclear and $^{1}H–^{13}C$ heteronuclear NMR experiments, and their nature was deduced from the coordination induced shifts (CIS) of carbon atoms that exhibit a characteristic pattern

Table 1
Proportions (%) of the molybdate and tungstate complexes of D-*glycero*-L-*manno*-heptose at various acidities (by ^{13}C NMR spectroscopy)

Metal ion	W			Mo		
pH	7	8	9	6.3	7	8
Free heptose	85	30	35	50	60	100
Complexes	15	70	65	50	40	0
Type L	nd [a]	25	traces	20	15	
Type M	nd	25	50	0	0	
Type A	nd	nd	nd	15	10	
Type G_1	nd	nd	nd	10	8	
Type G_2	nd	10 [b]	10 [b]	5	7	
Other types [c]	nd	10	5	0	0	

[a] nd: Not determined. The measurements were made within 1 h after mixing the reagents.
[b] The tungstate complex of type G is similar to the molybdate species G_2.
[c] Other types of tungstate complexes may belong to type A, type G_1, *threo* type, or mixed types.

for each type of complex. The assignments are compared in Table 2 with those for the complexes of D-mannose and D-gulose.

The tungstate species were studied at pH 8–9. At pH 9, the major species is a

Table 2
100.62-MHz ^{13}C NMR Chemical shifts (in ppm) and direct coupling constants $^1J_{C,H}$ (in Hz) for the complexes of D-*glycero*-L-*manno*-heptose, D-lyxose, D-mannose, and D-gulose [a]

Carbon atom	C-1	C-2	C-3	C-4	C-5	C-6	C-7
Heptose, u, α-*p*, δ (70%)	95.4	72.3	71.7	67.5	71.6	69.8	64.3
Heptose, u, β-*p*, δ (30%)	95.0	72.4	74.2	67.2	75.9	69.7	64.0
Molybdate complexes							
Heptose, type L, δ	**112.5**	**84.5**	**88.6**	80.2	**79.0**	71.3	63.6
Heptose, type G_1, δ	93.2	74.1	**78.1**	**90.7**	**83.1**	**82.6**	63.7
Heptose, type G_2, δ	90.0	72.4	**81.4**	**82.7**	**91.0**	**78.6**	64.5
Heptose, type A, δ	**95.3**	**94.0**	**81.9**	**80.3**	69.8	71.8	64.3
Mannose, type A, δ [b]	**94.6**	**93.6**	**81.6**	**80.5**	71.5	64.1	
Gulose, type A, δ [c]	**95.3**	**92.9**	**82.1**	**82.0**	nd	63.9	
Lyxose, type A, δ [d]	**95.4**	**93.4**	**82.0**	**81.9**	63.8		
Tungstate complexes							
Heptose, type L, δ	**112.5**	**83.8**	**87.4**	80.9	**78.5**	71.7	64.2
Heptose, type L, $^1J_{C,H}$	**182**	**154**	**157**	145	**145**	nd	143
Heptose, type M, δ	103.4	**89.3**	**83.7**	82.4	**80.3**	**77.3**	65.2
Heptose, type M, $^1J_{C,H}$	174	**154**	**143**	143	**145**	**159**	153
Heptose, type G, δ	94.5	73.0	**81.2**	**83.8**	**93.5**	**80.0**	63.9
Mannose, type L, δ [e]	**112.7**	**84.0**	**88.0**	79.7	**79.7**	65.2	
Mannose, type M, δ [f]	103.6	**89.7**	**79.5**	82.6	**77.5**	**74.3**	

[a] nd: Not determined. u: Uncomplexed. Accuracy δ ± 0.1 ppm; $^1J_{C,H}$ ± 1 Hz. All assignments were made by 2D homo- and hetero-nuclear experiments. Data for carbon atoms that bear chelating oxygen atoms are boldface.
[b] Values in agreement with ref. [6], [c] ref. [8], [d] ref. [6], [e] ref. [11], [f] ref. [11], revised by reversing C-4,5.

furanose complex of type M, accompanied by a complex of the acyclic ligand (10%). At pH 8, a furanose complex of type L is also detected (25%). This complex is slowly formed at the expense of type M in the solutions of pH 9. Traces of several minor complexes (10% overall amount) were apparent in the ^{13}C NMR spectrum, but the intensities of the corresponding signals were so small that the assignment could not be achieved.

The molybdate species were studied at pH 6–8. Only a free ligand can be detected at pH 8, but four complexes appear at pH 7. One is a furanose species of type L (20%), whereas three other species contained the acyclic ligand. The first one is formed at the *arabino* site (A, 10%), whereas two minor species are formed at the *galacto* site ($G_1 + G_2$, 15%). At pH 6.3, some oxidation of the aldose took place, since the solution slowly became blue, due to reduction of heptamolybdate to a mixed Mo(VI)–Mo(V) polyanion. At pH 6, precipitation of molybdenum oxide occurred.

The ^{13}C NMR spectra of all the complexes are compared in Table 2. Among the molybdate complexes, G_1 and G_2 are a pair of isomeric complexes analogous to those formed at a *galacto* site O-2,3,4,5 in which the lateral carbon atoms bear different substituents, as for example in D-galactose [4,9]. The third molybdate complex of the acyclic sugar (type A) is formed at a site involving the *lyxo* system O-2,3,4 and a hydroxyl group of the hydrated carbonyl, with the ligand adopting a sickle conformation at C-1,2,3,4. Other molybdate complexes of type A have been described with lyxose, mannose [6], and gulose [8], and the NMR data in Table 2 show their remarkable analogy. The tungstate complex of type G appears to possess a structure close to that of the molybdate species G_2.

The molybdate and tungstate complexes of type L are clearly isostructural. The data are in agreement with the heptose being in α-*f* form with four deshielded ($\Delta\delta > 6$ ppm) carbon atoms, i.e. C-1,2,3,5. The values of the direct coupling constants $^1J_{C,H}$ are generally enhanced by 2–10 Hz for carbon atoms that belong to the site of chelation. For reference, the coupling constants in the free ligand, which could not be measured because the proportions of furanose form are negligible at equilibrium, were assumed to be close to 142 Hz for all carbons, as in the pyranose form. Accordingly, the value (145 Hz) found for C-5 in the tungstate complex of type L is low but matches those found in other complexes of series L [11].

For the tungstate complexes of type M, the CIS patterns calculated when the ligand is assumed to be in β-*f* form indicate that C-2,3,5,6 are deshielded. Consequently, the direct coupling constants for C-3 and C-5 (< 150 Hz) are surprisingly low, although the corresponding chemical shifts ($\delta > 80$ ppm) clearly demonstrate that they bear chelating oxygen atoms. The same phenomenon was reported for the mannose complex [11]. Because the complex of type M prevails in the heptose system, the assignment by 2D NMR spectroscopy of its ^{13}C NMR spectrum was easier than in our previous work [11], in which the major species were of type L. Initially, this assignment was at variance with those previously reported for other complexes of type M, but a careful comparison and re-evaluation of earlier data [11] showed that the assignments of the signals for C-4,5 of mannose and C-5,6 of mannoheptulose must be reversed in the spectra of their complexes. Thus, we gathered in Table 3 the complete revised assignments for the four complexes of type M studied up to now, which should replace the data reported in Table

Table 3
^{13}C NMR Chemical shifts δ (in ppm) and direct coupling constants $^{1}J_{C,H}$ (in Hz) for the complexes of type M of aldoses and ketoses of *lyxo–manno* configuration [a]

Carbon atom	Metal	C-1	C-2	C-3	C-4	C-5	C-6	C-7
D-Mannose, δ	W	103.6	**89.7**	**79.5**	82.6	**77.5**	**74.3**	
$^{1}J_{C,H}$		174	**157**	**146**	148	**152**	**145**	
Heptose, δ	W	103.4	**89.3**	**83.7**	82.4	**80.3**	**77.3**	65.2
$^{1}J_{C,H}$		174	**154**	**143**	143	**145**	**159**	153
Heptulose, δ	W	64.5	110.5	**88.5**	**79.7**	82.2	**78.8**	**74.3**
$^{1}J_{C,H}$		142	–	**154**	**145**	145	**158**	**147**
Heptulose, δ	Mo	64.7	111.1	**88.7**	**81.5**	82.9	**79.7**	**73.8**
$^{1}J_{C,H}$		145	–	**154**	**145**	145	**158**	**147**

[a] Accuracy δ ±0.1 ppm; $^{1}J_{C,H}$ ±1 Hz. Frequencies are 90.556 MHz for mannose and heptulose, and 100.62 MHz for heptose. Heptose: D-*glycero*-L-*manno*-heptose. Heptulose: D-*manno*-heptulose. Data for carbon atoms that bear chelating oxygen atoms are boldface.

5 of ref. [11]. In that paper, it was also noticed that the direct coupling constants $^{1}J_{C,H}$ reported for C-5, or C-6 for the ketose, seemed rather small (< 150 Hz) for carbon atoms of the site of chelation. In fact, the revised values are 152–158 Hz. The data were completed with the ^{1}H chemical shifts for the tungstate and molybdate complexes of heptose and sugars of related configurations (Table 4). The chemical identity of complexes within series L and M is obvious. Hydrogen atoms borne by carbon atoms of the site of chelation are clearly deshielded and display characteristic CIS patterns, like the corresponding carbon atoms.

Attempts were made in order to define some of the minor constituents in the mixture of tungstate complexes formed at pH 8.5. It began by attributing a small signal at δ 73.1 in the ^{13}C NMR spectrum to a chelating CH_2OH group, according to a *J*-modulated spin echo experiment [25,26], on the basis that the corresponding C-7 atoms generally give signals at δ ca. 64 in the free heptoses. This C-7 signal corresponds to a yet unidentified complex, since all complexes presented in Table 2 possess uncomplexed O-7 atoms. In such a tungstate complex, the site of chelation involving O-7 should presumably also involve the neighbouring *threo* O-5,6 system. A confirmation of this assumption was sought by using the ^{183}W NMR data, but the 1D ^{183}W NMR spectra of the tungstate complexes could not be directly obtained because the solutions were too diluted, owing to the small available amount of heptose. However, several 2D heteronuclear $^{1}H\{^{183}W\}$ correlation experiments using the inverse mode (HMQC) were performed. This technique improves the sensitivity of the tungsten nuclei which are coupled to protons of the sugar and enhances the corresponding signals [23]. Spectral data from two selected 2D experiments at pH 8.5 are shown in Fig. 1. They differ by the optimization for $^{3}J_{W,H}$ coupling constants, close to 5 or 8 Hz, respectively. Many tungsten signals may be observed, some of which were readily assigned to species of known types, owing to the identification of the coupled protons. The corresponding chemical shifts are compared with those found for the tungstate complexes of lyxose and mannose in Table 5. The signals for the complex of type G at δ −78 are very close and are coupled to protons at, respectively, δ 5.30 and 5.35, but nevertheless were separated

Table 4
400.13-MHz ^{1}H NMR Chemical shifts δ (in ppm) for the tungstate and molybdate complexes of D-*glycero*-L-*manno*-heptose and related carbohydrates of *lyxo*–*manno* configuration [a]

Hydrogen atom	Type	Metal	H-1	H-2	H-3	H-4	H-5	H-6	H-7
Heptose	L	W	**6.60**	**5.12**	**5.85**	4.45	**4.45**	3.85	nd
D-Mannose	L	W	**6.61**	**5.10**	**5.82**	4.36	**4.55**	nd	
D-Lyxose	L	W	**6.60**	**5.11**	**5.84**	4.49	**4.42**		
							4.27		
Heptose	L	Mo	**6.16**	**4.95**	**5.33**	4.34	**4.28**	3.82	3.68
D-Mannose [b]	L	Mo	**6.20**	**5.01**	**5.41**	4.35	**4.46**	3.84	
								3.75	
D-Gulose [c]	L	Mo	**6.16**	**4.94**	**5.38**	4.44	**4.08**	3.99	
								3.91	
D-Lyxose [c]	L	Mo	**6.16**	**4.95**	**5.35**	4.40	**4.20**		
							3.95		
Heptose	M	W	5.50	**5.24**	**4.64**	3.90	**4.65**	**4.75**	3.62
D-Mannose	M	W	5.50	**5.29**	**4.81**	3.95	**4.77**	nd	
Heptulose	M	W	3.52	–	**5.24**	**4.78**	3.91	**4.78**	**3.80**
									3.59
Heptose	A	Mo	**5.43**	**4.65**	**4.95**	**4.34**	3.86	3.73	3.66
D-Mannose [b]	A	Mo	**5.45**	**4.71**	**5.01**	**4.33**	3.98	3.73	
								3.90	
Heptose	G	W	5.60	4.15	**5.35**	**5.05**	**5.30**	**4.45**	nd

[a] nd: Not determined, owing to overlap with other signals. Heptose: D-*glycero*-L-*manno*-heptose. Heptulose: D-*manno*-heptulose. Data for protons borne by carbon atoms of the site of chelation are boldface.
[b] In agreement with ref. [6]. [c] ref. [8].

(Fig. 1b). The chemical shifts for the complexes of type L are close to those for the acyclic species and are found in the −80 ppm range. In contrast, values for complexes of type M lie in a more characteristic range, around 10 ppm. The numerous additional signals observed at δ values between −80 and −90 may be attributed to tungsten atoms chelated by sites of *erythro* configuration. Like the molybdate species, the corresponding complexes may involve the sites of chelation O-1,2,3,4 (type A) or O-3,4,5,6 (type G).

Alditols with *threo* sites are known to form, at pH 8–9, complexes characterized by two ^{183}W NMR signals near −60 and −120 ppm, in which the ligand is tridentate [20,21,23]. Thus, we examined the −60 ppm range in Fig. 1 and found two signals at δ −52.8 and −56. The lack of signals at δ −120 was not unexpected, because in such complexes only the signal near δ −60 is coupled [21]. Thus, we believe that two minor complexes involve the tridentate O-5,6,7 site of the heptose, for which two structural possibilities may be considered. In the first one, the sugar is in furanose form and chelates a ditungstate moiety by the side-chain only. In the second one, the sugar is acyclic and owns a second available site at O-1,2,3,4 like that involved in the molybdate complexes of type A. This structure may allow the formation of a bis-dinuclear species of the heptadentate ligand, in which two ditungstate groups are chelated simultaneously

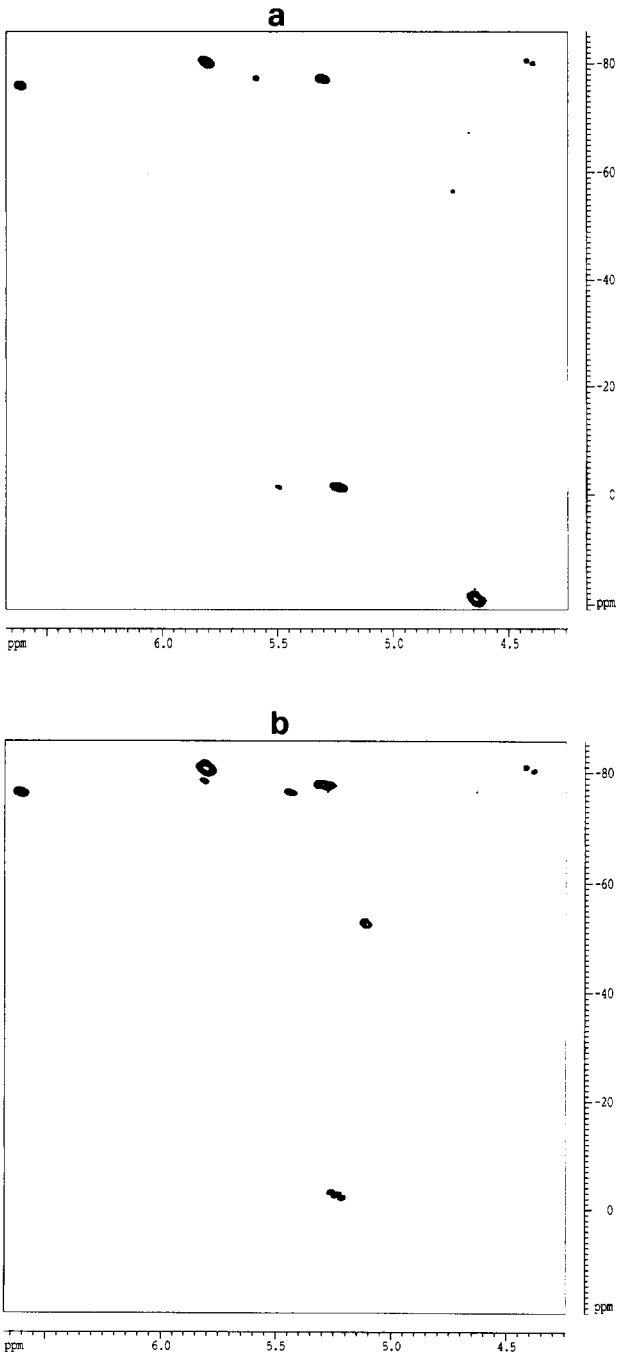


Fig. 1. 2D $^{1}H\{^{183}W\}$ correlation spectrum (HMQC) of the tungstate complexes of D-*glycero*-L-*manno*-heptose at pH 8.5 (8 scans, 1.5 h) with optimization for (a) 5 Hz; (b) 8 Hz. Frequencies are 400.13 MHz for ^{1}H and 16.67 MHz for ^{183}W.

Table 5
16.67-MHz ^{183}W NMR Chemical shifts δ and main vicinal coupling constants $^{3}J_{W,H}$ for the tungstate complexes of D-*glycero*-L-*manno*-heptose and related carbohydrates [a]

Tungsten atom	W-1		W-2	
Heptose complexes	δ (ppm)	$^{3}J_{W,H}$ (Hz)	δ (ppm)	$^{3}J_{W,H}$ (Hz)
Furanose, type L	−76.7	ca. 8 (H-1)	−81.5	ca. 8 (H-3)
Furanose, type M	17.6	ca. 8 (H-3)	−3.0	ca. 8 (H-2)
Acyclic, type G	−78.3	ca. 8 (H-5)	−77.8	ca. 5 (H-3)
D-Lyxose, type L [b]	−79.6	8.6 (H-1)	−71.1	7.9 (H-3)
D-Mannose, type L [b]	−73.7	6.4 (H-1)	−90.9	7.6 (H-3)
D-Mannose, type M [b]	15.0	6.3 (H-3)	0.3	9.4 (H-2)

[a] Reference: Na_2WO_4 in alkaline D_2O. Accuracy δ ±0.1 ppm, $^{3}J_{W,H}$ ±2 Hz for heptose, estimated from 2D experiments $^{1}H\{^{183}W\}$ in the inverse mode (HMQC), $^{3}J_{W,H}$ ±0.1 Hz for other sugars. All measurements at pH 8.5. 1D spectra were not obtained, due to the small available quantity of heptose.
[b] Ref. [11].

at O-1,2,3,4 and O-5,6,7. This type of tetratungstate complex was previously characterized with perseitol (D-*glycero*-D-*manno*-heptitol) [21]. The corresponding signals of tungsten atoms chelated by the O-1,2,3,4 site of *arabino* configuration were sought in the 2D correlation spectrum, and likely candidates were found at δ −70.9, coupled to a proton at δ 6.6, and at δ −76.8, coupled to a proton at δ 5.44.

4. Discussion

This study clearly demonstrates that D-*glycero*-L-*manno*-heptose forms several series of molybdate or tungstate complexes, in which it adopts the furanose or the acyclic form.

Comparison of the stabilities of the complexes.—Among tungstate complexes of the heptose, the species of type M is definitely stronger than that of type L, according to their relative proportions at equilibrium. In contrast, mannose and mannoheptulose yield major complexes of type L. For example, in the presence of 2.5 equiv of tungstate, both sugars afforded a mixture of species of type L (60%) and type M (40%) [11].

With molybdate, under the same conditions, mannoheptulose forms a complex of type M (45%) in addition to the type L species (55%), but mannose [11] and gulose [8] do not. The present study shows that the heptose does not form a molybdate complex of type M, confirming that complexes of type M are formed more readily with tungstate than with molybdate.

The acyclic forms of the heptose appear to be favoured in the molybdate complexes. It contrasts with shorter aldoses which mainly afford furanose complexes of type L. For example, lyxose and mannose form only small amounts (< 10%) of molybdate acyclic species [6] with the *arabino* O-1,2,3,4 site of chelation (type A). Such complexes involving HO-1 of the hydrated aldehyde group are also formed by erythrose and threose [7]. The heptose forms a similar complex (species A), together with other species

(complexes G_1 and G_2) involving the *galacto* site O-3,4,5,6 that is not available in shorter aldoses. Results obtained on alditols [15] and aldoses of the arabinose homomorphous series [4] show that ligands with *galacto* sites give strong molybdate complexes because of the favourable orientation of the chain at the extremities of the site of chelation. Since the proportions of species A and G involving the acyclic form are similar, these molybdate complexes possess similar stabilities.

The relative stabilities of the furanose complexes of types M and L depend on the length of the carbon chain of the aldose. The amount of species of type L (site of chelation O-1,2,3,5) is smaller with the heptose than with the pentose and hexoses. Within species of type M, only hexoses and heptoses may be compared, because the O-2,3,5,6 site of chelation does not exist in pentoses. The higher proportion of type M with the heptose is probably due to an entropic factor, since it is known that chelation by a secondary hydroxyl group is favoured with respect to that by a primary group, because a terminal CH_2OH group loses more degrees of freedom, when complexed, than an internal CHOH group [15,22]. Accordingly, the HO-6 group is primary in hexoses and secondary in heptoses.

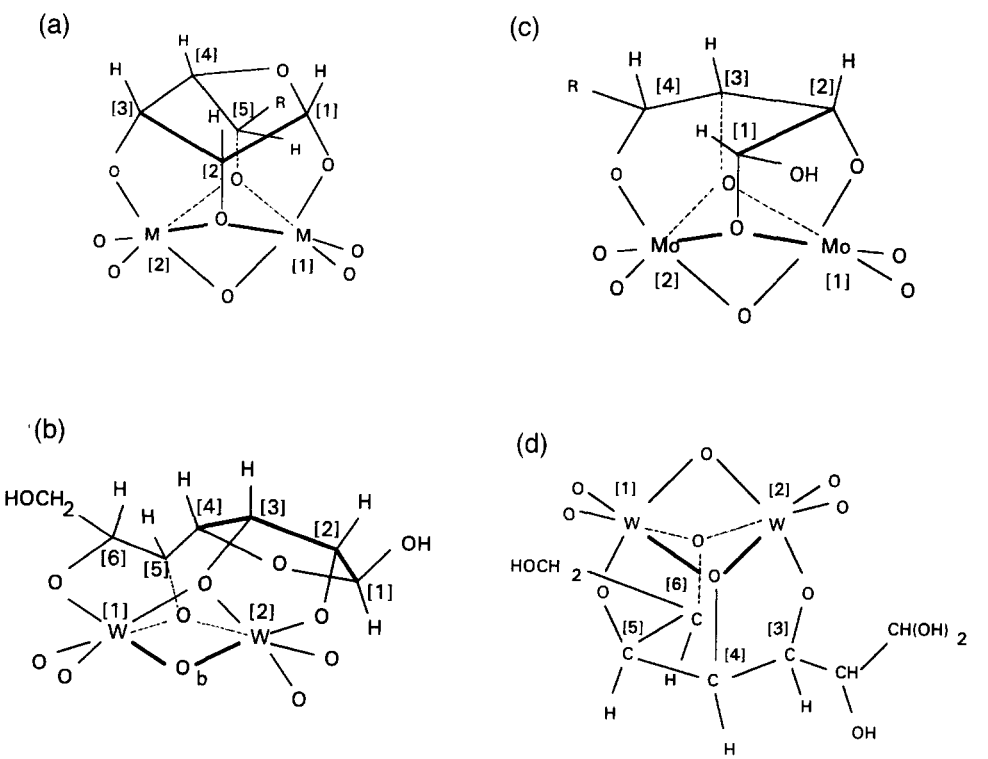


Fig. 2. Proposed structures for the molybdate and tungstate complexes of D-*glycero*-L-*manno*-heptose. R = $HOCH_2$–CHOH–CHOH. (a) type L (M = Mo or W); (b) type M; (c) type A; (d) the tungstate species of type G.

Structures of the complexes from ^{183}W NMR data.—In all complexes of type L, a tungsten atom is correlated with H-1 and is numbered W-1, whereas the other is correlated with H-3 and is numbered W-2. In agreement with our previous assignments of the sites of chelation of lyxose and mannose [11], the sites of chelation are O-1,2,5 for W-1, O-2,3,5 for W-2, and the bridging atoms are O-2,5. The structure of the complex of type L, deduced from NMR data (Fig. 2a), is fully consistent with that obtained by X-ray crystallography for a solid lyxose–dimolybdate complex [12].

Tungstate complexes of type M are characterized by two signals near 15 ppm (W-1) and 0 ppm (W-2). The latter signal cannot be confused with that of free tungstate, because 2D NMR experiments show a correlation with H-2 of the ligand. In fact, for both signals, coupling constants with protons of the aldose are apparent and were estimated from the correlation experiments. W-1 was correlated with H-3 and W-2 with H-2. The sites of chelation for each tungsten atom were specified by examination of molecular models, showing that W-1 is bound to O-3,5,6 and W-2 to O-2,3,5, as in the mannose complex. The likely structure is represented in Fig. 2b, in which the inorganic moiety is composed of two WO_6 octahedra sharing a face that includes O-3,5 and a bridging oxygen atom O_b. The dihedral angles W-2;O-2;C-2;H-2 and W-1;O-3;C-3;H-3 are consistent with the estimated vicinal coupling constants.

Likely structures for the complexes of types A and G are presented in Fig. 2c and d.

5. Conclusions

The present results show that important differences exist between molybdate and tungstate complexes of the same heptose, indicating that the chemistry of these elements is less similar than is generally postulated [19]. Thus, comparison of the stabilities of the complexes of both metals should be made with caution when their structural similarity is not established, because the ligand may be forced by chelation into unusual conformations in which free sugars are not normally stable. Since the major tungstate complex of heptose is a furanose species of type M, previously found as a minor constituent, previous erroneous NMR data for this series of complexes [11] were corrected. CIS patterns for carbon and proton are presented in order to assist the analysis of mixtures of complexes of types L, M, A, and G.

References

[1] S.J. Angyal, *Adv. Carbohydr. Chem. Biochem.*, 42 (1984) 15–68.
[2] J. Alföldi, L. Petruš, and V. Bílik, *Collect. Czech. Chem. Commun.*, 43 (1978) 1476–1480.
[3] J. Alföldi, V. Bílik, and L. Petruš, *Collect. Czech. Chem. Commun.*, 45 (1980) 123–126.
[4] M. Matulová and V. Bílik, *Chem. Pap.*, 44 (1990) 77–87.
[5] M. Matulová and V. Bílik, *Chem. Pap.*, 44 (1990) 97–103.
[6] V. Bílik and M. Matulová, *Chem. Pap.*, 44 (1990) 257–265.
[7] M. Matulová and V. Bílik, *Chem. Pap.*, 46 (1992) 253–256.
[8] M. Matulová and V. Bílik, *Carbohydr. Res.*, 250 (1993) 203–209.
[9] J.P. Sauvage, S. Chapelle, A.M. Dona, and J.F. Verchère, *Carbohydr. Res.*, 243 (1993) 293–305.

[10] J.P. Sauvage, S. Chapelle, and J.F. Verchère, *Carbohydr. Res.*, 237 (1992) 23–32.
[11] S. Chapelle and J.F. Verchère, *Carbohydr. Res.*, 277 (1995) 39–50.
[12] G.E. Taylor and J.M. Waters, *Tetrahedron Lett.*, 22 (1981) 1277–1278.
[13] J.F. Verchère and S. Chapelle, *Polyhedron*, 8 (1989) 333–340.
[14] M. Matulová and V. Bílik, *Chem. Pap.*, 44 (1990) 703–709.
[15] S. Chapelle, J.F. Verchère, and J.P. Sauvage, *Polyhedron*, 9 (1990) 1225–1234.
[16] V. Bílik, *Chem. Zvesti*, 26 (1972) 76–81; 183–186; 187–189; 372–375.
[17] M.L. Hayes, N.J. Pennings, A.S. Serianni, and R. Barker, *J. Am. Chem. Soc.*, 104 (1982) 6764–6769.
[18] E.L. Clark, Jr., M.L. Hayes, and R. Barker, *Carbohydr. Res.*, 153 (1986) 263–270.
[19] F.A. Cotton and G. Wilkinson, *Modern Inorganic Chemistry*, 5th ed., Wiley, New York, 1988.
[20] S. Chapelle and J.F. Verchère, *Inorg. Chem.*, 31 (1992) 648–652.
[21] S. Chapelle, J.P. Sauvage, and J.F. Verchère, *Inorg. Chem.*, 33 (1994) 1966–1971.
[22] S. Chapelle and J.F. Verchère, *Carbohydr. Res.*, 266 (1995) 161–170.
[23] S. Chapelle, J.P. Sauvage, P. Köll, and J.F. Verchère, *Inorg. Chem.*, 34 (1995) 918–923.
[24] V. Bílik and L. Petruš, *Chem. Zvesti*, 30 (1976) 359–365.
[25] C. Le Cocq and J.Y. Lallemand, *J. Chem. Soc., Chem. Commun.*, (1981) 150–152.
[26] S.L. Patt and J.N. Shoolery, *J. Magn. Reson.*, 46 (1982) 535–539.