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NMR spectroscopy study of the complexation of L-mannonic acid with tungsten(VI) and molybdenum(VI)

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Abstract

By using multinuclear (^{1}H, ^{13}C, ^{17}O, ^{95}Mo, ^{183}W) magnetic resonance spectroscopy (1D and 2D), L-mannonic acid was found to form nine complexes both with tungsten(VI) and molybdenum(VI), in aqueous solution, depending on pH and concentration conditions. Two isomeric 1:2 (metal:ligand) complexes involving the carboxylate and the adjacent OH group were present in the whole pH range covered (2–11). At high pH, three 2:1 complexes were detected, each one involving four OH groups of the ligand. At low and intermediate pH values, four additional complexes were found: two 4:2 isomers, more abundant with W(VI), involving the carboxylate group and all the hydroxyl groups, and two 2:1 isomers, more abundant with Mo(VI), involving the carboxylate group and three OH groups. © 1997 Elsevier Science Ltd.

Keywords: Tungsten; Molybdenum complexes; L-Mannonic acid; NMR

1. Introduction

Studies of the interaction of carbohydrates and their derivatives with metal ions have received an increased attention during the last few years, mainly due to the possible importance of such interactions in a variety of industrial, pharmaceutical and biological processes [1,2].

Aldonic acids have been found to have various applications, for example in preparations of medical and pharmaceutical importance [3,4], in detergents as environmental protectors [5], in industrial processes as corrosion inhibitors [6] and, especially, in cosmetic preparations [7].

We have been carrying out a systematic and comparative study of sugar acids and their complexation with metal oxoions, in aqueous solution, using multinuclear high field NMR spectroscopy (1D and 2D). Having studied the main aldaric acids [8–10] and alduronic acids and their complexation with tungstate and molybdate ions [11] followed by D-galactonic acid and its complexation with those metals [12], we now address an important aldonic acid: L-mannonic acid.

No reference has been found in the literature to complexes of mannonic acid with tungstate or molybdate ions. Its complexation with other metals has,

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however, been studied, namely with Co(III) (two isomeric $[Co(L\text{-mannonato})(en)_2]^{2+}$ complexes) [13] and with Eu(III) in the form of the chiral shift reagent propylenediaminetetraacetatoeuropium(III) [14].

2. Experimental

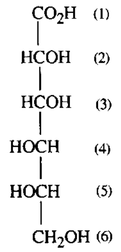
Analytical grade disodium tungstate and sodium molybdate dihydrates and commercially available L-mannonic acid (source L-mannonic acid-1,4-lactone) were used.

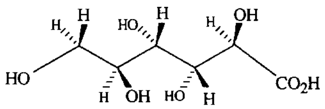
The pH was adjusted (cautiously, to reduce the possibility of drastic local disturbances of equilibria that may be slow to disappear) by addition of DCl and NaOD; the pH* values quoted are the direct pH-meter readings (room temperature) after standardization with aqueous (H_2O) buffers.

^1H and ^{13}C NMR spectra were obtained on a Varian Unity-500 NMR spectrometer (at 499.843 MHz) and on a Varian XL-200 (at 50.300 MHz), respectively. Solvent signal suppression was achieved by a selective saturation of the *H*DO resonance. ^{13}C Spectra were recorded using proton-decoupling techniques (Waltz-16) with suppression of the nuclear Overhauser effect. The methyl signal of *tert*-butyl alcohol was used as internal reference for ^1H (δ 1.3) and ^{13}C (δ 31.2), respectively, relative to Me_4Si. The ^{95}Mo and ^{183}W spectra were obtained on a Varian Unity-500 NMR spectrometer (32.576 and 20.825 MHz, respectively), using D_2O solutions of Na_2MoO_4 and Na_2WO_4 at pH* 9.0 and pH* 9.5, respectively, (δ 0) as external reference. The ^{17}O spectra were obtained on the same spectrometer (67.760 MHz), using D_2O (δ 0) as external reference. Detailed conditions can be found in previous papers [8–11]. The 2D NMR spectra, DQFCOSY [15] and HETCOR [16] and COLOC [17], were recorded on a Varian Unity-500 NMR spectrometer.

3. Results and discussion

Mannonic acid has been shown to exist preferentially in a planar zig-zag conformation in solution. Horton et al. came to this conclusion from a study of the ^1H NMR spectrum in pyridine solution, as compared with the ^{13}C spectra of the corresponding aqueous solution [18]. Van Duin et al. corroborated these results from a comparative study of several polyhydroxycarboxylates in aqueous solution using ^1H NMR spectroscopy [19] and from a ^{13}C and ^1H NMR study of several polyhydroxycarboxylates and their interaction with borate in aqueous solution [20]. The ^{13}C signals could not be unambiguously assigned at that time [21].





In order to characterize the complexes formed, a proper assignment of all the proton and carbon signals of the ligand is necessary, for various pH conditions. We achieved this target using C–H HETCOR spectra to remove the ambiguities concerning the carbon shifts. The proton and carbon chemical shifts, as well as the proton–proton coupling constants, are shown in Tables 1 and 2, for different pH values. Our results are in agreement with previous studies. It is found that the various NMR parameters change only slightly with pH, which is an indication that no major conformational changes occur.

We have carried out our studies of the complexation of L-mannonic acid with W(VI) and Mo(VI) in a

Table 1
^1H NMR parameters[a] for L-mannonic acid at 298 K

	H-2	H-3	H-4	H-5	H-6a	H-6b	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$\lvert J_{6a,6b}\rvert$
L-Mannonic acid [b]												
pH* 3.0												
δ	4.33	4.07	3.82	3.81	3.90 /	3.72	7.5	1.0	8.5	2.5 /	6.0	11.8
pH* 5.0												
δ	4.19	4.05	3.79	3.79	3.89 /	3.71	6.0	0.8	8.5	2.0 /	6.0	11.8
pH* 7.6												
δ	4.18	4.05	3.79	3.79	3.89 /	3.70	5.5	0.8	8.5	2.0 /	6.0	11.8

[a] δ Values, in ppm, relative to Me_4Si, using *tert*-butyl alcohol (δ_H 1.3) as internal reference; *J* values in Hz.
[b] 0.1 M L-Mannonic acid solution.

Table 2
^{13}C NMR chemical shifts [a] for L-mannonic acid at 298 K

	C-1	C-2	C-3	C-4	C-5	C-6
L-mannonic acid [b]						
pH* 3.0						
δ	178.93	73.56	71.31	72.19	71.81	64.49
pH* 5.0						
δ	180.68	75.27	71.97	72.37	71.97	64.47
pH* 7.5						
δ	180.73	75.31	71.90	72.34	71.90	64.42

[a] δ Values, in ppm, relative to Me_4Si, using *tert*-butyl alcohol (δ_C 31.2) as internal reference.
[b] 0.5 M L-Mannonic acid solution.

parallel manner owing to the expected similarities. Indeed, we have found the same number of complexes for the two systems, although the variation of their relative concentrations with concentration and pH conditions was not the same, ascribable in part to differences in the competing polymerization equilibria of tungstate and molybdate. In addition, the interpretation of the data has gained from a direct comparison of the two systems.

Depending on pH, concentration and molar ratios, mixtures of sodium molybdate or sodium tungstate and L-mannonic acid, in aqueous solution, show ^{1}H and ^{13}C signals ascribed to the complexed forms, in addition to those of the free ligand eventually present. The observation of distinct signals for bound and free ligand is a consequence of slow ligand exchange on the NMR time scale, which renders signal attribution more direct using this technique.

The way the ligand is bonded to the metals can be established from the proton and carbon chemical shifts, compared with the free ligand, at the same pH. The ^{183}W, ^{95}Mo and ^{17}O chemical shifts can help to elucidate the nature of the metal center in the complexes. It is noted that the quadrupolar molybdenum nucleus gives rise to broad signals, whereas the spin 1/2 tungsten-183 nucleus produces sharp signals. As

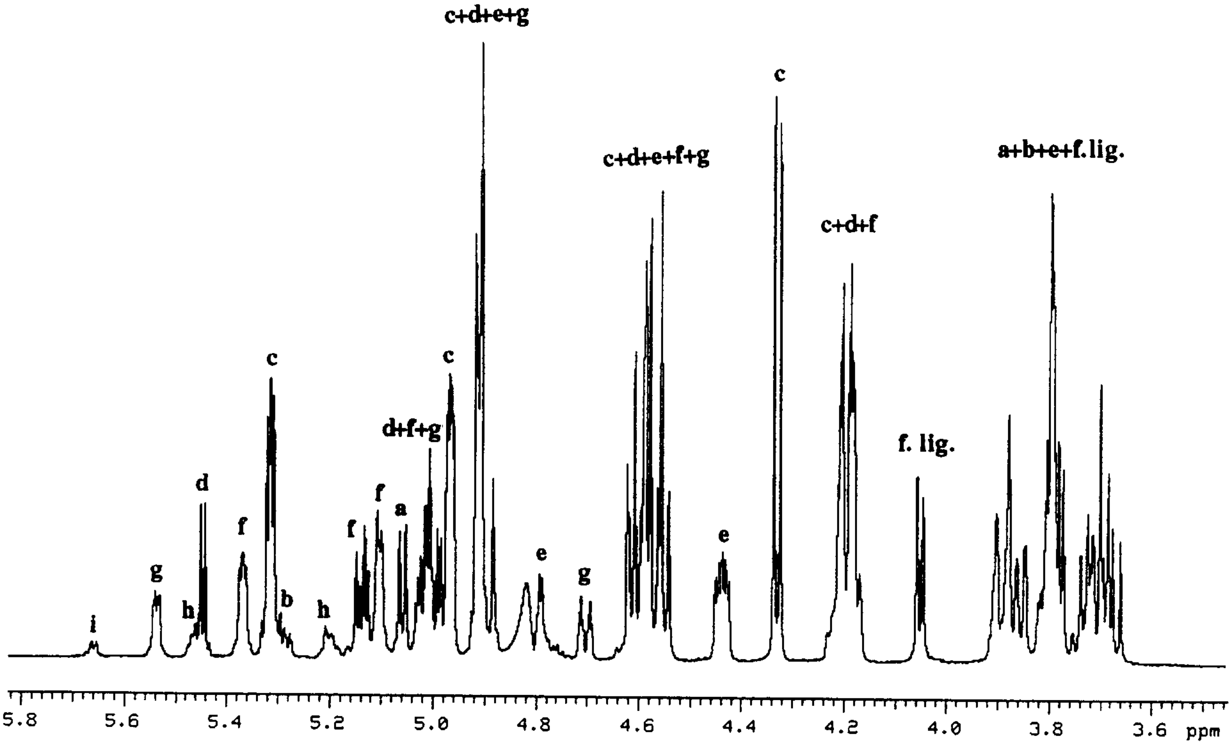


Fig. 1. ^{1}H NMR spectrum (499.843 MHz) of a D_2O 0.20 M:0.10 M solution of W(VI)/L-mannonic acid, pH* = 7.5, temp. 298 K, with suppression of the residual OH signal ($\delta \approx 4.80$ ppm).

a result, the vicinal tungsten–proton coupling constants can also help establishing some details of the structures, in addition to the vicinal proton–proton coupling constants which reflects the conformation of the bound ligand.

Spectra of M(VI)-L-mannonic acid (M = W or Mo) were recorded for total concentrations of the complexing species ranging from 3 to 0.10 M, metal:ligand molar ratios from 10 to 0.25 and pH* values in the ranges 3 to 11 for the case of W(VI) and 2 to 9 for Mo(VI). Under these conditions, nine different sets of signals were detected, for each system. Signal intensity considerations enabled the conclusion that these sets correspond to nine different complexes. Two of them, **a** and **b**, are formed at any pH, especially when the metal:ligand molar ratio is less than 1. Species **c**, **d** and **e** occur at pH* values greater than 5 (Mo) or 6 (W) and for metal:ligand molar ratios larger than 1. For the pH range 4–9, and for solutions having metal:ligand molar ratios larger than 1, two other species are formed: **f** and **g**. These species are more abundant with tungstate, appearing in the case of molybdate only for more concentrated solutions. At low pH, due to the stronger competing polymerization equilibria of tungstate, the differences of the two systems are more pronounced, especially when the metal:ligand molar ratio is larger than 1. Thus with tungstate, and for the pH range 3–3.5, W(VI) only forms complexes **a** and **b** in a significant concentration, whereas Mo(VI) also forms two abundant species **h** and **i**; species **i** disappears for pH values about 4, but **h** is present up to pH about 7.5. In the case of tungstate, homologous species of **h** and **i** appear in the pH range 4–9, but in minor concentrations. Fig. 1 illustrates the complexity of these systems and the complete assignment of bound and free ligand signals.

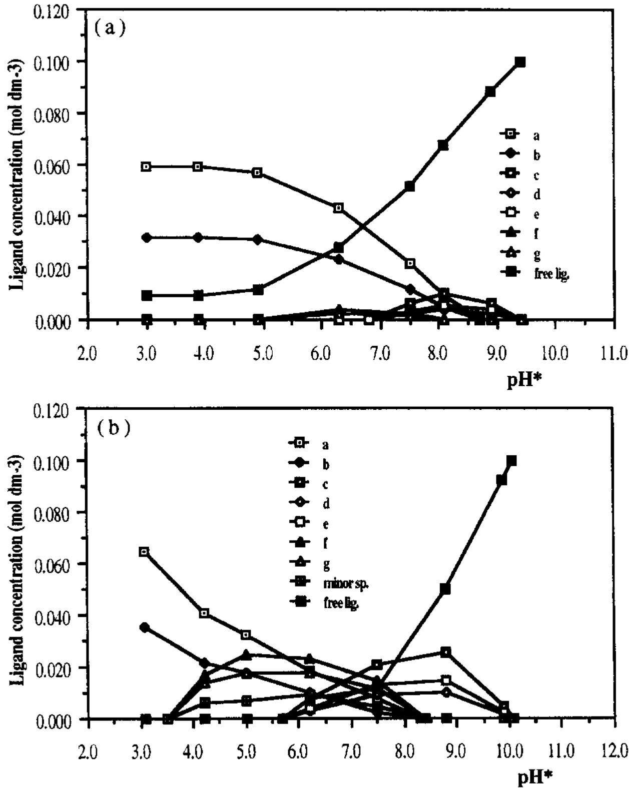


Fig. 2. Concentration of the ligand as a function of pH*, obtained by ^1H NMR for (a) a 0.05 M:0.10 M D_2O solution of sodium tungstate(VI) and L-mannonic acid, KNO_3 2 M, temp. 294 K and (b) a 0.20 M:0.10 M D_2O solution of sodium tungstate(VI) and L-mannonic acid, KNO_3 2 M, temp. 294 K.

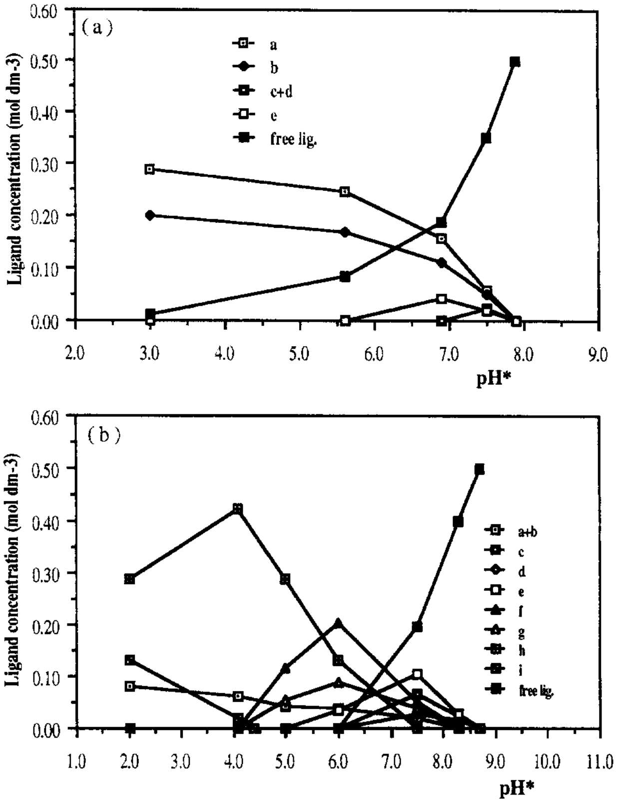


Fig. 3. Concentration of the ligand as a function of pH*, obtained by ^{13}C NMR for (a) a 0.25 M:0.50 M aqueous solution (33% D_2O) of sodium molybdate(VI) and L-mannonic acid, temp. 294 K and (b) a 1.0 M:0.50 M aqueous solution (33% D_2O) of sodium molybdate(VI) and L-mannonic acid, temp. 294 K.

The way in which the concentrations of the various species vary with pH*, for two different molar ratios, is shown in Figs. 2 and 3, for tungstate and molybdate, respectively. For Mo(VI), we used both less and more concentrated solutions, in order to detect all the species, namely **f** and **g**. In this case, because the ^1H

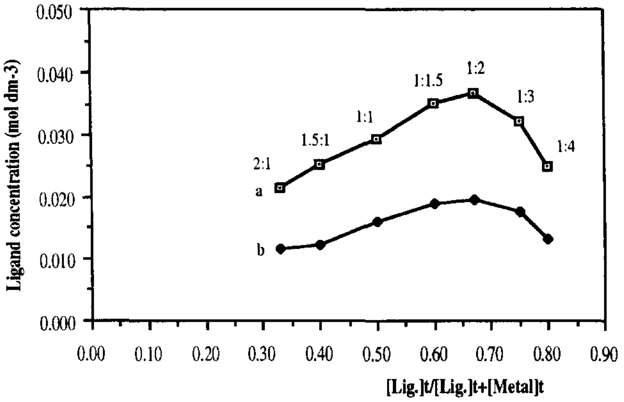


Fig. 4. Job's plot based on proton NMR spectral intensities for the system W(VI) + L-mannonic acid; total concentration of complexing species 0.10 M (D_2O solutions, 2 M in KNO_3, pH* = 3.0, temp. 298 K).

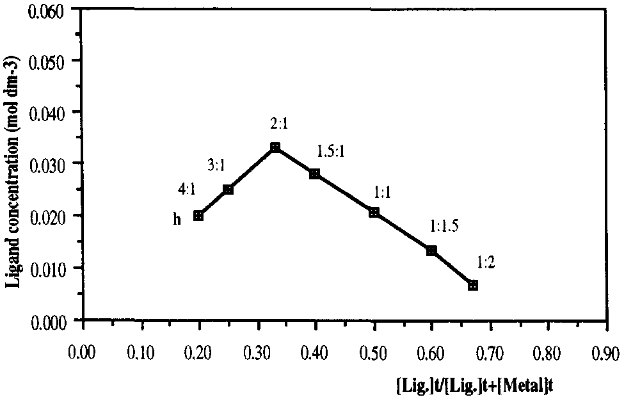


Fig. 5. Job's plot based on proton NMR spectral intensities for the system Mo(VI) + L-mannonic acid; total concentration of complexing species 0.10 M (D_2O solutions, 2 M in KNO_3, pH* = 5.0, temp. 298 K).

Table 3
^1H NMR parameters [a] for and W(VI) + L-mannonic acid at 298 K

	H-2	H-3	H-4	H-5	H-6a	H-6b	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$\lvert J_{6a,6b}\rvert$
W(VI) + L-mannonic acid												
complex **a** [b] (pH* 5.0)												
δ	5.06	4.17	3.85	3.81	3.89 /	3.72	5.3	1.5	9.0	2.9 /	6.6	11.9
$\Delta\delta$	0.87	0.12	0.06	0.02	0.00	0.01						
complex **b** [b] (pH* 5.0)												
δ	5.30	4.22	3.85	3.81	3.90 /	3.72	5.3	1.1	8.9	3.7 /	6.4	11.6
$\Delta\delta$	1.11	0.17	0.06	0.02	0.01	0.01						
complex **c** [c] (pH* 7.5)												
δ	4.33	4.91	4.97	5.31	4.56 /	4.20	6.1	1.0	4.3	0 /	2.6	10.8
$\Delta\delta$	0.14	0.86	1.18	1.52	0.67	0.50						
complex **d** [c] (pH* 7.5)												
δ	4.17	4.56	5.46	4.96	4.90 /	4.60	7.8	0	4.6	4.4 /	0	11.1
$\Delta\delta$	−0.01	0.51	1.67	1.17	1.01	0.90						
complex **e** [c] (pH* 7.5)												
δ	4.80	4.92	4.56	4.43	3.79 /	3.68	2.6	0	2.1	3.8 /	7.8	11.9
$\Delta\delta$	0.62	0.87	0.77	0.64	−0.10	−0.02						
complex **f** [c] (pH* 5.0)												
δ	5.14	5.02	5.10	5.37	4.55 /	4.19	7.8	0	3.8	0 /	2.6	11.0
$\Delta\delta$	0.95	0.97	1.31	1.58	0.66	0.48						
complex **g** [c] (pH* 5.0)												
δ	4.93	4.70	5.54	5.03	4.89 /	4.60	8.5	1.7	3.1	0 /	5.0	11.1
$\Delta\delta$	0.74	0.65	1.75	1.24	1.00	0.89						
complex **h** [d] (pH* 5.0)												
δ	5.18	5.45	4.72	4.04	4.05 /	3.92	4.4	0	9.0	2.8 /	6.4	12.0
$\Delta\delta$	0.99	1.40	0.93	0.25	0.16	0.21						
complex **i** [d] (pH* 5.0)												
δ	5.03	5.65	– [e]	– [e]	4.15 /	3.78	4.3	0	– [e]	2.8 /	6.4	12.0
$\Delta\delta$	0.84	1.60			0.26	0.07						

[a] δ Values, in ppm, relative to Me_4Si, using *tert*-butyl alcohol (δ_H 1.3) as internal reference; J values in Hz.
[b] 0.05 M:0.1 M W(VI)-L-mannonic acid solution.
[c] 0.20 M:0.1 M W(VI)-L-mannonic acid solution.
[d] 1.0 M:0.1 M W(VI)-L-mannonic acid solution.
[e] Not measured due to low concentration of **i** and superposition with other signals.

signals are too broad, the approximate concentrations of the complexes are based on ^{13}C signal intensities (excluding the carboxylate due to its longer relaxation times).

The previously mentioned observations suggest that **a** and **b** might be isomers of stoichiometry 1:2 (metal:ligand), whereas the remaining species, **c**, **d**, **e**, **f**, **g**, **h** and **i** would be n:1 complexes, with $n \geq 1$, presumably 2:1 species. Taking advantage of conditions for which only **a** and **b** are present (with tungstate), and other conditions for which **h** is dominant (with molybdate), Job's plots based on the proton NMR intensities could be attempted. These are shown in Figs. 4 and 5 and strongly support the proposal of 1:2 complexation for **a** and **b**, and 2:1 complexation for **h**.

The ^1H and ^{13}C NMR parameters are shown in Tables 3–6 and the ^{17}O, ^{183}W and ^{95}Mo data are presented in Tables 7–9, respectively. Whenever necessary, COSY and HETCOR experiments were performed to assign the proton and carbon shifts, and COLOC (correlation through long-range couplings) experiments were also performed to assign tungsten shifts via the correlation with protons.

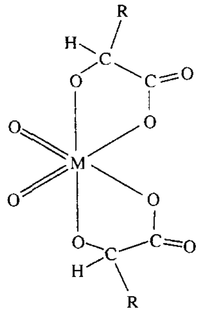
1:2 (Metal:ligand) complexes at any pH.—As far as complexes **a** and **b** are concerned, the tungsten and molybdenum shifts are characteristic of MO_2^{2+} centers [8–12,22–24] and the oxygen shifts are typical of terminal M = O groups, there being no evidence for any bridge oxygen atoms [9–12,25–29]. The high frequency shifts observed for the carboxylic and the adjacent carbinol carbon nuclei, upon complexation, are characteristic of the involvement of these groups in complexation [8–12,23,30–35]; the other carbon shifts are much smaller. Accordingly, only the proton H-2 undergoes a significant chemical shift, which is

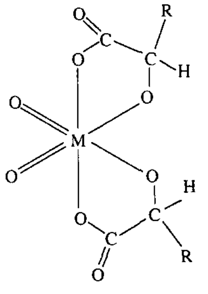
Table 4
^1H NMR parameters [a] for Mo(VI) + L-mannonic acid at 298 K

	H-2	H-3	H-4	H-5	H-6a	H-6b	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$\|J_{6a,6b}\|$
Mo(VI) + L-mannonic acid												
complex **a** [b] (pH* 5.0)												
δ	4.90	4.18	3.84	3.80	3.88 /	3.70	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]
$\Delta\delta$	0.71	0.13	0.05	0.01	−0.01	−0.01						
complex **b** [b] (pH* 5.0)												
δ	5.15	4.18	3.84	3.80	3.88 /	3.70	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]
$\Delta\delta$	0.96	0.13	0.05	0.01	−0.01	−0.01						
complex **c** [d] (pH* 7.5)												
δ	4.21	4.90	4.68	4.79	4.38 /	4.12	–[c]	–[c]	–[c]	0 /	2.2	10.4
$\Delta\delta$	0.03	0.85	0.89	1.00	0.49	0.42						
complex **d** [d] (pH* 7.5)												
δ	–[e]	–[e]	–[e]	–[e]	–[e]	–[e]						
$\Delta\delta$												
complex **e** [d] (pH* 7.5)												
δ	4.76	4.60	4.28	4.38	3.72 /	3.64	2.4	0	1.5	4.3 /	7.5	11.8
$\Delta\delta$	0.58	0.55	0.49	0.59	−0.17	−0.06						
complex **f** [f] (pH* 6.0)												
δ	4.90	4.68	4.82	4.98	4.36 /	4.11	–[c]	–[c]	–[c]	0 /	2.0	10.3
$\Delta\delta$	0.71	0.63	1.03	1.19	0.47	0.40						
complex **g** [f] (pH* 6.0)												
δ	–[c]	–[c]	–[c]	–[c]	4.78 /	4.56	–[c]	–[c]	–[c]	–[c]	–[c]	10.8
$\Delta\delta$					0.89	0.85						
complex **h** [d] (pH* 5.0)												
δ	5.04	5.34	4.36	3.92	3.82 /	3.63	4.1	0	9.0	2.8 /	6.4	12.0
$\Delta\delta$	0.85	1.29	0.57	0.13	−0.07	−0.08						

[a] δ Values, in ppm, relative to Me_4Si, using *tert*-butyl alcohol ($\delta_H = 1.3$) as internal reference; J values in Hz.
[b] 0.05 M:0.1 M Mo(VI)-L-mannonic acid solution.
[c] Broad signals.
[d] 0.20 M:0.1 M Mo(VI)-L-mannonic acid solution.
[e] Not measured due to low concentration of **d** and superposition with other signals.
[f] 1.0 M:0.5 M Mo(VI)-L-mannonic acid solution.

to high frequency. All these findings, associated to the fact that the two ligand molecules are magnetically equivalent, point to **a** and **b** as being diastereoisomers **1** and **2**


M=W, Mo
R=$(CHOH)_3CH_2OH$
1


M=W, Mo
R=$(CHOH)_3CH_2OH$
2

Since complex **a** is slightly more stable than **b**, steric considerations involving the R chains would suggest that **a** is **1** and **b** is **2**. These geometries are also consistent with only small changes of the proton coupling constants upon complexation and with a small vicinal W–H-2 coupling constant. In addition, the fact that H-2 in **1** is more affected by the magnetic anisotropy associated with M=O groups leading to a higher screening constant, is in accordance with a smaller δ value for complex **a**. Similar complexes have been found for related systems [11,12,22,23,31,33,34].

A rough estimate of the formation constants, based on the proton signal intensities, for the complexes **a** and **b** formed with tungstate, leads to conditional pK values of -4.2 and -4.0, respectively, for pH* 3.0 and assuming the equation $M + 2L = ML_2$.

2:1 (Metal:ligand) complexes at high pH.—Concerning complexes **c**, **d** and **e**, which are formed especially at high pH*, we note the shifts to high frequency of signals for C-3, C-4, C-5 and C-6, for **c** and **d** and the shifts to high frequencies of signals for C-2, C-3, C-4 and C-5, for species **e**, as well as those for the corresponding H nuclei. This shows that the coordination is established via the deprotonated OH groups in positions 3, 4, 5 and 6, for **c** and **d** and in positions 2, 3, 4 and 5, for **e**. This situation is similar to that found by Verchère et al. for the 2:1 complexes of alditols with tungstate and molybdate [36–41] and by us for the complexes of galactaric acid, D-galactonic acid and D-mannaric acid with those metal ions [9,10,12]. Species **c** and **d** are more stable in the

Table 5
^{13}C NMR chemical shifts [a] for W(VI) + L-mannonic acid, temp. 298 K

	C-1	C-2	C-3	C-4	C-5	C-6
W(VI) + L-mannonic acid						
complex **a** [b] (pH* 5.0)						
δ	185.37	85.59	72.02	72.37	71.81	64.44
$\Delta\delta$	4.69	10.32	0.05	0.00	−0.16	−0.03
complex **b** [b] (pH* 5.0)						
δ	184.76	86.99	72.02	72.42	71.81	64.44
$\Delta\delta$	4.08	11.72	0.05	0.05	−0.16	−0.03
complex **c** [c] (pH* 7.5)						
δ	179.99	75.53	82.71	81.93	91.77	70.07
$\Delta\delta$	−0.74	0.22	10.81	9.59	19.87	5.65
complex **d** [c] (pH* 7.5)						
δ	181.34	75.53	79.29	91.27	82.23	71.18
$\Delta\delta$	0.61	0.22	7.39	18.93	10.33	6.76
complex **e** [c](pH* 7.5)						
δ	178.84	84.69	80.25	80.54	84.93	63.24
$\Delta\delta$	−1.89	9.38	8.35	8.20	13.03	−1.18
complex **f** [c] (pH* 5.0)						
δ	184.53	83.51	83.95	82.16	91.75	70.11
$\Delta\delta$	3.85	8.24	11.98	9.79	19.78	5.64
complex **g** [c] (pH* 5.0)						
δ	186.25	81.67	78.12	91.24	82.16	72.16
$\Delta\delta$	5.57	9.70	6.15	18.87	10.19	7.69

[a] δ Values, in ppm, relative to Me_4Si, using *tert*-butyl alcohol (δ_C 31.2) as internal reference.
[b] 0.25 M:0.5 M W(VI)-L-mannonic acid solution.
[c] 1.0 M:0.5 M W(VI)-L-mannonic acid solution.

Table 6
^{13}C NMR chemical shifts [a] for Mo(VI) + L-mannonic acid, temp. 298 K

	C-1	C-2	C-3	C-4	C-5	C-6
Mo(VI) + L-mannonic acid						
complex **a** [b] (pH* 5.0)						
δ	184.65	86.60	72.06	72.44	72.06	64.44
$\Delta\delta$	3.97	11.33	0.09	0.07	0.09	−0.03
complex **b** [b] (pH* 5.0)						
δ	183.90	88.30	72.06	72.44	72.06	64.44
$\Delta\delta$	3.22	13.03	0.09	0.07	0.09	−0.03
complex **c** [c] (pH* 7.5)						
δ	180.48	75.65	83.06	85.97	92.28	70.68
$\Delta\delta$	−0.25	0.34	11.16	13.63	20.38	6.26
complex **d** [c] (pH* 7.5)						
δ	181.41	– [d]	– [d]	– [d]	– [d]	73.47
$\Delta\delta$	0.68					9.05
complex **e** [c] (pH* 7.5)						
δ	178.90	85.97	80.31	80.31	85.89	62.91
$\Delta\delta$	−1.88	10.66	8.41	7.97	13.99	−1.51
complex **f** [c] (pH* 6.0)						
δ	184.12	84.24	83.17	81.68	92.28	70.36
$\Delta\delta$	3.44	8.97	11.20	9.31	20.31	5.89
complex **g** [c] (pH* 6.0)						
δ	186.06	82.23	78.69	91.96	83.78	73.36
$\Delta\delta$	5.38	6.96	6.72	19.59	11.81	8.89
complex **h** [c] (pH* 5.0)						
δ	182.90	91.70	84.39	81.65	72.53	64.07
$\Delta\delta$	2.22	16.43	12.42	9.28	0.56	−0.40
complex **i** [c] (pH* 2.0)						
δ	183.46	85.84	88.76	84.00	72.01	66.21
$\Delta\delta$	4.53	12.28	17.45	11.81	0.20	1.72

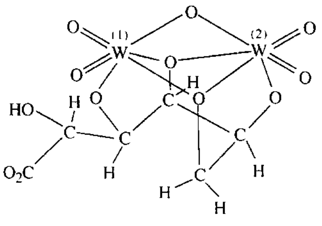
[a] δ Values, in ppm, relative to Me_4Si, using *tert*-butyl alcohol (δ_C 31.2) as internal reference.
[b] 0.25 M:0.5 M Mo(VI)-L-mannonic acid solution.
[c] 1.0 M:0.5 M Mo(VI)-L-mannonic acid solution.
[d] Not measured due to low concentration of **d** and superposition with other signals.

Table 7
^{17}O NMR chemical shifts [a] for W(VI) + L-mannonic acid and Mo(VI) + L-mannonic acid, temp. 298 K

	$-\overset{\|}{\underset{\vert}{\mathrm{M}}}={}^{17}\mathrm{O}$	$-\overset{\vert}{\underset{\vert}{\mathrm{M}}}-{}^{17}\mathrm{O}-\overset{\vert}{\underset{\vert}{\mathrm{M}}}-$
W(VI) + L-mannonic acid		
complex **a** [b] (pH* 5.0)	640	–
complex **b** [b] (pH* 5.0)	645	–
complexes **c** + **d** + **e** [c] (pH* 7,5)	643, 632, 618	249, 230
complexes **f** + **g** [c] (pH* 5.0)	625, 633	297, 420
complexes **h** + **i** [c] (pH* 5.0)	641, 630, 626, 616	257
Mo(VI) + L-mannonic acid		
complex **a** [d] (pH* 5.0)	833	–
complex **b** [d] (pH* 5.0)	842	–
complexes **c** + **d** + **e** [e] (pH* 7.5)	795, 789	303, 323
complexes **f** + **g** [e] (pH* 5.0)	793	435, 449
complexes **h** + **i** [e] (pH* 3.0)	835, 815	324

[a] δ Values, in ppm, relative to external reference D_2O.
[b] 0.25 M:0.5 M W(VI)-L-mannonic acid solution.
[c] 1.0 M:0.5 M W(VI)-L-mannonic acid solution.
[d] 0.25 M:0.5 M Mo(VI)-L-mannonic acid solution.
[e] 1.0 M:0.5 M Mo(VI)-L-mannonic acid solution.

case of W(VI) in opposition to Mo(VI) which favours the formation of species **e**. The sets of (sharp) tungsten signals observed (Table 8) indicate the presence of a $W_2O_5^{2+}$ centre in the three species, with non-equivalent tungsten atoms [10,12,37–41]. Accordingly, the oxygen spectra show signals due to terminal W=O and to bridge W–O–W oxygen atoms [10,12,25,26]. COLOC Experiments show correlations between W-1 and H-3 and between W-2 and H-5, for complex **c**, and between W-1 and H-4 and between W-2 and H-6a for complex **d**. Inspired by the structures found by X-ray diffraction for the complexes of molybdate with lyxose [42] mannitol [43] and erythritol [44] and the suggested structures in solution [9,10,12,36–41], and recognizing that **c** and **d** must be isomers possessing the central diol group in an *erythro* configuration (only differing by the reversed orientation of the site of chelation) we propose the structures **3** and **4**, for complexes **c** and **d**, respectively.



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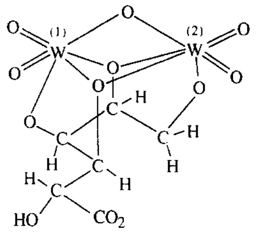
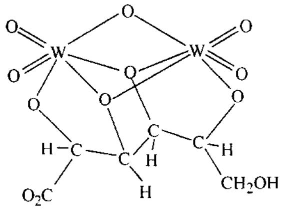


4

In both cases, the central part of the carbon chain must adopt a *sickle* arrangement so that the four OH groups point in the appropriate direction. This is required in view of the *erythro* configuration of the central diol group. As a consequence, the C-5 nucleus in complex **c** and C-4 in complex **d** undergo a larger low-field shift due to distortion with respect to the *zig-zag* geometry of the free ligand [36], the ligand O atoms involved in the W–O–W bridges being O-4 and O-6 for complex **c** and O-3 and O-5 for complex **d**. Simultaneously, protons H-3 and H-5, in complex **c** and H-4 and H-6a, in complex **d** become oriented in a *trans* configuration with respect to W-1 and W-2, respectively, as revealed by the observed W–H coupling constants and the cross peaks in the COLOC experiment (Table 8). Complex **c** is found to be more stable, in agreement with the stability rules proposed by Verchère et al. [36].

Regarding complex **e**, the broad ^{183}W signal precluded W–H correlations. The more uniform ^{13}C as ^1H shifts to high frequencies of the carbinol groups upon complexation point to a *zig-zag* conformation of the ligand, without appreciable loss of symmetry. Thus, we propose structure **5** for complex **e**.

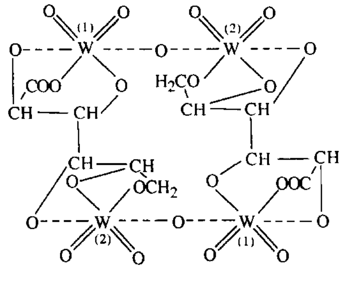


5

Similar structures were found by Burgmayer et al. by X-ray diffraction for the molybdate complex of 1,4-dithiothreitol [45] and proposed from NMR data by Verchère et al. for several tetradentate complexes of Mo(VI) [36,38] and W(VI) [41] with alditols possessing a central diol group of the coordination site in a *threo* configuration. In our previous NMR studies, we have found similar structures for the complexes that D-mannaric acid forms with Mo(VI) [9] and W(VI) [10], at high pH.

For complexes **c**, **d** and **e** formed with molybdate, we propose similar structures. In fact, the patterns of the ^1H and ^{13}C shifts induced by complexation are similar, the ^{95}Mo shifts are typical of $Mo_2O_5^{2+}$ groups [9,36,37,46,47] and the ^{17}O shifts are characteristic of Mo=O and O–Mo–O groups [26–29].

4:2 (Metal:ligand) complexes at intermediate pH. —For species **f** and **g**, detected at intermediate pH values for both systems (but more abundant with tungstate), all the carbon signals move to high frequency on complexation, as well as the corresponding proton signals. Concentration studies suggest that **f** and **g** are 4:2 species. In accordance, the ^{183}W spectra show two sets of tungsten signals whose δ values indicate the presence of $W_2O_5^{2+}$ groups in both complexes, with non-equivalent tungsten atoms [10,12,37–41]. Accordingly, the oxygen spectra show signals due to terminal W=O and to bridge W–O–W oxygen atoms [10,12,25,26]. COLOC Experiments show correlations between W-1 and H-3 and between W-2 and H-5, for complex **f** and between W-1 and H-2 and between W-2 and H-4, for complex **g**. The two ligand molecules in the 4:2 complexes are magnetically equivalent in spite of two ^{183}W signals being found for each complex. The structure proposed for one of these complexes is shown in structure **6** (and similarly for Mo(VI)) in which, for steric reasons, the carboxylate groups are *cis* to the bridge oxygen atoms. Two possibilities exist for the bonding of the OH-6 group: *cis* or *trans* to the bridge oxygen atoms. We have previously proposed similar structures for complexes of Mo(VI) with D-galactonic acid [12]. According to the ^{13}C shifts observed in both complexes, a lateral part of the carbon chain seems to adopt a *sickle* arrangement. This distortion relative to the *zig-zag* conformation leads to a large high frequency shift of the C-5 signal for complex **f** and of the C-4 signal for complex **g** and to significant W–H coupling constants.



6

2:1 (Metal:ligand) complexes at low and intermediate pH.—Complexes **h** and **i** are detected at low and intermediate pH values, especially with molybdate. The available ^{13}C and ^{1}H NMR parameters point to the involvement of O-2, O-3 and O-4 in complexation, besides the carboxylate group. Probably, **h** and **i** are tetradentate isomers possessing the central diol group in an *erythro* configuration, only differing by the reversed orientation of the site of chelation. For the first time, we detect the involvement of the carboxylate group on this kind of species. Unfortunately, its small abundance in the case of tungstate and the very congested region of the ^{183}W NMR spectrum from −68 to −90 ppm, preclude the total assignment of the W signals. COLOC Experiments show correlations between W-1 and H-2, for complex **h** and between W-2 and H-3, for complex **i**. Possible structures for complexes **h** and **i** are shown in structure **7** and **8**, respectively, and similarly for Mo(VI) as suggested by the similar patterns of the ^{1}H and ^{13}C shifts. The ^{95}Mo shifts are characteristic of $Mo_2O_5^{2+}$ groups [9,36,37,46,47] and the ^{17}O shifts are characteristic of Mo=O and O–Mo–O groups [26–29]. Complex **h** is more stable, in accordance with the stability rules proposed by Verchère et al. for alditols [36]. In addition, C-2 is expected to be

Table 8
^{183}W NMR chemical shifts [a] for W(VI) + L-mannonic acid, temp. 298 K

	$\delta^{183}W$	$^{3}J_{W-H}$
W(VI) + L-mannonic acid		
complex **a** [b] (pH^* 5.0)	41.3	3.9
complex **b** [b] (pH^* 5.0)	50.4	~ 0 ($\Delta\nu_{1/2}$ = 1.7 Hz)
complex **c** [c] (pH^* 7.5)	−80.2 (W-1)	7.4 (H-3)
	−71.3 (W-2)	9.1 (H-5)
complex **d** [c] (pH^* 7.5)	−70.4 (W-1)	9.2 (H-4)
	−70.6 (W-2)	9.2 (H-6a)
complex **e** [c] (pH^* 7.5)	−92.4	– [d]
complex **f** [c] (pH^* 5.0)	−72.9 (W-1)	7.3 (H-3)
	−70.5 (W-2)	9.8 (H-5)
complex **g** [c] (pH^* 5.0)	−77.3 (W-1)	7.9 (H-2)
		2.4
	−68.3 (W-2)	9.4 (H-4)
complex **h** [c] (pH^* 5.0)	−67.8 (W-1)	9.1 (H-2)
	– [e] (W-2)	
complex **i** [c] (pH^* 5.0)	– [e] (W-1)	
	−79.5 (W-2)	9.8 (H-3)

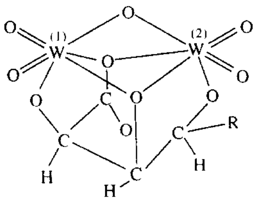
[a] δ Values, in ppm, relative to external reference Na_2WO_4, pH^* = 9.5; *J* values in Hz.
[b] 0.25 M:0.50 M W(VI)-L-mannonic acid solution.
[c] 2.0 M:1.0 M W(VI)-L-mannonic acid solution.
[d] Not resolved.
[e] Not assigned, due to low concentration of **h** and **i** and superposition with other signals.

Table 9
^{95}Mo NMR chemical shifts [a] for Mo(VI) + L-mannonic acid, temp. 298 K

	δ^{95}Mo	$\Delta\nu_{1/2}$
Mo(VI) + L-mannonic acid		
complex **a** [b] (pH* 5.0)	98	490
complex **b** [b] (pH* 5.0)	93	261
complexes **c** + **d** + **e** [c] (pH* 7.5)	35	638
	27	705
complexes **f** + **g** [c] (pH* 6.0)	38	363
	45	352
complexes **h** + **i** [c] (pH* 3.0)	27	305
	36	983

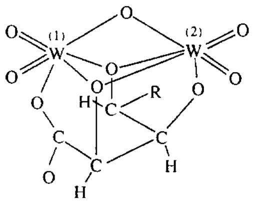
[a] δ Values in ppm, relative to external reference Na_2MoO_4, pH* = 9.0; $\Delta\nu_{1/2}$ in Hz.
[b] 0.25 M:0.5 M Mo(VI)-L-mannonic acid solution.
[c] 1.0 M:0.5 M Mo(VI)-L-mannonic acid solution.

more deshielded upon complexation for **h**, in agreement with the observed correlation between W-1 and H-2; similarly, C-3 is more shifted to high frequencies in the case of complex **i**.



R=CHOHCH$_2$OH

7



R=CHOHCH$_2$OH

8

4. Conclusion

The complexation of metal oxoions, namely tungstate and molybdate, with sugar acids has been the object of a thorough and systematic study for different pH and concentration conditions, using multinuclear (proton, carbon, oxygen and metal) magnetic resonance spectroscopy (1D and 2D). Having studied the main aldaric acids [8–10] and alduronic acids [11], D-galactonic acid was the first aldonic acid whose complexation was addressed [12] and L-mannonic acid is the subject of this study.

Nine complexes were identified for both tungsten(VI) and molybdenum(VI) systems, which means a greater complexity with respect to the previously studied systems of D-galactonic acid with molybdate and tungstate [12].

This is especially valid in the case of tungstate. Indeed, the great stability of 2:1 complexes with galactonic acid precludes the formation of additional species besides the two 1:2 diastereoisomers. The reason for the difference in the stability of the 2:1 complexes in both systems lies in a more favourable configuration of the four central OH groups in the case of D-galactonic acid (*threo-erythro-threo*) associated to a favourable entropy factor due to the non-involvement of the terminal groups [36]; in the case of mannonic acid, a similar configuration requires the involvement of the terminal OH group. On the other hand, the configuration of the four central OH groups of L-mannonic acid (*erythro-threo-erythro*) is not appropriate for the formation of dominant species. As a consequence, mannonic acid also forms 4:2 polymeric complexes and two other minor species.

In the case of molybdate, the 4:2 complexes are less stable than with tungstate, as expected on the basis of a greater tendency of tungstate to form polymeric species. Simultaneously, the minor species mentioned above become more abundant with molybdate. These are found to be 2:1 complexes in which the ligand molecules are bound to the metal through the carboxylate and the OH groups in positions 2, 3 and 4. It is noted that, in this way, a favourable configuration is involved (an *erythro* central diol group).

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