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NMR study of the complexation of D-galactonic acid with tungsten(VI) and molybdenum(VI)

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Abstract

By using multinuclear (1D and 2D) magnetic resonance spectroscopy, D-galactonic acid was found to form four complexes with tungsten(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, and, at high pH, two 2:1 complexes involving the four OH groups of the central part of the carbon chain. Homologous species were found with molybdenum(VI), in similar conditions, but four additional complexes were detected: two 4:2 isomers, at low pH, involving the carboxylate and all the hydroxyl groups, and two 2:1 complexes at intermediate pH. These complexes are not present in the case of W(VI) because of competition of polymerization equilibria of tungstate at low pH. Detailed structures are proposed for most of the complexes and formation constants are estimated for the W(VI) complexes. © 1997 Elsevier Science Ltd.

Keywords: Tungsten; Molybdenum; Complexes; D-Galactonic acid; NMR

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1. Introduction

Studies of the interaction of carbohydrates and their derivatives with metal ions have increased during the last few years, mainly due to the potential 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, they are present 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 some aldaric acids [8–10] and some uronic acids and their complexation with tungstate and molybdate ions [11], we now address an important aldonic acid: D-galactonic acid.

2. Experimental

Analytical grade sodium tungstate and sodium molybdate and commercially available D-galactonic acid (source D-galactono-1,4-lactone) were used.

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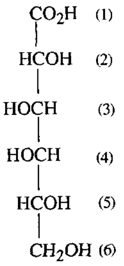
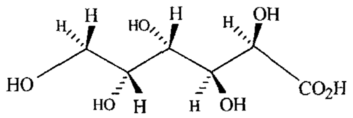
The pH was adjusted (cautiously, to reduce the possibility of drastic local disturbances of equilibria that may be slow to disappear) by addition of DCl and NaOD; the pH* values quoted are the direct pH-meter readings (room temperature) after standardization with aqueous (H_2O) buffers.

The ^1H and ^{13}C 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. The ^{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), 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, ($\delta = 0$) as external reference. The ^{17}O spectra were obtained on the same spectrometer (67.760 MHz), using D_2O ($\delta = 0$) as external reference. Detailed conditions can be found in previous papers [8–10]. The 2D NMR spectra, DQFCOSY [12], HETCOR [13], and COLOC [14] were recorded on a Varian Unity 500 NMR spectrometer.

3. Results and discussion

D-Galactonic acid (**1**) has been shown to exist preferably in a planar zigzag conformation in solution by Horton et al. [15] from a study of the ^1H NMR spectrum in pyridine solution, compared with the ^{13}C spectra of the corresponding aqueous solution. The ^{13}C signals could not be assigned unambiguously at that time, the same being said of other ^{13}C NMR studies of those systems reviewed by Bock and Pedersen [16].





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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. This we have done, 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. Whenever necessary, the proton assignments were established by COSY recordings, and the parameters were confirmed by spectrum simulation of the second-order patterns. Our results are in agreement with the previous studies. It was found that the various NMR parameters change only slightly with pH, which is an indication that no major conformational changes occur.

Complexation with W(VI).—No reference has been found in the literature to complexes of D-galactonic acid with tungstate or molybdate ions. Indeed, the only previous studies of complexation of this acid with metal ions have been limited to Fe(III) using potentiometric techniques [17], Ni(II) and Co(II) using potentiometric techniques and ^{13}C NMR spectroscopy [18], and Zn(II) whose metal–sugar salts were isolated and characterized by elemental analysis, FT IR spectroscopy, thermogravimetric analysis, and ^{13}C NMR spectroscopy [19].

Table 1
^1H NMR parameters [a] for D-galactonic acid [b] at 298 K

	H-2	H-3	H-4	H-5	H-6a	H-6b	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$\lvert J_{6a,6b}\rvert$
pH* 3.0	4.61	4.12	3.75	4.02	3.76	3.75	2.0	10.0	1.0	5.3	6.8	11.5
pH* 5.0	4.34	4.02	3.71	4.02	3.76	3.75	2.0	10.0	1.0	5.3	6.8	11.5
pH* 7.5	4.33	4.02	3.70	4.02	3.76	3.75	2.0	10.0	1.0	5.3	6.8	11.5
pH* 10.6	4.32	4.02	3.70	4.03	3.76	3.75	1.5	9.5	1.0	5.3	6.8	11.5

[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] 0.10 M D-Galactonic acid solution.

Table 2
^{13}C NMR chemical shifts [a] for D-galactonic acid [b] at 298 K

	C-1	C-2	C-3	C-4	C-5	C-6
pH * 3.0	179.46	72.18	72.62	70.71	71.35	64.76
pH * 5.0	181.04	72.84	72.96	71.14	71.53	64.79
pH * 7.5	181.19	72.84	72.84	71.14	71.53	64.79
pH * 10.6	181.19	72.84	72.84	71.14	71.53	64.79

[a] δ Values, in ppm, relative to Me_4Si, using *tert*-butyl alcohol (δ_C 31.2) as internal reference.
[b] 0.50 M D-Galactonic acid solution.

Depending on pH, concentration, and molar ratios, mixtures of sodium tungstate and D-galactonic acid, in aqueous solution, show additional ^1H and ^{13}C signals due to complexed forms, besides those of the free ligand. An illustration is given in Fig. 1. The observation of distinct signals for bound and free ligand is a consequence of slow ligand exchange on the NMR time-scale, which renders a speciation study more direct using this technique.

Spectra of W(VI)–D-galactonic acid were recorded for total concentrations of the complexing species ranging from 2.5 to 0.10 M, metal:ligand molar ratios from 4 to 0.25, and pH * values ranging from 3 to 10. Under these conditions, four different sets of signals were detected. Signal intensity considerations enabled the conclusion that these sets correspond to four different complexes. Two of them, **a** and **b**, are formed at any pH, especially when the metal:ligand molar ratio is less than 1. The other two, **c** and **d**, only occur at pH * greater than 4 and for molar ratios larger than 1. The way in which the concentrations of the various complexes vary with pH *, for two different molar ratios, is shown in Fig. 2.

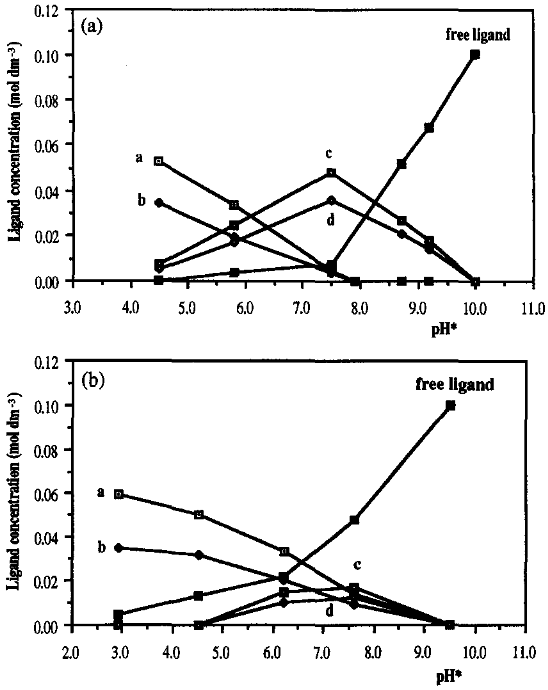


Fig. 2. Concentration of the ligand as a function of pH *, obtained by ^1H NMR for (a) a 0.20 M:0.10 M D_2O solution (2 M KNO_3) of sodium tungstate(VI) and D-galactonic acid at 298 K, and (b) a 0.05 M:0.10 M D_2O solution (2 M KNO_3) of sodium tungstate(VI) and D-galactonic acid at 298 K.

The above observations suggest that **a** and **b** might be isomers of stoichiometry 1:2 (metal to ligand), whereas **c** and **d** could be n:1 complexes, with $n \geq 1$. Taking advantage of conditions for which only **a** and **b** are present, and others in which **c** and **d** are dominant, Job's plots based on the proton NMR intensities could be attempted. These are shown in Figs. 3 and 4 and strongly support the proposal of 1:2 complexation for **a** and **b**, and 2:1 complexation for **c** and **d**.

A rough estimate of the formation constants for complexes **a** and **b**, based on the proton signal inten-

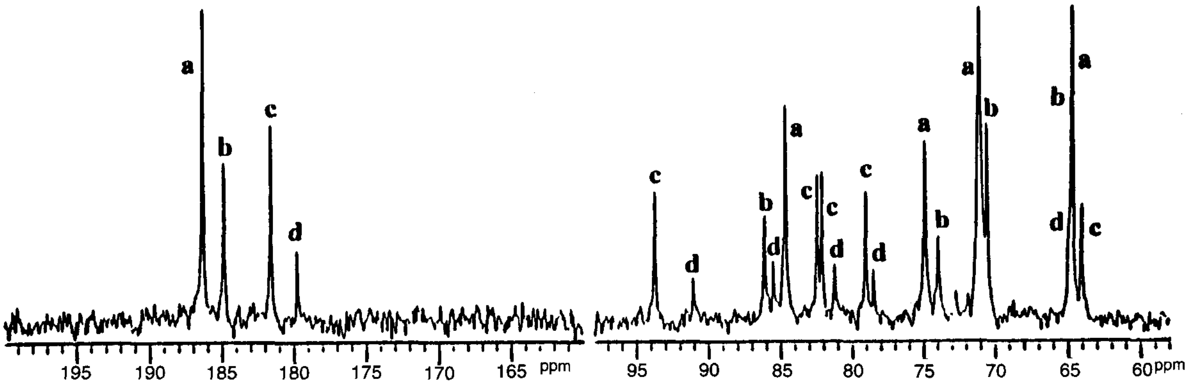


Fig. 1. ^{13}C NMR spectrum (50.30 MHz) of a 2.0 M:0.50 M aqueous solution (33% D_2O) of W(VI)–D-galactonic acid, pH * = 5.0, 294 K.

sities, leads to conditional pK values of -3.8 and -3.7, for pH* 3.6 and assuming the equation $M + 2L = ML_2$. Similarly, for **c** and **d**, with $2M + L = M_2L$, at pH* 7.5, we get pK -3.7 and -3.5, respectively.

The way in which the ligand is bonded to the metal can be established from the proton and carbon chemical shifts, compared with the free ligand at the same pH. The ^{183}W and ^{17}O chemical shifts can elucidate the nature of the metal centre in the complex. The vicinal proton–proton coupling constants can be explored to infer the conformation of the bound ligand. Vicinal tungsten–proton coupling constants can also help to establish some details of the structures. The ^{1}H, ^{13}C, ^{17}O, and ^{183}W NMR parameters are shown in Tables 3–6, respectively. Whenever necessary, COSY and HETCOR experiments were performed to assign the proton and carbon shifts. An example (DQFCOSY) is given in Fig. 5.

So far as complexes **a** and **b** are concerned, the tungsten shifts are characteristic of WO_2^{2+} centres [10,11,20] and the oxygen shifts are typical of terminal W=O groups [10,11,21,22]. 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 [8–11,23–28]; the other carbon shifts are much smaller. Accordingly, only the proton H-2 undergoes a significant chemical shift, which is to high frequency.

All these findings point to **a** and **b** being the diastereomers **2** and **3**. The two ligand molecules are magnetically equivalent, complex **a** being slightly more stable than **b** mainly for steric reasons involving the R chains. 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 (not measurable in the W signals having linewiths of 3.3 and 2.2 Hz, respectively, for complexes **a** and **b**). In addition, the fact that H-2 in structure **2** is more affected by the magnetic anisotropy associated with W=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 other related systems [11,20,24,26,27].

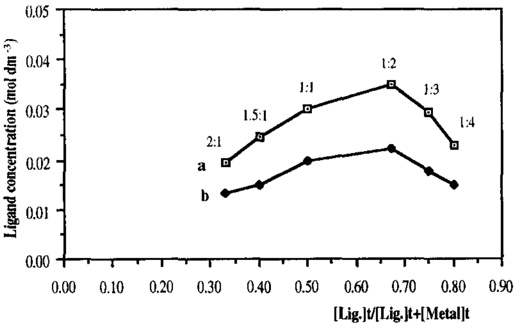


Fig. 3. Job's plot based on ^{1}H NMR spectral intensities for the system W(VI) + D-galactonic acid; total concentration of complexing species, 0.10 M (D_2O solutions, 2 M in KNO_3, pH* = 3.6, 298 K).

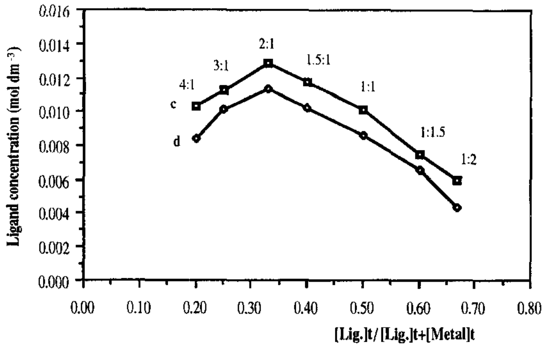
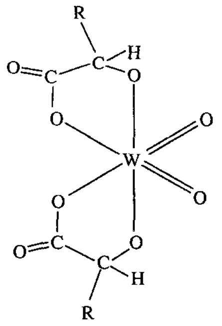


Fig. 4. Job's plot based on ^{1}H NMR spectral intensities for the system W(VI) + D-galactonic acid; total concentration of complexing species, 0.10 M (D_2O solutions, 2 M in KNO_3, pH* = 7.5, 298 K).



R=(CHOH)$_3$CH$_2$OH

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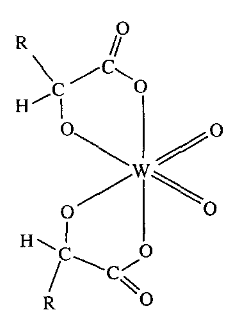


R=(CHOH)$_3$CH$_2$OH

3

Concerning the 2:1 complexes **c** and **d**, which are formed specially at high pH*, we note the shifts to high frequency of C-2, C-3, C-4, and C-5, as well as those for the corresponding H nuclei. This shows that the coordination is made via the deprotonated OH groups in positions 2, 3, 4, and 5. This situation is similar to that found by Verchère et al. [29–33] for the complexes of alditols with tungstate and molybdate and by us for the complexes of galactaric acid with those metal ions [9,10]. Both the ^{183}W and ^{17}O spectra help in further characterizing the structures.

Thus, the two sets of tungsten signals observed and the corresponding δ values indicate the presence of $W_2O_5^{2+}$ groups in both complexes, with non-equivalent tungsten atoms. Accordingly, the oxygen spectra show signals due to terminal W=O and to bridge W–O–W oxygen atoms [10,21,22].

Inspired by the structures found by X-ray diffraction for the complexes of molybdate with mannitol [34] and erythritol [35] and the suggested structures in solution [29–33], we propose structures **4** and **5** for complexes **c** and **d**, which are similar to those found for the system W(VI)–galactaric acid at high pH [10]. In both complexes, the central part of the carbon chain of the acid must adopt a sickle arrangement so that the four OH groups point in the appropriate direction. This is required in view of the *erythro*

Table 3
^{1}H NMR parameters [a] for W(VI) + D-galactonic acid and Mo(VI) + D-galactonic 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) + D-*Galactonic acid*												
Complex **a** [b] (pH * 5.0)												
δ	5.17	4.12	3.80	4.05	3.76	3.75	1.2	9.8	1.0	5.3	6.8	11.5
$\Delta\delta$	0.83	0.10	0.09	0.03	0.00	0.00						
Complex **b** [b] (pH * 5.0)												
δ	5.50	4.02	3.79	4.10	3.76	3.75	1.6	9.8	1.0	5.3	6.8	11.5
$\Delta\delta$	1.16	0.00	0.08	0.08	0.00	0.00						
Complex **c** [c] (pH * 7.5)												
δ	4.89	5.65	4.86	4.95	3.94	3.82	4.4	0	0	8.1	5.2	11.5
$\Delta\delta$	0.56	1.63	1.16	0.93	0.18	0.07						
Complex **d** [c] (pH * 7.5)												
δ	5.08	5.27	5.40	4.58	3.76	3.75	0	4.4	0	6.6	6.6	11.5
$\Delta\delta$	0.75	1.25	1.69	0.56	0.00	0.00						
Mo(VI) + D-*Galactonic acid*												
Complex **a** [d] (pH * 5.0)												
δ	5.03	4.07	3.74	4.07	3.76	3.75	– [e]	– [e]	– [e]	– [e]	– [e]	– [e]
$\Delta\delta$	0.69	0.05	0.03	0.05	0.00	0.00						
Complex **b** [d] (pH * 5.0)												
δ	5.31	4.07	3.74	4.07	3.76	3.75	– [e]	– [e]	– [e]	– [e]	– [e]	– [e]
$\Delta\delta$	0.97	0.05	0.03	0.05	0.00	0.00						
Complex **c** [f] (pH * 7.5)												
δ	4.76	5.09	4.71	4.63	3.93	3.80	4.4	0	0	8.1	5.3	11.3
$\Delta\delta$	0.43	1.07	1.00	0.61	0.17	0.05						
Complex **d** [f] (pH * 7.5)												
δ	4.83	5.16	4.86	4.40	3.76	3.75	0	4.3	0	6.6	6.6	11.5
$\Delta\delta$	0.50	1.14	1.16	0.38	0.00	0.00						
Complex **e** [f] (pH * 3.0)												
δ	5.25	4.84	5.14	5.18	4.77	4.43	4.4	0	0	2.7	0	10.3
$\Delta\delta$	0.64	0.72	1.39	1.16	1.01	0.68						
Complex **f** [f] (pH * 3.0)												
δ	5.35	5.13	4.54	4.80	4.03	3.87	6.3	3.7	0	0	2.8	10.0
$\Delta\delta$	0.74	1.01	0.79	0.78	0.27	0.12						
Complex **g** [f] (pH * 5.0)												
δ	5.04	4.57	4.51	5.00	4.40	3.87	3.1	10.5	0	0	3.2	10.4
$\Delta\delta$	0.70	0.55	0.80	0.98	0.64	0.12						
Complex **h** [f] (pH * 5.0)												
δ	4.90	5.11	4.52	4.73	3.95	3.84	4.0	0	0	8.4	5.1	11.6
$\Delta\delta$	0.56	1.09	0.81	0.72	0.19	0.06						

[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:0.10 M W(VI)–D-galactonic acid solution.
[c] 0.20 M:0.10 M W(VI)–D-galactonic acid solution.
[d] 0.05 M:0.10 M Mo(VI)–D-galactonic acid solution.
[e] Broad signals.
[f] 0.20 M:0.10 M Mo(VI)–D-galactonic acid solution.

configuration of the central diol group. As a consequence, the C-3 nucleus in complex **c** and C-4 in complex **d** undergoes a larger low-field shift due to distortion with respect to the zigzag geometry of the free ligand [29]. The two isomers arise because the ligand O atoms involved in the W–O–W bridges can be either O-2 and O-4, structure **4**, or O-3 and O-5, structure **5**. The increase of the J (H-2, H-3) value upon complexation is in accordance with a slight increase of the corresponding HCCH dihedral angle as shown by molecular models. Also, the observed vicinal W–H coupling constants between each W nucleus and protons H-3 and H-5, and protons H-2 and H-4, respectively, for structures **4** and **5**, point to WOCH dihedral angles close to 180°, in agreement with those models. The assignment of the structures **4** and **5** to complexes **c** and **d**, respectively, was possible by a COLOC experiment. This shows that, for

Table 4
^{13}C NMR chemical shifts [a] for W(VI) + D-galactonic acid and Mo(VI) + D-galactonic acid at 298 K

	C-1	C-2	C-3	C-4	C-5	C-6
W(VI) + D-Galactonic acid						
Complex **a** [b] (pH * 5.0)						
δ	186.46	84.90	75.13	71.19	71.36	64.81
$\Delta\delta$	5.42	12.06	2.17	0.05	−0.17	0.02
Complex **b** [b] (pH * 5.0)						
δ	184.94	86.33	74.29	71.36	70.76	64.81
$\Delta\delta$	3.90	13.49	1.33	0.22	−0.77	0.02
Complex **c** [c] (pH * 7.5)						
δ	181.66	82.55	93.90	79.20	82.18	64.05
$\Delta\delta$	0.47	9.71	21.06	8.06	10.65	−0.74
Complex **d** [c] (pH * 7.5)						
δ	179.81	81.31	85.67	91.14	78.52	64.86
$\Delta\delta$	−1.38	8.47	12.83	20.00	6.99	0.07
Mo(VI) + D-Galactonic acid						
Complex **a** [d] (pH * 5.0)						
δ	185.80	85.52	75.19	71.16	71.47	64.85
$\Delta\delta$	4.76	12.68	2.23	0.02	−0.06	0.06
Complex **b** [d] (pH * 5.0)						
δ	184.19	87.13	74.20	71.16	71.47	64.85
$\Delta\delta$	3.15	14.29	1.24	0.02	−0.06	0.06
Complex **c** [e] (pH * 7.5)						
δ	182.95	83.23	94.53	80.09	83.09	64.12
$\Delta\delta$	1.76	10.39	21.69	8.95	11.56	−0.67
Complex **d** [e] (pH * 7.5)						
δ	180.78	82.48	86.55	91.53	78.94	65.13
$\Delta\delta$	−0.41	9.64	13.71	20.39	7.41	0.34
Complex **e** [e] (pH * 3.0)						
δ	186.18	85.22	86.48	85.79	85.99	75.67
$\Delta\delta$	6.72	13.04	13.86	15.08	14.64	10.91
Complex **f** [e] (pH * 3.0)						
δ	187.88	81.87	85.97	84.55	86.57	70.09
$\Delta\delta$	8.42	9.69	13.35	13.84	15.22	5.33
Complex **g** [e] (pH * 5.0)						
δ	183.59	83.91	80.16	81.89	83.85	70.02
$\Delta\delta$	2.55	11.07	7.20	10.75	12.32	5.23
Complex **h** [e] (pH * 5.0)						
δ	183.59	83.31	93.81	87.67	82.32	64.08
$\Delta\delta$	2.55	10.47	20.97	16.53	10.79	−0.71

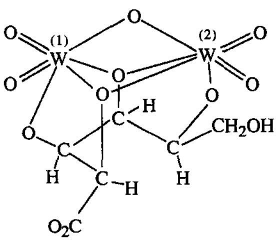
[a] δ Values, in ppm, relative to Me_4Si, using *tert*-butyl alcohol (δ_C 31.2) as internal reference.
[b] 0.25 M:0.50 M W(VI)–D-galactonic acid solution.
[c] 1.0 M:0.50 M W(VI)–D-galactonic acid solution.
[d] 0.25 M:0.50 M Mo(VI)–D-galactonic acid solution.
[e] 1.0 M:0.50 M Mo(VI)–D-galactonic acid solution.

Table 5
^{17}O NMR chemical shifts [a] for W(VI) + D-galactonic acid and Mo(VI) + D-galactonic acid at 298 K

	$-\overset{\|}{\underset{\|}{M}}={}^{17}O$	$-\overset{\|}{\underset{\|}{M}}-{}^{17}O-\overset{\|}{\underset{\|}{M}}-$
W(VI) + D-Galactonic acid		
Complex **a** [b] (pH * 5.0)	636	–
Complex **b** [b] (pH * 5.0)	647	–
Complexes **c** + **d** [c] (pH * 7.5)	615, 625, 628, 630	246, 300
Mo(VI) + D-Galactonic acid		
Complex **a** [d] (pH * 5.0)	839	–
Complex **b** [d] (pH * 5.0)	849	–
Complexes **c** + **d** [e] (pH * 7.5)	812, 798, 786, 670	320, 314
Complexes **e** + **f** [e] (pH * 3.0)	740, 715, 691, 660	291, 377
Complexes **g** + **h** [e] (pH * 5.0)	757, 729, 719, 700	414

[a] δ Values, in ppm, relative to external reference D_2O.
[b] 0.25 M:0.50 M W(VI)–D-galactonic acid solution.
[c] 1.0 M:0.50 M W(VI)–D-galactonic acid solution.
[d] 0.25 M:0.50 M Mo(VI)–D-galactonic acid solution.
[e] 1.0 M:0.50 M Mo(VI)–D-galactonic acid solution.

complex **c**, the (*trans*) W–H couplings arise between W-1 and H-3 and between W-2 and H-5 (Table 6). Similarly, for complex **d**, the (*trans*) W–H couplings arise between W-1 and H-2 and between W-2 and H-4 (Table 6).



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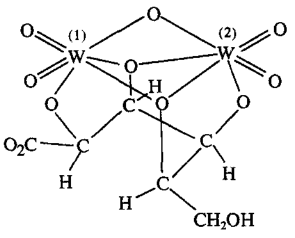

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Complexation with Mo(VI).—The study carried out using molybdate solutions was similar to that for tungstate. Depending on pH, concentration, and molar ratios, eight complexes were detected. The ^1H, ^{13}C, ^{17}O, and ^{95}Mo NMR parameters are given in Tables 3–5 and 7, respectively. Whenever necessary, COSY and C–H HETCOR experiments were performed to remove any ambiguities concerning the assignment of proton and carbon shifts.

Of those eight complexes, four are the homologous species of the complexes found with tungstate: two 1:2 diastereomers (complexes **a** and **b**), at any pH and, specially, when the metal:ligand molar ratio is less than 1; and two 2:1 complexes (complexes **c** and **d**) at higher pH. Due to the presence of other complexes, it was not possible to make a direct estimation of formation constants. The same fact precluded the use of Job's plots based on proton signal intensities, as was done with W(VI). The ^{17}O and ^{95}Mo chemical shifts (Tables 5 and 7) lend support to the proposal of structures similar to those advanced for the tungsten system. In particular, for complexes **c** and **d**, ^{17}O shifts characteristic of a Mo–O–Mo bridge were recorded [22,36,37], as well as ^{95}Mo shifts characteristic of a $Mo_2O_5^{2+}$ group [9,29,30]. Complexes **a** and **b** show no bridge oxygen signals [22,36,37] and have Mo shifts characteristic of MoO_2^{2+} centres [8,9,11,38].

For metal:ligand molar ratios larger than 1, four additional complexes are detected. These are taken to be polynuclear species which do not form in the case of W(VI), presumably because of competition with polymerization equilibria in the case of tungstate. One pair, complexes **e** and **f**, shows an increase of concentration relative to the other pair, complexes **g**

Table 6
^{183}W NMR chemical shifts [a] for W(VI) + D-galactonic acid at 298 K

	$\delta^{183}W$	$^3J_{W,H}$
W(VI) + D-Galactonic acid		
Complex **a** [b] (pH * 5.0)	48.1	~ 0
Complex **b** [b] (pH * 5.0)	57.6	~ 0
Complex **c** [c] (pH * 7.5)	−67.8 (W-1)	9.15 (H-3)
	−80.2 (W-2)	7.94 (H-5)
Complex **d** [c] (pH * 7.5)	−78.7 (W-1)	8.43 (H-2)
	−71.8 (W-2)	9.55 (H-4)

[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)–D-galactonic acid solution.
[c] 1.0 M:0.50 M W(VI)–D-galactonic acid solution.

and **h**, when the total concentration of the solution increases. This suggests that complexes **e** and **f** are 4:2 isomers whereas complexes **g** and **h** are 2:1 species.

Fig. 6 shows the way in which the concentrations of the various complexes change with pH, for two concentration conditions.

The two ligand molecules in the 4:2 complexes are magnetically equivalent and two ^{95}Mo signals are found for each complex (Table 7). As expected, bridge oxygen signals are detected, one for each complex (Table 5). All the carbon signals move to high frequency on complexation, as well as the corresponding proton signals. For one of these complexes, structure **6** is proposed, where, for steric reasons, the carboxylate groups are *cis* to the bridge oxygen atom. This is similar to a structure previously proposed for complexes of Mo(VI) with galactaric and D-mannaric acids [9]. Two possibilities exist for the bonding of the OH group: *cis* or *trans* to the bridge oxygen atom. We attribute the occurrence of two isomers to this factor, in view of the different ^{13}C shifts for that group in complexes **e** and **f**. The alternative possibility of a *cis*-type complex with both carboxylate groups bonded to the same $Mo_2O_5^{2+}$ moiety is excluded on the basis of molecular models

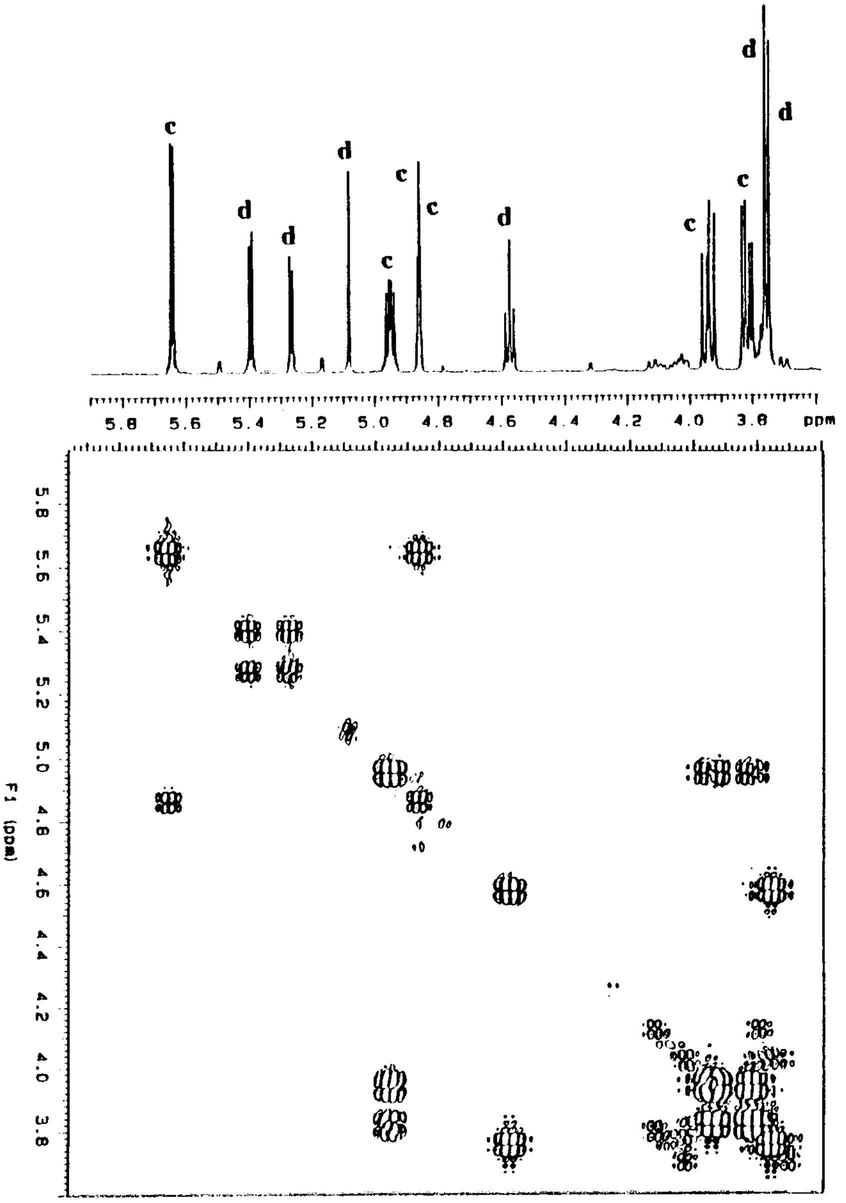


Fig. 5. DQFCOSY of a 0.20 M:0.10 M D_2O solution of W(VI)–D-galactonic acid (pH* = 7.5, 298 K).

Table 7
^{95}Mo NMR chemical shifts[a] for Mo(VI) + D-galactonic acid at 298 K

	$\delta\,^{95}$Mo	$\Delta\nu_{1/2}$
Mo(VI) + D-Galactonic acid		
Complex **a**[b] (pH* 5.0)	105	318
Complex **b**[b] (pH* 5.0)	100	225
Complex **c**[c] (pH* 7.5)	39	323
	27	225
Complex **d**[c] (pH* 7.5)	35	105
	31	218
Complexes **e** + **f**[d] (pH* 3.0)	74	386
	51	541
	64	245
	41	668
Complexes **g** + **h**[c] (pH* 5.0)	73	284
	50	427
	37	296
	28	359

[a] δ values relative to external reference Na_2MoO_4, pH* = 9.0; $\Delta\nu_{1/2}$ in Hz.
[b] 0.25 M:0.50 M Mo(VI)–D-galactonic acid solution.
[c] 1.0 M:0.50 M Mo(VI)–D-galactonic acid solution.
[d] 1.0 M:0.10 M Mo(VI)–D-galactonic acid solution.

and the magnetic equivalence of the two ligand molecules. Geometries adjusted to the observed vicinal H–H coupling constants are easily established.

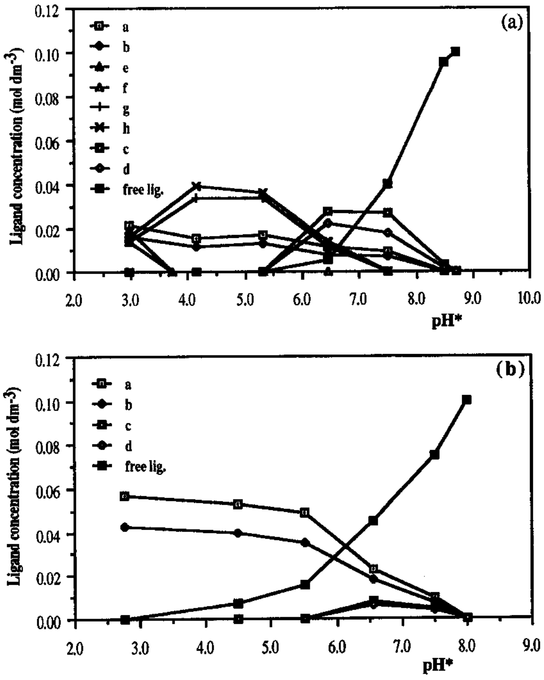
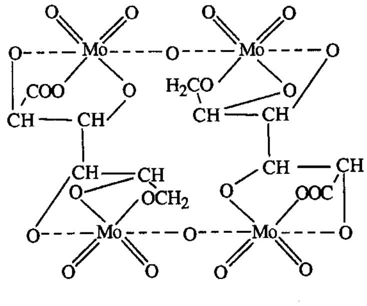


Fig. 6. Concentration of the ligand as a function of pH*, obtained by ^{1}H NMR for (a) a 0.20 M:0.10 M D_2O solution (2 M KNO_3) of sodium molybdate(VI) and D-galactonic acid at 298 K (2 M KNO_3), and (b) a 0.05 M:0.10 M D_2O solution (2 M KNO_3) of sodium molybdate(VI) and D-galactonic acid at 298 K.

As pH* is increased to 5, complexes **e** and **f** are gradually replaced by complexes **g** and **h**. One of these, **h**, gives rise to a ^{17}O signal characteristic of a Mo–O–Mo bridge. In accordance, the ligand adopts a sickle arrangement so that the four central OH groups can be involved in chelation, as revealed by the proton and carbon shifts. This distortion is confirmed by a large high-frequency shift of the C-3 signal. Therefore, this complex appears to have a structure (**7**) similar to one of the high pH complexes (**c**, **d**), presumably only differing by an additional involvement of the carboxylic group, as suggested by a higher shift of C-1.



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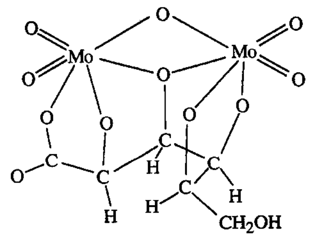

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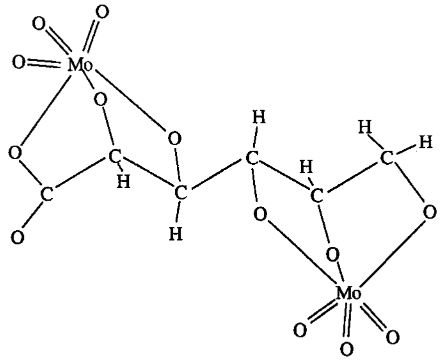

8

The other complex (**g**) differs in two ways: the terminal OH group is involved in complexation and the proton coupling constant $J_{3,4}$ is typical of a *trans* configuration of H-3 and H-4. This points to a structure **8** involving two separate MoO_3 groups bridged by a ligand molecule with a zigzag conformation. A similar structure was previously proposed for the systems Mo(VI)–EDTA [39] and Mo(VI)–D-glucaric acid [8].

4. Conclusion

Quite complex systems involving metal oxoions, namely tungstate and molybdate, and sugar acids in aqueous solution have 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 aldaric and some alduronic acids [8–11], we have now turned to aldonic acids; D-galactonic acid was the first study to be completed, while D-gluconic and D-mannonic acids will be the subject of future papers.

Four complexes were identified in the case of tungsten(VI) (two 1:2 and two 2:1) and characterized in some detail. In the case of molybdenum(VI), besides a set of four complexes homologous of the tungsten ones, four additional complexes (two 4:2 and two 2:1) were detected, at low pH, which are not present in the W(VI) system probably because of competition with polymerization equilibria.

Acknowledgements

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