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NMR spectroscopy study of the complexation of D-gluconic 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), D-gluconic acid is found to form 10 and 8 complexes, respectively, 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 and one 2:1 complex, involving the carboxylate group and three OH groups are present in the whole pH range covered (2–11). At high pH, three 2:1 complexes are detected, each one involving four hydroxyl groups of the ligand. At intermediate pH values, two additional 5:2 isomeric complexes are found involving the carboxylate group and all the hydroxyl groups. Tungsten(VI) in alkaline medium is also able to form two additional (tetradentate and tridentate) 2:1 species. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: Tungsten complexes; Molybdenum complexes; D-Gluconic acid; NMR

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 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, being 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].

The work presented here on the complexation of D-gluconic acid concludes our systematic study using multinuclear high field NMR spectroscopy (1D and 2D) which started with aldaric acids [8–10], was continued with alduronic acids [11], and was more recently extended to D-galactonic acid and L-mannonic acids [12,13].

The complexation of D-gluconic acid with tungstate and molybdate ions has been the subject of several studies. Polarimetric, polarographic, spectrophotometric methods and ^{13}C NMR spectroscopy have been used in those studies [14–18]. Its complexation with other metals has also been studied, namely with Co(III) [19], Fe(III) [20,21], Mn(II) [22–24], Zn(II) [25,26], Cu(II) [27], Cd(II) and Hg(II) [25], Co(II) and Ni(II) [28], Cr(III) [29], Al(III), Ga(III) and

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In(III) [30], and with Eu(III) in the form of the chiral shift reagents 1,2-propanediaminetetraacetatoeuropium(III) [31] and propylenediaminetetraacetatoeuropium(III) [32]. Previously, Sawyer [33] published a review on gluconate complexes of various metal ions, including molybdate and tungstate.

2. Experimental

Analytical grade disodium tungstate and disodium molybdate dihydrates and commercially available D-gluconic acid (from D-gluconic acid, potassium salt) were used.

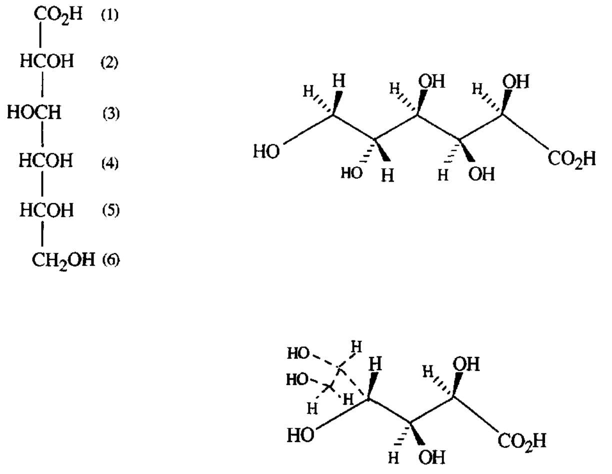
The pH was adjusted (cautiously, to reduce the possibility of drastic local disturbances of equilibria that may be slow to disappear) by addition of DCl and NaOD; the pH * values quoted are the direct pH-meter readings (room temperature) after standardization with aqueous (water) buffers.

The ^{13}C spectra were obtained on a Varian XL-200 instrument and the ^{1}H, ^{17}O, ^{95}Mo and ^{183}W spectra were obtained on a Varian Unity-500 NMR spectrometer. The detailed conditions can be found in previous papers [8–13]. The 2D NMR spectra, DQF-COSY [34], HETCOR [35] and COLOC [36], were recorded on a Varian Unity-500 NMR spectrometer.

3. Results and discussion

Gluconic acid has been shown to exist in at least two forms in solution, the planar straight chain form and the bent chain form (Scheme 1).

This conclusion has been established namely by Horton et al. [37] from a study of the ^{1}H NMR spectrum in pyridine solution, compared with the ^{13}C spectra of the corresponding aqueous solution, and by van Duin et al. [38,39] from a comparative study of several polyhydroxycarboxylates in aqueous solution using ^{1}H and ^{13}C NMR spectroscopy following previous studies reviewed by Bock and Pedersen [40]. An unambiguous assignment of these signals was made by Escandar et al. [30], in a subsequent study, using the ^{1}H–^{13}C two-dimensional NMR correlation.



Scheme 1.

The proton and carbon chemical shifts, as well as the proton–proton coupling constants, are shown in Tables 1 and 2, respectively, for different pH values. Our results are in agreement with the previous studies mentioned above. It is found that the various NMR parameters change only slightly with pH, which is an indication that no major conformational changes occur.

Depending on pH, concentration, and molar ratios, mixtures of sodium tungstate or sodium molybdate and D-gluconic acid, in aqueous solution, show additional ^{1}H and ^{13}C signals due to complexed forms, besides those of the free ligand eventually present.

Spectra of M(VI)–D-gluconic acid (M = W or Mo) were recorded for total concentration species ranging from 3.0 to 0.10 M, metal:ligand molar ratios from

Table 1
^{1}H NMR parameters[a] for D-gluconic acid at 298 K

D-Gluconic acid[b]	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 * = 3.3												
δ	4.38	4.15	3.81	3.82	3.88	3.72	4.0	3.0	7.4	2.5	5.5	11.8
pH * = 5.4												
δ	4.19	4.09	3.81	3.82	3.87	3.72	3.5	2.5	7.4	2.0	5.5	11.8
pH * = 7.4												
δ	4.18	4.09	3.81	3.82	3.87	3.72	3.5	2.5	7.4	2.0	6.0	11.8
pH * = 10.8												
δ	4.18	4.09	3.81	3.82	3.87	3.72	3.5	2.5	7.4	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] 0.10 M D-gluconic acid solution.

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

D-Gluconic acid[b]	C-1	C-2	C-3	C-4	C-5	C-6
pH* = 3.0						
δ	178.48	74.46	72.21	73.42	72.59	64.10
pH* = 5.0						
δ	180.12	75.53	72.45	74.03	72.67	64.10
pH* = 7.5						
δ	180.20	75.58	72.47	74.07	72.68	64.10
pH* = 10.2						
δ	180.36	75.58	72.47	74.07	72.68	64.10

[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-gluconic acid solution.

10 to 0.25, and pH* values ranging from 3 to 12 for the case of W(VI) and 2 to 9 for Mo(VI). Under these conditions, 10 different sets of signals were detected for W(VI) and 8 for Mo(VI). Signal intensity considerations enabled the conclusion that these sets correspond to 10 different complexes for W(VI) and 8 for Mo(VI). 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* 5.0–9.5 for W(VI) and 5.5–8.5 for Mo(VI) and for both systems for metal:ligand molar ratios larger than 1. For the pH ranges 3.5–7.5 and 4.0–8.0, for W(VI) and Mo(VI), respectively, and for solutions having metal:ligand molar ratios larger than 1, two other species are formed: **f** and **g**. The differences between the two systems are more pronounced at low and high pH, especially when the metal:ligand molar ratio is larger than 1. Thus, for the pH range 3–3.5, W(VI) forms only complexes **a** and **b** in significant concentration, whereas Mo(VI) also forms one abundant species **h**, which is present up to pH about 7.5. In the

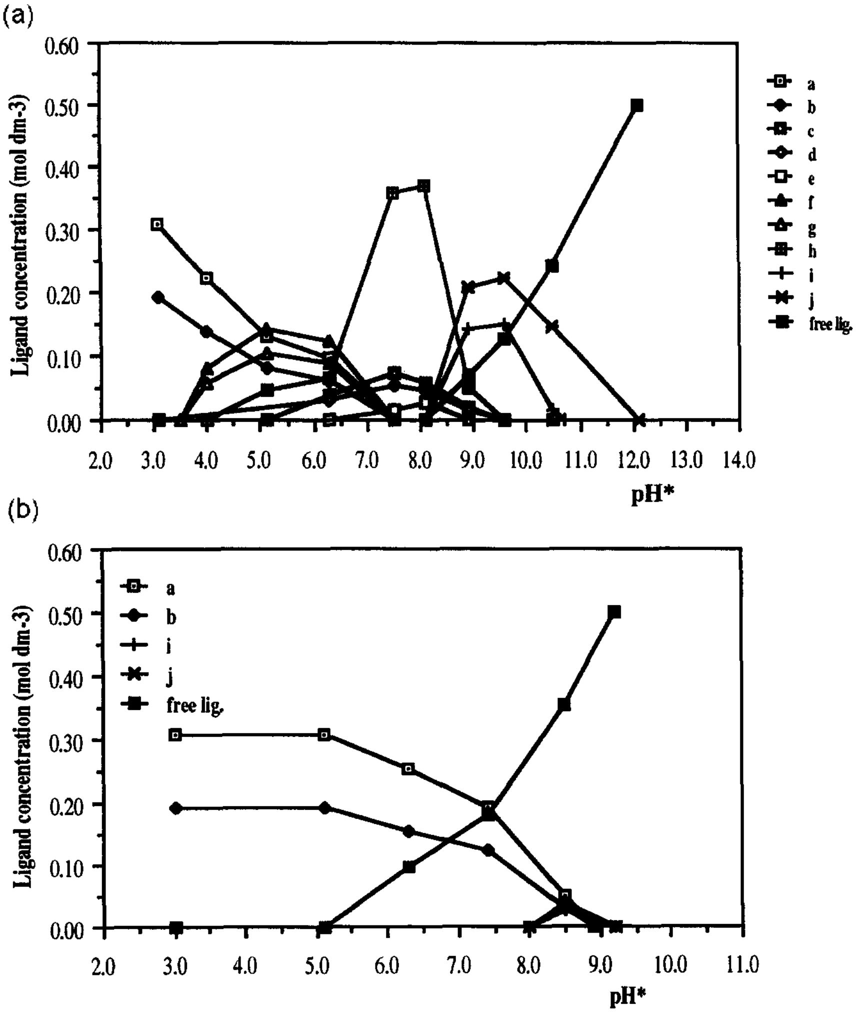


Fig. 1. Concentration of the ligand as a function of pH*, obtained by ^{13}C NMR for (a) a 1.0:0.50 M aqueous solution (33% deuterium oxide) of sodium tungstate(VI) and D-gluconic acid, temp. 294 K and (b) a 0.5:1.0 M aqueous solution (33% deuterium oxide) of sodium tungstate(VI) and D-gluconic acid, temp. 294 K.

case of tungstate, homologous species of **h** appear in the pH range 4–9.5, and in the pH range 8.0–12, two more species, **i** and **j**, appear. No homologous species of **i** and **j** with molybdate are detected.

The way in which the concentrations of the various species vary with pH *, for two different molar ratios, is shown in Figs. 1 and 2, for tungstate and molybdate, respectively. The approximate concentrations of the complexes are based on ^{13}C signal intensities (excluding the carboxylate due to its longer relaxation time), because the ^{1}H signals for some species, for both systems, are too broad.

The observations mentioned above suggest that **a** and **b** are probably isomers of stoichiometry 1:2 (metal:ligand), whereas the remaining species **c**, **d**, **e**, **f**, **g**, **h**, **i** and **j** would be n:1 complexes, with $n \geq 1$. Taking advantage of conditions for which only **a** and **b** are present, Job's plot based on the proton NMR intensities could be attempted (with tungstate). Clear maxima occur for the 1:2 molar ratio.

The ^{1}H 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, when possible, to assign tungsten shifts via the correlation with the proton resonances.

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 [8–13,41–43] and the oxygen shifts are typical of terminal M=O groups, there being no evidence for

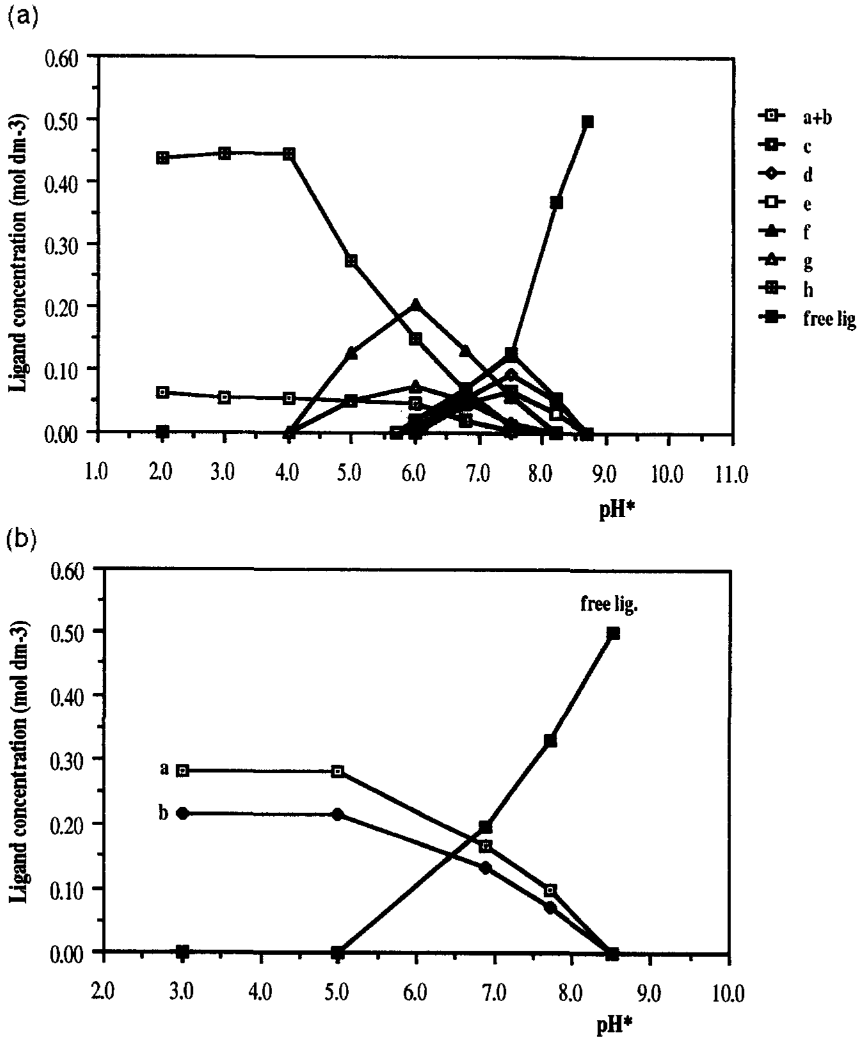


Fig. 2. Concentration of the ligand as a function of pH *, obtained by ^{13}C NMR for (a) a 1.0:0.50 M aqueous solution (33% deuterium oxide) of sodium molybdate(VI) and D-gluconic acid, temp. 294 K and (b) a 0.5:1.0 M aqueous solution (33% deuterium oxide) of sodium molybdate(VI) and D-gluconic acid, temp. 294 K.

Table 3
^{1}H NMR parameters[a] for W(VI) + D-gluconic acid, temp. 298 K

W(VI) + D-gluconic acid	H-2	H-3	H-4	H-5	H-6a	H-6b	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$\lvert J_{6a,6b}\rvert$
Complex **a**[b] (pH* 5.0)												
δ	5.05	4.23	3.92	3.84	3.88	3.73	3.5	3.2	7.5	2.0	5.6	11.8
$\Delta\delta$	0.86	0.14	0.11	0.02	−0.01	0.01						
Complex **b**[b] (pH* 5.0)												
δ	5.37	4.19	3.93	3.84	3.88	3.73	3.1	3.2	7.5	2.0	5.6	11.8
$\Delta\delta$	1.18	0.10	0.12	0.02	−0.01	0.01						
Complex **c**[c] (pH* 7.5)												
δ	4.35	4.98	5.07	5.38	4.55	4.20	5.5	0	4.3	0	2.2	10.6
$\Delta\delta$	0.17	0.89	1.26	1.56	0.68	0.48						
Complex **d**[c] (pH* 7.5)												
δ	4.23	4.42	5.45	4.97	4.88	4.60	8.2	0	4.4	0	4.9	11.1
$\Delta\delta$	0.05	0.33	1.64	1.15	1.01	0.88						
Complex **e**[c] (pH* 7.5)												
δ	[d]	[d]	[d]	4.48[e]	3.92	3.80	[d]	[d]	0	4.9	7.6	11.6
$\Delta\delta$				0.66	−0.05	0.08						
Complex **f**[c] (pH* 5.0)												
δ	5.24	5.10	5.30	5.37	4.57	4.20	5.5	0	4.6	0	2.0	10.2
$\Delta\delta$	1.05	1.01	1.49	1.55	0.60	0.48						
Complex **g**[c] (pH* 5.0)												
δ	5.20	4.66	5.74	4.99	4.89	4.60	8.7	0	4.6	0	5.2	11.5
$\Delta\delta$	1.01	0.57	1.93	1.17	1.02	0.88						
Complex **h**[c] (pH* 7.5)												
δ	4.96	4.59	4.29	3.70	3.86	3.63	5.0	0	7.6	3.5	6.7	11.6
$\Delta\delta$	0.78	0.50	0.48	−0.12	−0.01	−0.09						

[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:0.10 M W(VI)–D-gluconic acid solution.
[c] 0.20 M:0.10 M W(VI)–D-gluconic acid solution.
[d] Not assigned due to the low concentration of **e** and superposition with other signals.
[e] Broad signal.

any bridge oxygen atoms [9–13,44–48]. The high frequency shifts observed upon complexation for the carboxylic and the adjacent carbinol carbon nuclei, are characteristic of the involvement of these groups in complexation [8–13,42,49–54]; 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, associated to the fact that the two ligand molecules are magnetically equivalent, point to **a** and **b** being the diastereoisomers II and III (Schemes 2 and 3).

Since complex **a** is slightly more stable than **b**, steric considerations involving the R chains would suggest that **a** is II and **b** is III. 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 structure II 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 [11–13,41,42,50,52,53].

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 −5.7 and −5.5, respectively, for pH* 3.0 and assuming the equation $M + 2L = ML_2$.

2:1 (Metal:ligand) complexes at high pH.—Concerning complexes **c** and **d**, which are formed especially at high pH*, we note the shifts to high frequency of C-3, C-4, C-5 and C-6, as well as those for the corresponding ^{1}H nuclei. This shows that the coordination is established via the deprotonated OH groups in positions 3, 4, 5 and 6. Proton and ^{13}C resonances are not completely assigned for complex **e** due its low concentration. Probably, C-2, C-3, C-4 and C-5 and the corresponding ^{1}H nuclei are shifted to high frequencies. This situation is similar to that found by Chapelle et al. [55,58,60] and Chapelle and Verchère [56,57,59] for the 2:1 complexes of alditols with tungstate and molybdate and by us for the complexes of galactaric acid, D-galactonic acid, L-mannonic acid and D-mannaric acid with those metal ions [9,10,12,13]. For both systems, species **c** and **d** are more stable than species **e**. The sets of (sharp) tungsten signals observed (Table 8) indicate the presence of a $W_2O_5^{2+}$ center in species **c** and **d**, with non-equivalent tungsten atoms [10,12,13,55–60]. Accordingly, the oxygen spectra show signals due to terminal W=O and to bridging W–O–W oxygen atoms [10,12,13,44,45]. 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 [61] mannitol [62] and erythritol [63] and the suggested structures in solution [9,10,12,13,55–60], and recognizing that **c** and **d** must be isomers possessing the central diol group (0–4,5) in an *erythro* configuration (only differing by the reversed orientation of the site of chelation), we propose structures IV and V, for complexes **c** and **d**, respectively (Schemes 4 and 5).

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 [55], 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 accordingly to the stability rules proposed by Chapelle et al. [55].

Regarding complex **e**, the broad ^{183}W signal (and its small concentration) precluded W–H correlations. Probably, **e** is a tetradentate species possessing the central diol group (0–3,4) in a *threo* configuration, the ligand being in a *zig-zag* arrangement. We propose structure VI for complex **e**, by analogy with our previous NMR studies. We have found similar structures for the complexes that D-mannaric acid and L-mannonic acid form with Mo(VI) and W(VI), at high pH [9,10,13] (Scheme 6).

Table 4
^{1}H NMR parameters[a] for Mo(VI) + D-gluconic acid at 298 K

Mo(VI) + D-gluconic acid	H-2	H-3	H-4	H-5	H-6a	H-6b	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$\|J_{6a,6b}\|$
Complex **a**[b] (pH* 5.0)												
δ	4.90	4.19	3.90	3.83	3.87	3.72	[c]	3.0	7.5	2.7	6.6	11.8
$\Delta\delta$	0.71	0.10	0.09	0.01	0.0	0.0						
Complex **b**[b] (pH* 5.0)												
δ	5.19	4.16	3.90	3.83	3.87	3.72	[c]	3.0	7.5	2.7	6.6	11.8
$\Delta\delta$	1.00	0.07	0.09	0.01	0.0	0.0						
Complex **c**[d] (pH* 7.5)												
δ	4.31	4.61	4.82	4.97	4.37	4.11	6.1	0	5.8	0	2.1	10.4
$\Delta\delta$	0.13	0.52	1.01	1.15	0.50	0.39						
Complex **d**[d] (pH* 7.5)												
δ	4.20	4.26	5.19	4.90	4.56	4.51	8.2	0	[c]	0	4.1	10.7
$\Delta\delta$	0.02	0.17	1.38	1.08	0.69	0.79						
Complex **e**[d] (pH* 7.5)												
δ	[c]	[c]	[c]	4.42	3.88	3.72	[c]	[c]	[c]	[c]	[c]	[c]
$\Delta\delta$				0.60	0.01	0.0						
Complex **f**[d] (pH* 5.0)												
δ	[c]	[c]	[c]	[c]	4.41	4.13	[c]	[c]	[c]	0	[c]	10.2
$\Delta\delta$					0.54	0.41						
Complex **g**[d] (pH* 5.0)												
δ	[c]	[c]	[c]	[c]	4.80	4.54	[c]	[c]	[c]	[c]	[c]	10.5
$\Delta\delta$					0.93	0.82						

[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:0.10 M Mo(VI)–D-gluconic acid solution.
[c] Broad signals.
[d] 0.20 M:0.10 M Mo(VI)–D-gluconic acid solution.

Similar structures were found by Burgmayer and Stiefel [64] by X-ray diffraction for the molybdate complex of 1,4-dithiothreitol and proposed from NMR spectroscopy data by Chapelle et al. [55,60] and Chapelle and Verchère [57] for several tetradentate complexes of Mo(VI) and W(VI) with alditols possessing a central diol group of the coordination site in a *threo* configuration. For complexes **c**, **d** and **e** formed with molybdate, we propose similar structures. In fact, the available 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 [9,55,56,65,66] and the ^{17}O shifts are characteristic of Mo=O and O–Mo–O groups [45–48].

5:2 (Metal:ligand) complexes at intermediate pH. —For species **f** and **g**, detected at intermediate pH values for both systems, all the carbon signals move to high frequency on complexation, as well as the corresponding proton signals. 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 [10,12,13,56–60], with non-equivalent tungsten atoms, and two additional signals of half intensity whose δ values suggest the presence of a WO_2^{2+} group in each complex [10–13,41,42], as in complexes **a** and **b**. According to the ^{13}C shifts observed in both complexes, the C-3, C-4, C-5, C-6 fragment of the carbon chain seems to adopt a *sickle* arrangement. This distortion, relative to the *zig-zag* conformation of the free ligand, 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. COLOC experiments show correlations between W-1 and H-3 and between W-2 and

Table 5
^{13}C NMR chemical shifts[a] for W(VI) + D-gluconic acid at 298 K

W(VI) + D-gluconic acid	C-1	C-2	C-3	C-4	C-5	C-6
Complex **a**[b] (pH* 5.0)						
δ	185.25	86.24	72.55	73.64	73.22	64.12
$\Delta\delta$	5.13	10.71	−0.10	−0.39	0.55	0.02
Complex **b**[b] (pH* 5.0)						
δ	184.15	87.98	72.55	73.64	73.22	64.12
$\Delta\delta$	4.03	12.45	−0.10	−0.39	0.55	0.02
Complex **c**[c] (pH* 7.5)						
δ	179.50	77.28	82.28	83.30	91.82	70.07
$\Delta\delta$	−0.70	1.70	9.81	9.23	19.24	5.97
Complex **d**[c] (pH* 7.5)						
δ	180.16	76.77	80.23	91.25	83.80	72.08
$\Delta\delta$	−0.04	1.19	7.76	17.18	11.12	7.98
Complex **e**[c] (pH* 7.5)						
δ	179.20	[d]	[d]	[d]	[d]	64.73
$\Delta\delta$	−1.00					0.63
Complex **f**[c] (pH* 5.0)						
δ	183.87	82.49	82.18	82.13	91.74	70.07
$\Delta\delta$	3.75	6.96	9.73	8.10	19.07	5.97
Complex **g**[c] (pH* 5.0)						
δ	183.76	87.06	78.81	91.16	82.13	72.16
$\Delta\delta$	3.64	11.53	6.36	17.13	9.46	8.06
Complex **h**[c] (pH* 7.5)						
δ	187.29	85.23	84.31	82.93	74.09	64.24
$\Delta\delta$	7.09	9.65	10.24	10.25	1.62	0.14
Complex **i**[c] (pH* 8.9)						
δ	187.37	86.02[e]	82.74[e]	82.38	74.29	64.42
$\Delta\delta$	7.01	10.44	10.27	8.31	1.61	0.32
Complex **j**[c] (pH* 8.9)						
δ	183.37	88.18[e]	82.74[e]	82.74	73.39	64.86
$\Delta\delta$	3.01	12.60	10.27	8.67	0.71	0.76

[a] δ values in ppm relative to Me_4Si, using *tert*-butyl alcohol (δ_c 31.2) as internal references.
[b] 0.25 M:0.50 M W(VI)–D-gluconic acid solution.
[c] 1.0 M:0.50 M W(VI)–D-gluconic acid solution.
[d] Not assigned due to the low concentration of **e** and superposition with other signals.
[e] The assignments can be reversed.

Table 6
^{13}C NMR chemical shifts[a] for Mo(VI) + D-gluconic acid at 298 K

Mo(VI) + D-gluconic acid	C-1	C-2	C-3	C-4	C-5	C-6
Complex **a**[b] (pH* 5.0)						
δ	184.56	86.89	74.00	73.49	72.52	64.07
$\Delta\delta$	4.44	11.36	−0.03	0.82	0.07	−0.03
Complex **b**[b] (pH* 5.0)						
δ	183.37	88.78	73.49	73.15	72.52	64.07
$\Delta\delta$	3.25	13.25	−0.54	0.48	0.07	−0.03
Complex **c**[c] (pH* 7.5)						
δ	179.97	77.41	81.65	84.36	92.18	70.53
$\Delta\delta$	1.83	9.18	10.29	19.50	6.43	
Complex **d**[c] (pH* 7.5)						
δ	180.90	77.20	80.65	92.57	84.36	73.31
$\Delta\delta$	1.62	8.18	18.50	11.68	9.21	
Complex **e**[c] (pH* 7.5)						
δ	180.32	[d]	[d]	[d]	[d]	62.88
$\Delta\delta$	0.12					−1.22
Complex **f**[c] (pH* 5.0)						
δ	183.73	88.28	84.36	83.46	91.64	70.02
$\Delta\delta$	3.61	12.75	11.91	9.43	18.97	5.92
Complex **g**[c] (pH* 5.0)						
δ	183.64	88.23	79.20	92.11	83.46	72.46
$\Delta\delta$	3.52	12.70	6.75	18.08	10.79	8.36
Complex **h**[c] (pH* 7.5)						
δ	184.56	84.35	83.51	82.91	73.37	64.03
$\Delta\delta$	4.36	8.77	11.04	8.84	0.69	−0.07

[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 Mo(VI)–D-gluconic acid solution.
[c] 1.0 M:0.50 M Mo(VI)–D-gluconic acid solution.
[d] Not obtained due to its small intensity and superposition with other signals.

Table 7
^{17}O NMR chemical shifts[a] for W(VI) + D-gluconic acid and Mo(VI) + D-gluconic acid at 298 K

	$-\overset{\|}{\underset{\mid}{M}}={}^{17}O$	$-\overset{\mid}{\underset{\mid}{M}}-{}^{17}O-\overset{\mid}{\underset{\mid}{M}}-$
W(VI) + D-gluconic acid		
Complex **a**[b] (pH* 5.0)	638	
Complex **b**[b] (pH* 5.0)	647	
Complexes **c** + **d** + **e**[c] (pH* 7.5)	656, 638, 628	279
Complexes **f** + **g**[c] (pH* 5.0)	652, 637, 630, 617	298, 257
Complex **h**[c] (pH* 7.5)	579, 616	289
Complexes **i** + **j**[c] (pH* 8.9)	526, 550, 559, 570	289, 298
Mo(VI) + D-gluconic acid		
Complex **a**[d] (pH* 5.0)	832	
Complex **b**[d] (pH* 5.0)	845	
Complexes **c** + **d** + **e**[e] (pH* 7.5)	683, 677, 671	294, 321
Complexes **f** + **g**[e] (pH* 5.0)	832, 815, 796, 786	289, 317
Complex **h**[e] (pH* 3.0)	838, 813	413

[a] δ values relative to external reference deuterium oxide.
[b] 0.25 M:0.50 M W(VI)–D-gluconic acid solution.
[c] 1.0 M:0.50 M W(VI)–D-gluconic acid solution.
[d] 0.25 M:0.50 M Mo(VI)–D-gluconic acid solution.
[e] 1.0 M:0.50 M Mo(VI)–D-gluconic acid solution.

Table 8
^{183}W^a NMR chemical shifts for W(VI) + D-gluconic acid (298 K)

	δ^{183}W	$^3J_{W,H}$
W(VI) + D-gluconic acid		
Complex **a**^{b} (pH* 5.0)	47.1	2.4
Complex **b**^{b} (pH* 5.0)	56.9	~ 0($\Delta\nu_{1/2}$ = 1.9 Hz)
Complex **c**^{c} (pH* 7.5)	−74.4 (W-1)	8.5 (H-3)
	−60.8 (W-2)	8.0 (H-5)
Complex **d**^{c} (pH* 7.5)	−68.6 (W-1)	9.2 (H-4)
	−71.0 (W-2)	9.2 (H-6a)
Complex **e**^{c} (pH* 7.5)	−84.9	^{d}
Complex **f**^{c} (pH* 5.0)	−74.4 (W-1)	8.7 (H-3)
	−70.5 (W-2)	8.6 (H-5)
	36.4 (W-3)	^{d}
Complex **g**^{c} (pH* 5.0)	−74.2 (W-1)	8.7 (H-4)
	−76.0 (W-2)	8.5 (H-6a)
	44.8 (W-3)	^{d}
Complex **h**^{c} (pH* 7.5)	−61.8 (W-2)	0
	56.3 (W-1)	4.38 (H-2)
		3.40
Complex **i**^{c} (pH* 9.3)	6.9	^{d}
	71.8	^{d}
Complex **j**^{c} (pH* 9.3)	−46.2(W-1)	4.0
	−116.6 (W-2)	^{d}

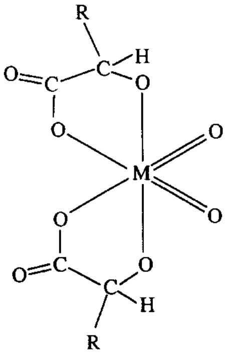
[a] δ values relative to external reference sodium tungstate, pH* = 9.5.
[b] 0.25 M:0.50 M W(VI)–D-gluconic acid solution.
[c] 2.0 M:1.0 M W(VI)–D-gluconic acid solution.
[d] Not resolved.

H-5, for complex **f**, and between W-1 and H-4 and between W-2 and H-6a, for complex **g**, as in complexes **c** and **d**. We can conclude that complexes **f** and **g** are species that resemble **c** and **d** and also **a** and **b** in so far as the carboxylate group and the adjacent OH group are involved in coordination. Thus, we propose the structures shown in Schemes 7 and 8, respectively for complexes **f** and **g**. In agreement with these structures, the oxygen spectra show signals due to terminal W=O and to bridge W–O–W oxygen atoms [10,12,13,44,45]. The two ligand molecules in the 5:2 complexes are magnetically equivalent in accordance with three ^{183}W signals being found for each complex, with relative intensities 2:2:1. Homologous complexes form with molybdenum(VI), as is shown by similar patterns of the ^{13}C shifts and by the ^{95}Mo and ^{17}O spectra. Previously,

Table 9
^{95}Mo NMR chemical shifts^a for Mo(VI) + D-gluconic acid (298 K)

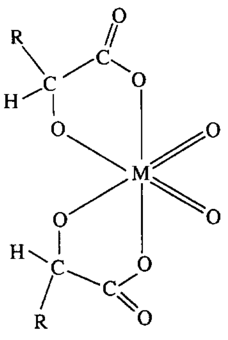
	δ^{95}Mo	$\Delta\nu_{1/2}$
Mo(VI) + D-gluconic acid		
Complex **a**^{b} (pH* 5.0)	103	327
Complex **b**^{b} (pH* 5.0)	99	263
Complexes **c** + **d** + **e**^{c} (pH* 7.5)	36	394
	34	1128
Complexes **f** + **g**^{c} (pH* 5.0)	36	709
	32	801
	94	1139
Complex **h**^{c} (pH* 3.0)	95	1163
	28	2095

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



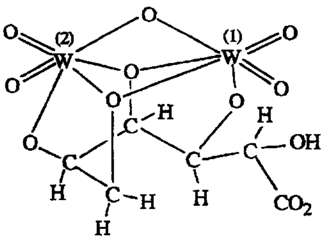
R=(CHOH)$_3$CH$_2$OH

Scheme 2.

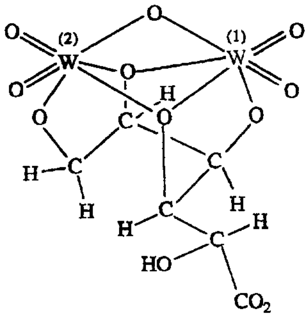


R=(CHOH)$_3$CH$_2$OH

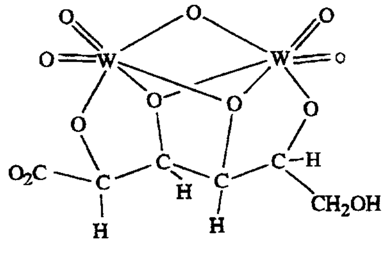
Scheme 3.



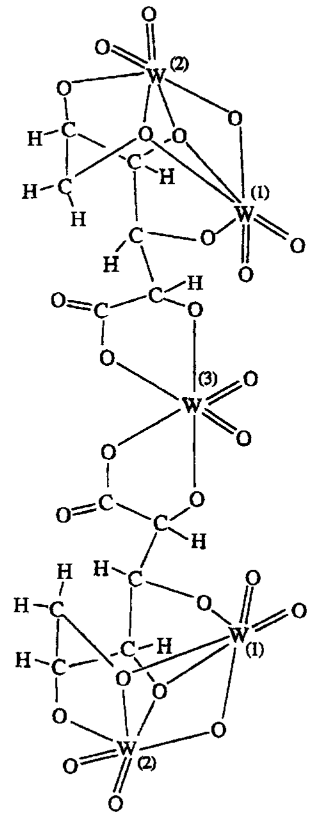
Scheme 4.



Scheme 5.



Scheme 6.



Scheme 7.

Hlaïbi et al. [67] have found similar W(VI) mixed complexes with D-*glycero*-D-*gulo*-heptonic acid. [1]

2:1 (Metal:ligand) complex at any pH.—Complex **h** is detected at any pH values, both with tungstate and 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. Complex **h** is probably a tetradentate species possessing the central diol group in an *threo* configuration, the ligand being in a *zig-zag* arrangement. The ^{183}W NMR spectrum shows two signals (Table 8). COLOC experiments show only a correlation between W-1 and H-2. A possible structure for complex **h** is shown in Scheme 9 and similarly for Mo(VI) as suggested by the similar patterns of the ^{13}C shifts. The ^{95}Mo

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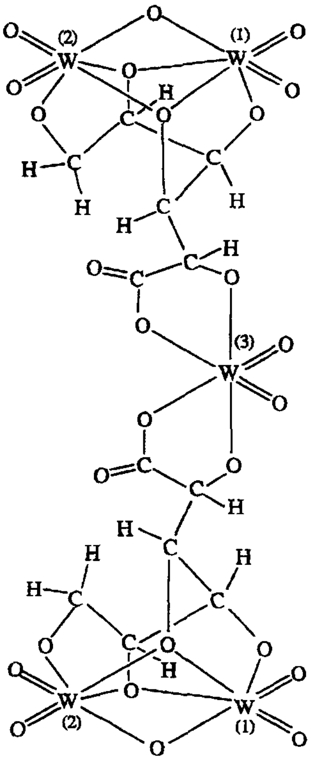
[1] In our previous studies of complexation of W(VI) and Mo(VI) with L-mannonic acid [13], we have proposed that the corresponding complexes **f** and **g** were species of stoichiometry 4:2. The results above led us to repeat the tungsten spectra and to reexamine all data. Clear evidence is now found for 5:2 complexation. In particular, three sets of ^{183}W signals are recorded for each complex with relative intensities 2:2:1 and the following δ values: -72.9, -70.5 and 46.4 ppm for complex **f** and -68.3, -77.3 and 44.1 ppm for complex **g**.

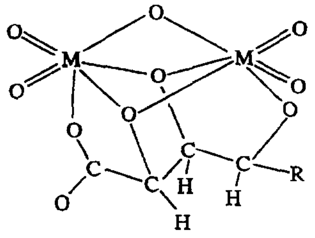


Scheme 8.

shifts are characteristic of $Mo_2O_5^{2+}$ groups [9,12,13,55,65,66] and the ^{17}O shifts are characteristic of Mo=O and O–Mo–O groups [9,12,13,44–48].

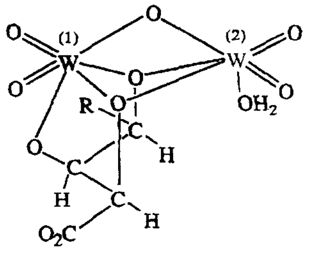
Tungstate complexes at pH 8 – 12.—In the pH range 8–12, tungstate is able to form two species with D-gluconic acid, **i** and **j**, that are not present with molybdate. Since the ^1H signals are very broad for all the molar ratios covered, a correct assignment is not possible.

The ^{13}C shifts (Table 5) indicate that **i** must be a tetradentate species, involving three deprotonated secondary OH groups (2, 3 and 4 or 2, 4 and 5) besides the carboxylate group. The uniform ^{13}C shifts to high frequencies upon complexation point to a *zig-zag* conformation of the ligand. The ^{183}W spectra show two non-equivalent signals (Table 8).



R=$CHOHCH_2OH$

Scheme 9.



R=$CHOHCH_2OH$

Scheme 10.

Regarding complex **j**, the ^{13}C shifts (Table 5) show that it must be a tridentate species, involving three secondary OH groups. As for **i**, the ^{13}C shifts point to a *zig-zag* conformation of the ligand. The ^{183}W shifts (Table 8) resemble those found by Chapelle and Verchère [57] and Chapelle et al. [58,60] for the tridentate complexes of alditols having a threo diol group. Thus, for complex **j**, we propose structure X (Scheme 10).

4. Conclusion

The system addressed in this paper completes a systematic study of the complexation of metal oxoions, namely, tungstate and molybdate, with the main sugar acids, aldaric [8–10], alduronic [11], and aldonic [12,13] acids.

Cervilla and co-workers have studied tungstate complexes with gluconic acid, in solution with an excess of gluconic acid, using polarimetric and spectrophotometric methods [17] and in solution with an excess of tungstate, using polarimetric and ^{13}C NMR studies [18]. They have found two species of stoichiometry 1:2 (metal:ligand) in solutions with excess of ligand. With excess of metal they have identified, besides two 2:2 complexes, two 2:1 isomers in the pH range 5–7, and a species of doubtful stoichiometry.

In our study, ten complexes and eight complexes were identified for tungsten(VI) and molybdenum(VI) systems, respectively. This means, as was the case of L-mannonic acid [13], a greater complexity with respect to the previously studied systems of D-galactonic acid with molybdate and tungstate [12]. This is especially true 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 favorable configuration of the four central OH groups in the case of D-galactonic acid (*threo–erythro–threo*) associated to a favorable entropy factor due to the non-involvement of the terminal groups [55]; in the case of gluconic acid, as with mannonic acid [13], a similar configuration requires the involvement of the terminal OH group. On the other hand, the configuration of the four central OH groups of D-gluconic acid (*threo–threo–erythro*) is not appropriate to the formation of dominant species. As a consequence, gluconic acid also forms additional n:1 species with $n > 1$.

Of these additional complexes (with respect to galactonic acid), one is a 2:1 species. This is particularly stable involving a tetradentate ligand having the carboxylate group and OH-2, OH-3 and OH-4 groups as coordination sites. Although a terminal group (carboxylic group) is coordinated to the metal, the complex is stable because it involves a favorable CO_2H,OH-2,OH-3,OH-4 (*threo–threo–threo*) arrangement. This is the first example of a tetradentate species, involving the carboxylate group and possessing the central diol group in a *threo* configuration. With L-mannonic acid, we had detected two 2:1 isomeric species, possessing the central diol group in an *erythro* configuration in which the ligand molecules are bound to the metal by the same groups.

The remaining complexes are 5:2 mixed species in the sense that the ligand coordinates both as an alditol and as an α-hydroxycarboxylic acid. A similar result is found for the systems W(VI) and Mo(VI) with mannonic acid, thus, correcting our previous proposal of 4:2 complexation [13].

Besides these species formed for both tungstate and molybdate, tungstate is also able to form two more 2:1 species, in alkaline medium, one of them tetradentate and the other tridentate.

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