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Carbohydrate Research 329 (2000) 387–397

CARBOHYDRATE RESEARCH

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

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Received 11 May 2000; accepted 22 June 2000

Abstract

By using multinuclear (^{1}H, ^{13}C, ^{17}O, ^{95}Mo, ^{183}W) magnetic resonance spectroscopy (1D and 2D), D-gulonic acid is found to form ten and seven complexes, respectively, with tungsten(VI) and molybdenum(VI), in aqueous solution, depending on pH and metal–ligand molar ratios. Two isomeric 1:2 (metal–ligand) complexes involving the carboxylate and the adjacent OH group are present in the pH range 2–9. At intermediate and high pH, molybdate forms a 2:1 tetradentate complex involving the four secondary hydroxyl groups, whereas tungstate forms one 2:1 terdentate species. At low and intermediate pH values, three 2:1 complexes are found for both metals, involving the carboxylate group and three secondary hydroxyl groups, as well as a 5:2 species involving the carboxylate group and all the secondary hydroxyl groups; the concentration of this species increases in time mainly at the expense of 2:1 and 1:2 complexes. Tungstate can also form two additional species, probably a 5:2 species involving the carboxylate group and all the hydroxyl groups, and a 2:1 pentadentate species involving the carboxylate group and all the secondary hydroxyl groups. In alkaline solutions, tungstate is able to form an additional 2:1 pentadentate complex involving all the hydroxyl groups.

Keywords: Tungsten; Molybdenum; Complexes; D-Gulonic 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 years, mainly due to the importance of such interactions in a variety of industrial, pharmaceutical and biological processes [1–3].

Aldonic acids are found to have several applications, for example being present in preparations of medical and pharmaceutical importance, viz. Refs. [4,5], in detergents as environmentally compatible tensioactive agents, viz. Ref. [6], in industrial processes as corrosion inhibitors viz. Ref. [7] and, especially, in cosmetic preparations viz. Ref. [8]. L-Gulonic acid is furthermore an intermediate in the biosynthesis of L-ascorbic acid (vitamin C) from D-glucuronic acid [9].

The work presented here on the complexation of D-gulonic acid is an extension to less common sugars of our systematic study using multinuclear high field NMR spectroscopy (1D and 2D) which started with aldaric acids [10–12], was continued with alduronic acids [13], and was more recently extended to aldonic acids [14–16].

The complexation of gulonic acid with some metals has been the subject of several studies, namely with Zn(II) [17], Cu(II) [18] and with Eu(III) in the form of the chiral shift reagent propylenediaminetetraacetatoeuropium (III) [19].

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0008-6215/00/$ - see front matter

PII: S0008-6215(00)00191-9

Table 1
^{1}H NMR parameters [a] for D-gulonic acid in D_2O solution (0.10 M), 298 K

	H-2	H-3	H-4	H-5	H-6a	H-6b	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$\lvert J_{6a,6b}\rvert$
D-Gulonic acid												
pH* 3.0												
δ	4.34	3.95	3.90	3.91	3.78	3.69	5.9	3.5	1.3	4.0	6.6	11.8
pH* 5.0												
δ	4.18	3.93	3.87	3.88	3.77	3.68	5.3	3.1	1.3	3.9	6.5	11.8
pH* 7.5												
δ	4.17	3.93	3.87	3.88	3.77	3.68	5.3	3.1	1.3	3.9	6.5	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.

2. Experimental

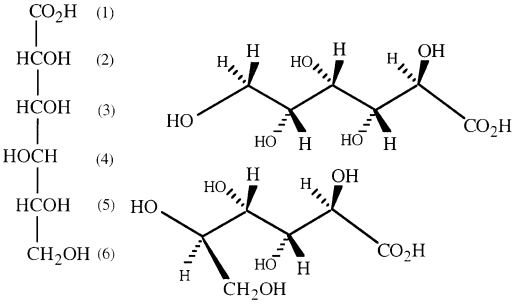
Analytical grade disodium tungstate and disodium molybdate dihydrates and commercially available D-gulono-1,4-lactone as source of D-gulonic acid were used.

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 (rt) after standardization with aqueous (H_2O) 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 on a Varian Unity-500 NMR spectrometer. The detailed conditions can be found in previous papers [10–16]. The 2D NMR spectra, DQFCOSY [20] and HETCOR [21] were recorded on a Varian Unity-500 NMR spectrometer.

3. Results and discussion

Gulonic acid has been shown to exist in at least two forms in solution, the planar straight chain form and the bent chain form.



I

This conclusion has been established by van Duin et al. from a comparative study of several polyhydroxycarboxylates in aqueous solution using ^{1}H and ^{13}C NMR spectroscopy [22,23] following previous studies reviewed by Bock et al. [24]. The ^{13}C signals could not be assigned unambiguously at that time. In order to characterize the complexes formed, a proper assignment of all proton and carbon signals is necessary for various pH conditions. This has been done, using the ^{1}H–^{13}C two-dimensional NMR correlation.

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-gulonic acid, in

Table 2
^{13}C NMR chemical shifts [a] for D-gulonic acid in D_2O solution (0.50 M), 298 K

	C-1	C-2	C-3	C-4	C-5	C-6
D-Gulonic acid						
pH* 3.0						
δ	178.38	73.96	73.55	71.71	73.87	64.11
pH* 5.0						
δ	180.27	75.01	73.90	72.02	74.20	64.11
pH* 7.5						
δ	180.38	75.06	73.90	72.03	74.21	64.11

[a] δ values, in ppm, relative to Me_4Si, using *tert*-butyl alcohol (δ_C 31.2) as internal reference.

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-gulonic acid (M = W or Mo) were recorded for total concentration species ranging from 3.0 to 0.10 M, metal–ligand molar ratios from 10 to 0.25, and pH* values ranging from 2 to 11 for the case of W(VI) and 2 to 9 for Mo(VI). Under these conditions, seven different sets of signals were detected for Mo(VI) and ten for W(VI). Signal intensity considerations enabled the conclusion that these sets correspond to seven different complexes for Mo(VI) and ten for W(VI).

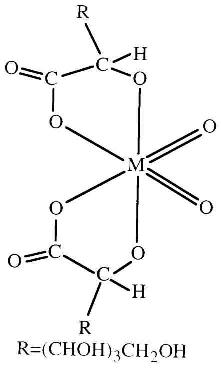
The ^{1}H and ^{13}C NMR parameters are shown in Tables 3 and 4 and the ^{17}O, ^{183}W and ^{95}Mo data are presented in Tables 5–7, respectively. Whenever necessary, COSY and HETCOR experiments were performed to assign the proton and carbon shifts.

For both tungstate and molybdate, species **a** and **b** are formed in the pH range 2–9, especially when the metal–ligand molar ratio is less than 1. In the case of W(VI), several species are detected for solutions having metal–ligand molar ratios larger than 1: species **c** occurs in the pH* range 4–9, species **d** is present in the pH* range 2–6, species **g**, **h** and **i** are present for the pH range 3.0–7.5, minor species **e** and **f** are detected for the pH range 2.0–4.0 and species **j** is formed in the pH range 8–11. Similarly, for Mo(VI), the major species **c** and **d** occur for the pH* range 4–9 and 3–7, respectively, for metal–ligand molar ratios larger than 1. Three additional minor species, **e**, **f** and **g** are also detected for the pH range 3–7, for solutions having metal–ligand molar ratios larger than 1.

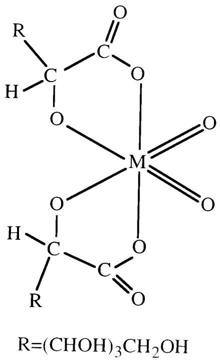
The way in which the concentrations of the various species vary with pH* is shown in Figs. 1 and 2, for tungstate and for molybdate, respectively, for two different molar ratios. The approximate concentrations of the complexes are based on ^{1}H signal intensities.

The observations mentioned above suggest that **a** and **b** are isomers of stoichiometry 1:2 (metal–ligand), whereas the remaining species **c**, **d**, **e**, **f**, **g**, **h**, **i** and **j** are probably **n**:**m** complexes, with **n** > **m**.

1:2 (W, Mo–ligand) complexes (pH 2–9).—As far as complexes **a** and **b** are concerned, the tungsten and molybdenum shifts are characteristic of MO_2^{2+} centers [10–16,25,26] and the oxygen shifts are typical of terminal M=O groups, there being no evidence for any bridge oxygen atoms [11–16,27–31]. 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 [10–16,32,33]; the other carbon shifts are much smaller. Accordingly, only 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**.



II



III

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**. 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 [14–16].

2:1 (W, Mo: ligand) complexes (pH 4–9).—For complex **c** with tungstate, C-3, C-4 and C-5 and the corresponding ^{1}H nuclei are shifted to high frequencies. The ^{183}W shifts resemble those found previously for the terdentate complex detected for the system W(VI)–D-gluconic acid at high pH [16] and by Verchère and co-workers for the terdentate complexes of alditols having a threo diol group [34–36]. Complex **c** is probably a terdentate species possessing the central diol

Table 3
^{1}H NMR parameters [a] for W(VI)–D-gulonic acid and Mo(VI)–D-gulonic acid, 298 K

	H-2	H-3	H-4	H-5	H-6a	H-6b	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$\|J_{6a,6b}\|$
W(VI)–D-gulonic acid												
Complex **a** [b] (pH* 5.0)												
δ	5.06	4.08	3.94	3.89	3.77	3.69	4.9	4.6	1.3	4.2	7.2	11.8
$\Delta\delta$	0.88	0.15	0.07	0.01	0.0	0.01						
Complex **b** [b] (pH* 5.0)												
δ	5.30	4.11	3.94	3.89	3.77	3.69	4.3	4.1	1.3	4.2	7.2	11.8
$\Delta\delta$	1.12	0.18	0.07	0.01	0.0	0.01						
Complex **c** [c] (pH* 6.0)												
δ	4.22	4.85	4.80	4.58	3.78	3.69	[d]	[d]	[d]	[d]	[d]	[d]
$\Delta\delta$	0.04	0.92	0.93	0.70	0.01	0.01						
Complex **d** [c] (pH* 5.0)												
δ	5.39	5.20	4.32	4.69	3.77	3.69	5.0	0	9.7	2.8	5.7	10.3
$\Delta\delta$	1.21	1.27	0.45	0.81	0.0	0.01						
Complex **e** [c] (pH* 5.0)												
δ	[e]	5.61	4.23	3.88	[e]	[e]	[e]	[e]	[e]	[e]	[e]	[e]
$\Delta\delta$		1.68	0.36	0.00								
Complex **f** [c] (pH* 5.0)												
δ	[e]	5.09	4.80	4.11	[e]	[e]	[e]	[e]	[e]	[e]	[e]	[e]
$\Delta\delta$		1.68	0.36	0.23								
Complex **g** [c] (pH* 5.0)												
δ	5.42	4.00	5.28	4.80	3.86	3.72	4.9	0	2.9	[e]	[e]	[e]
$\Delta\delta$	1.24	0.07	1.41	0.92	0.09	0.04						
Complex **h** [c] (pH* 5.0)												
δ	5.20	4.82	4.78	5.02	4.70	4.22	2.9	[e]	[e]	[e]	[e]	[e]
$\Delta\delta$	1.02	0.89	0.91	1.13	0.93	0.54						
Complex **i** [c] (pH* 5.0)												
δ	5.31	4.68	4.88	4.78	3.82	3.68	[e]	[e]	2.9	5.5	8.6	[e]
$\Delta\delta$	1.13	0.75	1.01	0.90	0.05	0.00						
Complex **j** [c] (pH* 9.0)												
δ	4.80	5.00	4.70	4.60	4.35	4.25	[d]	[d]	[d]	[d]	[d]	[d]
$\Delta\delta$	0.63	1.07	0.83	0.72	0.58	0.57						
Mo(VI)–D-gulonic acid												
Complex **a** [f] (pH* 5.0)												
δ	4.91	4.09	3.91	3.88	3.77	3.68	[d]	4.0	1.7	3.9	6.7	11.8
$\Delta\delta$	0.73	0.16	0.04	0.00	0.00	0.00						
Complex **b** [f] (pH* 5.0)												
δ	5.14	4.09	3.91	3.88	3.77	3.68	[d]	4.0	1.7	3.9	6.7	11.8
$\Delta\delta$	0.96	0.16	0.04	0.00	0.00	0.00						
Complex **c** [d] (pH* 7.5)												
δ	4.77	4.53	4.33	4.23	3.77	3.76	2.5	0	0	[d]	[d]	[d]
$\Delta\delta$	0.59	0.60	0.46	0.35	0.00	0.08						
Complex **d** [g] (pH* 5.0)												
δ	5.05	4.83	4.20	4.62	3.77	3.71	5.00	9.5	3.5	6.0	12.1	
$\Delta\delta$	0.87	0.90	0.33	0.74	0.00	0.03						
Complex **e** [g] (pH* 5.0)												
δ	5.05	5.23	4.51	3.97	3.87	3.76	4.3	0	6.0	3.4	3.5	12.1
$\Delta\delta$	0.88	1.30	0.64	0.09	0.10	0.08						
Complex **f** [g] (pH* 5.0)												
δ	4.99	4.45	4.50	3.91	[e]	[e]	3.0	10.5	0	[e]	[e]	[e]
$\Delta\delta$	0.81	0.52	0.63	0.03								
Complex **g** [g] (pH* 5.0)												
δ	5.09	4.02	4.77	4.56	[e]	[e]	4.0	1.8	0	[e]	[e]	[e]
$\Delta\delta$	0.91	0.09	1.00	0.68								

[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] 0.05:0.10 M W(VI)–D-gulonic acid solution.
[c] 0.20:0.10 M W(VI)–D-gulonic acid solution.
[d] Broad signals.
[e] Not obtained due to its superposition with other signals.
[f] 0.05:0.10 M Mo(VI)–D-gulonic acid solution.
[g] 0.20:0.10 M Mo(VI)–D-gulonic acid solution.

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

	C-1	C-2	C-3	C-4	C-5	C-6
W(VI)–D-gulonic acid						
Complex **a** [b] (pH* 5.0)						
δ	184.81	85.46	73.60	71.57	74.59	64.32
$\Delta\delta$	4.54	10.45	−0.30	−0.45	0.39	0.21
Complex **b** [b] (pH* 5.0)						
δ	184.15	86.85	73.60	71.57	74.59	64.32
$\Delta\delta$	3.95	11.84	−0.30	−0.45	0.39	0.21
Complex **c** [c] (pH* 6.0)						
δ	179.38	75.65	85.12	80.21	85.27	63.26
$\Delta\delta$	−0.89	0.64	11.22	8.19	11.07	−0.85
Complex **d** [c] (pH* 3.0)						
δ	181.66	87.70	83.90	83.59	86.93	64.40
$\Delta\delta$	3.28	13.74	10.35	11.88	13.13	0.29
Complex **g** [c] (pH* 5.0)						
δ	183.27	87.65	73.70	82.09	87.65	64.92
$\Delta\delta$	3.00	12.64	−0.20	10.07	13.45	0.81
Complex **h** [c] (pH* 5.0)						
δ	185.33	83.77	83.62	83.42	81.97	75.63
$\Delta\delta$	5.06	8.76	9.72	11.40	7.77	11.52
Complex **i** [c] (pH* 5.0)						
δ	182.76	86.12	85.98	84.44	87.13	64.72
$\Delta\delta$	2.49	11.11	12.08	12.42	12.93	0.61
Complex **j** [c] (pH* 9.0)						
δ	181.97	88.44	84.86	83.04	81.27	78.63
$\Delta\delta$	1.59	13.38	10.96	11.01	7.06	13.95
Mo(VI)–D-gulonic acid						
Complex **a** [d] (pH* 5.0)						
δ	184.15	86.35	73.67	71.70	74.46	64.32
$\Delta\delta$	3.88	11.34	−0.23	−0.32	0.26	0.21
Complex **b** [d] (pH* 5.0)						
δ	183.32	88.03	73.67	71.70	74.46	64.32
$\Delta\delta$	3.05	13.02	−0.23	−0.32	0.26	0.21
Complex **c** [e] (pH* 5.0)						
δ	181.20	88.96	83.69	84.18	87.84	64.13
$\Delta\delta$	0.93	13.9	59.79	12.16	13.64	0.02
Complex **d** [e] (pH* 7.5)						
δ	179.20	85.92	85.22	79.54	85.92	63.28
$\Delta\delta$	−1.18	10.86	11.32	7.51	11.71	−0.83
Complex **e** [e] (pH* 5.0)						
δ	182.74	84.94	91.83	82.34	74.89	63.65
$\Delta\delta$	2.47	9.93	17.93	10.32	0.69	−0.46
Complex **f** [e] (pH* 5.0)						
δ	183.75	87.34	80.25	78.93	74.05	63.65
$\Delta\delta$	3.48	12.33	6.35	6.91	−0.15	−0.46
Complex **g** [e] (pH* 5.0)						
δ	184.81	[f]	[f]	[f]	[f]	63.65
$\Delta\delta$	4.54					−0.46

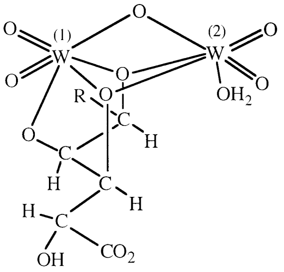
[a] δ Values, in ppm, relative to Me_4Si, using *tert*-butyl alcohol (δ_C 31.2) as internal reference.
[b] 0.25:0.50 M W(VI)–D-gulonic acid solution.
[c] 1.0:0.50 M W(VI)–D-gulonic acid solution.
[d] 0.25:0.50 M Mo(VI)–D-gulonic acid solution.
[e] 1.0:0.50 M Mo(VI)–D-gulonic acid solution.
[f] Not obtained due to its low concentration and superposition with other signals.

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

	$-\mathrm{M}={}^{17}\mathrm{O}$	$-\mathrm{M}-{}^{17}\mathrm{O}-\mathrm{M}-$
W(VI)–D-gulonic acid		
Complex **a** [b] (pH* 5.0)	641	
Complex **b** [b] (pH* 5.0)	648	
Complex **c** [c] (pH* 7.5)	597, 579, 554, 527	298
Complexes **d**, **g**, **h**, **i** [c] (pH* 5.0)	651, 622, 597	312, 293, 235
Complex **j** [c] (pH* 9.0)	528, 555, 582, 598	267
Mo(VI)–D-gulonic acid		
Complex **a** [d] (pH* 5.0)	831	
Complex **b** [d] (pH* 5.0)	843	
Complex **c** [e] (pH* 7.5)	790, 800	298
Complex **d** [e] (pH* 3.0)	833, 824, 816, 800	319
Complexes **e**, **f** [e] (pH* 5.0)	747, 751	392

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

group in a threo configuration and the ligand in a zig–zag arrangement (structure **IV**). Such conclusion is supported by the ^{17}O shifts which are characteristic of W=O and W–O–W groups [11–16,27,28].



R=CH$_2$OH
IV

For complex **c** with molybdate, C-2, C-3, C-4 and C-5 and the corresponding ^{1}H nuclei are shifted to high frequencies, providing evidence that the co-ordination is established via the OH groups in positions 2, 3, 4 and 5. Structure **V** is proposed, i.e. a tetradentate species possessing the central diol group in a threo configuration, the ligand being in a zig–zag arrangement, as was established previously for aldaric and aldonic acids [11,14–16] and for alditols [34–40], inspired on the known crystal structure of the molybdate complex with 1,4-dithiothreitol [41]. This is supported by the ^{95}Mo chemical shift that suggests the presence of a $Mo_2O_5^{2+}$ center.

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

	$\delta\,^{183}$W	$^3J_{\mathrm{W-H}}$
W(VI)–D-gulonic acid		
Complex **a** [b] (pH* 5.0)	39.6	2.8
Complex **b** [b] (pH* 5.0)	52.1	~0 ($\Delta\nu_{1/2}=1.9$ Hz)
Complex **c** [c] (pH* 7.5)	−50.2 (W-1)	[d]
	−108.9 (W-2)	[d]
Complex **d** [c] (pH* 5.0)	−35.2 (W-1)	[d]
	−119.6 (W-2)	[d]
	57.9 (W-3)	[d]
Complex **g** [c] (pH* 5.0)	64.3 (W-1)	[d]
	−89.3 (W-2)	6.8
Complex **h** [c] (pH* 5.0)	−84.1	[d]
	54.1	[d]
Complex **i** [c] (pH* 5.0)	30.9	[d]
	45.8	[d]
Complex **j** [c] (pH* 9.0)	106.7 (W-1)	[d]
	93.0 (W-2)	[d]

[a] δ values relative to external reference Na_2WO_4, pH* 9.5, J values in Hz.
[b] 0.25:0.50 M W(VI)–D-gulonic acid solution.
[c] 2.0:1.0 M W(VI)–D-gulonic acid solution.
[d] Not resolved.

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

	$\delta\,^{95}$Mo	$\Delta\nu_{1/2}$
Mo(VI)–D-gulonic acid		
Complex **a** [b] (pH* 5.0)	97	460
Complex **b** [b] (pH* 5.0)	92	295
Complex **c** [c] (pH* 7.5)	21	450
Complex **d** [c] (pH* 5.0)	8	612
	24	285
	98	384
Complexes **e**, **f** [c] (pH* 5.0)	25	386

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

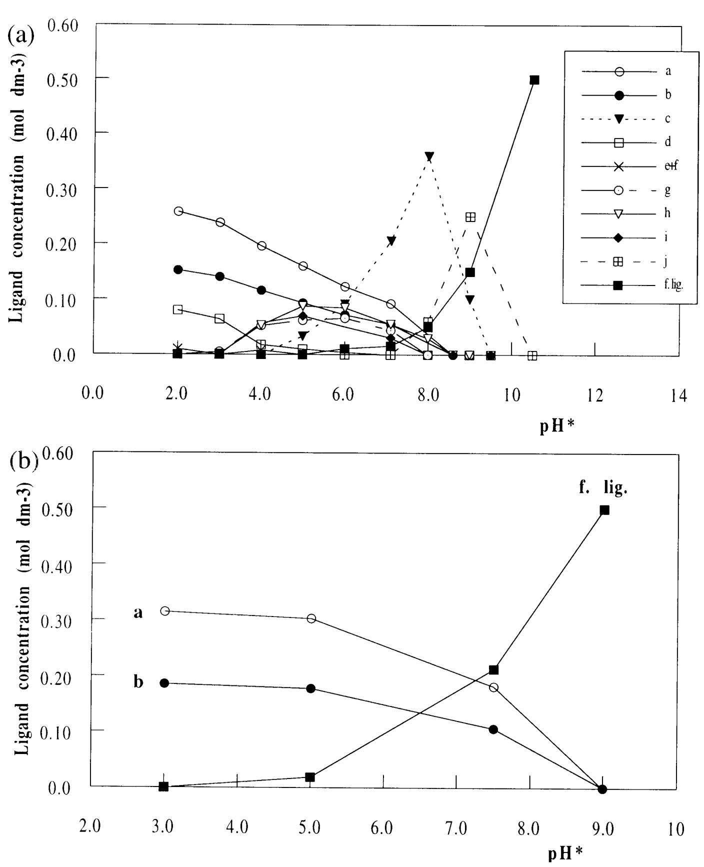
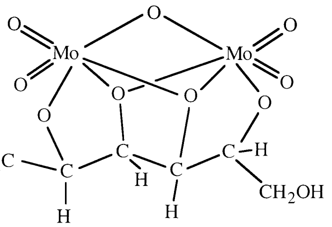


Fig. 1. Concentration of the ligand as a function of pH*, obtained by ^1H NMR for (a) 1.0:0.50 M D_2O solution of sodium tungstate(VI) and D-gulonic acid, temp 298 K; and (b) 0.25:0.50 M D_2O solution of sodium tungstate(VI) and D-gulonic acid, temp 298 K.

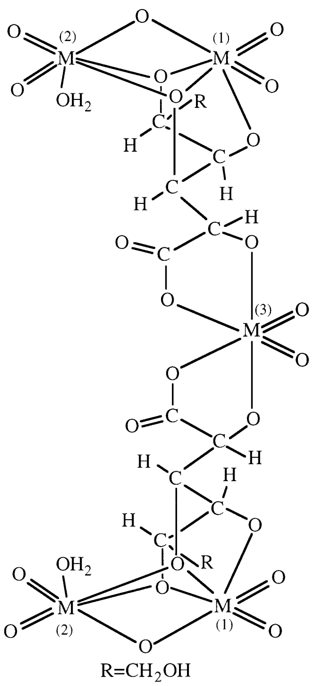
Also the ^{17}O shifts are characteristic of Mo=O and Mo–O–Mo groups [11,13–16,27,29–31].



V

Previously, Verchère and co-workers have found a similar behaviour with threo alditols, which form terdentate and tetradentate species, respectively, with tungstate and molybdate [34–36].

5:2 (metal–ligand) complex (pH 2–7).— Concerning complex **d**, with both W(VI) and Mo(VI), we note the shifts to high frequency of C-1, C-2, C-3, C-4 and C-5, as well as those for the ^1H nuclei in positions 2, 3, 4 and 5. This shows that the coordination is established via the carboxylic and the OH groups in positions 2, 3, 4 and 5. The ^{183}W spectra are consistent with two $W_2O_5^{2+}$ groups with non-equivalent tungsten atoms as in complex **c** and one additional WO_2^{2+} group as in complexes **a** and **b**. The ^{95}Mo shifts — 98, 24 and 8 ppm — require a more detailed discussion. The signal at 98 ppm can be assigned to a MoO_2^{2+} group as in complexes **a** and **b**. The two other signals can be related to those of ^{183}W of $W_2O_5^{2+}$ groups in complex **d**, through the already established general relationship $\delta_W = 1.8\delta_{Mo} - 137.3$ [42]. We can thus infer that complex **d** with Mo(VI) and W(VI) are homologous. The unusual terdentate chelation of Mo(VI) becomes possible in view of the presence of an additional metal centre (MoO_2^{2+}) in complex **d**. Thus, we propose the 5:2 structure shown in scheme VI for complex **d**. In agreement with this structure, the oxygen spectra show signals due to terminal M=O and to bridge M–O–M oxygen atoms [11–16,27–31]. The two ligand molecules in **d** are equivalent magnetically. According to the ^{13}C shifts observed, they seem to adopt a zig–zag arrangement.



VI

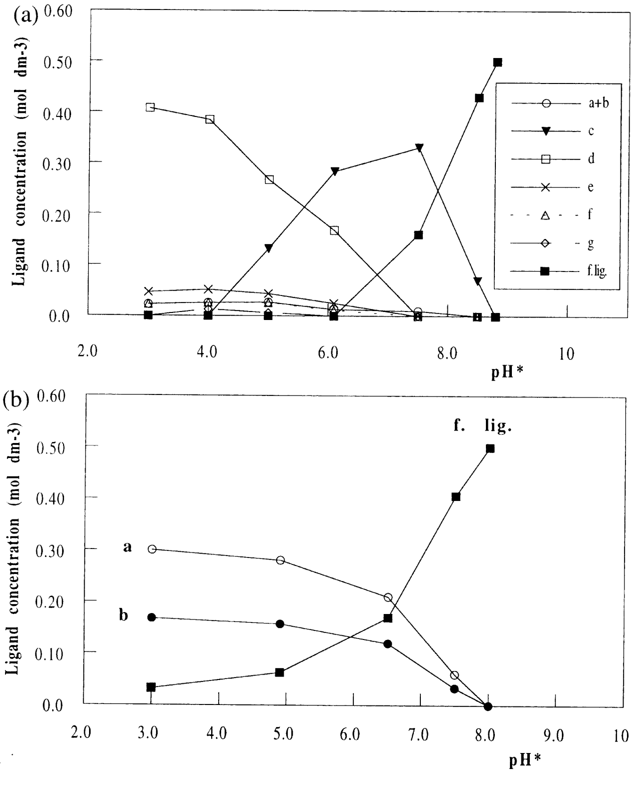
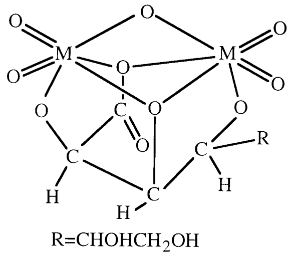


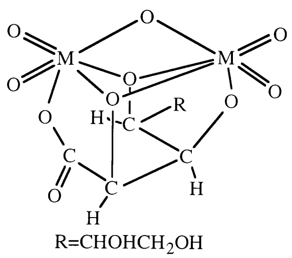
Fig. 2. Concentration of the ligand as a function of pH*, obtained by ^{1}H NMR for (a) 1.0:0.50 M D$_2$O solution of sodium molybdate(VI) and D-gulonic acid, temp 298; K and (b) 0.25:0.50 M D$_2$O solution of sodium molybdate(VI) and D-gulonic acid, temp 298 K.

Other mixed complexes have been found previously for alditols and aldonic acids. A bis-dinuclear tungstate species in which a single ligand molecule of perseitol uses different sites of chelation, two different W$_2$O$_5^{2+}$ centers in a tetradentate erythro site and a terdentate threo site, was characterized [35]. Species of 5:2 stoichiometry having two W$_2$O$_5^{2+}$ centers and an additional WO$_2^{2+}$ center were also characterized in aqueous solution for the systems tungsten(VI)–D-glycero-D-gulo-heptonic acid [43], W(VI)–L-mannonic acid and W(VI)–D-gluconic acid [16].

Additional 2:1 (W, Mo: ligand) complexes (pH 2–8).—Species **e** and **f** and **g** are detected in the pH range 2–8, for both metals. The ^{1}H and the available ^{13}C NMR parameters point to the involvement of O-2, O-3 and O-4, besides the carboxylate group in species **e** and **f**. Similar species were detected previously with L-mannonic acid [15], as 2:1 tetradentate isomers possessing the central diol group in an erythro configuration, the only difference being the reversed orientation of the site of chelation. We propose structures **VII** and **VIII**.

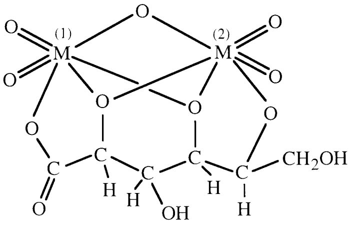


VII



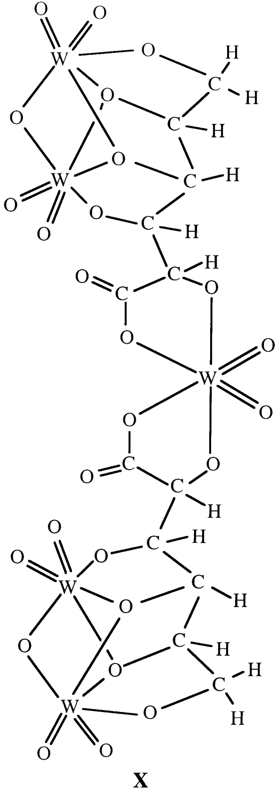
VIII

Concerning species **g**, more abundant with tungstate, the ^{1}H and the ^{13}C NMR parameters show the involvement of O-2, O-4 and O-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 (−89.3 and 64.3 ppm) which resemble those found previously for a tetradentate species with D-gluconic acid involving the carboxylate and three secondary OH groups and possessing the central diol group in a threo configuration [16]. We, therefore, propose structure **IX**.



IX

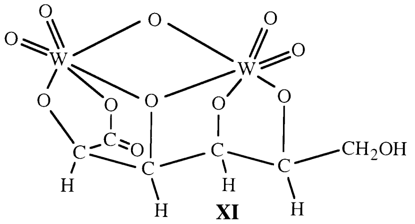
Other tungsten complexes (pH 3.5–10.5).— Tungstate can also form two additional species in the pH range 3.5–8.5, that are not detected with molybdate: species **h** and **i**. The ^{1}H and the ^{13}C NMR parameters show the involvement of all the OH groups, besides the carboxylate group in species **h**, and the carboxylate and the secondary OH groups in species **i**. The ^{183}W shifts can be used to identify the metal centers present in these species. Four signals are detected in the ^{183}W spectra: a broad signal at − 84.1 ppm and three sharp signals at 30.9, 45.8 and 54.1 ppm. The single broad signal at − 84.1 ppm can be assigned to $W_2O_5^{2+}$ centers involving the tetradentate (O- 3,4,5,6) (threo-threo-threo) site of the ligand [12,15,16,36]. One of the remaining signals detected with positive chemical shifts can be associated with an additional WO_2^{2+} group as in complexes **a** and **b**. These data suggest the formation of a new mixed species (structure **X**).



X

This proposal is consistent with the uniform ^{13}C shifts upon complexation which point to a zig–zag arrangement of the ligand. This is an unusual structure in so far as the central diol group of the tetradentate ligand in the $W_2O_5^{2+}$ centers shows a threo configuration.

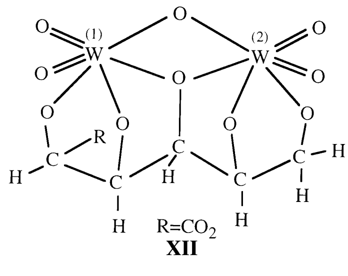
The two remaining ^{183}W signals can be assigned to species **i**. For this complex the ^{1}H and ^{13}C NMR shifts point to the involvement of the carboxylate and the secondary OH groups, the CH_2OH group remaining free. A possible structure is **XI**.



XI

This would be the first example reported of a W(VI) pentadentate complex also involving the carboxylate group.

In the pH range 8–10.5, tungstate is also able to form one additional species with D-gulonic acid (species **j**) which is not present with molybdate. Since the ^{1}H signals are broad for all the molar ratios covered, a correct assignment is not possible. The carbon-13 shifts indicate that **j** must be a pentadentate species, involving all the OH groups, the carboxylate group being free. The ^{183}W shifts confirm **j** to be a pentadentate complex, involving the ligand in an erythro–threo–threo–threo configuration [36,44]. Verchère and co-workers have characterized previously this species in a multinuclear NMR study of tungsten(VI) terdentate and pentadentate complexes of carbohydrates at high pH [44]. Accordingly, structure **XII** is proposed for complex **j**. In support of structure **XII** the recorded ^{17}O shifts are characteristic of W=O and W–O–W groups [27,28].



XII

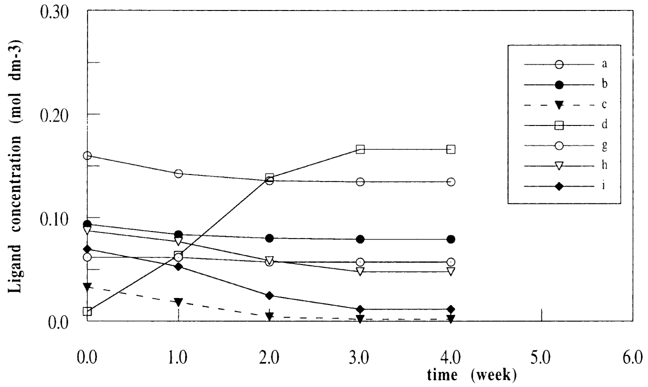


Fig. 3. Concentration of bound ligand as a function of time, obtained by ^{1}H NMR for a 1.0:0.50 M D_2O solution of sodium tungstate(VI) and D-gulonic acid, pH* 5.0, temp 298 K.

Kinetic variations with tungstate.—As is observed in much of the aqueous chemistry of W(VI) but contrary to the systems studied previously, kinetic variations were noticed for the system W(VI)–D-gulonic acid. Complex **d** is favoured kinetically, becoming the dominant species in a 1.0:0.50 M (metal–ligand) at pH 5, after 3 weeks, as is shown in Fig. 3. It is noted that **d** (5:2 complex) is being formed mainly at the expense of **a** (1:2 complex) and **c** (2:1 complex).

4. Conclusions

The system addressed in this paper is an extension to less common sugar acid configurations of a previous systematic study of the complexation of metal oxoions, namely tungstate and molybdate, with the main sugar acids, aldaric [10–12], alduronic [13], and aldonic [14–16] acids.

In the present study, ten and seven complexes were identified for tungsten(VI)–D-gulonic acid and molybdenum(VI)–D-gulonic acid systems, respectively, depending on pH and metal–ligand molar ratio. Such a complexity is common to most systems of this kind, an exception being tungstate–D-galactonic acid for which only four stable complexes are formed [14]. In accordance with the findings for Mo(VI) and W(VI) complexes of alditols [38,44], this latter result is in part a consequence of a favourable ligand configuration of the central OH groups (threo–erythro–threo). Such a configuration allows a maximum number of metal–ligand bonds and entropic gains whenever the terminal groups are not involved.

Irrespectively of pH, 1:2 (metal–ligand) complexation occurs, the ligand behaving as an α-hydroxycarboxylic acid (O-1 and O-2 as binding sites).

At intermediate to high pH, D-gulonic acid forms a terdentate 2:1 (metal–ligand) species with tungstate (binding sites O-3, O-4 and O-5) and a tetradentate 2:1 (metal–ligand) species with molybdate (binding sites O-2, O-3, O-4 and O-5), as was observed previously for alditols possessing the central diol group of the chelation site in a threo configuration [34]. The occurrence of terdentation with W(VI) is consistent with stronger metal-oxygen bonding for W(VI) relative to Mo(VI). The configuration of the four central OH groups (erythro–threo–threo) of D-gulonic acid is not particularly favourable and several competing species can appear, as was the case with L-mannonic and D-gluconic acids.

At low to intermediate pH and for both metals, D-gulonic acid is also found to form 5:2 (metal–ligand) mixed species, in the sense that the ligand coordinates both as an alditol (two 2:1 moieties, $Mo_2O_5^{2+}$ centres) and as an α-hydroxycarboxylic acid (one 1:2 moiety, MoO_2^{2+} centre). It is interesting to note that in these species the 2:1 moieties involve terdentation both for W(VI) and Mo(VI).

Additional 2:1 complexes are observed with both metals. Similarly to L-mannonic acid, two isomers are detected in which the ligand is bound to the metal by O-1, O-2, O-3 and O-4. For this favourable configuration (threo–erythro–threo) the ligand shows a sickle arrangement. A new competing 2:1 species appears in which O-1, O-2, O-4 and O-5 are involved with the metal, the ligand having a zig–zag arrangement.

Tungstate is also able to form two more 2:1 species in which the ligand is pentadentate. At high pH, the coordination is established by O-2, O-3, O-4, O-5 and O-6; at intermediate pH, the coordination sites are O-1, O-2, O-3, O-4 and O-5.

Finally, evidence for one additional W(VI) 5:2 complex is also found, in which the 2:1

moieties involve O-3, O-4, O-5 and O-6. This chelation pattern becomes possible only because of a synergic effect due to the presence of a 1:2 moiety.

In the case of tungstate, the relative concentration of the various complexes at low and intermediate pH vary with time. An equilibrium state is being attained in about three weeks in favour of the 5:2 complex whose 2:1 moieties involve a terdentate ligand. Such a complex is homologous to the dominant 5:2 complex formed with molybdate at low and intermediate pH.

Acknowledgements

This work has been supported by a grant from Fundação para a Ciência e Tecnologia, the Portuguese agency for scientific research (Project PRAXIS QUI 63/96).

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