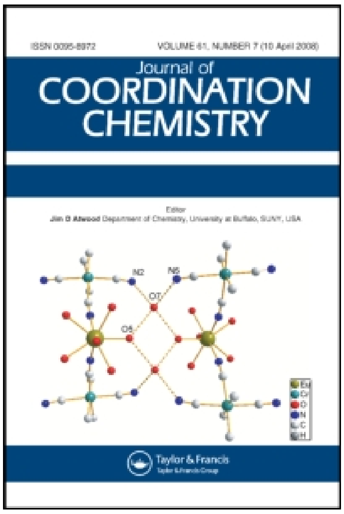

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MULTINUCLEAR NMR STUDY OF COMPLEXATION OF *D*-GALACTARIC AND *D*-MANNARIC ACIDS WITH TUNGSTEN(VI) OXOIONS

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MULTINUCLEAR NMR STUDY OF COMPLEXATION OF *D*-GALACTARIC AND *D*-MANNARIC ACIDS WITH TUNGSTEN(VI) OXOIONS

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The coordination compounds formed between W(VI) and *D*-galactaric and *D*-mannaric acids, in aqueous solution, have been studied by ^{1}H, ^{13}C, ^{17}O and ^{183}W NMR spectroscopy. In the pH range 3–8 for *D*-galactaric acid and 2–10 for *D*-mannaric acid, the acids are found to form n:n species (mainly 2:2) with tungstate, in which the ligands are bound to the metal by the two carboxylate groups and their adjacent OH groups. Above pH 6.5, a 2:1 species is also formed, in which all the OH functions are coordinated to the metal, the two carboxylate groups remaining free. The formation of symmetrical or asymmetrical species is discussed, taking into account the configuration of the ligands. Structures for the various complexes are formulated.

KEYWORDS: complexes, tungsten(VI), sugar derivatives, *D*-galactaric acid, *D*-mannaric acid, *threo* and *erythro* configurations

INTRODUCTION

The coordination chemistry of molybdenum(VI) and tungsten(VI) with ligands such as sugar derivatives, in aqueous solution, is a field of considerable interest from a chemical point of view and on account of its relevance in biological systems, health and the environment and because of its industrial applications.

In our comparative study of complexation of sugar acids with molybdenum(VI) and tungsten(VI), multinuclear NMR spectroscopy as a single technique proved to have clear advantages over other methods for studying these systems. This is mainly due to relatively slow exchange phenomena that enable distinct spectra to be obtained for different species.

We have previously studied the complexation of *D*-glucaric acid with molybdenum(VI) and tungsten(VI)[1] and of *D*-galactaric and *D*-mannaric acid with molybdate.[2]

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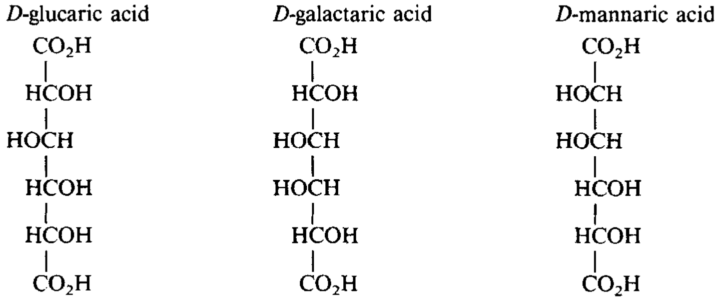


Fischer projections of the ligands

In the present work we report the complexation of *D*-galactaric and *D*-mannaric acids with tungstate, using ^{1}H, ^{13}C, ^{17}O and ^{183}W NMR spectroscopy, and discuss the relation between the ligand configuration and complexation behaviour.

^{1}H and ^{13}C signals due to free and bound ligand and their changes with molar ligand:metal ratio and pH, together with the number and intensity of the ^{183}W NMR signals, enabled the determination of the number of complexes. From ^{1}H and ^{13}C shifts it was possible to establish the ligand coordination sites and ^{17}O and ^{183}W shifts provided information about the metal centre. Information about the stoichiometry of the species was obtained by comparing ^{13}C with ^{17}O and/or ^{183}W NMR spectra of the same solutions.

EXPERIMENTAL

Analytical grade sodium tungstate and commercially available *D*-galactaric acid were used. *D*-mannaric acid was synthesized, in the dilactone form, starting from *D*-mannitol, according to Linstead *et al.*[3]

To reduce the intensity of the O*H* NMR signal, the salts were dried at 120°C, the ligands were lyophilized from solutions in deuterium oxide and D_2O solutions were used throughout. The pH was adjusted (cautiously, to reduce the possibility of drastic local disturbances of equilibria that may be slow to disappear) by addition of solutions of DCl and NaOD; the pH* values quoted are the direct pH-meter readings (room temperature) after standardization with aqueous (H_2O) buffers.

Most ^{1}H and ^{13}C spectra were obtained on a Varian XL-200 NMR spectrometer, and some on a Varian VXR-400 S NMR spectrometer. Except for some ^{1}H and ^{13}C spectra, recorded at 2, 40, 60 and 80°C, all spectra were obtained at probe temperature (21 ± 1°C). ^{13}C spectra were recorded using proton-decoupling techniques (Waltz-16) with suppression of the nuclear Overhauser effect. 2-Sodium 2,2-dimethyl-2-silapentane-5-sulphonate (DSS) (δ = 0 ppm) and *p*-dioxane (δ = 67.4 ppm) were used as internal references for ^{1}H and ^{13}C shifts, respectively. The ^{183}W spectra were obtained on a Varian VXR-400 S NMR spectrometer, using D_2O solutions of Na_2WO_4 at pH* = 9.5 (δ = 0 ppm) as external reference. The ^{17}O spectra were obtained on a Varian Unity-500 NMR spectrometer, using D_2O (δ = 0 ppm) as external reference. Typically, spectral widths of 20000 Hz, acquisition times of 0.4 s, pulse, delays of 8–12 s, and 2000 pulses were used when recording ^{13}C spectra. For ^{17}O and ^{183}W spectra, the corresponding parameters were 100000 and 10000 Hz, 0.02 and 0.9 s, 0 and 1.0 s, 750000–1000000 and about 25000, respectively.

RESULTS AND DISCUSSION

Proton and carbon-13 spectra of aqueous solutions of sodium tungstate and *D*-galactaric acid or *D*-mannaric acid, for variable molar ratios (from 4 to 0.5) and pH values (range 3–8 for *D*-galactaric acid and 2–10 for *D*-mannaric acid), clearly show the formation of various complexes. Due to the limited solubility of *D*-galactaric acid in water and especially in D_2O it was not possible to obtain spectra for metal:ligand molar ratios beyond 0.5 and for pH values above 8. For pH values below about 3, the precipitation of polytungstates occurs.

In the case of W(VI)/*D*-galactaric acid, three complexes appear (**a**, **b** and **c**) in the whole pH range studied, one (**a**) being largely dominant. At about pH* = 6.5, two new species appear: **d**, for metal:ligand ratios ≥ 1 and the minor species **e** for metal:ligand ratios between 1 and 0.5. For pH* values larger than about 8.5, precipitation occurs. The variation of the concentration of the species **a**, **b**, **c**, **d** and **e** with pH* is shown for two different compositions in Figures 1A and 1B.

Similar results were obtained for the system W(VI)/*D*-mannaric acid, except that the minor complex **e** is not detected in this system. The variation of the concentration of the species **a**, **b**, **c** and **d** with pH* is shown in Figures 2A and 2B.

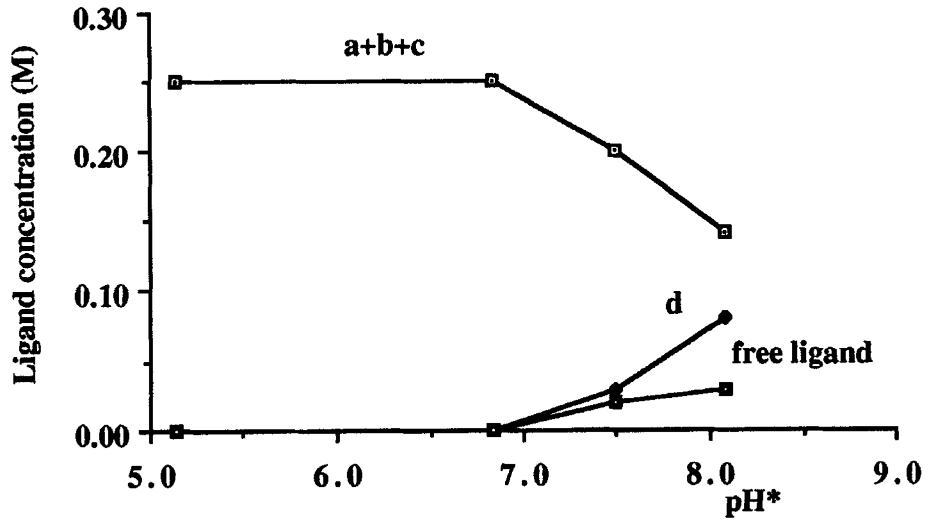
The way the NMR signal intensities (namely ^{13}C) change with metal:ligand molar ratio, both for bound ligand and for free ligand, suggest that **a**, **b** and **c** have an n:n metal:ligand stoichiometry, whereas the **d** complexes have a n:1 (n>1) composition; with similar reasoning the minor species **e**, which appears in the system W(VI)/*D*-galactaric acid, seems to be a 1:2 complex. For example, the ^{13}C spectrum of a 0.25M:0.50M W(VI)/*D*-mannaric acid solution, at pH* 5, shows approximately equal intensities of bound and free ligand signals and the ^{17}O spectrum of the same solution has no signal for the free metal oxoions. Similar species have been found for the systems Mo(VI)/*D*-glucaric acid[1] and Mo(VI)/*D*-galactaric and *D*-mannaric acids.[2]

Further conclusions can be made using the ^{1}H and ^{13}C chemical shifts relative to the free ligand (under identical conditions) as well as from the ^{17}O and ^{183}W parameters. In particular, δ values for these nuclei can be related to the structure of the metal centres. In favourable cases, the H-H coupling constants provided an indication of the conformation adopted by the ligand in the complexes.[4,5]

Tables 1 and 2 show the ^{1}H and ^{13}C NMR parameters and Tables 3 and 4 give the ^{183}W and ^{17}O NMR parameters, respectively. Complexes **a**, **b** and **c** and **e** show very broad ^{1}H signals, due to exchange processes. High frequency shifts for the carboxylic nuclei and for $C_{(2)}$ and $C_{(5)}$ relative to the free ligand were observed (Table 2). These shifts are typical of participation of the two carboxylic groups and their adjacent OH groups in complexation.[1,2,6–11] The ^{183}W NMR signals for these three complexes (Table 3) lie in the same region for the two systems (40–59 ppm range). It is possible to detect three distinct signals (two of them presenting W-H couplings in the system W(VI)/*D*-galactaric acid) besides the signals assigned to uncomplexed tungstate (three signals assigned to the heptatungstate ion[12–14]). The coupling constants $^{3}J_{W-H}$ are in the range 4–6 Hz. Other $^{3}J_{W-H}$ values reported in the literature lie in the range 1.5–8 Hz.[15–17] The assignments were made on the basis of signal intensities and by comparison with ^{13}C spectra.

For species **a**, **b** and **c** only one ^{183}W signal appears for each species; this indicates that these species are either monomeric or polymeric with equivalent metal centres. These results together with the number of ^{13}C NMR signals (Table 2) show that the C_{2v} symmetry of *D*-galactaric acid and the C_2 symmetry of *D*-mannaric acid are not

A



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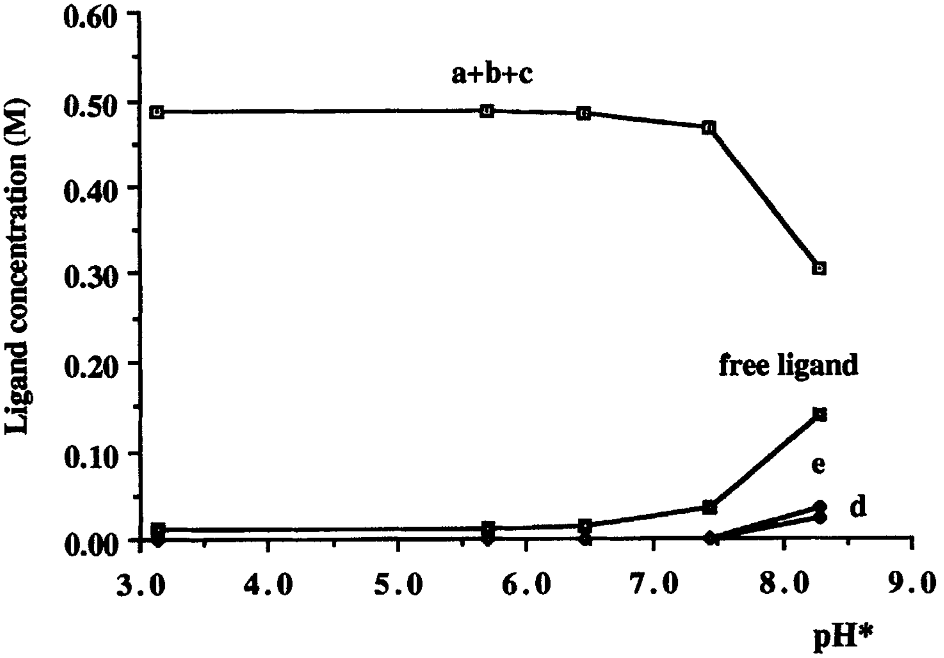


Figure 1 A: Concentration of species as a function of pH*, obtained by ^{13}C NMR for a 1.0M/0.25M aqueous solution (33% D_2O) of sodium tungstate (VI) and *D*-galactaric acid (Temp. 294K). B: Concentration of species as a function of pH*, obtained by ^{13}C NMR for a 0.50M/0.50M aqueous solution (33% D_2O) of sodium tungstate(VI) and *D*-galactaric acid (Temp. 294K).

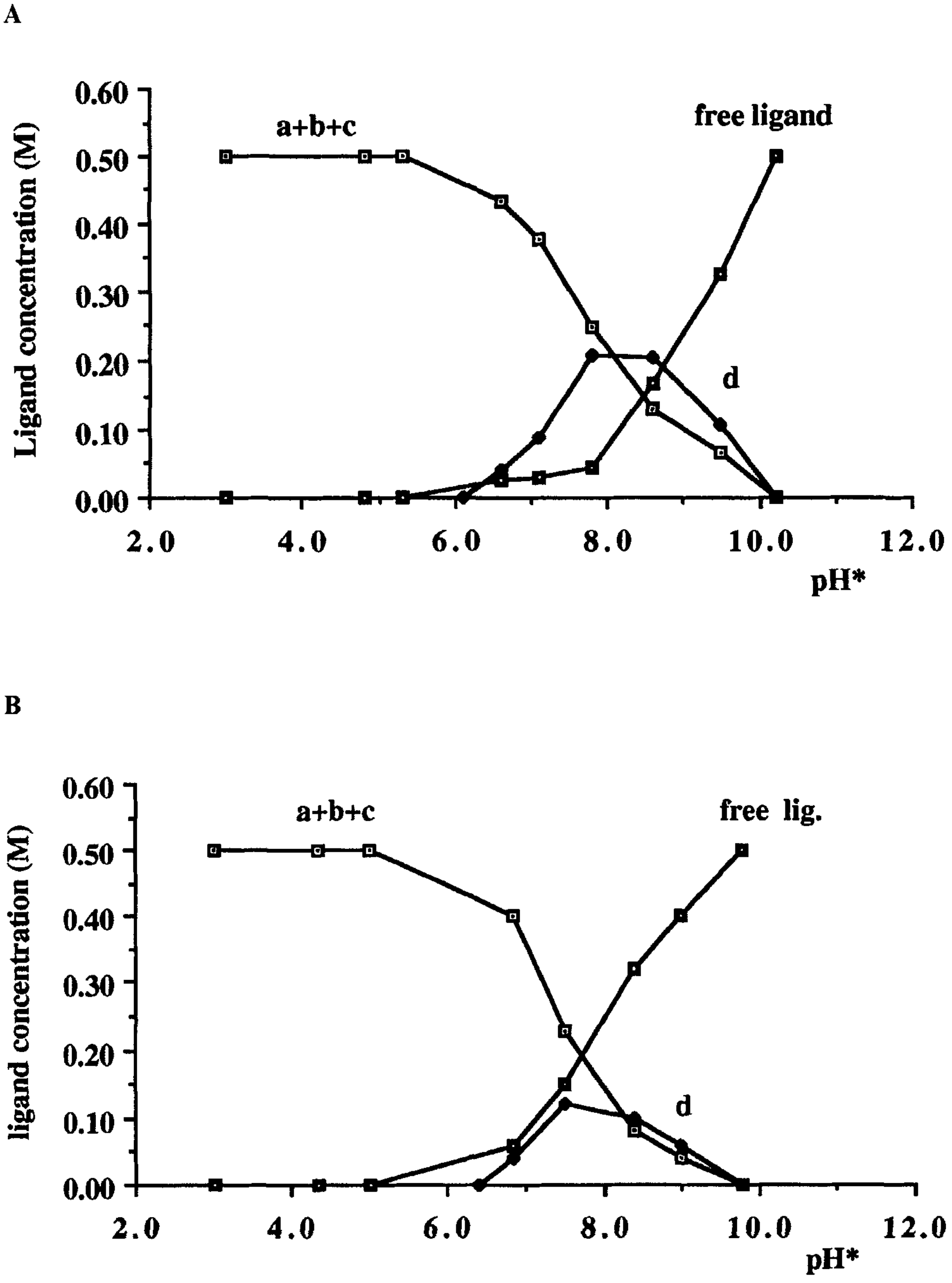


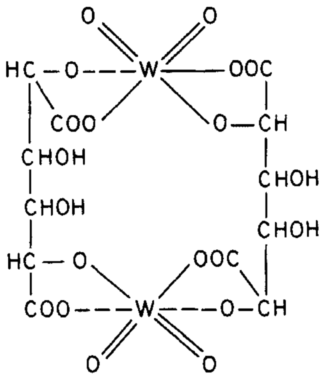
Figure 2 A: Concentration of species as a function of pH*, obtained by ^{13}C NMR for a 1.0M/0.50M aqueous solution (33% D_2O) of sodium tungstate(VI) and *D*-mannaric acid (Temp. 294K): B: Concentration of species as a function of pH*, obtained by ^{13}C NMR for a 0.50M/0.50M aqueous solution (33% D_2O) of sodium tungstate (VI) and *D*-mannaric acid (Temp. 294K).

Table 1 ^1H NMR parameters[a] for W(VI) + *D*-galactaric acid and W(VI) + *D*-mannaric acid.

	$H_{(2)}$	$H_{(5)}$	$H_{(3)}$	$H_{(4)}$	J_{2-3}	J_{4-5}	J_{3-4}
D-galactaric acid							
pH* = 2.0, Temp. 294K							
δ	4.16		3.97				
pH* = 5.0, Temp. 294K							
δ	4.26		3.94		1.1	1.1	~7^b
pH* = 7.5, Temp. 274K							
δ	4.26		3.94		1.1	1.1	~7^b
D-mannaric acid							
pH* = 2.0, Temp. 294K							
δ	4.34		4.00		5.6	5.6	-
pH* = 5.0, Temp. 294K							
δ	4.10		3.93		5.6	5.6	~2^b
pH* = 7.5, Temp. 294K							
δ	4.10		3.93		5.6	5.6	~2^b
W(VI) + D-galactaric acid							
complex **d**[c] (pH* = 7.9, Temp. 275K)							
δ	4.78	5.05	5.65	5.23	0	0	4.5
Δδ	0.79	0.52	1.71	1.29			
W(VI) + D-mannaric acid							
complex **d**[d] (pH* = 7.5, Temp. 274K)							
δ	4.69		4.81		2.2	2.2	0
Δδ	0.59		0.88				

[a] δ Values, in ppm, relative to DSS, J values in Hz. [b] According to ref. 24. [c] 0.40M/0.10M W(VI)/*D*-galactaric acid solution. [d] 0.40M/0.10M W(VI)/*D*-mannaric acid solution.

lost upon formation of complexes **a**, **b** and **c**. The ^{17}O NMR spectra (at pH* 5), besides the signals assigned to the heptatungstate ions,[14] show three signals that can be assigned to terminal oxygen nuclei in the metal centre; no resonance typical of bridge oxygen is observed (Table 4). By analogy with the Mo(VI) systems,[2] we propose Structure I for the dominant species **a**. These results are in part different



Structure I

Table 2 ^{13}C NMR chemical shifts[a] for W(VI) + *D*-galactaric acid and W(VI) + *D*-mannaric acid (295K).

	$C_{(1)}$	$C_{(6)}$	$C_{(2)}$	$C_{(5)}$	$C_{(3)}$	$C_{(4)}$
D-galactaric acid						
pH* = 2.0	179.75		72.43		72.00	
pH* = 5.0	180.33		72.53		72.21	
pH* = 7.5	180.53		72.72		72.32	
D-mannaric acid						
pH* = 2.0	177.01		72.06		71.98	
pH* = 5.0	179.73		74.56		72.40	
pH* = 7.5	179.88		74.66		72.40	
W(VI) + D-galactaric acid						
complex **a**[b] (pH* = 5.1)						
δ	184.97		84.83		74.85	
Δδ	4.64		12.30		2.64	
complex **b**[b] (pH* = 5.1)						
δ	185.73		84.03		74.37	
Δδ	5.40		11.50		2.16	
complex **c**[b] (pH* = 5.1)						
δ	184.27		85.39		74.04	
Δδ	3.94		12.86		1.83	
complex **d**[c] (pH* = 7.5)						
δ	181.01	179.07	78.51	80.88	93.54	85.22
Δδ	0.48	-1.46	5.79	8.16	20.22	12.90
complex **e**[b] (pH* = 7.5)						
δ	186.69		82.02		74.66	
Δδ	6.16		9.30		2.34	
W(VI) + D-mannaric acid						
complex **a**[d] (pH* = 5.0)						
δ	184.00		84.70		72.65	
Δδ	4.27		10.14		0.25	
complex **b**[d] (pH* = 5.0)						
δ	182.96		86.50		72.97	
Δδ	3.23		11.94		0.57	
complex **c**[d] (pH* = 5.0)						
δ	184.69		84.47		73.26	
Δδ	4.96		9.91		0.86	
complex **d**[d] (pH* = 7.5)						
δ	177.85		80.67		84.41	
Δδ	-2.03		6.01		12.01	

[a] δ Values relative to TMS (using δC(dioxane = 67.4 ppm). [b] 1.0M/0.25M W(VI)/*D*-galactaric acid solution. [c] 0.80M/0.20M W(VI)/*D*-galactaric acid solution. [d] 0.40M/0.10M W(VI)/*D*-mannaric acid solution.

from the observed complexation behaviour of *D*-galactaric and *D*-mannaric acids with Mo(VI), at low pH.[2] In this case, besides 1:1 (or n:n) species, a n:1 (4:2) species is formed in the pH* range 2–6.5, in which the two carboxylate and all OH groups are bound to the metal. Usually, complexations studies of Mo(VI) and W(VI) are performed in parallel, taking into account their similar properties, but it is known that the tungstate has a larger tendency to form polymeric species (polytungstates) than molybdate, for solutions under the same conditions (concentration, pH, ionic strength and temperature).

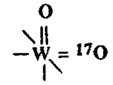
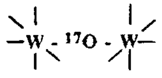
In the case of complex **d** the relatively small complexation shifts for $C_{(1)}$ and $C_{(6)}$ and the large shifts of $C_{(2)}$, $C_{(3)}$, $C_{(4)}$, $C_{(5)}$, $H_{(2)}$, $H_{(3)}$, $H_{(4)}$ and $H_{(5)}$ nuclei (Tables 1

Table 3 ^{183}W NMR chemical shifts[(a)] for W(VI) + *D*-galactaric acid and W(VI) + *D*-mannaric acid (298K).

	$\delta^{183}W$	J_{W-H} (Hz)
W(VI) + D-galactaric acid		
complex **a**[b] (pH* = 5.0)	54.9	4.3
complex **b**[c] (pH* = 5.0)	50.1	6.1 4.2
complex **c**[c] (pH* = 5.0)	58.9	[d]
complex **d**[e] (pH* = 7.5)	- 61.7 - 74.0	9.1 8.6
W(VI) + D-mannaric acid		
complex **a**[f] (pH* = 5.0)	40.6	[d]
complex **b**[f] (pH* = 5.0)	53.2	[d]
complex **c**[f] (pH* = 5.0)	53.5	[d]
complex **d**[f] (pH* = 7.5)	- 84.9	[d]

[a] δ Values relative to external reference Na_2WO_4, pH* = 9.5 [b] 1.0M/0.50M W(VI)/*D*-galactaric acid solution. [c] 0.50M/0.50M W(VI)/*D*-galactaric acid solution. [d] not resolved. [e] 1.0M/0.25M W(VI)/*D*-galactaric acid solution. [f] 1.6M/0.40M W(VI)/*D*-mannaric acid solution.

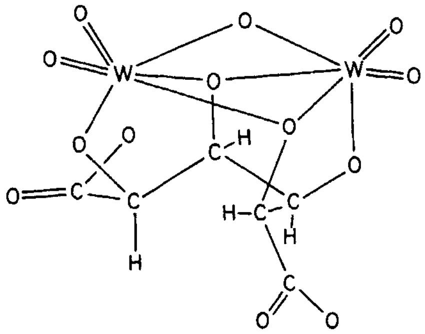
Table 4 ^{17}O NMR chemical shifts[a] for W(VI) + *D*-galactaric acid and W(VI) + *D*-mannaric acid (298K).

		
W(VI) + *D*-galactaric acid		
complexes **a** + **b** + **c**[b] (pH* = 5.0)	679, 642, 632	
complex **d**[c] (pH* = 8.5)	497	412
W(VI) + *D*-mannaric acid		
complexes **a** + **b** + **c**[d] (pH* = 5.0)	739, 650, 643	
complex **d**[c] (pH* = 7.5)	617	241

[a] δ Values relative to external reference D_2O. [b] 0.50M/0.50M W(VI)/*D*-galactaric acid solution. [c] 1.0M/0.25MW(VI)/*D*-galactaric acid solution. [d] 0.50M/0.50M W(VI)/*D*mannaric acid solution.

and 2) point to a complexation through the four OH groups alone, just as previously found for the systems Mo(VI)*D*-galactaric acid and Mo(VI)/*D*-mannaric acid.[2]

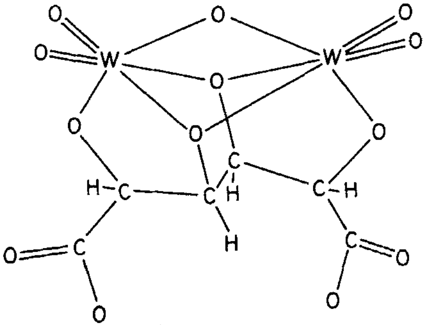
For the system W(VI)/*D*-galactaric acid, species **d** shows two ^{183}W NMR signals (δ = - 61.7 and δ = - 74.0 ppm; Table 3) that can be assigned to an asymmetrical ditungstate complex. The coupling constants $^3J_{W\text{-}H}$ are 9.1 and 8.6 Hz. These results are in agreement with those found by Chapelle and Verchère,[17] for *erythro* tungstate alditol complexes; they assumed that these high $^3J_{W\text{-}H}$ values reflect dihedral angles close to 180°. The known crystal structure of the *D*-mannitol[18] and erythritol[19] molybdate complexes, possessing a complexing site involving a central *erythro* group, can be used as models. Structure II is a schematic representation of the proposed chelation of the ditungstate anion by four hydroxyl groups of *D*-galactaric acid. Similar structures were proposed for *erythro* tungstate alditol complexes,[17] for the molybdate complex of *D*-galactaric acid found at high pH*[2] and for molybdate complexes of alditols with an *erythro* central diol group.[20,21] The complex has a dinuclear core bridged by three oxygen atoms, two of them being



Structure II

deprotonated hydroxy groups of the ligand. For the latter, two possibilities exist: $OH_{(2)}$ and $OH_{(4)}$ or $OH_{(3)}$ and $OH_{(5)}$. The four carbon atoms of the complexing site must adopt a sickle arrangement allowing their four hydroxyl groups to point in the same direction. By making use of the model of Altona and coworkers[4,5] relating vicinal H-H coupling constants to dihedral angles, when substituents are present, the dihedral angles, $H_{(3)}C_{(3)}C_{(4)}H_{(4)}$, $H_{(2)}C_{(2)}C_{(3)}H_{(3)}$ and $H_{(4)}C_{(4)}C_{(5)}H_{(5)}$ are estimated to change from 20 to 42°, 54 to 80° and 54 to 101°, respectively, if $OH_{(2)}$ and $OH_{(4)}$ bridge the two metal centres.

Complex **d** for *D*-mannaric acid is similar but shows a single ^{183}W NMR signal with a chemical shift −84.9 ppm (Table 3), that can be assigned to two symmetrical metal centres. The W-H couplings are not detected in this case. The complexation occurs without appreciable loss of symmetry. Following refs. 4 and 5 we calculate a dihedral angle of about 100° for $H_{(3)}C_{(3)}C_{(4)}H_{(4)}$ and about 61° for both $H_{(2)}C_{(2)}C_{(3)}H_{(3)}$ and $H_{(4)}C_{(4)}C_{(5)}H_{(5)}$. Structure III is a shematic representation of



Structure III

such a complex. The complex has a dinuclear core bridged by three oxygen atoms, two of them being the central deprotonated hydroxy groups of the ligand, $OH_{(3)}$ and $OH_{(4)}$. The four carbon atoms of the complexing site must adopt a zig-zag arrangement. Accordingly, these pairs of carbon nuclei (as well as the corresponding pairs of protons; Tables 1 and 2) were found to be equally deshielded. Similar structures were proposed for the molybdate complex of *D*-mannaric acid found at high pH* and for molybdate complexes of alditols with a central *threo* diol group.[20] In favour of $W_2O_5^{2+}$ centres for complexes **d** in the two systems, are the ^{17}O chemical shifts (Table 4), in particular the values assigned to bridge oxygen atoms.[14]

The results for the system W(VI)/*D*-galactaric acid agree in part with those of Cervilla and coworkers.[22] These authors studied the complexation between W(VI) and *D*-galactaric acid using spectrophotometric methods and NMR spectroscopy and concluded that one 1:2 and two 2:2 (metal:ligand) species occur and that W(VI) is not able to form complex species with galactaric acid having all alcoholic groups bound to the metal. The coordination of the ligand to the metal is shown to be through the two carboxylate groups and the two adjacent OH groups (2,5), leaving the central hydroxyl groups (3,4) always uncoordinated. Complex **d** is not mentioned by them.

CONCLUSION

D-galactaric and *D*-mannaric acids are found to form analogous complexes with tungstate: n:n complexes all over the pH range studied (3–8 and 2–10, respectively; the dominant one is 2:2), and 2:1 complexes at high pH (6.5–8.5). In the former complexes, both carboxylate groups and the adjacent OH groups are bound to the metal; the two central OH groups remain free, in a symmetrical fashion. In the 2:1 complexes at high pH, only the alcoholic groups are involved in complexation.

Previously, we studied the complexation of these ligands with Mo(VI).[2] The main difference between W(VI) and Mo(VI) is that no 2:1 complex at low pH is detected with W(VI). However, 2:1 complexes at high pH are formed, just as with Mo(VI), involving only the four OH groups of the chain. The difference at low pH is probably mainly due to the greater tendency of W(VI) to form polymeric oxoions.

Our results with aldarates at high pH can be compared to those obtained with alditols as ligands.[17] We note that, although the two acids studied here have C_2 symmetry structures, only *D*-mannaric acid gives rise to symmetrical complexes with W(VI). *D*-galactaric acid, on the other hand, leads to asymmetrical species. Chapelle and Verchère have studied molybdate[20,21] and tungstate[17] complexes of alditols. With Mo(VI) they found two types of binuclear species in which all four OH groups of the ligand were bound to Mo and differing in the configuration of the central diol groups (*threo* or *erythro*). In a similar study, Bílik and coworkers[23] have found two types of binuclear dimolybdate species: a symmetrical one if the ligand can adopt a zig-zag arrangement (only one ^{95}Mo NMR signal) and an asymmetrical one if the ligand adopts a sickle arrangement (two ^{95}Mo NMR signals). *Erythro* alditols form homologous molybdate and tungstate complexes, but with *threo* alditols the ligand acts as terdentate and two well separated ($\Delta\delta \sim 60$ ppm) ^{183}W signals are recorded.[17]

As for Mo(VI)[2], the ditungstate complex of *D*-galactaric acid, in which the central diol group has an *erythro* configuration, is asymmetrical, and, therefore, gives rise to two ^{183}W signals. The ^{183}W chemical shifts are comparable to those of the galactitol ditungstate complex.[17] The spatial arrangement of the ligand in the complexes is sickle, giving rise to differential shielding of carbon nuclei and protons.

On the other hand, *D*-mannaric acid, a symmetrical ligand with a *threo* configuration of the central diol group, gives rise to a symmetrical 2:1 complex, the ligand being in a zig-zag arrangement. Accordingly, only one ^{183}W signal is detected. The ^1H and ^{13}C complexation shifts provide strong evidence that mannaric acid acts as a tetradentate ligand adopting a zig-zag conformation. This result is at variance with that found for the ditungstate complexes of *threo* alditols[17] in which the alditol acts as a terdentate ligand.

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