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Indirect photometry and multinuclear ^{13}C and ^{183}W NMR study of tungstate complexes of sugar acids Stabilities and structures

Miloudi Hlaïbi [a,b,*], Mustapha Hor [a], Amina Riad [a], Fatiha Toumri [a], Jean-François Verchère [b], Stella Chapelle [c]

[a] *Laboratoire d'Interface Matériaux et Chimie de l'Environnement, Université Hassan II, Faculté des Sciences Aïn Chock, B.P. 5366, Maârif, Casablanca, Morocco*
[b] *Laboratoire des Polymères, Biopolymères, Membranes, UMR 6522 du CNRS, Université de Rouen, Faculté des Sciences, F-76821 Mont-Saint-Aignan, France*
[c] *Laboratoire R.M.N. et spectroscopie de masse, IRCOF, 1 rue Tesnières, Université de Rouen, Faculté des Sciences, F-76821 Mont-Saint-Aignan, France*

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Abstract

The tungstate complexes of the sugar acids, *meso*-tartaric and L-gulonic acids, have been studied in aqueous solutions. Indirect photometry has been used to determine the stability constants and the stoichiometry of these colourless complexes. Multinuclear ^{13}C and ^{183}W NMR spectroscopies have been used to specify the structures of the complexes and the sites of chelation of the ligand. For *meso*-tartaric acid, complexes of the lactic type with a mononuclear and with a dinuclear tungsten core have been identified. In these type lactic complexes, only the hydroxyl groups of the carboxyl function and the atom carbon in α position belong to the site of chelation of the tungstate complexes. Both α-hydroxyacid moieties of the *meso*-tartaric acid are involved in the chelation.

For L-gulonic acid, lactic type complexes with a mononuclear and a dinuclear tungsten core have been observed at acidic pH. Upon increasing the pH, the lactic complexes disappear: first the mononuclear, then the dinuclear complexes. In pH range 4–8, for gulonic acid, dual lactic, *threo* (tetradentate) type complexes occur, the dual lactic, *erythro* and lactic, *threo* complexes exist. At pH 10, for gulonic acid, a single complex has been identified in which the ligand is pentadentate. In this complex, all carbon atoms of the ligand are involved in the site of chelation except the carboxyl atom.

Keywords: Tungstate complexes; Indirect photometry; Multinuclear ^{13}C and ^{183}W NMR; Site of chelation; Lactic type complexes; *Erythro* and *threo* type complexes

1. Introduction

The chemistry of living organisms is based on the chemistry of proteins, lipids and carbohydrates. Carbohydrates play an important role, for instance, in the regulation of metabolism and energetic balance. Occasionally, carbohydrates act as ligands and chelate metal ions with their hydroxyl groups. This process may be used for the transport of carbohydrates through ion exchange membranes.

The subject of this work is the complexation of some sugar derivatives by the tungstate ion (WO_4^{2-}). The complexation reaction of tungstate with a sugar ligand L is given by:

$$x\,WO_4^{2-} + y\,L + z\,H^+ \Leftrightarrow (x, y, z)^{(2x-z)-} + n\,H_2O \quad (1)$$

where L represents a neutral compound (sugar or alditol). The values of x, y, and z, and the sites of chelation depend on the nature of the derivative. The formation constants of the complexes are derived from indirect photometry measurements and quantify the stabilities of the complexes. The sites of chelation and the structures of the complexes are determined by ^{13}C and ^{183}W NMR. The relative proportions of the various tungstate complexes in case of mixtures with a given ligand provide an

* Corresponding author. Tel.: +212 2 23 06 80; fax: +212 2 23 06 74.
E-mail address: miloudi58@hotmail.com (M. Hlaïbi).

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Fig. 1. *Threo* configuration (a) and *erythro* configuration (b) of hydroxyl groups.

indication for their relative stabilities. It is found that the stability strongly depends on the configuration of the hydroxyl groups of the ligands. This property is used to separate carbohydrates by chromatography on cellulose impregnated with tungstate [1].

Alditols are sugar derivatives, which are obtained by reducing the aldehyde group of an aldose. Their general formula is $HOCH_2{-}(CHOH)_n{-}CH_2OH$. The tungstate complexes of alditols have been extensively studied [2–5]. In general, one ligand chelates two tungsten ions. Internal OH groups are preferred with respect to end of chain HO groups for entropic reasons [6]. The way in which the tungsten ions are chelated depends on the presence of *threo* or *erythro* configurations for the internal diol systems. The *threo* or *erythro* configurations are illustrated in Fig. 1; the names are chosen after the sugars with corresponding internal OH configuration: threose and erythrose.

In order to chelate tungstate ions, the donating hydroxyl groups must point in the same direction with respect to the carbon chain. This is the case for *threo* sites, which can chelate tungstate with the carbon chain in the natural *zig–zag* conformation. The density (the number of hydroxyl groups which chelate tungstate) is pH-dependent. At $pH < 7$, the ligand is tetradentate, at $7 < pH < 9$ the ligand is tridentate and at $pH > 9$ pentadentate species are formed [4,5]. On the other hand, for *erythro* sites to chelate the tungstate ion, the carbon chain has to adopt a *sickle* conformation. This results, for the tetradentate ligand, in an asymmetrical chelation by four OH groups of the *erythro* site. The various complexes are represented in Fig. 2.

Upon increasing the chain length, two chelation sites may become available next to each other. For the heptitol perseitol, one complex has been identified in which both an *erythro* tetradentate and a *threo* tridentate type chelation occur. Thus, in this complex the ligand is heptadentate and because of the two ditungstate moieties involved, it is called a bis-dinuclear complex [4].

Aldonic acids are acidic derivatives of sugars, possessing the general formula $HOCH_2{-}(CHOH)_n{-}COOH$. The way in which tungstate interacts with the carboxyl moiety has been studied for ligands possessing one or two carboxyl groups and hydroxyl groups only at position α [7]. These α-hydroxyacids are simple models of aldonic acids. Several complexes are found in which tungstate is always chelated by the α-hydroxyl group and the hydroxyl group of the carboxyl moiety. In this paper, these complexes will be called lactic type complexes (lactic acid is $CH_3{-}CHOH{-}COOH$). The ligand being bidentate, this may result in *mononuclear bis chelate* complexes in which one tungsten atom is involved, or *dinuclear bis chelate* complexes in which two tungsten atoms are bridged. A particular complex is found in the case of DL-tartaric acid. This ligand possesses two α-hydroxyacid moieties which are both involved in complexation, so the formation of a bis-mononuclear complex has been suggested. The complexes are represented in Fig. 3.

If the α carbon atom is chiral, the two substituents which are not involved in chelation can be oriented in two different ways towards tungsten. This can result in the observation of different complexes which are diastereoisomers. The nature of the groups at the α carbon atom is also important for the stability of the complexes. It was found that the stability of the complexes increases significantly if hydrogen atoms are replaced by alkyl groups [7]. If the α carbon atom does not bear a hydroxyl group, no chelation of tungstate occurs. Even the presence of a hydroxyl group in the β position does not induce chelation.

When a ligand possesses both an α-hydroxyacid moiety and a polyol part, several possibilities for chelation are present. It appears that the way of complexation depends on the pH of the medium. An example of such a ligand is a heptonic acid possessing of a chain of seven carbon atoms. In alkaline medium, the α-hydroxyacid moiety is not involved in complexation, and the polyol part of the ligand is found to chelate a ditungstate moiety at the pentadentate *O*-2,3,4,5,6 site. In acidic medium, three types of complexes are found. The first type only involves

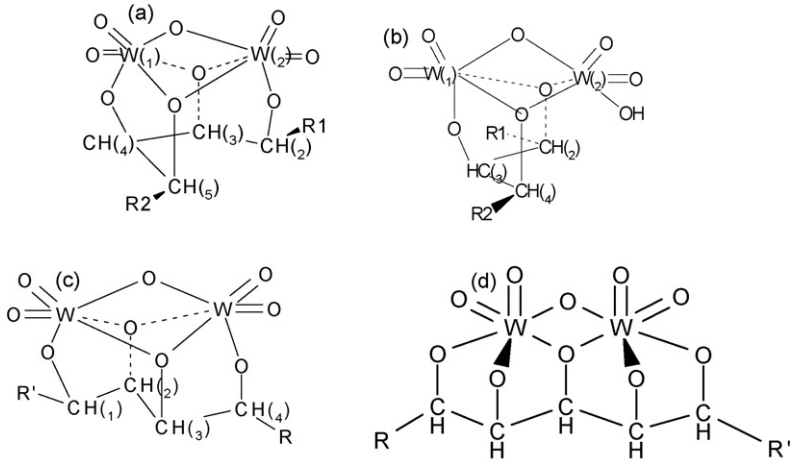

Fig. 2. Tungstate alditol complexes: *Erythro* site, ligand tetradentate (a); *Threo* site, ligand tridentate (b); *Threo* site, ligand tetradentate (c) and *Threo* site, ligand pentadentate (d).

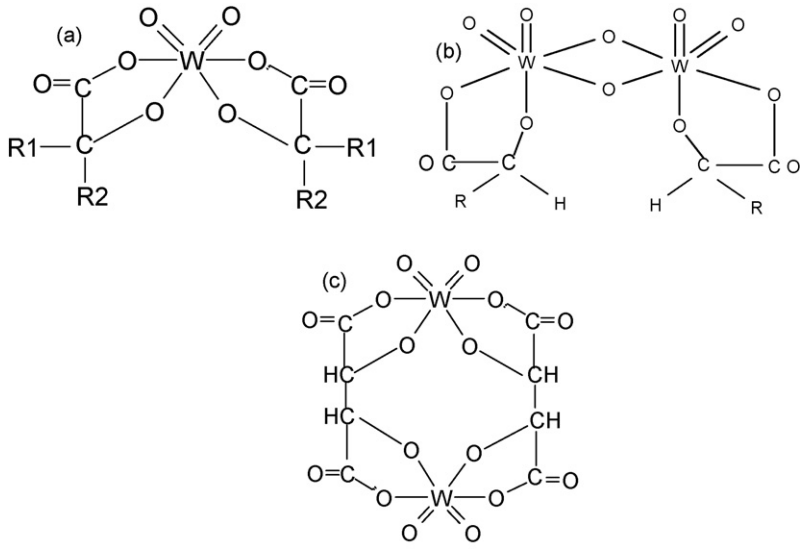

Fig. 3. Tungstate α-hydroxyacid complexes: mononuclear bis chelate (a), dinuclear bis chelate (b), bis mononuclear (c).

the polyol tetradentate *O*-4,5,6,7 site of the ligand. The second type involves the α-hydroxyacid moiety and both the mononuclear dichelate and the dinuclear monochelate complexes are observed. Finally, in the third type of complex, both the α-hydroxyacid site and the tetradentate polyol site are involved in complexation [8]. The complex has been identified as consisting of a mononuclear bis chelate part at one side, both ligands also chelating two bridged tungstate atoms in a tetradentate way (*erythro* site). Thus, the two ligands are hexadentate and the complex possesses the overall stoichiometry (5/2) (tungstate/ligand). As a general trend, above pH 6, the lactic complexes appear not to be favored whereas the *erythro* complexes are favored [8].

In this work, *meso*-tartaric acid (four carbon atoms) and L-gulonic acid (six carbon atoms) have been studied. The Fischer projections of the compounds are drawn in Fig. 4.

1.1. Indirect photometry

The complexation reaction of tungstate with an acidic ligand is given by Eq. (2):

$$x\,WO_4^{2-} + y\,L^- + z\,H^+ \rightleftarrows (x, y, z)^{(2x+y-z)-} + n\,H_2O \qquad (2)$$

where L^- represents the ligand with the carboxyl group in the dissociated form. The formation constant K_{xyz} (or stability constant β_{xyz}) of the complex is defined as the equilibrium constant:

$$K_{xyz} = [(x, y, z)][WO_4{}^{2-}]^{-x}[L^-]^{-y}[H^+]^{-z} \qquad (3)$$

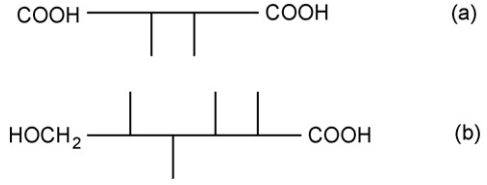

Fig. 4. *meso*-Tartaric acid (a) and L-gulonic acid (b).

Additionally, a conditional equilibrium constant K'_{xyz} is defined in case of constant pH value (buffered solution):

$$K'_{xyz} = [(x, y, z)][WO_4{}^{2-}]^{-x}(C_L)^{-y} \qquad (4)$$

where C_L represents the analytical concentration of the uncomplexed ligand ($C_L = [L^-] + [HL]$), with $K_a = [H^+][L^-][HL]^{-1}$; C_L can be written as: $C_L = [L^-]\,(1 + [H^+]K_a{}^{-1})$. Using this equation, equation (3) can be written as:

$$K_{xyz} = [(x, y, z)][WO_4{}^{2-}]^{-x}[H^+]^{-z}(C_L)^{-y}(1 + [H^+]K_a{}^{-1})^{+y} \qquad (5)$$

At pH values $\gg pK_a$, $[H^+]K_a{}^{-1} \ll 1$ and Eq. (5) can be rewritten as:

$$K_{xyz} = [(x, y, z)][WO_4{}^{2-}]^{-x}(C_L)^{-y}[H^+]^{-z} = K'_{xyz}[H^+]^{-z}$$

and

$$\log\, K_{xyz} = \log\, K'_{xyz} + z\mathrm{pH} \qquad (6)$$

At pH values $\ll pK_a$, $[H^+]K_a{}^{-1} \gg 1$ and Eq. (5) can be rewritten as:

$$K_{xyz} = [(x, y, z)][WO_4{}^{2-}]^{-x}[H^+]^{-z}(C_L)^{-y}([H^+]K_a{}^{-1})^{+y}$$

and

$$\log\, K_{xyz} = \log\, K'_{xyz} + y\,pK_a + (z - y)\mathrm{pH} \qquad (7)$$

The complexation equilibrium can be studied using a spectrophotometric method. Because both the carbohydate ligands and their complexes do not possess a characteristic UV–vis absorption spectrum, a second ligand is introduced. This second ligand must absorb in the UV–vis spectrum and form an absorbing complex (called the sacrificial complex) with tungstate. This photometric method, based on ligand–ligand displacement, is said to be in the indirect mode. The dissociation of the sacrificial complex by a carbohydrate ligand causes large variations in the

UV–vis spectrum, which allow the calculation of the concentration of the sacrificial complex. Using the known formation constant of this complex, the concentration of the colourless complex can be obtained. For this purpose, the sacrificial ligand must form a single tungstate complex of lower stability than the tungstate complexes under study.

In this work, 2,5-dihydroxy-1,4-benzoquinone (H_2D) has been used as sacrificial ligand. This ligand is a diprotic acid with pK_a values of 2.95 (H_2D/HD^-) and 4.87 (HD^-/D^{2-}). In our experimental pH range (3.8–5.2), the small proportion of H_2D form could be neglected. The complexation of dihydroxybenzoquinone is represented by:

$$WO_4{}^{2-} + D^{2-} + 2H^+ \rightleftarrows (1,1,2)^{2-} + 2H_2O \quad (8)$$

The formation constant of the (*1,1,2*) complex is defined as:

$$K_{112} = [(1,1,2)][WO_4{}^{2-}]^{-1}[D^{2-}]^{-1}[H^+]^{-2} \quad (9)$$

The conditional equilibrium constant is given by:

$$K'_{112} = [(1,1,2)][WO_4{}^{2-}]^{-1}(C_D)^{-1} \quad (10)$$

where C_D represents $[D^{2-}] + [HD^-]$.

When the carbohydrate ligand is added to a solution of the sacrificial complex, the dihydroxybenzoquinone complex will dissociate. To calculate the concentration of the complexed benzoquinone, the absorption values of the totally complexed (A_F) and completely dissociated (A_I) benzoquinone had to be determined. Then the following equations were used:

$$[(1,1,2)] = C_{D\,initial}(A - A_I)(A_F - A_I)^{-1} \quad (11)$$

$$[C_{D\,present}] = C_{D\,initial}(A_F - A)(A_F - A_I)^{-1} \quad (12)$$

Since the conditional equilibrium constant of the sacrificial complex is known, the tungstate concentration can be calculated using Eqs. (10)–(12). Knowing [*(1,1,2)*] and $[WO_4{}^{2-}]$, the concentration of the complex under study can be determined using the tungstate mass balance equation:

$$\boldsymbol{x}(x,y,z) = C_W - [(1,1,2)] - [WO_4{}^{2-}] \quad (13)$$

C_w being the initial tungstate concentration. In a similar way, the concentration of the free ligand is obtained by:

$$[C_{L\,present}] = C_{L\,initial} - \boldsymbol{y}(x,y,z) \quad (14)$$

In each experiment, the ligand is added stepwise in order to measure the absorption at different values (at least 12) of the overall initial concentration C_L of ligand. The correct K'_{xyz} is calculated by varying $\boldsymbol{x}$ and $\boldsymbol{y}$ in order to obtain a constant value for all values of C_L. If K'_{xyz} is determined at different pH values, the slope of the log K'_{xyz} vs. pH plot reveals the number of protons z involved in the complex by use of Eqs. (6) and (7), since the value of K is independent of pH. Now the total stoichiometry of the complex has been determined.

1.2. Nuclear magnetic resonance

The complexes formed by the ligands under study are examined by recording one-dimensional (1D) ^{13}C and ^{183}W NMR spectra. Because of the spin number $I = 1/2$ of both nuclei, each magnetically distinct atom shows a sharp signal in the spectrum. Thus, in a broadband ^1H decoupled ^{13}C spectrum, each carbon atom generally gives rise to one signal. In a complexed ligand, the carbon atoms involved in chelation are deshielded, which causes a change in their chemical shift. This change is called the coordination induced shift (CIS) and is a tool in elucidating the sites of chelation. The CIS also helps in determining the structure of the ligand in the complex, as a typical deshielding pattern corresponds to each type of complex. For the different complexes described in the introduction, the CIS patterns of the carbon atoms involved are summarized in Table 1. ^{183}W is a heavy nucleus and its chemical shift is very sensitive to its environment. Each typical way of chelating tungstate gives rise to a signal in a typical region of the spectrum. Therefore, a ^{183}W spectrum of an aqueous solution of the ligand and tungstate is very helpful in the identification of the number and structures of the metal–ligand complexes. The chemical shift (δ) ^{183}W values for the different types of complexes can also be found in Table 1.

The 1D ^{13}C spectra can be recorded either ^1H coupled or ^1H decoupled. If the spectrum is recorded with coupling, the hydrogen atoms directly bound to the carbon atoms will induce splitting of the carbon signals. From the splitting pattern, it can be seen how many hydrogen atoms are bound to the carbon atom. Decoupling the protons however simplifies the spectrum. During a decoupling experiment, the protons are strongly irradiated while the resonance of the ^{13}C nuclei is observed. Being saturated, the protons transfer their energy by way of dipole–dipole interactions. Thus, the populations of the ^{13}C isotope increase

Table 1
^{13}C CIS patterns and ^{183}W chemical shifts of different types of tungstate complexes of carbohydrate derivatives

	($\Delta\delta$) ^{13}C CIS (ppm)					(δ) ^{183}W (ppm)
Erythro site						
Ligand tetradentate	10	10	20	10		−79 ± 7 two signals
Threo site						
Ligand tridentate	10	14	10			−58 ± 3 and −119 ± 2 two signals
Ligand tetradentate	12	11	11	12		−90 ± 2, one signal
Ligand pentadentate	14	10	13	11	15	+90 ± 13 two signals
Lactic site	COOH			CHOH		
Mononuclear bis chelate	5			12		+34 ± 8 two signals
Dinuclear bis chelate	5			12		−120 ± 1 one signal

and the intensity of the carbon signals is enhanced. This relative variation η of the intensity given by the expression (17), translated the nuclear Overhauser effect η (nOe):

$$\eta = \frac{I - I_0}{I_0} \tag{17}$$

The amount of signal enhancement is determined by the gyromagnetic ratios of the nuclei involved. The maximum relative values of the nOe is given by:

$$\eta_{\max} = \frac{1}{2}\left[\frac{\gamma\,(\text{irradiated})}{\gamma\,(\text{observed})}\right] \tag{18}$$

For C–H, $\eta_{\max} = 1.987$.

A special pulse sequence allows to differentiate between carbon atoms bearing an odd number of hydrogen and carbon atoms bearing an even number of H's: the J modulated spin-echo sequence. By choosing the right experimental parameters, the echo of CH_n ($n = 1$ or 3) shows a positive signal whereas CH_m ($m = 0$ or 2) displays a signal in negative direction [9]. Below, the ^{13}C CIS patters and ^{183}W chemical shifts of different types of complexes are given and some relations between the values and the types of complexes will be explained. For the schematical drawings of the different complexes, see Figs. 2 and 3.

Tetradentate *erythro* type complexes show an asymmetrical CIS pattern. The asymmetrical chelation causes the two bridged tungsten atoms to be in a similar, but not identical environment. This explains why the two tungsten signals are separated by a small gap. In tridentate *threo* type complexes, the chelation is symmetrical with respect to the ligand carbon chain, but now the two bridged tungsten atoms are not chelated in a similar way. One of them is chelated by three oxygen atoms of the ligand whereas the other is chelated by only two oxygen atoms of the ligand. The less deshielded ^{183}W signal at −120 ppm is assigned to the latter tungsten atom. In the pentadentate complex, an asymmetry may be caused by a difference in the groups at both sides of the ligand carbon chain [2–5] (Fig. 2a–c). In the case of a mononuclear bis chelate complex involving lactic sites, the two ^{183}W signals represent two tungsten atoms in similar environments, assigned to the two diastereoisomers mentioned before [7]. If the α carbon atom of an α-hydroxyacid is not chiral, its ^{183}W spectrum shows only one signal (Fig. 3c). This signal lies at +81 ppm when the carbon atom bears two hydrogen atoms and at −14 ppm if it bears two methyl groups.

2. Experimental

2.1. Sugar acids

meso-Tartaric acid (Sigma) and L-gulonic γ-lactone (Aldrich) were commercially obtained and of analytical grade (puriss. ≥98%). The acids were used without further purification.

2.2. Indirect photometry

The spectrophotometric experiments have been performed on a Secomam S 1000G spectrophotometer, using quartz cells of optical path length $l = 1$ cm. The absorption measurements have been performed at room temperature at wavelength $\lambda_{\max} = 320$ nm. Stock solutions of $Na_2WO_4{\cdot}2H_2O$ (Prolabo puriss. ≥98%) and 2,5-dihydroxy-1,4-benzoquinone (Aldrich, puriss. ≥ 98%) were prepared at concentrations of $(5 \pm 0.1) \times 10^{-3}$ M and $(2 \pm 0.1) \times 10^{-3}$ M, respectively. In a typical experiment, a solution ($v = 100$ mL) of the sacrificial tungstate-dihydroxyquinone complex was prepared, $[WO_4^{2-}] = 6 \times 10^{-5}$ M, [DHQ] = 6×10^{-5} M, [NaOAc] = 0.1 M. The initial solution also contained a calculated amount of 1 M HCl in order to obtain the desired pH value (pK_a of AcOH = 4.6 ± 0.02, experimental pH range: 3.8–5.2 ± 0.02). pH values were measured with a Metrohm 620 pH-meter equipped with a combined glass electrode and calibrated with commercial buffers (pH 4.00 and 7.00). Then aliquots ($v = 0.100$–0.200 mL) of an aqueous solution of the ligand acid ($C_m = 10 \pm 0.1$ g/L) were added, using a Gilson micropipet of 0.20 mL. After each addition, the resulting solution was left at least 5 min in order to reach equilibrium (and thus a constant absorption value). Addition was repeated until a maximum volume of 2.00 mL of the ligand solution was added. Hence, the changes in the total volume could be neglected. When an excess of ligand was added, complete dissociation of the coloured sacrificial complex occurred and the colourless solution contained only the mixture of colourless tungstate complex of the studied ligand and free dihydroxyquinone.

The formation constants were calculated using a laboratory made computer program in GW basic. The absorption values for the undissociated (A_F) and the totally dissociated (A_I) sacrificial tungstate–dihydroxyquinone complex were used as determined in experiments using pure dihydroxyquinone for A_I and an excess of tungstate for A_F (performed at pH intervals of 0.20). Assuming various integers for the tungstate and ligand stoichiometry, a value of the formation constant was calculated from the absorption value recorded for each added amount of ligand. The results were rejected when a systematic variation of $\log K'$ occurred with increasing added amount of ligand or when individual values of $\log K'$ differed from the mean value by more than 2%.

2.3. NMR spectroscopies

NMR spectra were recorded at 297 K, using a Bruker ARX-400 spectrometer equipped with 5-mm and 10-mm multinuclear probes. The frequencies used were 400.16 MHz (^1H), 100.62 MHz (^{13}C) and 16.65 MHz (^{183}W). As references have been used aqueous solutions of sodium dimethylsilapentane-5-sulfone (DSS) (^1H), 2,2,3,3-tetradeuterio-3-(dimethyl)-propionate (TMSP) (^{13}C) and a 2 M solution of disodium tungstate in alkaline deuterium oxide (WO_4^{2-}) (^{183}W). The chemical shifts have been determined using the substitution method [10].

1D ^{13}C spectra have been recorded with the following parameters: sweeping range 26000 Hz, acquisition time 0.30–0.60 s, digital resolution 0.5–1.6 Hz/pt, relaxation delay 2 s. ^1H coupled and decoupled ^{13}C spectra are obtained with nuclear Overhauser enhancement, in the former case by gating off the decoupler

during data acquisition. Accordingly, J-modulated spin-echo experiments have been performed in order to determine whether the number of attached protons of the carbon atoms is odd or even.

1D ^{183}W spectra have been recorded with sweeping range 8500 Hz, acquisition time 1 s, digital resolution 0.5 Hz/pt, relaxation delay 1 s and a pulse duration of 40 μs. To reduce the effect of probe acoustic ringing on the baseline, several left shifts were applied on the free induction decay before Fourier transformation.

Samples were prepared by weighing the appropriate amount of ligand and Na_2WO_4 (Prolabo), adding H_2O and D_2O, mixing and finally adjusting the pH with concentrated HCl or NaOH. Unless otherwise specified, the concentrations were 1 M (ligand) and 2 M (Na_2WO_4) in water containing D_2O (10%, v/v), sample volumes being 0.5 mL (5 mm probe) or 2 mL (10 mm probe). pH values were measured using a Radiometer MI 412 combined glass electrode (external diameter: 2 mm) and a Metrohm 632 pH-meter calibrated with commercial buffers (pH 4.00 and 7.00).

3. Results and discussion

3.1. meso-Tartaric acid

3.1.1. Indirect photometry

The complexation of *meso*-tartaric acid has been studied by indirect photometry at pH values 3.80–5.20 with pH intervals of 0.4. The dissociation of the sacrificial complex upon adding the ligand is represented in Fig. 5.

The way in which the absorption decreases depends on the formation constant of the studied complex as well as on the absorption values of the free and totally complexed dihydroxybenzoquinone (DHQ). These maximum (A_F) and minimum (A_I) absorption values are pH-dependent and their values are summarized in Table 2.

In initial experiments, the absorption value of the DHQ complex was found to decrease significantly after several days. A likely explanation was that DHQ has decomposed in the daylight. Therefore, the fresh DHQ solutions were kept in the dark and the problem was not observed again. The measured absorption values A were analysed with the computer program. An example of the calculated values for $\log K' \pm 0.01$ is provided in Table 3. In order to obtain constant values for $\log K'$ for all added volumes of ligand, occasionally adjustments of A_F and A_I are made. An explanation for the need to make these adjustments may be small inaccuracies in the pipetted amount of stock solution of DHQ.

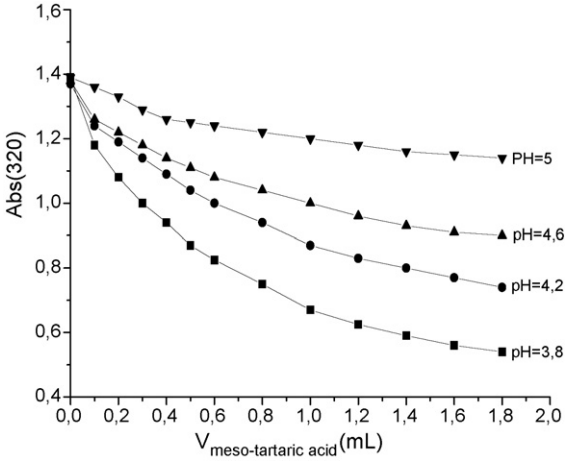

Fig. 5. Absorption of the tungstate–DHQ complex (λ = 320) as a function of the added volume of *meso*-tartaric acid. $C_{0\,acid} = 10\,g\,L^{-1}$; $C_{DHQ} = 6.0 \times 10^{-5}\,mol\,L^{-1}$; $v_{initial} = 100\,ml$.

Table 2
A_F and A_I absorption values vs. pH; $[WO_4^{2-}]/[DHQ] = 6 \times 10^{-5}/6 \times 10^{-5}$ M, $I = 0.1$ M (NaCl), $\lambda_{max} = 320$ nm

pH	$A_I \pm 0.002$	$A_F \pm 0.002$
4.50	0.54	1.66
4.60	0.61	1.67
4.75	0.72	1.69
4.80	0.73	1.69
4.90	0.82	1.68
5.00	0.86	1.67
5.20	1.05	1.73
5.50	1.22	1.74

For *meso*-tartaric acid, at all pH values, constant results for $\log K'$ are found only if the composition of the complex is chosen to be $(x,y) = (1,1)$, x being the number of tungstate atoms and y the number of ligands. The values of $\log K'$ are plotted as a function of pH in Fig. 6. From Eqs. (6) and (7) it follows that the slopes of the graph reveal the number z of protons which are involved in each complex. Below the pK_a of the ligand, the slope of the graph is one unit smaller than the slope of the graph above the pK_a; in the latter case, the slope directly reveals the value of z. Thus, where the two slopes cross each other lies the value of the pK_a. For *meso*-tartaric acid, a pK_a value of 4.45 is found, corresponding to the literature value $pK_a = 4.49 \pm 0.05$, measured under similar experimental conditions [11]. Validation of the indirect photometric method was achieved by comparison with potentiometric measurements relative to the formation of the mannitol tungstate complex [12].

Table 3
The $\log K'$ values of the stability constant at pH 4.40, $A_I = 0.645$ and $A_F = 1.355$ of the (*1/1*) tungstate complex with the *meso*-tartaric acid

V (mL)	[Tar] (M)	A (320 nm)	$\alpha = (A - A_I)/(A_F - A_I)$	$\log K'_{11z} \pm 0.01$
0.10	5.95×10^{-5}	1.038	0.644	6.07
0.20	1.19×10^{-4}	0.929	0.521	6.05
0.30	1.785×10^{-4}	0.858	0.442	6.05
0.40	2.38×10^{-4}	0.806	0.383	6.06
0.50	2.974×10^{-4}	0.767	0.339	6.06
0.60	3.57×10^{-4}	0.736	0.304	6.07
0.80	4.76×10^{-4}	0.691	0.254	6.07
1.00	5.95×10^{-4}	0.660	0.219	6.07
1.20	7.14×10^{-4}	0.636	0.192	6.08
1.40	8.33×10^{-4}	0.618	0.172	6.07
1.60	9.52×10^{-4}	0.605	0.157	6.07
1.80	1.07×10^{-3}	0.595	0.146	6.06

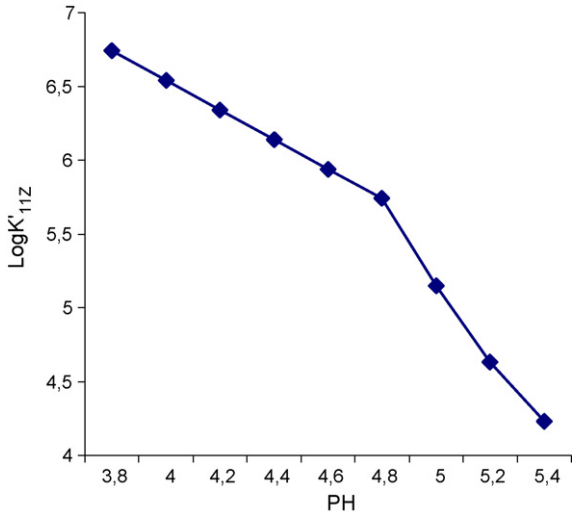

Fig. 6. Tungstate complex of *meso*-tartaric acid: log K' as a function of pH.

The number of protons was determined to be 2. Hence, the total composition of the tungstate complex of the *meso*-tartaric acid was $(x,y,z) = (1,1,2)$. The corresponding formation constant (or stability constant $\log \beta_{112}$) was found by applying Eqs. (6) and (7). Using $pK_a = 4.49$, $\log K_{112}$ was found to be 15.03 ± 0.05. This result for *meso*-tartaric acid is different from that for DL-tartaric acid that gave a (*2*,*2*,*4*) complex in which both ligands chelate two tungsten atoms each [7,12].

3.1.2. Nuclear magnetic resonance

The proton decoupled ^{13}C spectrum of *meso*-tartaric acid shows two spectral lines as expected because the symmetry of the molecule causes the carbon atoms 2/3, and the carbon atoms 1/4, to be magnetically equivalent. The most deshielded signal lies in the spectral region typical for carboxyl carbon atoms. Indeed, in the proton coupled spectrum, this signal remains a singlet whereas the other signal is splitted into a doublet. Thus, the latter signal belongs to the carbon atoms, which bear a proton. The increased intensity of the CHOH signals with respect to the COOH signals is caused by the nuclear Overhauser effect. The ^{13}C and ^{183}W spectra of *meso*-tartaric acid in the presence of tungstate are given in Fig. 7.

In the presence of tungstate, the chemical shifts of the ^{13}C signals of the carbon atoms involved in the sites of chelation, change. Here, no unshifted signals are detected, implying that all carbon atoms are involved in complexation. The values of the chemical shifts for the complexed and uncomplexed forms of the ligand are given in Table 4. The CIS pattern corresponds to the deshielding pattern reported before for lactic or α-hydroxyacid sites ($\Delta\delta \approx 5$ and 12 ppm, Table 1). Thus, *meso*-tartaric acid does not show the CIS pattern observed by Hlaïbi et al. for DL-tartaric acid ($\Delta\delta \approx 9$ and 15 ppm) [7]. Apart from the main signals given in Table 4, other minor signals are observed with CIS < 0.90 ppm. For carbon atoms 2/3 and 1/4, six signals can be distinguished that could correspond to three complexes in which the ligand is not totally symmetrical.

The tungstate signals with $\delta_W = +49.9$ and +34.5 ppm are typical for the two diastereoisomers of a mononuclear bis chelate

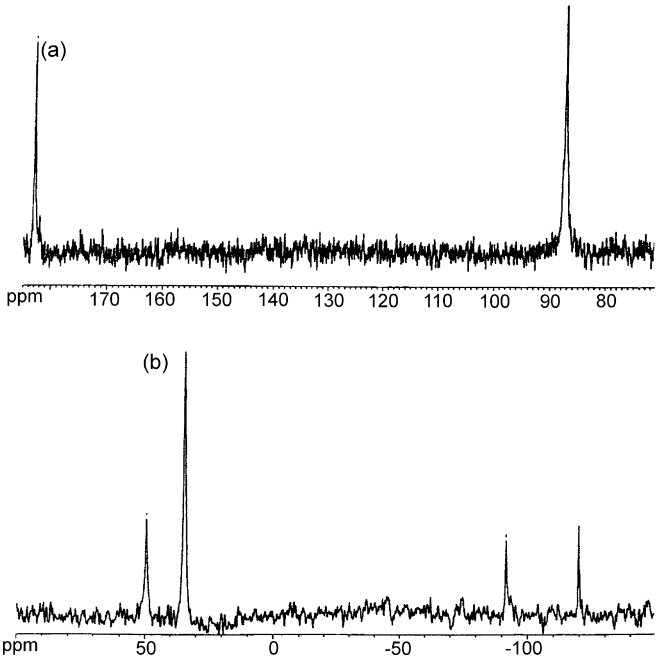

Fig. 7. *meso*-Tartaric acid ($c = 1$ M) and tungstate ($c = 2$ M), pH 4.30: ^{13}C spectrum (a) and ^{183}W spectrum (b).

complex in which one tungstate atom is chelated by the four oxygen atoms of two lactic sites. Combining this with the ^{13}C NMR results that show that all carbon atoms are involved in the sites of complexation, a bis-mononuclear complex can be proposed in which both tungsten atoms are chelated by two α-hydroxyacid sites of different ligands, each ligand thus chelating both tungsten atoms (Fig. 8a). However, the (2/2) (tungstate/ligand) composition of this complex does not match the (*1*,*1*,*2*) stoichiometry of the complex found by indirect photometry. It is possible that this discrepancy is due to the large difference in concentrations used in both methods: ($[WO_4^{2-}] = 6.0 \times 10^{-5}$ M in photometric experiments whereas $[WO_4^{2-}] = 2$ M in the NMR sample. The (*2*,*2*,*4*) complex observed by NMR in concentrated solution can be thought of as a dimer of two (*1*,*1*,*2*) complexes (Fig. 8b) formed in diluted solutions.

The $\delta_W = -119.9$ ppm signal is characteristic for a dinuclear tungsten core in which each tungsten atom is chelated by the two oxygen atoms of a lactic site [7]. Combining this with the fact that all carbon atoms are involved in chelation, a structure can be proposed of a complex of two dinuclear cores which are both chelated by the lactic sites of two different ligands (Fig. 8c).

Table 4
meso-Tartaric acid: chemical shifts of the free (pH 4.80) and complexed (pH 4.30, $C_L = 1$ M, $C_{WO_4^{2-}} = 2$ M) ligand

	C 1,4	C 2,3	(δ) ^{183}W (ppm)
Free ligand			
δ (ppm); J (Hz)	178.2	75.7; 146	
Complexed ligand			
δ (ppm); J (Hz)	182.8	87.2; 146	+49.4 and+34.5 two diastereoisomers
$\Delta\delta$ (ppm)	4.59	11.5	−119.9 one signal

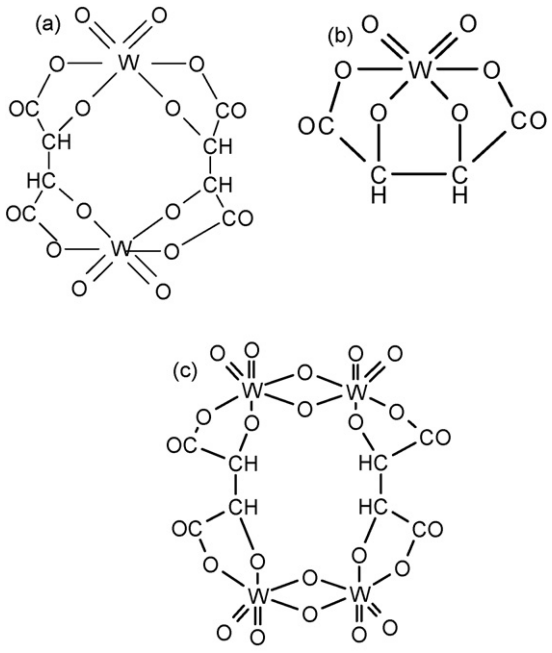

Fig. 8. Proposed structures for the tungstate complexes with *meso*-tartaric acid: bis mononuclear (a); mononuclear (b) and bis dinuclear (c).

Thus, this complex would have a (4/2) (tungstate/ligand) composition. The signal at −91.8 ppm corresponds to heptatungstate [13], indeed, this signal disappears when the excess of tungstate is changed into equal concentrations of ligand and tungstate. At this lower tungstate concentration, also the $\delta_W = -119.9$ ppm signal has appeared as expected for the (*4*,*2*) complex.

3.2. Gulonic acid

3.2.1. Indirect photometry

The complexation of gulonic acid has been studied photometrically at pH values 3.80–5.00 with pH intervals of 0.20. First attempts were made to perform the experiments with a ligand solution prepared by dissolving the acidic ligand (in lactone form) into water. In this way, determination of log *K* would also allow to calculate the energy of ring opening of the lactone [12,14]. However, after adding aliquots of this acidic solution to the sacrificial complex, the dissociation of the coloured complex was very slow and even after hours, equilibrium was not reached. Thus, the formation of the tungstate complex (which requires ring opening of the ligand) is not favourable enough to overcome the energy of ring opening. Consequently, before starting the experiments, the solution of gulonic acid was neutralized with a solution of NaOH. Hence, the ligand was in acyclic form and the formation of the tungstate–ligand complex reached equilibrium within approximately 5 min after each addition. A representation of the dissociation of the sacrificial complex as a function of the added amount of neutralized gulonic acid is represented in Fig. 9.

Upon analyzing the data with the GW.Basic program, a similar pH dependence of the stability of the complex was found as for the tungstate–*meso*-tartaric acid complex. The composition (***x***,***y***) was found to be (*2*,*2*) at pH ≤ 4.20. Attempts to perform the experiment at pH 3.60 failed because after each addition of ligand, equilibrium was reached slowly. The absorption did not reach a constant value within 30 min after ligand addition. A possible explanation is, that at this acidic pH, the cyclization of the ligand is favourable and thus competes with the complexation reaction for which the ligand has to be in the acyclic form. The number of protons involved in the complex was determined to be 2. Applying equation (6), the formation constant, log K_{222} for the (*2*,*2*,*2*) complex of gulonic acid, is 24.44 ± 0.05. The corresponding log K'_{22z} values are presented in Fig. 10a.

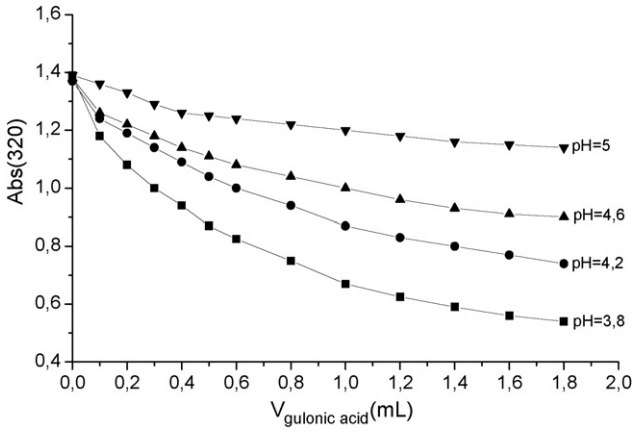

Fig. 9. Absorption of the tungstate–DHQ complex (λ = 320) as a function of the added volume of gulonic acid. $C_{0\,\mathrm{acid}} = 5.6 \times 10^{-2}$ mol L^{-1}; $C_{\mathrm{DHQ}} = 6.0 \times 10^{-5}$ mol L^{-1}; $v_{\mathrm{initial}} = 100$ ml.

At pH values 4.20–4.60, the composition (***x***,***y***) = (*1*,*1*) gave constant values for log K′. The log K'_{11z} values are presented as a function of pH in Fig. 10b. One proton is involved in complexation and using Eq. (6), log K_{111} for the (*1*,*1*,*1*) complex is found to be 9.96 ± 0.05.

It has to be remarked that the log K' value at pH 4.60 is only found to be constant at an added volume of ligand >0.60 mL. This, and the fact that for pH 4.20 also a (*2*,*2*) complex has been determined, indicates that a mixture of complexes is present. Since the program only takes into account the formation of a major complex, the existence of a mixture diminishes the accuracy of the determined formation constants.

3.2.2. NMR spectra

In order to explain the carbon spectra of the complexed gulonic acid, the chemical shifts of the complexed ligand must be compared with those of the free ligand. Therefore, the chemical shifts of the different carbon atoms of the free ligand have been determined. For this determination, a preliminary ^{1}H assignment was needed. It was shown above that the ligand must be in the acyclic form in order to complex tungstate. Thus, the experiments have been performed at pH 12, where the aldonate ion is known to possess the open structure. The ^{1}H and ^{13}C spectra of the free ligand are illustrated in Fig. 11a and b.

From the 1D proton coupled ^{13}C spectrum, it can be seen that the deshielded carboxyl carbon atom (C-1) possesses a chemical shift of 179.9 ppm. The triplet splitting of the CH_2OH

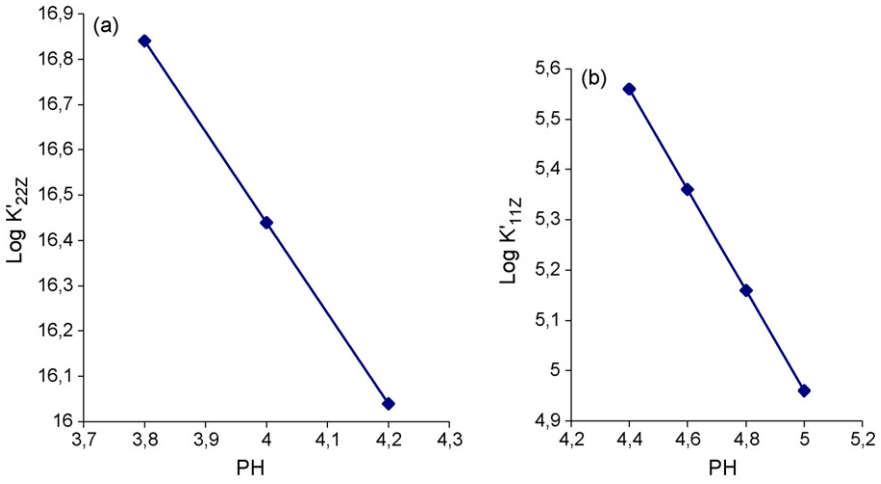

Fig. 10. log K′ values of the tungstate–gulonic acid complexes as a function of pH, composition (*2*,*2*,*2*) (a) and composition (*1*,*1*,*1*) (b).

carbon atom (C-6) reveals the chemical shift of this atom (63.7 ppm).

From the 1D proton spectrum, the quartet splitting pattern ($^2J_{H\text{-}6\text{-}6'}$ = 11.78 ppm) of both hydrogens belonging to C-6 shows their chemical shifts at 3.50 and 3.41 ppm. Similarly, all other hydrogen atoms can be readily assigned since for gulonate, all hydrogen atoms possess a single chemical shift. The assignment of C-6 is confirmed by cross peaks between C-6 and both hydrogen atoms at 3.50 and 3.41 ppm. The chemical shifts are summarized in Table 5.

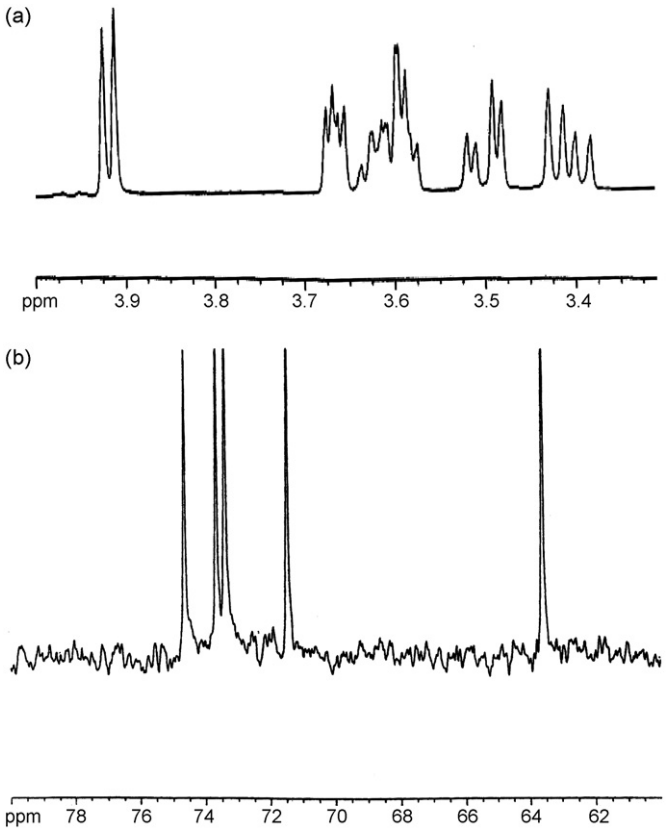

Fig. 11. Gulonate ion, pH = 12: 1D ^{1}H spectrum (a) and 1D ^{13}C spectrum (b).

3.2.2.1. Tungstate–ligand complexes. The complexation of gulonic acid has been studied at pH values 4, 6, 8 and 10. The nature of the complexes is found to be pH-dependent. At acidic pH, both mononuclear and dinuclear lactic type complexes have been identified and also a *threo* type complex in which the ligand is tetradentate. Upon increasing the pH, first the dinuclear and then the mononuclear lactic complexes disappear. At alkaline pH finally, a *threo* complex is formed in which the ligand is pentadentate and the tetradentate *threo* complex has disappeared. The ligand is predominantly present in the pentadentate complex, while free ligand also exists. No other complexes are formed and each carbon atom possesses one clear signal, so it has been possible to reveal the exact CIS pattern of the complexed ligand. The characterization of the tungstate–gulonic acid complexes has been performed and a selection of the corresponding ^{183}W spectra is given in Figs. 12 and 13.

3.2.2.2. pH 4. The major ^{183}W signal lies at −120 ppm, representing a dinuclear lactic type complex (Fig. 12). In the region 35–65 ppm, the ^{183}W signals probably belong to mononuclear lactic type complexes [7,8,15–18]. Finally, a signal is observed at −89 ppm, indicating the presence of a tetradentate *threo* type complex. In the ^{13}C spectrum, at least four different carboxyl signals exist which are shifted 2.6–5.2 ppm with respect to the carboxyl atom in the free ligand. Several signals are observed in the region 78–80 ppm, where the signals of the C-2 atoms involved in lactic complexes are expected. More shifted carbon signals are observed in the region 82–87 ppm; in this region, the signals belonging to the carbon atoms involved in the tetradentate *threo* complex are expected. The C-6 possesses three clear signals between 63 and 65 ppm and one signal of small inten-

Table 5
^{13}C and ^{1}H chemical shifts of L-gulonate, pH 12

	C-1	C-2	C-3	C-4	C-5	C-6
δ ^{13}C (ppm)	179.9	74.6	73.5	71.4	73.6	63.7
δ ^{1}H (ppm)	–	3.92	3.66	3.59	3.62	3.50 and 3.41

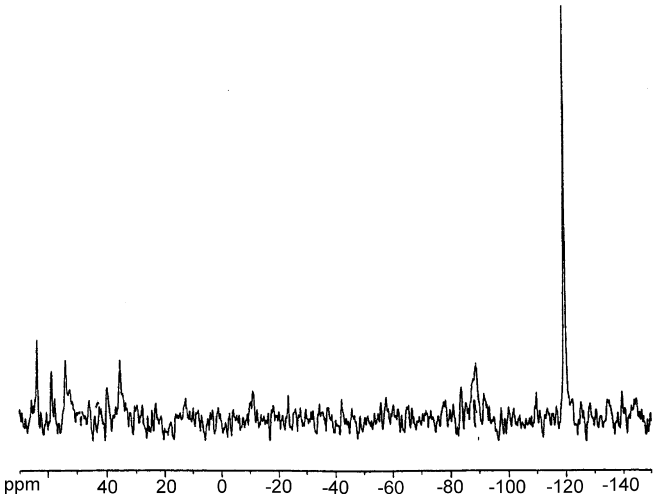

Fig. 12. Gulonic acid (1 M) and tungstate (2 M), pH 4, ^{183}W spectrum.

sity which is shifted by approximately 12 ppm. The latter signal probably belongs to a C-6 which is involved in the tetradentate *threo* type complex [3,4,5,19].

3.2.2.3. pH 6. At this pH, ^{183}W signals are observed at −92 and −89 ppm with a relative intensity of 2:1. This is typical for the presence of the free heptatungstate ion [13]. The ^{183}W signal at −120 ppm, typical for a dinuclear lactic type complex, has disappeared. The signals assigned to the mononuclear lactic complex are still present. The relative intensity of the ^{183}W signal at −89 ppm has increased with respect to the spectrum at pH 4. A similar increase in intensity is observed for the 12 ppm-shifted ^{13}C signal of the carboxylic C-6. This indicates that the relative amount of tetradentate *threo* type complex has increased and that the site of chelation indeed includes C-6. Thus, the site of chelation is *O*-3,4,5,6. Finally, a C-1 signal has appeared at 179 ppm. This signal probably belongs to the free C-1 in the single *threo* tetradentate complex. In contrast, no such signal was present at pH 4, indicating that the *threo* complex at pH 4 exists as a dual *threo* lactic type complex.

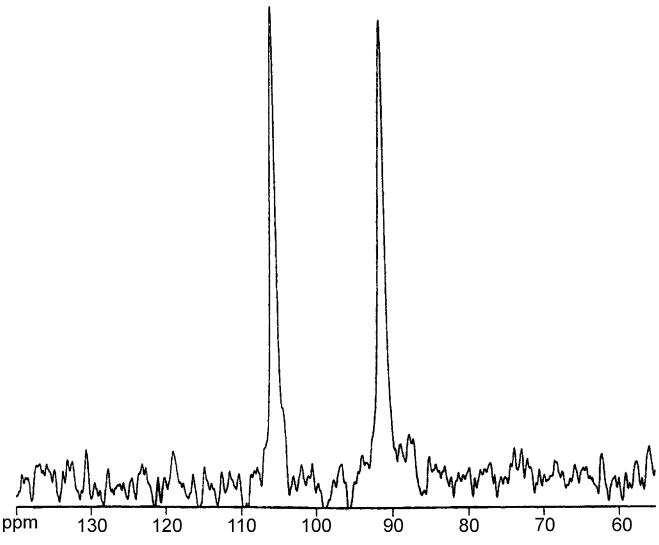

Fig. 13. Gulonate (1 M) and tungstate (2 M), pH 10, ^{183}W spectrum.

Table 6
^{13}C chemical shifts of the tungstate–gulonate complex at pH 10 and the CIS of the carbon atoms with respect to the δ values of the free ligand

	C-1	C-2	C-3	C-4	C-5	C-6
δ ^{13}C (ppm)	181.7	88.16	84.5	81.0	82.8	78.3
$\Delta\delta$ (ppm)	1.8	13.5	11.0	9.6	9.2	14.6

3.2.2.4. pH 8. At pH 8, three carboxyl ^{13}C signals exist. Their CIS are all smaller than 1.7 ppm which means that these COOH groups do not chelate tungsten. Thus, lactic type complexes do not exist anymore. Next to free gulonic acid, complexed ligand is present in the ^{13}C spectral region 80–85 ppm. This could correspond to the presence of the tetradentate *threo* type complex as also identified at pH 4 and pH 6.

3.2.2.5. pH 10. The ^{183}W spectrum of gulonic acid and tungstate at pH 10 shows three clear signals (Fig. 13). The signal at 0 ppm is that of the uncomplexed tungstate ion WO_4^{2-}. The other two signals (of equal intensity) at 91 and 105 ppm indicate the presence of a *threo* complex in which the ligand is pentadentate [20]. Due to the asymmetry of the ligand, the two tungsten atoms are not magnetically equivalent. The ^{13}C spectrum shows signals for free gulonate. However, the majority of the ligand is in the complexed form. The carboxyl atom of the complexed gulonic acid possesses a chemical shift which is only 1.90 ppm shifted with respect to the carboxyl signal of the free ligand. Thus, C-1 is not involved in the site of chelation and the site of chelation in the pentadentate complex is *O*-2,3,4,5,6. From the short range coupling spectrum of gulonic acid, the C-6 signal was assigned because this carbon atom is coupled to two hydrogen atoms in contrast to C-2–C-5 which bear only one hydrogen atom. The CIS of C-6 was thus calculated to be 14.6 ppm. Knowing the symmetry of the CIS pattern of the pentadentate site, the chemical shift of 88.1 ppm was likely assigned to C-2, giving a CIS of 13.5 ppm. The corresponding ^{13}C chemical shifts are given in Table 6.

For all tungstate complexes of gulonic acid formed between pH 4 and 10, that were detected by NMR, the corresponding ^{183}W chemical shifts are given in Table 7. The structures of the *threo* tetradentate and pentadentate complexes are represented in Fig. 14.

Table 7
^{183}W chemical shifts of the tungstate complexes of gulonic acid in the pH range 4–10

Type of complexes	pH	(δ) ^{183}W (ppm)
Mononuclear bis chelate	4	+35 ± 8 two signals
Dinuclear bis chelate		−120 ± 1 one signal
Threo-tetradentate complex	6–8	−89 ± 2 one signal
Threo-pentadentate complex	10	+91 and +105 two signals

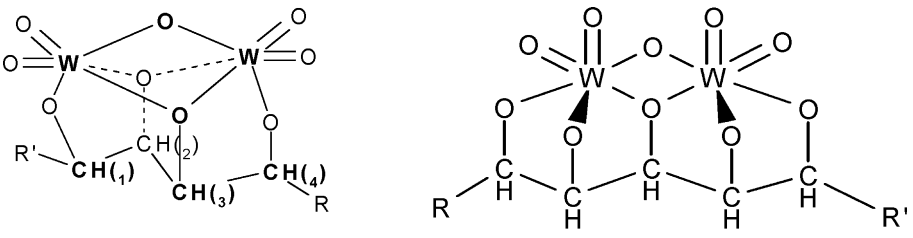

Fig. 14. Structures of the tungstate gulonic acid complexes: *Threo* site, tetradentate complex (a) and *Threo* site, pentadentate complex (b).

3.2.3. Comparison of photometric and NMR results

The (*2*,*2*,*2*) complex identified with indirect photometry (pH 3.80–4.20) can well correspond with a dinuclear lactic type complex. With NMR, this complex ($\delta\ ^{183}W = -120$ ppm) was also found to be the major complex present at pH 4. Additionally, the stability constant ($\log K_{222} = 20.23 \pm 0.05$) lies close to the stability constants found for similar complexes with *meso*-tartaric acid.

A (*1*,*1*,*1*) complex has been identified with indirect photometry at pH 4.2–4.8, whereas no such complex has been observed in the NMR experiments. A possible explanation is that the (*2*,*2*,*2*) complex present under the concentrated conditions of the NMR experiments, dissociates into two (*1*,*1*,*1*) complexes under the diluted conditions of the indirect photometry experiments at pH values above 4.20. Finally, at pH 5.0, a (*2*,*1*) complex is found with indirect photometry. Since this complex was found at only one pH value, the number of protons involved in the complex could not be determined. However, at pH 5–8, dinuclear *threo* type complexes (tetradentate ligand) have been detected by NMR spectroscopy. Assuming that the (*2*,*1*) complex is of the same type, its stability constant would be $\log K_{212} = 20.47 \pm 0.05$, if two protons are involved.

4. Conclusion

The tungstate complexes of *meso*-tartaric and L-gulonic acids have been studied by ^{13}C and ^{183}W NMR in the pH range 4–10. The stability constants of the complexes were determined by indirect photometry in the pH range 3.60–5.20. For the (*1*,*1*,*2*) tungstate–*meso*-tartaric complex in the pH range 3.80–5.20, the stability constant is $\log K_{112} = 15.03 \pm 0.05$. Both α-hydroxyacid moieties chelate either a mononuclear tungstate core or a dinuclear (bridged) tungstate core (pH 4). The stability constants of the tungstate–gulonic acid complexes are $\log K_{222} = 24.44 \pm 0.05$ at pH 3.80–4.20 and $\log K_{111} = 9.96 \pm 0.05$ in the pH range 4.2–4.80. At pH 4, mononuclear and dinuclear lactic complexes exist. A tetradentate *threo* type complex also occurs as a dual lactic *threo* complex. The site of chelation for the *threo* part is *O*-3,4,5,6. Upon increasing the pH, the lactic complexes disappear, first the mononuclear one (pH 6), then the dinuclear one (pH 8). The dual lactic *threo* tetradentate complex is still present at pH 8, but has disappeared at pH 10. At pH 10, a complex exists in which the ligand is pentadentate, the site of chelation being *O*-2,3,4,5,6. These results demonstrate the strong dependence of the nature of the complexes on the configurations of the internal HO groups. For *meso*-tartaric acid, the observed complexes are different from those reported for DL-tartaric acid [7].

The carboxyl group of aldonic acids induces the formation of tungstate complexes different from those formed with alditols. In acidic medium, complexes analogous to those observed for α-hydroxyacids are formed. Upon increasing ionisation of the carboxyl group, dual lactic *threo* type complexes appear. At alkaline pH, the carboxyl group is not involved in complexation anymore and the complexes are similar to those formed with alditols.

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