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Complexes of Tungsten(VI) with Mucic Acid: a Spectrophotometric and Polarimetric Study in Aqueous Solution

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Abstract

Spectrophotometric work on mucic acid–W(VI) system shows the formation of three different oxo-anion complexes in aqueous solution; their stability is dependent upon pH. One of the complexes is monomeric tungstodimucate and the other two are 2/2 species. An anomalous cryoscopic behaviour, similar to that of W(VI) tartaric system, has been observed for the dimeric complex formed at higher pH. The stoichiometries and conditional dissociation constants have been polarimetrically determined by means of competitive reactions between the mucic and tartaric ligands. ^{1}H and ^{13}C NMR spectra have been interpreted for the similar complex species of both mucic and tartaric acids.

Introduction

We have demonstrated in a previous paper [1] that in an excess of ligand, gluconic acid, $CH_2OH(CHOH)_4CO_2H$, shows some preference towards the coordination of carboxylate group. But when the metal is in excess, a very stable complex is formed at pH = 5–6 with a ligand molecule; it is coordinated by two hydroxy alcoholic groups α-positioned to each metal atom which are bound to each other by a μ-oxo bridge [2] like that formed by mannitol or sorbitol [3, 4]. This fact confirms that the metal–alkoxy bond is less labile than the more favoured metal–carboxylate bond [5].

In this paper, we have studied the complex species formed between tungsten(IV) and mucic acid, $HO_2C(CHOH)_4CO_2H$, in order to determine whether the presence of a second carboxylic group in a ligand containing four hydroxy alcoholic groups would allow the formation of a complex with 2:1 stoichiometry (metal:ligand), or whether, on the contrary, it would show a behaviour analogous to that of tartaric acid which does not form species with a stoichiometric ratio of metal:ligand > 1.

Regarding the bibliography, only a few papers have been found which suggest the formation of a 2:1 (metal:ligand) complex between molybdenum(VI) and mucic acid [6, 7], but these results have to be interpreted cautiously. On the other hand, the number of studies of tungsten(VI) we can find in literature are limited.

Experimental

Spectrophotometric UV measurements were made with a Pye-Unicam SP8-100 automatic recording photoelectric spectrophotometer using 1 ± 0.002 cm silica glass cells. The precision of absorbance is 0.5%.

The rotatory power of the samples was measured with a Perkin-Elmer 141 digital photoelectric polarimeter, with the precision of the measurements at ±0.002 deg. The cell was thermostatically set at 26 ± 0.05 °C with a length of 10 ± 0.002 cm. Measurements were taken at five different wavelengths (589, 578, 564, 436 and 365 nm). The results obtained for each one of these wavelengths were comparable.

The pH of the samples was measured with a Radiomether pH-meter 82 with a pH accuracy of ±0.01. All the samples were prepared to be 1 M in $NaClO_4$ for maintaining the ionic strength of the medium. The pH was adjusted to the required value by adding a proper amount of concentrated NaOH and/or $HClO_4$ (70%). Specific conditions of the samples are indicated in the text.

By using a Universal Temperature Measuring Instrument with a Knauer Thermo-electric Cooling Unit, cryoscopic decreases were determined, the standard sample volume being 0.15 ml. For concentrated solutions, the measuring error is less than 1%.

200 MHz ^{1}H NMR spectra were recorded through a Bruker AC-200 spectrometer. This tool was also used to record the ^{13}C NMR spectra at an operating frequency of 50.32 MHz.

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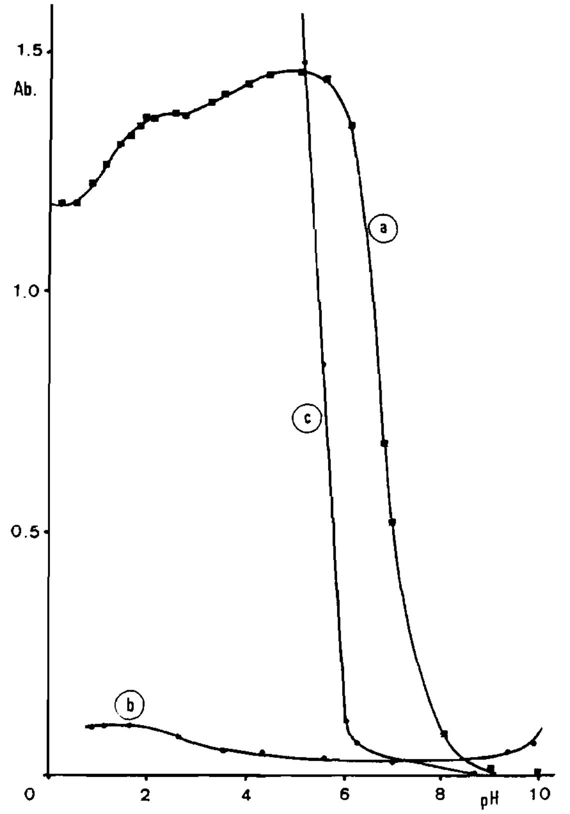

Fig. 1. Absorbance *vs.* pH. $\lambda = 240$ nm. Curve *a*: Difference of absorbance between Na_2WO_4 (8×10^{-4}) + mucic acid (8×10^{-3} mol dm^{-3}) and mucic acid (8×10^{-3} mol dm^{-3}); curve *b*: mucic acid (8×10^{-3} mol dm^{-3}); curve *c*: Na_2WO_4 (8×10^{-4} mol dm^{-3}).

Results and Discussion

Absorbance for the Different Complexes

Curve *a* in Fig. 1 shows the increase of absorbance between the solutions of 8×10^{-3} mol dm^{-3} in mucic acid plus 8×10^{-4} mol dm^{-3} in Na_2WO_4; solutions of the same concentrations of ligand in the absence of metal are shown in curve *b*. As a reference, curve *c* shows the absorbance of solutions containing 8×10^{-4} mol dm^{-3} in free metal.

Considering that the ligand has a much lower specific coefficient than that of the complex species, we can assume that curve *a* corresponds only to absorbance variation with the pH due to the different complexes. The existence of four breaks on this curve is related to the presence of three complexes with different molar absorbances, being those stable at pH 5.0, 2.5 and 1.0, respectively. At $\text{pH} > 7.0$, $\Delta A = 0$ and there is no interaction between tungstate and mucate ions. In the pH range 7.0–5.0, absorbance increase reveals the formation of complex **I** according to the following equilibrium:

$$WO_4^{2-} + nH^+ + z\text{Lig} \rightleftharpoons 1/a \text{ complex I}$$

At $5.0 > \text{pH} > 2.5$ range, the absorbance variation might be related to the formation of a second complex in equilibrium with the first one:

$$\text{Complex I} + mH^+ + z\text{Lig} \rightleftharpoons 1/b \text{ complex II}$$

In an analogous way, from pH = 2.5 to pH = 1.0, the absorbance decrease implies the existence of a third complex which has its highest concentration at $\text{pH} < 1.0$:

$$\text{Complex II} + pH^+ + z\text{Lig} \rightleftharpoons 1/c \text{ complex III}$$

The dependence of the absorbance upon the pH for the different complex species (curve *a*), according to the previously described procedure [8–10], can be used to calculate parameters *n* and *a* in each one of the above described equilibria. The results we obtained are summarized in Table I and show that the formation of the complexes **I**, **II** and **III** (from WO_4^{2-} and $C_6O_8H_8^{2-}$ ions) requires 2.0, 2.0 and 2.5 equivalents of H^+ for every mole of tungsten complexed, respectively. Complex **I** is monomeric and complexes **II** and **III** have a dinuclear character.

TABLE I. Calculated Values of the Equilibrium Coefficients in the Formation and Interconversion Equilibria

$7.5 > \text{pH} > 5.0$	$A_I = 1.450$	$a = 1$	$n = 1.92$
$5.0 > \text{pH} > 2.5$	$A_{II} = 1.360$	$b = 2$	$m = 1.06$
$2.5 > \text{pH} > 0.5$	$A_{III} = 1.185$	$c = 1$	$p = 1.17$

Stoichiometry and Stability Constants of the Complexes

The stoichiometric ratio of the complexes has been determined by applying the traditional molar ratio method [11] at pH values at which the tungsten(VI) is present almost entirely as a single complex species.

At a pH = 2.5 (complex **I**) and 0.95 (complex **III**), absorbance variation as a function of the metal–ligand relationship reaches its maximum when it becomes metal:ligand = 1, indicating how stable these two complexes are at the above pH values.

In order to simultaneously find out the stoichiometry, degree of condensation and conditional stability constant, we have applied a generalization concerning the molar-ratio method [12] and the Asmus method [13], which have been deduced from formation equilibria of weak complex species of the kind:

$$mA + nB \rightleftharpoons A_mB_n \qquad (1)$$

Bearing in mind that in such a system the complexes are very stable at $\text{pH} < 5.0$, the application of the above-mentioned methods has been possible for complex **I** only at a more basic pH. The results obtained from Table II at a pH = 6.15 for both methods show

TABLE II. Absorbance or Rotatory Power Increases Obtained at a Constant pH as a Function of the Ligand/Metal Ratio

Complex I[a]			Complex II[b]			Complex III[c]		
v	Mc/w	ΔA	v	T/W	ΔD	v	T/W	ΔD
0.2	1	0.090	0.2	0.4	0.080	0.2	0.4	0.067
0.4	2	0.142	0.4	0.8	0.116	0.4	0.8	0.110
0.6	3	0.220	0.6	1.2	0.145	0.6	1.2	0.140
0.8	4	0.296	0.8	1.6	0.174	0.8	1.6	0.165
1.0	5	0.362	1.0	2.0	0.206	1.0	2.0	0.192
2.0	10	0.575	1.5	3.0	0.238	2.0	4.0	0.252
3.0	15	0.637	2.0	4.0	0.258	3.0	6.0	0.284
4.0	20	0.654	3.0	6.0	0.290	4.0	8.0	0.298
5.0	30	0.682	4.0	8.0	0.386	5.0	10.0	0.307
8.0	40	0.702	6.0	12.0	0.386	6.0	12.0	0.319
10.0	50	0.704	8.0	16.0	0.333	8.0	16.0	0.329
12.0	60	0.706	10.0	20.0	0.339	10.0	20.0	0.333

[a] pH = 6.15; λ = 240 nm; $\Delta A = A_{\text{mea}} - A_{\text{lig}} - A_{\text{W}}$; $[\text{Na}_2\text{WO}_4] = 4 \times 10^{-4}$ M; v ml H_2MH_4 0.05 M. [b,c] pH = 3.0 and 0.90, respectively. In both series: $\Delta D = D_{\text{mea}} - D_{\text{lig}}$; λ = 365 nm; $[\text{Na}_2\text{WO}_4] = [\text{H}_2\text{MH}_4] = 2 \times 10^{-3}$ M; v ml TH_2 0.1 M. In all series V_{T} = 25 ml and ionic strength 1 M in NaClO_4.

that this is a monomeric complex of 1:2 stoichiometry (metal:ligand) with a dissociation constant $K_{\text{i}} = 3.8 \times 10^{-6}$ (mol dm^{-3})$^{-2}$ (molar-ratio method).

As regards the stoichiometry determination, including the degree of condensation, of the other two strong complexes, we have applied a recent modification of the above-mentioned methods using interconversion equilibria between different complexes of the type [14]:

$$m\text{A}_z\text{C}_y + n\text{B} \rightleftharpoons \text{A}_{mz}\text{B}_y + my\text{C} \quad \text{(molar-ratio method)} \tag{2}$$

or

$$\delta\text{AzC}y + n\delta\text{B} \rightleftharpoons \text{A}_{z\delta}\text{B}_{n\delta} + \delta y\text{C} \quad \text{(Asmus method)} \tag{3}$$

Concerning the application of a generalized molar-ratio method to a general equilibrium (2), the following equation has been deduced.

$$K^* = \left\{ \frac{C^0_{\text{A}_z\text{C}_y}{}^{\{1+m(y-1)\}} y^{my}}{K_{\text{eq}}} \right\}^{1/n} = \frac{C_{\text{B}}(X) - n/mXC^0_{\text{A}_z\text{C}_y}}{\{X^{1+my}/m(1-\text{X})^m\}^{1/n}} \tag{4}$$

in which $C^0_{\text{A}_z\text{C}_y}$ is the initial constant concentration of complex A_zC_y, and $C_{\text{B}}(X)$ is the added concentration of B. This implies a molar fraction (X) of complex A_{mz}B_n:

$$X = \frac{|\text{A}_{mz}\text{B}_n|}{|\text{A}_{mz}\text{B}_n|_{\text{lim}}} = \frac{|\text{A}_{mz}\text{B}_n|}{C^0_{\text{A}_z\text{C}_y}/m} = \frac{\Delta Y}{\Delta Y_{\text{lim}}} \; (0 < X < 1) \tag{5}$$

where ΔY is a physical property directly proportional to the concentration of the formed complex (A_{mz}B_n). According to eqn. (4), a plot K^* *vs.* X will be a horizontal line only for stoichiometric coefficients which make K_{eq} be a constant for every X value.

In an analogous way, on applying the generalization to the Asmus method, equilibrium (3), we can obtain:

$$\frac{\Delta Y^{y+1/\delta}}{v^n} = \frac{C^0_{\text{A}_z\text{C}_y}(b_0/V_{\text{T}})^n \epsilon^{(y+1/\delta)}}{(y\delta)^y (K_{\text{i}})^{1/\delta}} - \frac{(b_0/V_{\text{T}})^n \delta \epsilon^{(y-1+1/\delta)}}{(y\delta)^y (K_{\text{i}})^{1/\delta}} \Delta Y \tag{6}$$

where ϵ is the physical property specific value ($\Delta Y = \epsilon|\text{A}_{z\delta}\text{B}_{n\delta}|$), v is the volume of a solution b_0 mol dm^{-3} of B added to a constant concentration of complex A_zC_y, and V_T is the total volume. The graphic representation of $\Delta Y^{y+1/\delta}/v^n$ *vs.* ΔY gives a straight line only for δ and n values (z and y are known) which correspond to the right stoichiometry.

The stability constants, $K_{\text{eq}} = 1/K_{\text{i}}$, for these interconversion equilibria are related to the dissociation constants of each complex by the following relation:

$$K_{\text{i}}(\text{A}_{mz}\text{B}_n) = K_{\text{i}}(\text{A}_z\text{C}_y)^m 1/K_{\text{eq}}$$

or

$$K_{\text{i}}(\text{A}_{z\delta}\text{B}_{n\delta}) = K_{\text{i}}(\text{A}_z\text{C}_y)^\delta 1/K_{\text{eq}} \tag{7}$$

By applying these competitive reactions between two different ligands B and C, the stoichiometry determination of complexes formed by ligands without optical activity can be allowed by means of

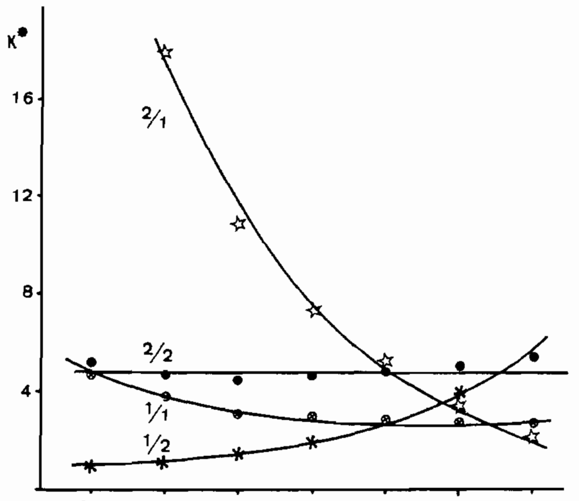

Fig 2. Molar-ratio generalized method. pH = 3.0. Rotatory power values at λ = 365 nm.

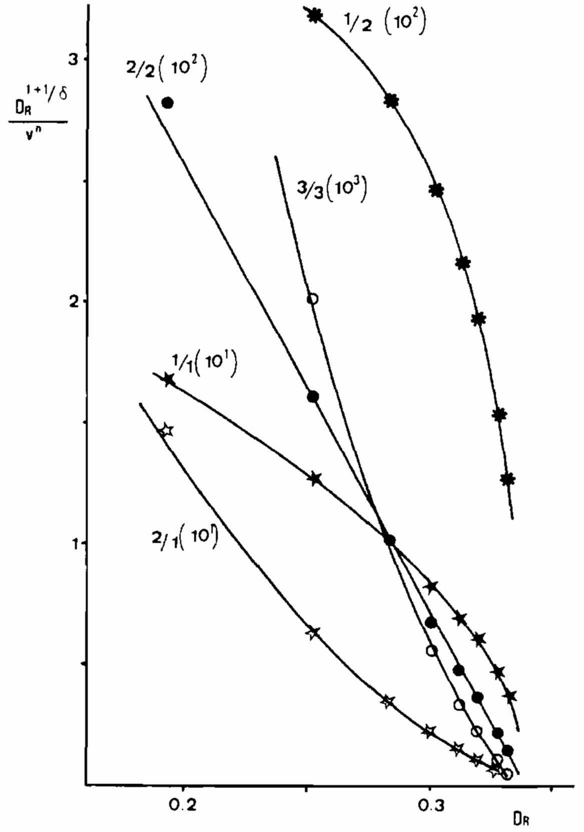

Fig. 3. Asmus modified method. pH = 3.0. Rotatory power values at λ = 365 nm.

polarimetry, using an additional optically active ligand which, in turn, forms two complex species with tungsten(VI) at pH 3.0 and 1.0 whose 2:2 stoichiometries are already known [15–18].

Table II shows, therefore, the rotatory power variations of solutions containing an initial concentration constant of tungstate and mucic acid in stoichiometric proportions, which are due to the addition of variable concentrations of tartaric acid Figures 2 and 3 show, as an illustrative example, the application of the molar-ratio method, eqn. (4), and the Asmus method, eqn. (6). The 2:2 stoichiometry of the complex species formed between mucic acid and tungsten(VI) occurs at pH 3.0 and 1.0, so that the following equilibrium is fulfilled:

$$W_2Mc_2 + 2T \rightleftharpoons W_2T_2 + 2Mc$$

where Mc and T are mucic and tartaric acids, respectively.

The conditional instability constant calculated for the above equilibrium is $K_i = 8 \pm 2$ (pH = 3.0 and 0.9), and it indicates a greater stability of complexes with mucic and tartaric acid, considering the relation ship

$$K_i(\text{mucic}) \simeq 10^{-1}\, K_i(\text{tartaric}) \qquad (7)$$

With respect to the dissociation constant of the monomeric complex at pH = 6.15, a comparison with the constant obtained for the similar tartaric complex formed at the same pH, $K_i = 4.2 \times 10^{-5}$ (mol $dm^{-3})^2$ (pH = 6.0) [13, 15], enables us to conclude that for this 1:2 (metal:ligand) species a proportionality constant 10^{-1} is also fulfilled.

Saline Cryscopy

Cryoscopic decreases (K) in the transition temperature of the Glauber salt for a series of solutions containing the $C_6O_8H_8^{2-}$:WO_4^{2-}:H^+ ratios have been established, corresponding to the complexes formed at pH = 3.0 (complex **II**, 1:1:2 ratio) and pH = 1.0 (complex **III**, 1:1:2.5 ratio). The results obtained for the series **II** ($K_0 = 0.03 \pm 0.01$) and **III** ($K_0 = 0.16 \pm 0.01$) confirm the dinuclear mucic complex formed at pH < 1.0 and the anomalous cryoscopic decrease produced by the dinuclear mucic complex II (pH = 3.0), which, in turn, has led some authors to suggest a very high degree of condensation for some complexes, due to the polimerization of the metal ion [16–18].

Nevertheless, the cryoscopic behaviour of the tungsten(VI)–mucic acid system is similar to that found for the tartrate derivatives [30], in which the small cryoscopic decrease produced by the complex **II** has been interpreted assuming a strong hydrogen bonding interaction between the dimeric units.

Nuclear Magnetic Resonance

In order to obtain structural information about the coordination of mucic acid and tunsgen(VI), the ^1H and ^{13}C NMR spectra at different pH values have

TABLE III. ^{13}C NMR Chemical Shifts (ppm) from Free and Complexed Mucic and Tartaric Acids[a]

pH	Free ligand				Complex species								
	Mucic acid		Tartaric acid		Mucic acid (excess of metal)			Tartaric acid (excess of metal)		Tartaric acid (excess of ligand)			
	COOH	HCOH	COOH	HCOH	COOM	HCOM	HCOH	COOM	HCOM	COOM	HCOM	HCOH	COOH
8.20			179.44	74.57						184.29	86.22	76.33	178.46
										183.04	85.96	75.57	178.90
7.00			179.48	74.61						184.16	87.49	76.25	178.46
										183.49	86.15		
6.75								183.60	87.10				
6.00	180.61	72.34	179.35	74.58	184.63	84.66	74.66	183.75	97.08	184.25	87.72	76.39	178.88
		72.68								183.03	86.22	75.64	178.41
5.40			179.36	74.62						184.30	87.77	76.43	178.87
										183.04	86.26	75.67	178.41
4.50			179.13	74.50						184.22	87.70	76.37	178.32
										182.98	86.25	75.60	
3.50			176.83	73.34	184.71	84.58	74.24	183.80	87.11	183.54	85.40	75.36	176.83
2.50			176.12	73.00				183.83	87.09	183.27	86.80	74.93	176.12
										181.83	85.58	74.29	
2.00					184.63	84.66	74.47						
1.00			175.25	72.49						182.01	85.86	74.23	175.64
										183.01	85.08		

[a] ^{13}C chemical shifts in ppm relative to TMS. Dioxan ($\delta = 67.3$ ppm) was used as internal reference.

been obtained. The proton NMR spectra show different signals corresponding to free and coordinate HCOD groups even though the metal is in excess.

At basic pH, ^{13}C NMR spectra for the mucate ion show only three resonances at 180.61, 62.34 and 72.68 ppm from the carboxyl group and from the α- and β-alcoholic groups as well. Due to the limited solubility of mucic acid in water, ^{13}C NMR spectra only for solutions containing a metal:ligand ratio $\geqslant 1$ could be obtained. For solutions with excess of tungsten(VI), the chemical shift values appear to be ~5 ppm low-field for the carboxyl resonance and ~10 ppm for one of the alcoholic resonances from the free ligand.

Irrespective of both pH and when the W(VI): ligand ratio $\geqslant 1$ (Table III), there are even signals from uncoordinated alcoholic carbons (Fig. 4a); therefore, we can infer that in excess of tungsten(VI) mucic acid is not able to form a complex species of 2:1 stoichiometry (metal:ligand) in which the four alcoholic groups are coordinated. These results clearly contrast with those observed for other ligands with at least four alcoholic groups in adjacent carbon atoms, such as gluconic acid [2], mannitol [4] and sorbitol [3].

On the other hand, the two resonances at lower field have been assigned to the carboxyl (184.6 ppm) and alcoholic (84.6 ppm) groups, both coordinated to tungsten(VI), pointing out that in excess of tungsten(VI), such coordination is shared by both of the carboxyl groups and some of the alcoholic ones.

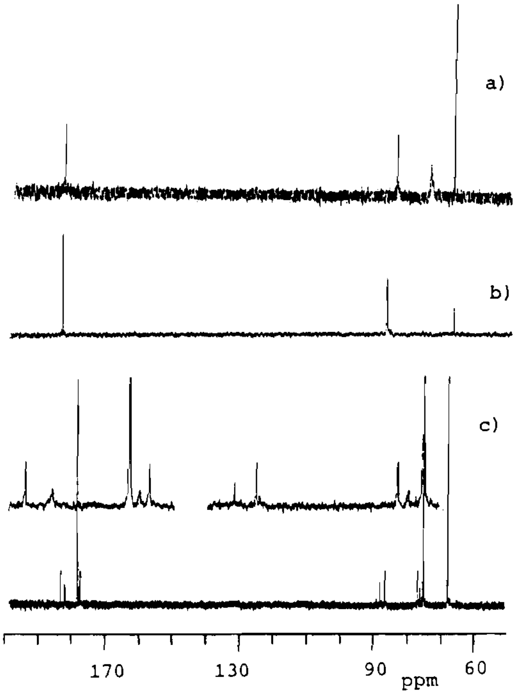

Fig. 4. Natural abundance ^{13}C NMR spectra: (a) tungsten(VI): mucic acid = 2; (b) tungsten (VI): tartaric acid = 2; (c) tartaric acid: tungsten(VI) = 5 solutions; pH = 3.5.

Taking into account that these complex species have 2:2 stoichiometries, the coordination to each metal atom by both of the carboxyl groups and some of the alcoholic ones becomes unlikely since it implies a very hard stretch in the organic ligand chain.

In order to explain the above-mentioned spectra, we have studied the ^{13}C NMR spectra of the complex species formed by the tungsten(VI)–tartaric acid system, since this ligand has a behaviour in aqueous solution similar to that of mucic acid in regard to the amount, pH range and stoichiometry of the complex species; their anomalous cryoscopic behaviour is also similar [30].

In excess of tartaric acid and at different pH values, ^{13}C NMR spectra show resonances at 178 and 74 ppm corresponding to the free ligand, and four more resonances arising from the complex species that is formed depending upon the pH value (Table III). The chemical shifts for these four signals with respect to the free ligand show that tartaric acid bonds to tungsten only by a carboxylic group and one α-alcoholic group, while the other two hydroxyl groups remain uncoordinated (Fig. 4c). This coordination is quite similar to other α-hydroxyacid ligands such as malic and citric acids [31, 32].

However, for solutions with metal:ligand ratio > 1, the spectra show resonances only at 183.8 and 87.1 ppm (Fig. 4b). These values are shifted at a lower field from the free ligand resonances, showing that every hydroxy group in tartaric acid is implicated in that coordination. These signals have been assigned to one dimeric complex species in which tartaric acid acts as a bridge ligand between metal atoms [18, 33].

Polarimetric studies [16, 17] demonstrate that the three complex species formed by tartaric acid are independent of which reagent is in excess, and at these pH values a μ-oxo bridge between metal atoms must exist. Therefore, we can assume that in excess of tungsten(VI) there are some intermolecular exchange processes among different units in which the four hydroxy groups take part, resulting in only two signals in the spectrum.

Conclusions

Absorbance variation with pH (curve a, Fig. 1) has shown the formation of three different complex species which have their highest concentrations at pH 5.0, 3.0 and 1.0. We have established the different formation and interconversion equilibria in every pH range and determined the amount of acid equivalents needed to form every complex species (Table I). According to these data and since the stoichiometries of the complexes are already known, we can write the following general scheme including the formation and interconversion reactions between different species, $7.0 > pH > 5.0$

$$WO_4^{2-} + 2C_6O_8H_8^{2-} + 2H^+ \rightleftharpoons [WO_2(C_6O_8H_7)_2]^{4-} + 2H_2O$$

I

$5.0 > pH > 2.5$

$$[WO_2(C_6O_8H_7)_2]^{4-} + H^+ \rightleftharpoons 0.5[W_2O_5(OH)_2(C_6O_8H_8)_2]^{4-} + C_6O_8H_9^-$$

II

$2.5 > pH > 1.0$

$$[W_2O_5(OH)_2(C_6O_8H_8)_2]^{4-} + H^+ \rightleftharpoons [W_2O_5(OH)(C_6O_8H_8)_2]^{3-} + H_2O$$

III

It turns out to be the same as those described for other α-hydroxyacids with molybdenum(VI) and tungsten(VI) [9, 23, 24], and especially the same as the tungsten(VI)–tartaric acid system [9] for which the analogous tartrate bidentate complexes $[WO_2(T)_2]^{4-}$, $[W_2O_5(OH)_2(TH)_2]^{4-}$ and $[W_2O_5(OH)(TH)_2]^{3-}$ have been established [16, 17].

The above equilibria have been formulated assuming that the monomeric complexes of molybdenum(VI) and tungsten(VI) have a *cis*-dioxo MO_2 core, and the dimeric ones have a μ-oxo bridge with at least one oxo-terminal group on each metal atom [25, 27]. For the dimeric complex formed at a more acidic pH, we have suggested the presence of a double bridge; this has been fully corroborated in the case of different molybdenum(VI) complexes [24, 28, 29], for which both binuclear species have been isolated and their IR spectra recorded.

On the other hand, only tartaric and mucic complexes show an anomalous cryoscopic decrease, while all the complex species formed by citric and malic acids in excess of tungten(VI) [31] (where their ^{13}C NMR spectra show that coordination will only occur through hydroxyl α-positioned groups while the β-carboxylate group remains free) produce correct cryoscopic decreases. Therefore, we can advance that both ligands, that is mucic and tartaric acids, have the same coordination to the metal atom with participation of the carboxylic and alcoholic groups in α-position. There are, however, some important differences due to the presence of a second $CHOH-CO_2H$ group in the molecule of the ligand, which causes a high intermolecular association for only one of these dimeric complex species.

^1H and ^{13}C NMR spectra for mucic and tartaric acids agree with these results. Thus, we can assume the existence of an intermolecular exchange process more favoured in solutions with tungsten(VI):ligand ratio ≥ 1. The comparison of ^{13}C NMR spectra in an excess of tungsten(VI) for both ligands shows that the β-alcoholic groups of mucic acid always remain uncoordinated.

From these results it must therefore be emphasized that mucic acid, in spite of having four hydroxy-alcoholic groups, does not form a complex of 2:1 stoichiometry (metal:ligand) and the complex species formed are fully analogous to those found for tartaric acid. It confirms the greater tendency toward carboxylate coordination in diacid ligands, regardless of the number of hydroxy-alcoholic groups.

On the other hand, recent work with ^{13}C NMR DEPT spectroscopy has demonstrated that the dinuclear complex of 2:1 stoichiometry (metal: ligand) formed by mannitol and sorbitol implies a coordination by the CH_2OH terminal group and three hydroxy-alcoholic α-positioned groups [4].

In fact, gluconic acid displays ^{13}C NMR spectra when tungsten(VI) is in excess, and it demonstrates a coordination by CH_2OH group when the analogous 2:1 species of mannitol and sorbitol are formed.

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