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

M. Luisa Ramos, M. Madalena Caldeira and **Victor M. S. Gil***

Department of Chemistry, University of Coimbra, 3000 Coimbra (Portugal)

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Abstract

Proton and ^{13}C NMR spectra of aqueous solutions of sodium molybdate and D-glucaric acid for variable molar ratios and pH values (range 1–9) clearly show the existence of five complexes dominating for specific concentration and pH conditions: a 2:1 metal to ligand complex, **a**, dominant at low pH (pH ≈ 2) for dilute solutions; two other complexes, **b** and **c**, which seem to have 2:2 and 1:1 composition, respectively, and which dominate at low pH for higher concentrations; another 2:1 complex, **d**, formed at intermediate pH (pH ≈ 4.5–6); still another 2:1 complex, **e**, formed at higher pH (pH ≈ 6–8.5). From the ^1H and ^{13}C chemical shifts observed on complexation, the binding sites of D-glucaric acid to the metal are established. From the proton–proton coupling constants the approximate conformation of the bound ligand is determined. The structures proposed on this basis are partially supported by ^{95}Mo chemical shifts, and the structure changes for the 2:1 complexation with pH are rationalized. Similar results are expected with W(VI) but due to close chemical shifts and exchange phenomena, only a 2:1 complex at low pH is adequately characterized.

Introduction

The coordination chemistry of molybdenum(VI) and tungsten(VI) in aqueous solution is a field of considerable interest, both from a purely scientific and an applied point of view. Among the ligands, hydroxycarboxylic acids have received special attention. In particular, our group has been exploiting the capabilities of NMR spectroscopy in a systematic study of the complexation of Mo(VI) and W(VI) salts with several α-hydroxycarboxylic acids [1–5], in close relation to previous work using other techniques. One advantage of NMR over most of the other methods for studying these systems is that, due to relatively slow exchange phenomena, distinct spectra are often obtained for different species.

Now we extend those studies to D-glucaric acid, an important polyhydroxycarboxylic acid. Whereas no reference was found in the literature for the system W(VI)/D-glucaric acid, the formation of a 2:1 (metal to ligand) complex was reported in the case of Mo(VI) on the basis of polarimetric methods [6]. However, no further structural information was obtained; in addition, in the light of our previous experience involving simpler ligands, more than just one complex is likely to form, depending on the pH and concentration conditions.

The present brief account anticipates a systematic comparative study of complexation of sugar acids (aldonic, alduronic and aldaric acids) with molybdenum(VI) and tungsten(VI) using multinuclear NMR.

Experimental

Analytical grade sodium tungstate and sodium molybdate and commercially available monopotassium salt of D-glucaric acid were used. To reduce the intensity of the *OH* NMR signal, the former were dried at 120 °C, the latter was lyophilized from a solution 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. Whenever necessary, the ionic strength was kept approximately constant by making the solution 1 M in KNO_3. The ^1H and ^{13}C spectra were obtained on

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*Author to whom correspondence should be addressed.

a Varian XL-200 NMR spectrometer and some of them on a Varian VXR-400S NMR spectrometer. Except for some ^{1}H spectra (recorded at 1 and 30 °C for removing overlap with the residual solvent signal) all spectra were obtained at probe temperature (21 ± 1 °C). The ^{13}C spectra were recorded using proton-decoupling techniques with suppression of the nuclear Overhauser effect; in this manner temperature fluctuations of the sample were reduced to c. ± 1 °C. p-Dioxane and DSS were used as internal references for ^{13}C and ^{1}H shifts, respectively. The [95]Mo spectra were obtained on a Varian VXR-400S NMR spectrometer, using a D_2O solution of Na_2MoO_4 at $pH^* = 9$ 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 [95]Mo, the corresponding parameters were 50000 Hz, 0.2 s, 0.5 s and 1700–90000 pulses.

Fig. 1. Job's plot based on proton NMR spectral intensities for the system Mo(VI) + D-glucaric acid; total concentration of complexing species 0.010 M (D_2O solutions, 1 M in KNO_3, $pH^* = 2.0$, temperature 313 K).

Results and discussion

Proton and ^{13}C NMR spectra of aqueous solutions of sodium molybdate and D-glucaric acid for variable molar ratios (from 4:1 to 1:4) and pH values (range 1–9) clearly show the formation of various complexes. As a result of slow chemical exchange, distinct spectra are detected for the bound ligands as well as for free ligand whenever in excess. The occurrence of five distinct bound situations for glucaric acids is found, which, together with the different variation of the corresponding signals on changing concentration, molar ratios and pH, points to the existence of five complexes dominating for specific concentration and pH conditions. The study was assisted by the assignment of ^{1}H and ^{13}C NMR signals previously done for the free ligand by other authors [7–9].

At low pH ($pH^* = 2.0$) and for moderately dilute solutions (below 0.1 M for metal + ligand), one complex, **a**, is largely dominant. A Job's plot (for a total concentration of 0.010 M) based on the intensities of the corresponding ^{1}H NMR signals is shown in Fig. 1 and clearly indicates a strong 2:1 metal to ligand complexation. Figure 2 shows a neat ^{1}H spectrum for complex **a** in conditions when it is essentially the only complex forming, with very little free ligand present. The assignment of the signals was based on homonuclear decoupling techniques.

For more concentrated solutions, the formation of two further complexes is detected (**b** and **c**), eventually dominating over complex **a**; the concentration of one of them (**c**) increases with increasing ligand content (Fig. 3).
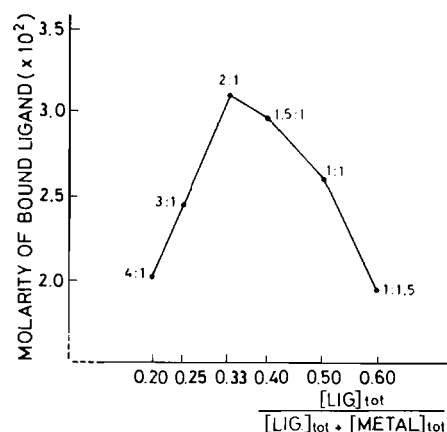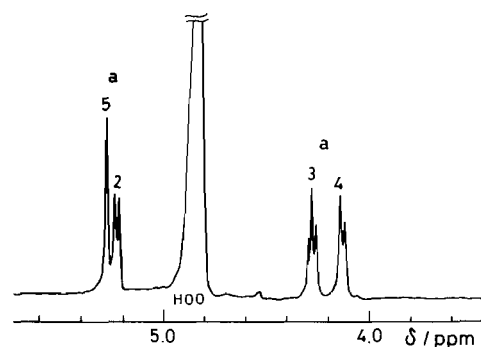

Fig. 2. 200 MHz ^{1}H NMR spectrum of a 0.10 M:0.050 M D_2O solution of sodium molybdate(VI) and D-glucaric acid ($pH^* = 2.0$, temperature 313 K).
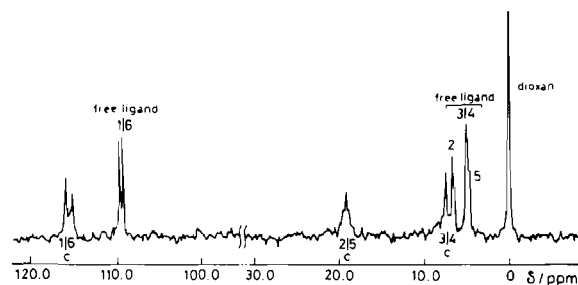

Fig. 3. 50.3 MHz ^{13}C spectrum of a 0.25 M:0.50 M aqueous solution (30% D_2O) of sodium molybdate(VI) and D-glucaric acid ($pH^* = 2.0$, temperature 293 K).

At intermediate pH values ($pH^* = 4.5$–6.0), another complex, **d**, is formed especially in solutions of high relative metal content as is shown in Fig. 4. In this range of pH and for high metal content solutions, complex **d** dominates over species **a** and **b** (the ^{1}H signals for **a** and **b** become broad presumably due to an exchange mechanism of intermediate rate,
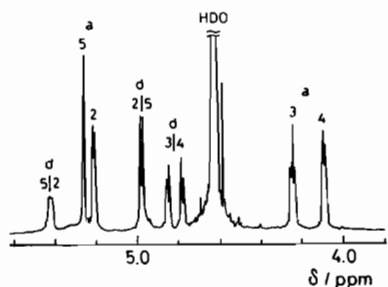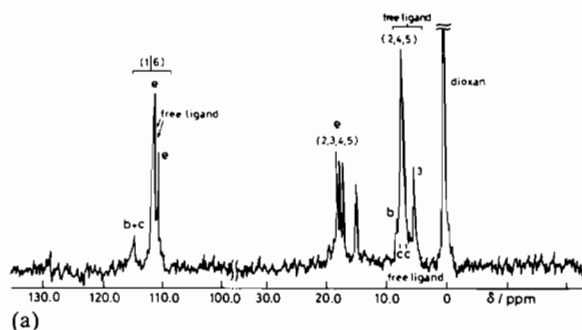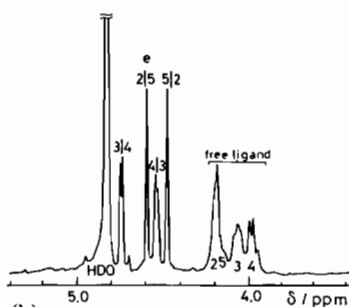
Fig. 4. 400 MHz ^{1}H NMR spectrum of a 0.099 M:0.033 M D$_2$O solution of sodium molybdate(VI) and D-glucaric acid (pH* = 4.9, temperature 313 K).

Fig. 5. (a) 50.3 MHz ^{13}C NMR spectrum of a 2.0 M:0.50 M aqueous solution (30% D$_2$O) of sodium molybdate(VI) and D-glucaric acid (pH* = 8.4, temperature 293 K); (b) 200 MHz ^{1}H NMR spectrum of a 2.0 M:0.50 M D$_2$O solution of sodium molybdate(VI) and D-glucaric acid (pH* = 8.4, temperature 274 K).

when the conditions are such that **a** and **b** are present in very small concentrations).

At pH above 6, complexes **a** and **d** disappear, but complexes **b** and **c** are still detected up to pH* = 8.5, especially for high ligand relative concentrations. In addition, a new species, **e**, is formed for solutions of high metal content. Figure 5 shows ^{1}H and ^{13}C spectra where signals of species **e** are visible.

The above results seem to indicate that besides a 2:1 metal to ligand complex **a**, complexes **d** and **e** also have 2:1 composition. Complex **b** is probably a *n:n* species, whereas **c** seems to be a 1:1 complex.

In favour of the latter hypothesis is the fact that a 0.25:0.50 Mo(VI)/D-glucaric acid solution, at pH* = 5.4, where species **c** dominates over species **b**, has a ^{13}C NMR spectrum showing a large amount of free ligand and a ^{95}Mo spectrum with no signal for free metal.

More firm and detailed conclusions can be gained from the ^{1}H and ^{13}C chemical shifts relative to the free ligand (in identical pH conditions), from the ^{95}Mo shifts which can be related to the structure of the metal centres, and from the vicinal HH coupling constants which are a rough indication of the conformations assumed by glucarate in the complexes.

Tables 1 and 2 show the ^{1}H and ^{13}C NMR parameters. The observed high frequency shifts for the carboxylic carbon nuclei and for C(2) and C(5) on going from free ligand to complex **a**, as well as the proton shifts for positions 2 and 5, are typical of involvement of the two carboxyl groups and the respective OH adjacent groups in complexation [1–5, 10]. The same can be said about complexes **b** and **c**, with $\Delta\delta$C being now more similar for C(2) and C(5) than is the case with complex **a**. Complex **d** exhibits similar shifts for C(1) and C(6) and larger shifts for the OH bearing carbon nuclei which suggests involvement of all hydroxyl groups in complexation, besides the carboxyl groups; accordingly, H(3) and H(4) show larger positive shifts than for complexes **a**, **b**, **c**. Finally, the almost zero shifts of C(1) and C(6) and the large shifts of the remaining carbon nuclei in the case of complex **e** point to complexation through the four OH groups alone; the non-involvement of the carboxylate groups is in accordance with smaller δH values for H(2) and H(5) than in the other cases.

The HH coupling constants given in Table 1 can now be explored to gain some insight on the conformation of the bound ligand around the various CC axes, by roughly considering the way the vicinal proton–proton couplings vary with dihedral angles (minor changes are also due to electronic effects accompanying complexation). The D-glucaric acid conformation in aqueous solution has been regarded roughly to be an equilibrium of the conformers found in potassium glucarate and calcium glucarate crystals [8]. For complex **a**, the big change is in J_{4-5} from 4.2 Hz to ≈ 0 on complexation. This requires a H(4)C(4)C(5)H(5) dihedral angle near 90° in the complex. The (equal) values for J_{2-3} and J_{3-4} are typical of an essentially *gauche* arrangement of the corresponding nuclei.

The broad signals recorded for complex **b**, possibly due to exchange phenomena, did not allow the determination of proton coupling constants. The partial results for complex **c** point to almost no

TABLE 1. ^{1}H NMR parameters^a for Mo(VI) + D-glucaric acid

	δH(2)		δH(5)	δH(3)		δH(4)	J_{2-3}	J_{4-5}		J_{3-4}
pH* = 2.0, temperature 313 K										
Free ligand	4.53		4.41	4.19		4.01	2.8	4.2		5.5
Complex a^b	5.24		5.29	4.28		4.13	4.2	0		4.2
pH* = 4.9, temperature 294 K										
Free ligand	4.15		4.13	4.07		3.94	3.0	4.8		3.3
Complex a^c	5.24		5.29	4.28		4.13	4.2	0		4.2
Complex b^d	4.94	/^{g}	5.04	4.21	/	4.11	f	f		f
Complex c^d	4.94	/	5.04	4.18	/	3.99	f	4.4	/	5.5
Complex d^b	5.43	/	4.99	4.81		4.81	4.2	4.2		9.8
pH* = 8.4, temperature 274 K										
Free ligand	4.14		4.12	4.06		3.94	3.0	4.8		4.5
Complex e^e	4.57	/	4.46	4.51	/	4.74	0	0		2.4

^{a}δ values, in ppm, relative to DSS, J values in Hz. ^{b}0.10 M/0.050 M Mo(VI)/D-glucaric acid solution. ^{c}1.0 M/0.25 M Mo(VI)/D-glucaric acid solution, temperature 313 K. ^{d}0.13 M/0.26 M Mo(VI)/D-glucaric acid solution. ^{e}1.0 M/0.25 M Mo(VI)/D-glucaric acid solution. ^{f}Not measured due to broad signals. ^{g}The oblique line refers to the possibility of a reverse assignment.

TABLE 2. ^{13}C NMR chemical shifts^a for Mo(VI) + D-glucaric acid, temperature 295 K

	δC(1)		δC(6)	δC(2)		δC(5)	δC(3)		δC(4)
pH* = 2.0									
Free ligand	176.24	/^{f}	176.65	74.04		72.06	72.29		72.29
Complex a^b	182.80	/	181.75	87.12	/	80.28	75.35	/	76.15
pH* = 4.9									
Free ligand	178.53	/	178.73	74.63		74.36	72.49		74.55
Complex b^c	182.71	/	181.91	87.28	/	86.84	75.51	/	e
Complex c^c	182.71	/	181.91	86.49		86.49	73.76	/	74.72
Complex d^d	182.55	/	181.59	91.17	/	88.20	83.31	/	86.00
pH* = 8.5									
Free ligand	179.43	/	179.65	74.55		74.55	72.67		74.55
Complex e^d	178.72	/	179.65	85.48	/	85.12	82.42	/	84.54

^{a}δ values relative to TMS (using δC(dioxane) = 67.4 ppm). ^{b}1.0 M/0.50 M Mo(VI)/D-glucaric acid solution. ^{c}0.25 M/0.50 M Mo(VI)/D-glucaric acid solution. ^{d}2.0 M/0.50 M Mo(VI)/D-glucaric acid solution. ^{e}Not measured due to superposition. ^{f}The oblique line refers to the possibility of a reverse assignment.

conformational changes around C(3)C(4) and C(4)C(5) on complexation. As far as complex d is concerned, the large J_{3-4} value shows the presence of an approximately *trans* arrangement of H(3) and H(4), the other pairs remaining essentially *gauche* as in the free ligand. Finally for complex e, the J values point to a *gauche* conformation of H(3) and H(4) and dihedral angles of about 90° for the remaining pairs.

The fact that the conformation of glucaric acid changes drastically (around (C(4)C(5)) when forming the 2:1 complex a means that the two molybdenum centres do not bind independently to the terminal fragments of glucaric acid. They must be directly bonded, probably through an oxygen bridge, thus

forcing the ligand to a new conformation. Structure I is consistent with all the observations, but the possibility of Mo being pentacoordinated can not be ruled out.

I
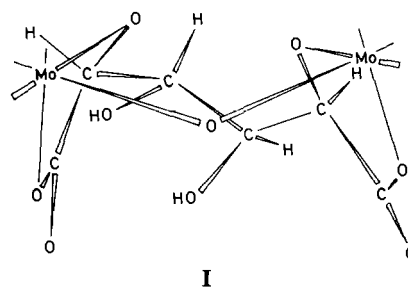
When increasing pH, the OH groups in positions 3 and 4 become also available for complexation in d and this replaces the oxygen bridge between the Mo atoms of I. Now the two moieties of glucarate bound independently to Mo centres and I gives place to II, a *trans* arrangement of H(3) and H(4) being the result of minimized steric repulsions of the two bulky chelate groups. This structure is similar to that proposed for $[(MoO_3)_2EDTA]^{4-}$ [11].

II
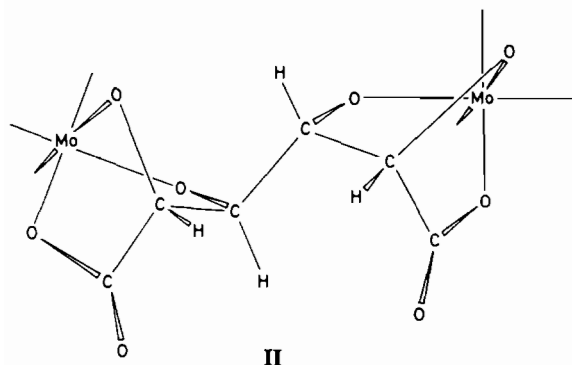
A further increase of pH leads to the breaking of the carboxyl group bonds to Mo and, as a consequence, the formation of oxygen bridges and new changes of ligand conformation. Thus, the structure of complex e is likely to be similar to that found for the erythritolate dimolybdate complexes in the solid state [12] and in solution [13].

III

IV
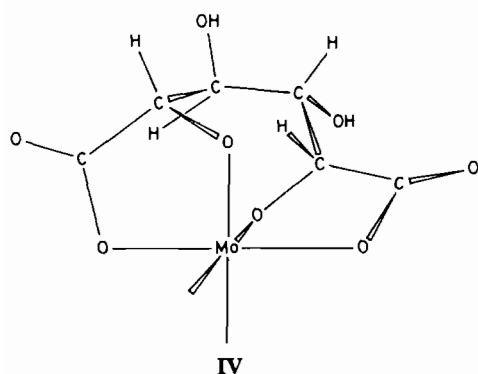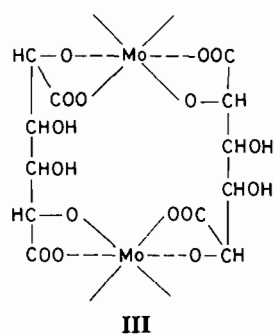
For complex b we propose the structure III, whereas structure IV agrees with the available data for complex c.

Table 3 shows the ^{95}Mo NMR chemical shifts and linewidths and Fig. 6 illustrates the case where pH* = 4.9. The value δ = 77 ppm recorded for complex a is to be compared with a value of 120 ppm claimed to be characteristic of a $Mo_2O_5^{2+}$ core in single oxo-bridged species [14]. The difference can be attributed to the fact that in a the molybdenum moieties are also ligand bridged.

Complexes b and c give ^{95}Mo signals at 105 and 115 ppm. Both of them have a MoO_2^{2+} core proposed.

TABLE 3. ^{95}Mo NMR chemical shifts[a] for Mo(VI) + D-glucaric acid, temperature 313 K

	δMo	$\Delta\nu_{1/2}$ (Hz)
pH* = 2.0		
Complex a[b]	76.52	182
pH* = 4.9		
Free metal	10.00	186
Complex a[c]	76.80	260
Complexes b + c[c]	105.00	878
Complex d[c]	44.94	391
pH* = 5.4		
Complex c[d]	114.97	489
pH* = 7.5		
Free metal	0.20	63
Complex e[e]	28.90	896

[a]δ values relative to external reference Na$_2$MoO$_4$, pH* = 9.0. [b]0.50 M/0.25 M Mo(VI)/D-glucaric acid solution. [c]0.30 M/0.10 M Mo(VI)/D-glucaric acid solution. [d]0.25 M/0.50 M Mo(VI)/D-glucaric acid solution. [e]2.0 M/0.50 M Mo(VI)/D-glucaric acid solution.
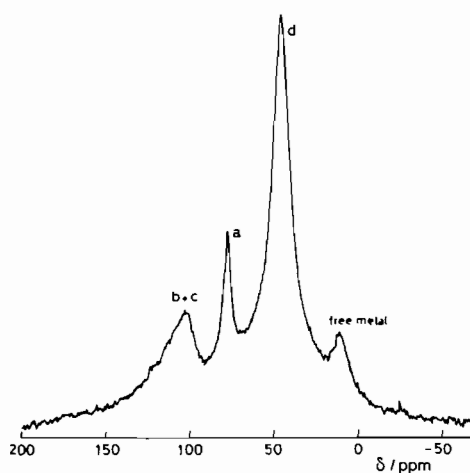

Fig. 6. 26.06 MHz ^{95}Mo spectrum of a 0.30 M:0.10 M aqueous solution (30% D$_2$O) of sodium molybdate(VI) and D-glucaric acid (pH* = 4.9, temperature 303 K).
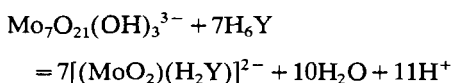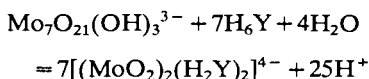
Comparing these results with data for $[MoO_2(O,N)_4]$ type species from Geller *et al.* [15], it seems reasonable to assign the difference to the minor effects of substituting oxygen for nitrogen in the coordinating ligand.

For a MoO_3 centre (d) we propose the ^{95}Mo signal at 45 ppm. This is in agreement with a Mo(VI) atom shielding in a MoO_3 core relative to $Mo_2O_5^{2+}$, supported by literature data [11, 14–16]. Complex **e** gives a ^{95}Mo signal at 29 ppm.
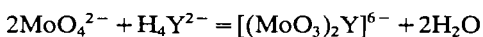
For complex **a**, the chemical equation

$$2Mo_7O_{21}(OH)_3^{3-} + 7H_6Y + H_2O$$

$$= 7[Mo_2O_5(H_2Y)(H_2O)_2]^{2-} + 2H^+$$
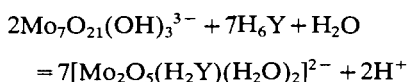
is consistent with the increasing acidity observed during complexation for dilute solutions, at $pH^* = 2$, as previously referred by Fedorov [6] for complex formation in the pH range 2.0–4.0. A conditional pK value of -10.3 ± 0.2 is obtained from the concentrations of free and bound ligand for various molar ratios, at $pH^* = 2.0$, measured form the ^1H NMR signals, the ionic strength being kept approximately constant with 1 M KNO_3. Complex formation reactions for species **b** and **c** may be represented, respectively, by the following equilibria:

$$Mo_7O_{21}(OH)_3^{3-} + 7H_6Y + 4H_2O$$

$$= 7[(MoO_2)_2(H_2Y)_2]^{4-} + 25H^+$$

$$Mo_7O_{21}(OH)_3^{3-} + 7H_6Y$$

$$= 7[(MoO_2)(H_2Y)]^{2-} + 10H_2O + 11H^+$$

For the **d** complex, at higher pH

$$2MoO_4^{2-} + H_4Y^{2-} = [(MoO_3)_2Y]^{6-} + 2H_2O$$

For the system $W(VI) + D$-glucaric acid we expect qualitatively similar results. This is however not clearly revealed by NMR mainly because of the proximity of signals and broadening due to exchange phenomena. The only unambiguous evidence obtained is for a 2:1 tungsten to ligand complex **a** dominant at $pH^* = 2.0$ in dilute solutions. The corresponding δH values are 5.61, 5.38, 4.30 and 4.11, respectively for H(2), H(5), H(3) and H(4) and the δC values are 183.6 and 182.7 for the pair C(1), C(6), 86.0 and 78.9 for the pair C(2), C(5) and 75.4 and 76.0 for the pair C(3), C(4). The proton coupling

constants are $J_{2-3} = 3.8$, $J_{4-5} = 0$, $J_{3-4} = 4.1$ Hz. These values are similar to those found for complex **a** with Mo(VI) and an identical structure is proposed.

Acknowledgements

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