INTERACTION OF TUNGSTEN(VI) AND MOLYBDENUM(VI) WITH NITRILOTRIACETIC ACID AND GLUTAMIC ACID IN DIFFERENT SODIUM PERCHLORATE AQUEOUS SOLUTIONS

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Using potentiometric and spectrophotometric techniques, the complexation of tungsten (VI) with nitrilotriacetic acid (NTA) has been carried out in aqueous solution for pH = 7.5 at 25 °C and different ionic strengths ranging from (0.1 to 1.0) mol dm^{-3} ($NaClO_4$). The composition of the complex was determined by the continuous variations method. It was shown that tungsten (VI) forms a mononuclear complex with NTA of the type (WO_3L^{3-}) at pH = 7.5.

The complexation of molybdenum (VI) with nitrilotriacetic acid (NTA) and glutamic acid has been studied using potentiometric and spectrophotometric techniques. The same conditions have been used for these two complexes except that pH was 6.0. Polarimetric technique also confirmed the complexation of molybdenum(VI) with glutamic acid.

In all aforementioned complex formation reactions the dependence of the protonation and stability constants on ionic strength is described by a Debye – Huckel type equation. Finally a comparison for the ionic strength dependence have been made.

KEY WORDS: Ionic Strength; Nitrilotriacetic Acid; Glutamic Acid; Tungsten(VI); Molybdenum(VI); Complexation; Stability Constant

1. Introduction

Desulfovibrio gigas formate dehydrogenase is the first representative of a tungsten-

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containing enzyme from a mesophile that has been structurally characterized.[1] Itis a heterodimer of 110 and 24 kDa subunits. The existence of a universal pterin dithiolene cofactor ligand for the molybdenum and tungsten oxotransferases supports a biological significance of the fundamental chemistry of mono and bis (dithiolene) complexes of these elements.[2] Tungsten(VI) also forms complexes with tryptophan [3] and porphyrin.[4]

Molybdenum is present in cofactors of several enzymes. Some of them are involved in important biochemical processes such as nitrogen fixation. As a result, structural, thermodynamic and kinetic studies of the complexation between molybdate and different chelating ligands have been the subject of several investigations.[5-18]

Considerable studies have been performed on the stability constants of metals with α-aminoacids and aminopolycarboxylic acids, but only little work has been reported on the ionic strength dependence of stability constants of tungsten(VI) and molybdenum(VI) with nitrilotriacetic acid and glutamic acid.[5-7] Marcu *et al.* [8] studied the radiochromatographic and electroradiochromatographic of sodium tungstate solutions under the action of NTA. Studies on the structural and bonding characteristics of various Mo (VI)-aminopolycarboxylic acid complexes has led to the evaluation of stability constants from proton nuclear magnetic resonance (NMR) data.[9-10] On the basis of these studies Kula *et al.* [11] determined the stability constants of W(VI)-NTA complexes by potentiometric techniques. Collin *et al.* [12] reported the stability constant of this system at 25 °C and at an ionic strength of 0.5 mol dm^{-3} $NaClO_4$. Zare *et al.* [13] studied the W(VI)-NTA and Mo(VI)-NTA systems and evaluated their stability constants at 25 °C and at an ionic strength of 3 mol dm^{-3} $NaClO_4$ using the potentiometric technique. Chan *et al.* [14] proved that stable one to one molybdenum chelate is formed with NTA using the NMR technique. Raymond [15] confirmed the existence of MoO_3 core for the complexation of Mo (VI) with the tridentate ligand NTA. Funahashi *et al.* [16] studied the reaction of molybdate (VI) with nitrilotriacetate spectrophotometrically in aqueous solution of pH 6-8 at $I = 1.00$ M ($NaClO_4$) and 25 °C. In a potentiometric study of molybdenum (VI) chelates with glutamic acid, Rabenstein *etal.* [17] reported the stability constant at 25 °C and at ionic strength of 0.2 mol dm^{-3} KNO_3. Raymond *etal.* [15] has synthesized and proved the composition of the complex using the spectroscopic technique. Gharib *etal.* [18] have proved the composition of glutamic acid complex and reported its stability constant, using the polarimetric and spectrophotometric techniques.

The present work deals with the complexation of tungsten(VI) and molybdenum(VI) with NTA and molybdenum(VI) with glutamic acid in an ionic strength range of (0.1 to 1.0) mol dm^{-3} sodium perchlorate at 25 °C. A simple Debye-Huckel type equation was established for the dependence of formation constants on ionic strength. This equation makes it possible to estimate a stability constant at a fixed ionic strength when its value is known at another ionic media in the range $(0.1<I<1.0)$ mol dm^{-3}.

2. Experimental Procedures

2.1. Reagents. Sodium perchlorate, perchloric acid, sodium hydroxide, sodium tungstate, sodium molybdate, nitrilotriacetic acid and glutamic acid were obtained from E.Merck as analytical reagent grade materials and were used without further purification. Dilute perchloric acid solution was standardized against $KHCO_3$. In all experiments double-distilled water with specific conductance equal to (1.3 ± 0.1) $\mu\Omega^{-1}cm^{-1}$ have been used.

2.2. Measurements

A Horiba pH-meter, D-14, was used for pH measurements. The pH-meter has a sensitivity of 0.01. The hydrogen ion concentration was measured with a Horiba combination electrode, model S8720. A 0.01 mol dm^{-3} perchloric acid solution containing 0.09 mol dm^{-3}

sodium perchlorate (for adjusting the ionic strength to 0.1 mol dm $^{-3}$) was employed as a standard solution of hydrogen ion concentration. The same procedure was performed for the other ionic strengths.[13] The calibration has been done for the whole pH (pH = -log[H^+]) range used. Spectrophotometric measurements were performed on a UV-vis Shimadzu 2101 spectrophotometer with an Acer Mate 486 SX/250 computer using thermostated, matched 10-mm quartz cells. Polarimetric measurements were performed with an Atago model Polax-D polarimeter equipped with a sodium lamp. A water-jacketed cell of 200 mm length and 20 cm^3 total volume was used.

For each experiment two solutions of metal + ligand were prepared with the same concentration, but the ionic strength of the first was maintained with sodium perchlorate and that of the second with sodium hydroxide or perchloric acid. The pH of the first solution was adjusted with the second one. The second solution consists of metal + ligand + NaOH for increasing pH, while for decreasing pH the second one consists of metal + ligand + $HClO_4$. The absorbance of the first solution was measured after adjusting the pH.

In all cases, the procedure was repeated at least three times and the resulting average values and corresponding standard deviations are shown in the text and Tables.

3. Results and Discussion

The dissociation equilibria of nitrilotriacetic acid and glutamic acid have been studied in different kinds of background electrolytes but there are no reports about the ionic strength dependence of the dissociation constants of NTA and glutamic acid.[5-7] The following equilibria were studied:

$$H_3L \rightleftharpoons H^+ + H_2L^- \qquad K_1 = [H^+][H_2L^-]/[H_3L] \qquad (1)$$

$$H_2L^- \rightleftharpoons H^+ + HL^{2-} \qquad K_2 = [H^+][HL^{2-}]/[H_2L^-] \qquad (2)$$

$$HL^{2-} \rightleftharpoons H^+ + L^{3-} \qquad K_3 = [H^+][L^{3-}]/[HL^{2-}] \qquad (3)$$

Where L^{3-} represents the fully dissociated ligand anion. The dissociation constants K_1, K_2 and K_3 have been determined using potentiometric techniques and calculated using the Solver, Microsoft Excel 2000 powerful optimization package, to perform non-linear least-squares curve fitting.(19-20) For the glutamic acid only K_1 and K_2 have been determined. These values are listed in Tables I and II together with the values reported in the literature, which are in good agreement with those reported before.

3.1. Complexation of Tungsten(VI) with NTA

Using the continuous variations method, we determined the absorbances of solutions of W (VI) and NTA of total concentration 0.006 mol dm^{-3} in the UV range (260 to 265 nm) at a constant pH of 7.5. When solutions of tungstates are made weakly acid, polymeric anions are formed, but from more strongly acid solutions substances often called tungstic acid are obtained.(21) The behavior of the tungstate systems is similar to that of the molybdate systems. Again the degree of aggregation in solution increases as the pH is lowered, and numerous tungstates have been crystallized from the solutions at different pH s.(21)

It is now certain that WO_4^{2-} ion is tetrahedral in aqueous solution. (21) In the usual potentiometric method for evaluating metal-ligand stability constants, the competition between metal ion and hydrogen ion for the ligand is studied, and the pH region of interest is from about 1 to 5.(11) In the W (VI) systems, however, the complication of metal polymerization is introduced in acidic solutions. Because the polymerization equilibria are not well understood, this pH region is not useful for stability determinations. In more alkaline solutions, on the other hand, a pH-dependent process involving the competition between tungstate formation and metal-ligand complexation-i.e., a competition between OH^- and ligand for the metal ion- can be utilized. This process was determined from the NMR studies to be important from about pH 6 to 9 and can be represented by:[11]

$$MO_3L^{x-} + OH^- \rightleftharpoons MO_4^{2-} + HL^{1-x} \quad (4)$$

where M represents W and L represents the aminopolycarboxylic acid ligand. In the pH region above 6 no evidence was found for any Mo species containing fewer than three oxygen atoms-e.g., MoO_2^{2+}- as has been proposed for other systems.[(22)] The molybdenum coordinating species in all the aminopolycarboxylic acid systems above pH 6 is MoO_3, and by analogy we have assumed that the corresponding coordinating unit in the tungsten systems is WO_3.

Using the potentiometric technique, results obtained for simple one to one metal-ligand chelates are more precise than for higher complexes, such as those formed with EDTA. In fact, for the multicomplex systems the NMR data are probably more reliable than the potentiometric data as indicated by the range of calculated values for the EDTA systems.[(11)] A comparison of the formation constants shows that within experimental error there is essentially no difference between the stabilities of the corresponding Mo (VI) and W (VI) chelates. This does not seem too surprising in view of the similarities of the two ions and their nearly equal ionic radii .[(11)] However, NMR studies show that tungstene chelates are significantly more labile with respect to individual metal-ligand bonds than are the molybdenum chelates. The slowness with which pH equilibrium was attained in the NTA chelates may be explained by the higher negative charge of this complex compared to the other complexes and the subsequently slower reaction with OH^-:

$$MO_3NTA^{3-} + OH^- \longrightarrow MO_4^{2-} + HNTA^{2-} \quad (5)$$

For NTA ligand system, NMR studies also indicate that only one metal-ligand species exists above pH 6, MO_3L^{x-}.[(11)] Thus, W (VI) will bond with this tridentate ligand as a 1:1 complex:

$$WO_4^{2-} + NTA^{3-} + 2H^+ \rightleftharpoons WO_3NTA^{3-} + H_2O \quad (6)$$

with the stability constant, K_s, as:

$$K_S = [WO_3NTA^{3-}]/[WO_4^{2-}][NTA^{3-}][H^+]^2 \quad (7)$$

The values of $\log K_S$ at different ionic strengths together with the values of literature are shown in Table VIII. These values have been calculated similar to the molybdenum (VI) complex. Calculations for the molybdenum complex are described in the next section.

3.2. Complexation of Molybdenum (VI) with Nitrilotriacetic Acid and Glutamic Acid

(1)Polarimetric Studies. The effect of pH on the optical activity of glutamic acid and its complex with molybdenum(VI) shows the difference of optical rotation for the ligand and the complex.This difference reaches a maximum in the pH range 5.0-6.0,which means that we have the largest amount of complex formation in this pH range.

(2)Spectrophotometric Studies. Using the continuous variations method, we determined the absorbances of solutions of Mo(VI) and NTA of total concentration 0.006 mol dm^{-3} in the UV range (260 to 265 nm) at a constant pH of 6. The total concentration for glutamic acid was 0.02 mol dm^{-3}. Different sets of species have been proposed in order to assign the equilibria in molybdate solutions. The equilibria of molybdenum(VI) in acidified molybdate solutions are complex since various polynuclear species are formed.[16] At higher pH the complex dissociates as a result of the competitive formation of MoO_4^{2-}.[21] The observed absorbances were corrected from eq 8 and are summarized in Table III for the W(VI)-NTA and Mo(VI)-NTA systems and Table IV for the Mo(VI)-Glutamic acid system and plotted in Figure.1:

$$A_c = A_{obs} - \varepsilon_0[\text{Metal}] \quad (8)$$

A_c, A_{obs}, and ε_0 are the absorbance of the complex, the observed absorbance and the molar absorptivity of the metal, respectively. ε_0 values were calculated at the mole fraction of the metal equal to 1 and are shown in Table V for tungsten(VI) and Table VI for molybdenum(VI). In Figure.1 a maximum at a mole fraction of the metal equal to 0.5 was obtained, indicating a 1:1 complex. The molar absorptivity of the complex, ε_1, were calculated from the linear part of the aforementioned plot at low mole fraction of the metal, where essentially all the metal ions were in the form of a complex, and are listed in Tables V, VI and VII. At the maximum point of the plot, the concentration of the complex is:

$$[C] = A_c / \varepsilon_1 \quad (9)$$

The molybdate anion MoO_4^{2-} maintains a tetrahedral configuration in neutral and alkaline solutions.[21] Complexes of molybdate with chelating ligands have an octahedral configuration. The complex formation therefore will have to occur by an addition of the ligand to the molybdate ion, thereby increasing its coordination number from 4 to 6. It has been postulated that the monoprotonated species $HMoO_4^-$ exists in the form of an octahedral hydrate species in solution. From consideration of thermodynamic parameters for protonation of molybdate, Cruywagen *etal.*[23] have suggested that it is the second protonation constant which is anomalous and that the change in coordination number occurs with addition of the second proton. Whichever of these viewpoints is correct, the diprotonated species H_2MoO_4 should be octahedral.

Although Mo(VI) forms complexes with the same chelating agents as most other metal ions, its chemistry is differentiated from other transition ions by its strong association with oxygen. Thus in most Mo(VI) complexes, MoO_2^{2+} or MoO_3 is the central coordinating unit, which with octahedral geometry, severely limits the number of coordination sites available to the ligands. An interesting consequence of this behavior is illustrated by the complex formed between Mo(VI) and EDTA in which two Mo ions can coordinate with EDTA.[24] This is in distinct contrast to the normal metal- EDTA chelates in which only one metal ion coordinates with each ligand. Kula [10] concluded that for EDTA (between pH 9 and 5) two complexes with 1:1 and 2:1 metal-ligand ratio are formed. The structures which were proposed for the Mo_2- EDTA chelate led to speculation concerning the possibility of forming one to one Mo(VI) chelates with methyliminodiacetic acid (MIDA) and nitrilotriacetic acid (NTA) and proton NMR studies of these chelates confirmed that the predominate EDTA chelate does indeed contain two Mo ions and that stable one to one molybdenum chelates are formed with MIDA and NTA. [9,24] Thus, Mo(VI) will bond with this tridentate ligand(NTA) as a 1:1 complex:

$$MoO_4^{2-} + NTA^{3-} + 2H^+ \rightleftharpoons MoO_3NTA^{3-} + H_2O \qquad (10)$$

with the stability constant, K_s, as:

$$K_S = [MoO_3NTA^{3-}]/[MoO_4^{2-}][NTA^{3-}][H^+]^2 \qquad (11)$$

For the glutamic acid the species is MoO_3Glu^{2-} with the stability constant as:

$$K_S = [MoO_3Glu^{2-}]/[MoO_4^{2-}][Glu^{2-}][H^+]^2 \qquad (12)$$

The following equations are valid for the total concentration of the metal(C_M) and the total concentration of the ligand (C_L) at the maximum point on the plot of Figure.1:

$$C_M = [Metal] + [C] \qquad (13)$$

$$C_L = [L] + [C] \qquad (14)$$

By substituting eqs 9, 13 and 14 in eqns 7, 11 and 12 we can calculate the values of K_S. The values of $\log K_S$ at different ionic strengths together with the values of literature are shown in Tables VIII, IX and X.

3.3. Ionic Strength Dependence of Dissociation and Stability Constants

The dependence of the dissociation and stability constants on the ionic strength can be described according to the previous works: [5, 20, 25-33]

$$\log K_S(I) = \log K_S(I_1) - AZ^*(\frac{I^{0.5}}{1+BI^{0.5}} - \frac{I_1^{0.5}}{1+BI_1^{0.5}}) + C(I - I_1) + D(I^{1.5} - I_1^{1.5}) + E(I^2 - I_1^2)$$

(15)

where I and I_l are the actual and reference ionic strengths, respectively and according to eq 16 :

$$pM^{m+} + qL^{n-} + rH^+ \rightleftharpoons (M_pL_qH_r)^{pm-qn+r} \quad (16)$$

$Z^* = pm^2 + qn^2 + r - (pm + qn + r)^2$, where m and n are the charges on the metal ion and the ligand respectively. Considering, A = 0.5115 and B = 1.489 eq 15 can be simplified :

$$\log K_S(I) = \log K_S(I_1) - Z^*(\frac{I^{0.5}}{2+3I^{0.5}} - \frac{I_1^{0.5}}{2+3I_1^{0.5}}) + C(I - I_1) + D(I^{1.5} - I_1^{1.5}) + E(I^2 - I_1^2)$$

(17)

where C, D and E are empirical coefficients and their values were obtained by minimizing the error squares sum,(U), and the Gauss-Newton nonlinear least squares method in a suitable computer program :

$$U = \sum_i (a_i - b_i)^2 \qquad (i = 1,2,3,...) \quad (18)$$

where a is a quasi-experimental quantity and b_i is a calculated one. The values of C, D and E are shown in Tables XI and XII.

4. Conclusions

Sodium molybdate has three sites to form its complexes in aqueous solution. The same situation exists for sodium tungstate. On the other hand, glutamic acid and nitrilotriacetic acid are potentially tridentate ligands with three donor sites. Thus, Mo(VI) and W(VI) will bond with these tridentate ligands and it seems unlikely that the complexes of 1:2 and 1:3 stoichiometry exist in the pH which has been used.

Tables VIII and IX show that in both W(VI) + NTA and Mo(VI) + NTA systems a maximum at I = 0.7 is obvious, but another maximum can be seen at I = 0.3 for the latter. In the Mo(VI) + glutamic acid system, no maximum can be detected. It seems that at the minimum points , attraction and repulsive forces between the ions are equal. The attraction forces are dominant before the minimum points and the systems are stabilized. The repulsive forces are more important after the minimum points, therefore the stability of the systems are decreased.

According to the obtained values of C, D, E and eq 17 it is possible to estimate a stability constant at a fixed ionic strength when its value is known at another ionic media in the desired range.

Legends to Figures

Fig 1. Continuous variations plots of the absorbances of (A) MoO_3NTA^{3-}, (B) WO_3NTA^{3-}, (C) MoO_3Glu^{2-} Abs, versus the mole fractions of W(VI) and Mo(VI), X, at 25 °C, an ionic strength of 0.1 mol dm^{-3} $NaClO_4$ and 265 nm.

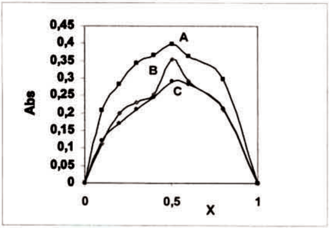
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
Abs
A
B
C
0
0,5
1
X

Table I. Dissociation Constants K_3, K_2, and K_1 of NTA at Different Ionic Strengths, I, of $NaClO_4$

I / mol dm $^{-3}$	$logK_3$	$logK_2$	$logK_1$	Experimental Conditions	Ref
0.1	1.98 ± 0.02	2.92 ± 0.05	10.00 ± 0.02		This work
0.3	1.83 ± 0.04	2.84 ± 0.03	9.85 ± 0.01		This work
0.5	1.76 ± 0.01	2.79 ± 0.02	9.70 ± 0.03		This work
0.7	1.63 ± 0.02	2.61 ± 0.01	9.55 ± 0.02		This work
1.0	1.55 ± 0.02	2.59 ± 0.04	9.25 ± 0.02		This work
			9.81 ± 0.10	I = 0.15 M, t = 25 °C	11
	2.05 ± 0.05	2.63 ± 0.02	9.17 ± 0.04	I = 3 M $NaClO_4$, t = 25 °C	13
	1.65	2.94	10.33	t = 20 °C	34

Table II. Dissociation Constants K_2 and K_1 of L-Glutamic acid at Different Ionic Strengths, I, of $NaClO_4$

I / mol dm $^{-3}$	$logK_2$	$logK_1$	Experimental Conditions	Ref
0.1	4.24 ± 0.05	9.64 ± 0.05		This work
0.3	4.03 ± 0.05	9.27 ± 0.05		This work
0.5	3.76 ± 0.05	9.19 ± 0.05		This work
0.7	3.74 ± 0.05	9.04 ± 0.05		This work
1.0	3.60 ± 0.05	8.98 ± 0.05		This work
	4.15	9.49	I = 0.15 M $NaClO_4$, t = 25 °C	18
	4.21	9.54	I = 0.1 M $NaNO_3$, t = 25 °C	35
	4.05	9.46	I = 0.1 M $NaClO_4$, t = 30 °C	36
	4.15	9.61	I = 0.1 M KNO_3, t = 25 °C	37
	3.71	9.63	I = 0.1 M $NaClO_4$, t = 30 °C	38

Table III. Continuous Variations Data for the W(VI) + NTA System at pH 7.5, Mo(VI) + NTA System at pH 6, an Ionic Strength of 0.1 M $NaClO_4$ and 265 nm

Mole Fraction of Metal	A[a]	
	W(VI) + NTA	Mo(VI) + NTA
0.00	0.000	0.000
0.10	0.112	0.207
0.20	0.200	0.283
0.30	0.230	0.343
0.40	0.254	0.365
0.50	0.356	0.398
0.60	0.292	0.364
0.80	0.212	0.297
1.00	0.000	0.000

[a]The corrected absorbance of [W(VI)] + [NTA] = 0.006 mol dm $^{-3}$.
[a]The corrected absorbance of [Mo(VI)] + [NTA] = 0.006 mol dm $^{-3}$.

Table IV. Continuous Variations Data for the Mo(VI) + L-Glutamic Acid System at pH 6, Wavelength 265 nm, an Ionic Strength of 0.1 M $NaClO_4$

Mole Fraction of Mo (VI)	A[a]	Mole Fraction of Mo (VI)	A[a]
0.00	0.000	0.60	0.284
0.05	0.099	0.80	0.213
0.10	0.121	0.90	0.111
0.20	0.169	0.95	0.054
0.40	0.245	1.0	0.000
0.50	0.291		

[a]The corrected absorbance of [Mo(VI)] + [L-glutamic acid] = 0.02mol dm $^{-3}$.

Table V. Molar Absorptivities of W(VI), ε_0 , and WO_3NTA^{3-}, ε_1 , at pH 7.5, Different Wavelengths, and Various Ionic Strengths, I, of $NaClO_4$

	ε_0		ε_1	
I / mol dm $^{-3}$	260 nm	265 nm	260 nm	265 nm
0.1	660.8	486.6	1116.6	1116.6
0.3	527.5	365.0	1221.6	1268.3
0.5	505.8	345.0	1533.3	1583.3
0.7	478.3	320.0	716.6	750.0
1.0	522.5	355.0	2316.6	2350.0

Table VI. Molar Absorptivities of Mo(VI), ε_0, and MoO_3NTA^{3-}, ε_1, for the Mo (VI) + NTA System at pH 6, Different Wavelengths and Various Ionic Strengths, I, $NaClO_4$

	ε_0		ε_1	
I / mol dm $^{-3}$	260 nm	265 nm	260 nm	265 nm
0.1	388.3	205.8	1928.3	1726.6
0.3	346.7	166.7	1166.6	983.3
0.5	380.0	199.2	3066.6	2916.6
0.7	386.7	211.7	2346.6	2188.3
1.0	402.5	223.3	1830.0	1710.0

Table VII. Molar Absorptivities of MoO_3Glu^{2-}, ε_1 , for the Mo (VI) + L-Glutamic Acid System at pH 6, Different Wavelengths and Various Ionic Strengths, I, $NaClO_4$

	ε_1	
I / mol dm $^{-3}$	260 nm	265 nm
0.1	273.5	98.8
0.3	285.1	109.5
0.5	268.1	94.4
0.7	269.9	97.4
1.0	265.1	98.8

Table VIII. Average Values of $\log K_S$ at pH 7.5 and Different Ionic Strengths for the Complexation of Tungsten (VI) with NTA, t = 25 °C

I / mol dm $^{-3}$	$\log K_S$	Experimental Conditions	Ref
0.1	19.00 ± 0.30		This work
0.3	19.37 ± 0.10		This work
0.5	19.65 ± 0.25		This work
0.7	20.10 ± 0.10		This work
1.0	19.40 ± 0.20		This work
	18.86 ± 0.05	I = 0.15 M, t = 25 °C	11
	19.10 ± 0.2	I = 1.0 – 2.5 M, t = 35 °C	11
	17.75	I = 0.5 M $NaClO_4$, t = 25 °C	12
	19.03 ± 0.15	I = 3 M $NaClO_4$, t = 25 °C	13

Table IX. Average Values of $\log K_s$ at pH 6 and Different Ionic Strengths, for the Complexation of Molybdenum(VI) with NTA, t = 25 °C

I / mol dm $^{-3}$	$\log K_s$	Experimental Conditions	Ref
0.1	18.72 ± 0.20		This work
0.3	19.36 ± 0.10		This work
0.5	18.08 ± 0.30		This work
0.7	18.31 ± 0.20		This work
1.0	17.97 ± 0.10		This work
	18.60 ± 0.20	I = 3 M $NaClO_4$, t = 25 °C	13
	18.09 ± 0.04	I = 1 M $NaClO_4$, t = 25 °C	16

Table X. Average Values of $logK_s$ at pH 6 and Different Ionic Strengths, for the Complexation of Molybdenum(VI) with L-Glutamic Acid, t = 25 °C

$I / mol\ dm^{-3}$	$logK_s$	Experimental Conditions	Ref
0.1	17.54 ± 0.30		This work
0.3	16.94 ± 0.40		This work
0.5	16.93 ± 0.50		This work
0.7	16.84 ± 0.35		This work
1.0	16.76 ± 0.40		This work
	16.78	I = 0.2 M $NaClO_4$, t = 25 °C	17
	16.73	I = 0.15 M $NaClO_4$, t = 25 °C	18

Table XI. Parameters for the Dependence on the Ionic Strength of Dissociation and Stability Constants for the W(VI) + NTA and Mo(VI) + NTA Systems at 25 °C

Species	C	D	E	Z*
K_3	2.933	-4.807	2.161	6
K_2	4.860	-9.257	4.673	4
K_1	-0.292	0.280	-0.578	2
WO_3NTA^{3-}	-8.294	28.021	-18.886	6
MoO_3NTA^{3-}	33.961	-67.906	35.411	6

Table XII. Parameters for the Dependence on the Ionic Strength of Dissociation and Stability Constants for the Mo (VI) + L-Glutamic Acid System at 25 °C

Species	C	D	E	Z*
K_2	-0.782	-0.453	0.702	2
K_1	-3.346	5.097	-2.241	4
MoO_3Glu^{2-}	-10.792	19.924	-9.911	6

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