Molybdenum(VI) and Tungsten(VI) Complex Formation.* Part 5.[1] The Reaction with Lactate in 1.0 mol dm^{-3} Sodium Chloride Medium

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Complex formation of molybdate and of tungstate with lactate have been investigated in the pH$_c$ range 2–7.5 by potentiometric and enthalpimetric titrations at 25 °C in 1.0 mol dm^{-3} NaCl. The potentiometric data were treated with the computer program SUPERQUAD taking into account the side-reactions of molybdate and tungstate with hydrogen ions. For both systems the 'best' reaction model comprises only one major complex and a number of minor complexes. Thermodynamic quantities have been determined for each of the major complexes. For the molybdenum(VI) complex, $[MoO_2(C_3H_4O_3)_2]^{2-}$, the values for the formation constant and enthalpy change are log β_{122} = 15.71 and $\Delta H^\circ = -72$ kJ mol^{-1} respectively and for the tungsten(VI) complex, $[WO_2(C_3H_4O_3)_2]^{2-}$, the values are log β_{122} = 17.47 and $\Delta H^\circ = -80$ kJ mol^{-1}. The equilibrium constant and enthalpy change for the protonation of lactate have also been determined, log K = 3.60 and $\Delta H^\circ = -1.7$ kJ mol^{-1}. The energetics of complexation is discussed in terms of the thermodynamic quantities.

Complex formation between molybdate and lactate in the region pH 7–3 has been reported by several authors[2–7] and a mononuclear complex $[MoO_2L_2]^{2-}$, where HL = $CH_3CH(OH)CO_2^-$, has been identified. Proton and ^{13}C NMR spectroscopy have provided information about the structure of the complex in solution as well as an approximate value for its stability constant.[7] The formation of two dinuclear complexes, $[Mo_2O_5L_2(H_2O)_2]^{2-}$ at pH ≈2 and its protonated form in 0.5 mol dm^{-3} $HClO_4$ have been suggested by Beltrán-Porter *et al.*[5] on the grounds of a spectrophotometric and cryoscopic study. By using the counter ion $[Co(en)_3]^{3+}$ (en = ethane-1,2-diamine) these authors isolated compounds for which the chemical analyses agreed with the composition of the above-mentioned mono- and di-nuclear complexes.

The tungsten(VI) lactate system has received much less attention,[7–9] but the existence at pH ≈5 of a mononuclear dilactate complex $[WO_2L_2]^{2-}$ analogous to the molybdenum complex has been deduced from proton and ^{13}C NMR measurements.[7] The stoichiometry of a much weaker complex occurring at the same pH could not be established from these measurements.

The aim of the present study was to supplement and extend the knowledge about these systems, first by determining formation constants of all complexes that can be identified by potentiometry in the range pH 7–2 and second by determining the enthalpy and entropy changes for the major complexes from calorimetric measurements using the now known formation constants. A comparison of the thermodynamic quantities for the two systems ought to provide valuable insight into the energetics of the co-ordination chemistry of molybdenum(VI) and tungsten(VI).

Experimental

Reagents and Solutions.—All reagents were of analytical grade (Merck) and solutions were prepared with water obtained from a Millipore Milli-Q system. Sodium molybdate and sodium tungstate stock solutions were prepared from the recrystallized salts $Na_2MoO_4{\cdot}2H_2O$ and $Na_2WO_4{\cdot}2H_2O$ and standardized gravimetrically as described previously.[10,11] Hydrochloric acid was standardized indirectly against potassium hydrogenphthalate by titration with sodium hydroxide. Sodium chloride was purified as described previously.[11] Sodium lactate (Riedel de Haen) was used as received; the stock solution (≈50% w/w) was standardized with hydrochloric acid. The concentration of a diluted solution was again checked by refinement in the calculation of the pK_a value of lactic acid using the program SUPERQUAD.[12]

Potentiometric Titrations.—Mixtures of sodium molybdate and sodium lactate (50–90 cm^3) were titrated with hydrochloric acid at 25 °C using a Metrohm 636 Titroprocessor. All solutions were made 1.0 mol dm^{-3} with respect to chloride ions by addition of the appropriate amount of recrystallized sodium chloride. To exclude carbon dioxide from the system, a stream of purified nitrogen was passed through 1.0 mol dm^{-3} NaCl and then bubbled slowly through the titration solution. The initial concentrations (mol dm^{-3}) of molybdate and lactate were as follows: 0.005, 0.1; 0.01, 0.01; 0.01, 0.02; 0.01, 0.05; 0.05, 0.01; 0.05, 0.05; and 0.05, 0.10. The titrations were done in duplicate covering the range pH$_c$ 7.0–1.0. A total of 600 data points were used in the computations.

The initial concentrations (mol dm^{-3}) of tungstate and lactate were as follows: 0.001, 0.003; 0.003, 0.009; 0.005, 0.01; 0.009, 0.07; 0.01, 0.02; and 0.01, 0.10; the pH$_c$ range covered was 8–2. Below pH$_c$ ≈2 precipitation of tungstate occurred, presumably as the trioxide. Most of the titrations were carried out in duplicate and 530 data points were used in the computations. Lower concentrations of tungstate or a greater excess of lactate had to be used than in the case of molybdate to prevent the slow reactions occurring in tungstate solutions acidified to $Z > 1.2$ (Z = degree of protonation).[11] For the determination of the protonation constant of lactate (which also served as a check on the concentration of various diluted lactate solutions) six titrations with hydrochloric acid were carried out.

The free hydrogen-ion concentrations, h, was determined by measuring the potential, E, to ±0.2 mV using a Ross combination electrode (Orion) with a 3.0 mol dm^{-3} potassium chloride bridge solution. Equation (1) was used to calculate h from the

$$E = E^\circ + 59.16 \log h + E_j \qquad (1)$$

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* This series has been previously entitled 'Molybdenum(VI) Complex Formation'.

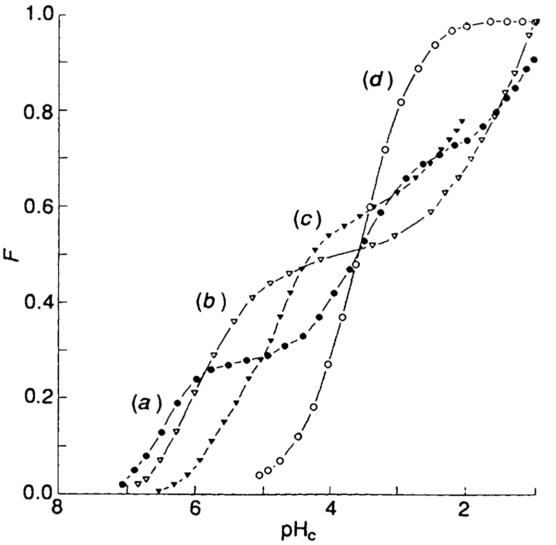

Fig. 1 Plots of function F *versus* pH$_c$ for some representative potentiometric titrations. Initial concentrations (molybdate:lactate): (*a*) 0.01:0.05, (*b*) 0.01:0.02, (*c*) 0.01:0.01 and (*d*) 0:0.05 mol dm^{-3}

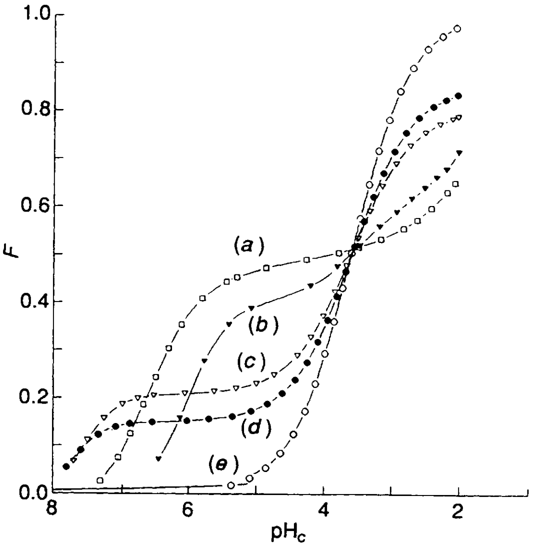

Fig. 2 Plots of function F *versus* pH$_c$ for some representative potentiometric titrations. Initial concentrations (tungstate:lactate): (*a*) 0.005:0.01, (*b*) 0.001:0.003, (*c*) 0.009:0.07, (*d*) 0.009:0.10 and (*e*) 0:0.05 mol dm^{-3}

measured potential at each titration point. Values for E° and E_j were determined from titrations of 1.0 mol dm^{-3} NaCl with HCl as described by Rossotti.[13] For brevity, $-\log h$ is denoted by pH$_c$.

Calorimetric Titrations.—An isothermal titration calorimeter, Tronac model 550, described elsewhere[14] was used for the enthalpy measurements. Solutions containing molybdate (or tungstate) and lactate (25.0 cm^3) were titrated with hydrochloric acid from a precision microburette (2.5 cm^3) and the data collected as described previously.[10] The initial concentrations of molybdate and lactate were 0.01 and 0.05 mol dm^{-3} respectively and those of tungstate and lactate 0.01 and 0.0497 mol dm^{-3}. The pH$_c$ range covered was 7.5–2.0. To determine the enthalpy involved in the protonation of lactate a 0.10 mol dm^{-3} sodium lactate solution was titrated with 1.0 mol dm^{-3} hydrochloric acid. Again all solutions were made 1.0 mol dm^{-3} with respect to chloride by addition of the appropriate amount of recrystallized sodium chloride. Titrations were carried out in duplicate. The data were corrected for the endothermic heat of dilution of hydrochloric acid titrated into sodium chloride by using results of previous blank titrations.[1,15]

Results and Discussion

Potentiometric Investigation.—The various protonation, condensation and complexation reactions that can take place when a solution containing molybdate (or tungstate) and lactate is acidified can be represented by the general equation (2). For

$$p\,\mathrm{MoO_4}^{2-} + q\,\mathrm{HL}^- + r\,\mathrm{H}^+ \rightleftharpoons [\mathrm{complex}]^{(2p+q-r)-} \quad (2)$$

brevity, species with overall formation constants β_{pqr} are denoted by the coefficients describing their stoichiometry, for example [0,1,1] for lactic acid. In the treatment of the data it is important to take into account all side-equilibria of lactate, molybdate and tungstate. The protonation constant of lactate was determined in separate titrations. The value obtained, log $\beta_{011} = 3.597 \pm 0.005$ can be compared with that determined in 1.0 mol dm^{-3} NaClO$_4$, namely 3.63 ± 0.02.[16]

For the equilibria involving uncomplexed molybdate the species $[\mathrm{HMoO_4}]^-$, $[\mathrm{MoO_2(OH)_2(H_2O)_2}]$, $[\mathrm{MoO_2(OH)(H_2O)_3}]^+$, $[\mathrm{HMo_2O_7}]^-$, $[\mathrm{Mo_7O_{24}}]^{6-}$, $[\mathrm{HMo_7O_{24}}]^{5-}$, $[\mathrm{H_2Mo_7O_{24}}]^{4-}$, $[\mathrm{H_3Mo_7O_{24}}]^{3-}$, $[\mathrm{Mo_8O_{26}}]^{4-}$ and $[\mathrm{HMo_2O_6}]^+$ were taken into account using previously determined equilibrium constants pertaining to a 1 mol dm^{-3} NaCl medium at 25 °C.[17–19] Acidification of tungstate to $Z > 1.2$ leads to the formation of polyanions which are involved in slow equilibria. Therefore lactate had to be present in sufficient excess in all titrations to suppress these reactions by reducing the free tungstate concentrations to a minimum through complexation. The higher the tungstate concentration the greater the excess of lactate which is needed to inhibit the slow reactions. Known equilibrium constants[11] for the species $[\mathrm{W_6O_{20}(OH)_2}]^{6-}$, $[\mathrm{W_7O_{24}}]^{6-}$, $[\mathrm{HW_7O_{24}}]^{5-}$ and $[\mathrm{H_2W_{12}O_{42}}]^{10-}$ have been used in the calculations to account for uncomplexed tungstate at $Z < 1.2$. Under the experimental conditions the concentrations of these polyions were relatively small. For the two titrations pertaining to a two-fold excess of lactate the maximum percentage concentration of the heptamer (in terms of total W) was about 8% at pH$_c$ ≈6 and less than 1% for all other titrations.

The results of some representative titrations are shown in Figs. 1 and 2 as plots of F against pH$_c$. The function F [equation (3)] represents the fraction of the total negative charge

$$F = [H - h + (K_w/h)]/(2B + C) \quad (3)$$

neutralized due to reaction with protons where H, B and C are the analytical concentrations of hydrogen ions, molybdate or tungstate, and lactate respectively. It is seen that complex formation results in the uptake of protons at much higher pH$_c$ than in the case of lactate alone. At low pH$_c$ on the other hand, protonation of the complexes is more difficult than protonation of lactate. The inflexions exhibited by the curves pertaining to excess of lactate show that after all molybdate or tungstate has reacted very little protonation takes place until the pH$_c$ is low enough ($\gtrsim 5$) for free lactate to become protonated and F then increases again.

The titration data were treated with the computer program SUPERQUAD[12] to search for the reaction model that would give the best description of the data. It soon became apparent that for both systems only one species namely a $[1,2,2]^{2-}$ complex, corresponding to the formulae $[\mathrm{MoO_2L_2}]^{2-}$ and $[\mathrm{WO_2L_2}]^{2-}$, predominates in the range pH$_c$ 2–7. For this complex $F = 0.5$ which explains the crossing at this point of the curves that correspond to complete complexation of molybdate or tungstate (Figs. 1 and 2). Curve (*c*) in Fig. 1 pertains to a solution containing uncomplexed molybdate species *e.g.* $[\mathrm{HMoO_4}]^-$ and $[\mathrm{Mo_7O_{24}}]^{6-}$. The further addition of the two dilactate species $[1,2,1]^{3-}$ and $[1,2,3]^-$ to the reaction model for the molybdate system, together with some other minor

Table 1 Reaction models and values for the formation constants of the various molybdenum(VI) and tungsten(VI) lactate complexes

	$\log \beta_{pqr} \pm 3\sigma$	
Complex	Mo^{VI}	W^{VI}
$[1,2,1]^{3-}$	7.46 ± 0.46	
$[1,2,2]^{2-}$	15.71 ± 0.01	17.47 ± 0.01
$[1,2,3]^{-}$	16.78 ± 0.09	18.38 ± 0.11
$[1,1,2]^{-}$	11.76 ± 0.03	13.03 ± 0.07
[1,1,3]	12.66 ± 0.32	14.56 ± 0.13
$[2,2,2]^{4-}$	16.07 ± 0.14	—
$[2,2,3]^{3-}$	21.70 ± 0.14	25.47 ± 0.11
$[2,2,4]^{2-}$	24.97 ± 0.30	—
$[2,1,3]^{2-}$	18.44 ± 0.38	—
$[2,1,4]^{-}$	21.53 ± 0.12	—
[2,1,5]	23.12 ± 0.14	—
[0,1,1]	3.603 ± 0.005	3.596 ± 0.005
[0,1,1]	3.597 ± 0.004*	

* Value calculated from titration data of lactate alone.

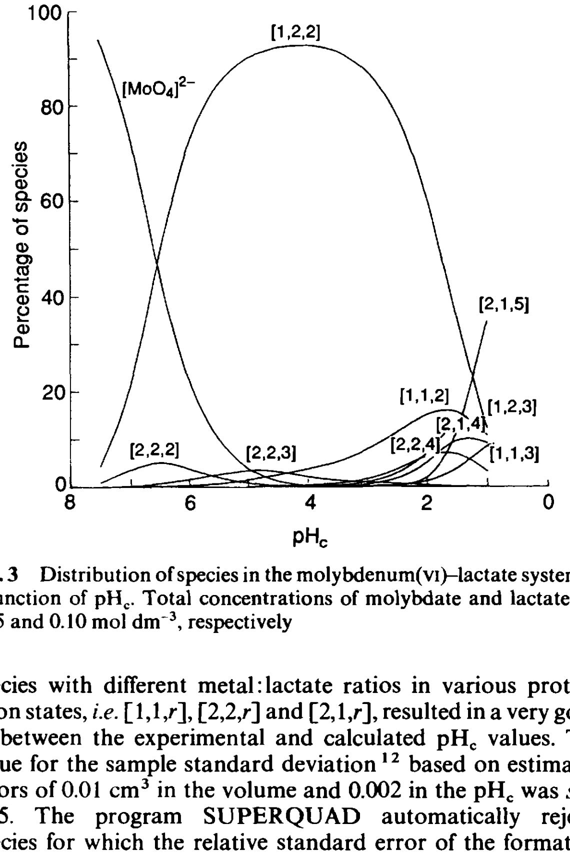

Fig. 3 Distribution of species in the molybdenum(VI)–lactate system as a function of pH_c. Total concentrations of molybdate and lactate are 0.05 and 0.10 mol dm^{-3}, respectively

species with different metal:lactate ratios in various protonation states, *i.e.* [1,1,*r*], [2,2,*r*] and [2,1,*r*], resulted in a very good fit between the experimental and calculated pH_c values. The value for the sample standard deviation[12] based on estimated errors of 0.01 cm^3 in the volume and 0.002 in the pH_c was s = 1.25. The program SUPERQUAD automatically rejects species for which the relative standard error of the formation constant is greater than 33% (or $3\sigma \gtrsim 0.43$ log units). Two of the species retained in the model namely $[1,2,1]^{3-}$ and $[2,1,3]^{2-}$ have relative standard deviations of 30 and 26% respectively, which are very close to the rejection limit. Since the maximum concentration of these species never exeeded 3% in any of the titrations their inclusion in the model does not seem justified. For the sake of completeness, however, the formation constants of all species retained in the best reaction model are listed in Table 1. The molybdate:lactate stoichiometry of the complexes is typical of that observed for other α-hydroxy carboxylate ligands such as tartrate and citrate.[1,10,15] However, the latter ligands differ from lactate in that several stable complexes are formed in the range pH_c 2–7. This difference stems from the extra carboxylate or hydroxyl groups of these ligands which allow a greater variety of co-ordination and protonation possibilities. Typical of these systems is the formation (through successive protonation) of a series of complexes of comparable stability, all having the same metal to ligand ratio.

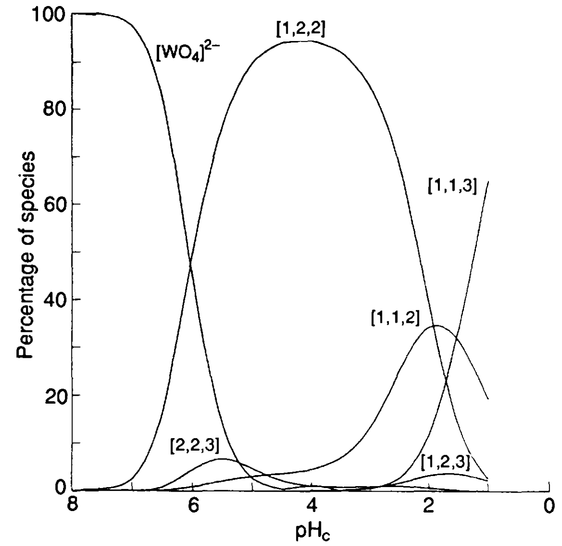

Fig. 4 Distribution of species in the tungstate(VI)–lactate system as a function of pH_c. Total concentrations of tungstate and lactate are 0.001 and 0.003 mol dm^{-3}, respectively

In the case of the tungstate system slow reactions necessitated restrictions on the experimental conditions so that fewer minor species were detected. The species retained in the best model, however, all have analogues in the model for the molybdenum system and all the formation constants have relative standard deviations of less than ≈10%; the value of s = 1.8 indicated a satisfactory fit. The models and values for the formation constants of the various complexes are listed in Table 1.

To check for consistency the protonation constant of lactate was refined together with the constants of the complexes in the final computer run. The values obtained for log β_{011} namely 3.596 and 3.603 are in excellent agreement with that obtained from the separate titrations, 3.597.

The distributions of the complexes as a function of pH_c at concentrations chosen to illustrate the stability regions are shown in Figs. 3 and 4. The formation constant of the $[MoO_2L_2]^{2-}$ complex, log β_{122} = 15.71, can be compared with the approximate value of 14.7 calculated from NMR measurements by Gil and co-workers.[6,7] These authors also obtained some information about the structures of both the tungsten and molybdenum $[1,2,2]^{2-}$ complexes. It can be assumed that the carboxyl oxygens are *trans* to the terminal oxygens of the *cis* MoO_2 and WO_2 units similar to the situation in tartrate,[20] malate[21] and citrate[22,23] complexes of known crystal structures (Fig. 5).

The values of the stability constants show that the tungstate lactate complexes are significantly more stable than the molybdenum lactate complexes; the difference between the values of the formation constant of the $[1,2,2]^{2-}$ complex, for instance, is about 1.8 log units. The thermodynamics underlying this difference is discussed in the next section.

Enthalpimetric Investigation.—The results of the enthalpimetric titrations are shown in Fig. 6 where the total amount of heat measured, *Q*, is plotted against the molar ratio of acid added to molybdate or tungstate. Both curves show a break at a mole ratio of approximately 1:2 in accordance with the stoichiometry of the major complex identified from the potentiometric measurements. The heat evolved in the formation of the tungsten complex is greater than that for the molybdenum complex. Included in the measured heat is the contribution from the protonation of lactate which is relatively small despite the five-fold excess of lactate. An excess of lactate is essential to ensure complete complexation of molybdate and tungstate

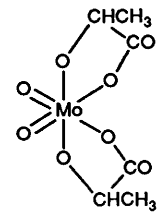

Fig. 5 Structure of $[MoO_2(C_3H_4O_3)_2]^{2-}$ complex

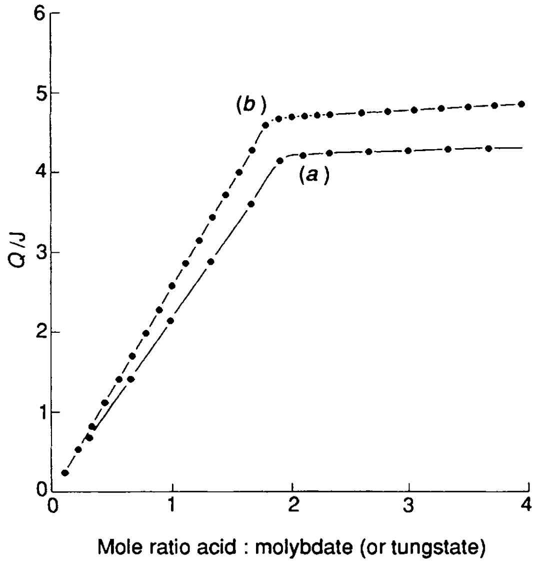

Fig. 6 Measured heat, Q, as a function of the molar ratio of acid to molybdate (or tungstate) for the titration of (*a*) 0.01 mol dm^{-3} molybdate and 0.05 mol dm^{-3} lactate, and (*b*) 0.01 mol dm^{-3} tungstate and 0.0497 mol dm^{-3} lactate with 1.0 mol dm^{-3} HCl

upon acidification thereby excluding side-reactions involving polyanion formation. To account for the heat involved in the protonation of free lactate the enthalpy change for the reaction in 1 mol dm^{-3} NaCl was determined in a separate titration. The value obtained, $\Delta H^\circ = -1.7$ kJ mol^{-1}, can be compared with those given by Smith and Martell,[24] 0.33 and -7.1 kJ mol^{-1} at ionic strengths $I = 0$ and 2.0 mol dm^{-3} respectively. Owing to the very small concentrations of the minor complexes under the conditions of the enthalpimetric titrations, calculation of their ΔH° values was not justified, especially at low pH$_c$ where several equilibria overlap and very little heat is measured. The enthalpy change for the formation of the $[1,2,2]^{2-}$ complex for each metal was calculated from the data represented by the first straight-line segment of the curves (Fig. 6) and for which the concentrations of the other complexes were less than ≈2%.

Table 2 Thermodynamic quantities (kJ mol^{-1}) for complex formation in 1.0 mol dm^{-3} NaCl at 298.15 K

Complex	ΔG°	ΔH°	$T\Delta S^\circ$
$[MoO_2L_2]^{2-}$	-89.67 ± 0.06	-72 ± 2	18 ± 2
$[WO_2L_2]^{2-}$	-99.72 ± 0.06	-80 ± 2	20 ± 2
HL^-	-20.53 ± 0.02	-1.7 ± 0.2	18.8 ± 0.2

The thermodynamic quantities for the formation of the $[1,2,2]^{2-}$ complexes of tungsten(VI) and molybdenum(VI) are listed in Table 2. The entropy change for complexation is about the same for tungsten and molybdenum and it is the difference in enthalpy change which is responsible for the greater stability of the tungstate complex. The enthalpy change for the tungstate complex is about 8 kJ mol^{-1} more favourable than for the molybdate complex. This result, which reflects the greater tendency of tungsten(VI) to expand its co-ordination number from four to six, has also been observed for citrate complexes of molybdenum and tungsten.[16] The tungsten complexes are more stable than the molybdenum complexes by an amount varying from 7 to 17 kJ mol^{-1}. In the case of the condensation of the tetrahedral $[WO_4]^{2-}$ and $[MoO_4]^{2-}$ ions to form the heptapolyanions $[W_7O_{24}]^{6-}$ and $[Mo_7O_{24}]^{6-}$ in which all the molybdenum and tungsten atoms are octahedrally co-ordinated the difference in enthalpy change is 99 kJ mol^{-1} which is equivalent to about 14 kJ mol^{-1} for the conversion of a tetrahedron into an octahedron.[11] The main driving force for all these reactions is the enthalpy change which emanates from the additional bond energy when the co-ordination number is increased from four to six. A question which arises is why a dilactate complex is formed and not a monolactate complex in which the metal is also six-co-ordinated, for example in the case of molybdenum, $[MoO_3L(H_2O)]^{2-}$, the analogue of the very stable oxalate complex[10,25] $[MoO_3(C_2O_4)(H_2O)]^{2-}$. The answer lies in the very favourable enthalpy change for the formation of the dilactate complex; for the $[MoO_3(C_2O_4)(H_2O)]^{2-}$ complex the entropy change is the same as that for the dilactate complex, $[MoO_2L_2]^{2-}$, but the enthalpy change is about 12 kJ mol^{-1} less favourable. Furthermore, for the formation of the monolactate complex $[MoO_3L(H_2O)]^{2-}$, six-co-ordination is achieved at the cost of the very strongly bound hydroxyl proton of lactate (pK ≈ 11). However, when the dilactate complex $[MoO_2L_2]^{2-}$ is formed the bond energy lost by the dissociation of *two* hydroxyl protons is regained (with profit) through the formation of a water molecule, resulting in the favourable enthalpy change observed. This argument can also be applied to other α-hydroxy carboxylate ligands for which the same situation prevails, in particular the tartrate ion for which it has been shown that $[1,2,r]$ complexes are formed with molybdenum but not $[1,1,r]$ complexes.[1]

Conclusion

The results of this investigation show that both molybdenum(VI) and tungsten(VI) form one major complex with lactate, *i.e.* $[MoO_2(C_3H_4O_3)_2]^{2-}$ and $[WO_2(C_3H_4O_3)_2]^{2-}$, as well as several minor complexes. Thermodynamic quantities for the major complexes have been determined. The tungsten complex is more stable than the molybdenum complex due to a *ca.* 8 kJ mol^{-1} more favourable enthalpy change. The tendency of lactate (and some other α-hydroxy carboxylate ligands) to form a di- rather than a mono-ligated complex can be rationalized in terms of its bidentate behaviour towards molybdenum(VI) [and tungsten(VI)] and the enthalpy involved in the expansion of the co-ordination number of the metal from four to six.

Acknowledgements

Financial support by the Foundation for Research Development and the University of Stellenbosch is gratefully acknowledged.

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Received 29*th June* 1992; *Paper* 2/03417D