Molybdenum(VI) Complex Formation. Part 7.[1] Equilibria and Thermodynamic Quantities for the Reactions with Nitrilotriacetate

Johannes J. Cruywagen,* J. Bernard B. Heyns and Elisabeth A. Rohwer
Department of Chemistry, University of Stellenbosch, Stellenbosch 7600, South Africa

Complex formation between molybdate and nitrilotriacetate (nta) has been investigated in the range pH 1.0–9.0 by potentiometric, spectrophotometric and enthalpimetric titrations at 25 °C in 1.0 mol dm^{-3} NaCl. The 'best' reaction model comprises seven complexes, of which three are mononuclear and four dinuclear. The formation constants of the complexes, denoted by β_{pqr}, where the subscripts p, q and r refer to the stoichiometric coefficients in the general formula $[(\text{MoO}_4)_p(\text{nta})_q\text{H}_r]^{(2p+3q-r)-}$, have the values $\log \beta_{112} = 17.78$, $\log \beta_{113} = 21.02$, $\log \beta_{114} = 22.57$, $\log \beta_{227} = 45.16$, $\log \beta_{228} = 47.95$, $\log \beta_{215} = 30.74$ and $\log \beta_{216} = 33.09$. Enthalpy and entropy changes for complexes occurring in sufficiently high concentrations were calculated from the calorimetric data using these formation constants: $\Delta H^\circ_{112} = -69$, $\Delta H^\circ_{113} = -71$, $\Delta H^\circ_{227} = -123$ and $\Delta H^\circ_{228} = -132$ kJ mol^{-1}. Thermodynamic parameters for the protonation of nta in 1.0 mol dm^{-3} NaCl have also been determined: $\log \beta_{011} = 8.78$, $\log \beta_{012} = 11.04$, $\log \beta_{013} = 12.73$ and $\log \beta_{014} = 13.69$; $\Delta H^\circ_{011} = -24.2$, $\Delta H^\circ_{012} = -24.4$ and $\Delta H^\circ_{013} = -26.6$ kJ mol^{-1}.

Nitrilotriacetate [nitrilotriacetic acid, $\text{H}_3\text{nta} = \text{N(CH}_2\text{CO}_2\text{H)}_3$] has three oxygen donor atoms in addition to the selective nitrogen donor atom and it can complex all metal ions by forming up to three stable five-membered chelate rings.[2] Complexation of molybdenum(VI) by nta has been investigated by various researchers and the existence of a particularly stable complex, $[\text{MoO}_3(\text{nta})]^{3-}$, is well established.[3–9] Values for its formation constant pertaining to different ionic media have been determined by potentiometry.[4,5,8] A value for the enthalpy change of the complexation reaction has been deduced from the change in the stability constant with temperature; the kinetics of this reaction has also been investigated and a mechanism proposed.[8]

It has been concluded from NMR investigations that the structure of this complex is probably similar in aqueous and non-aqueous solvents and at least grossly similar to that found in the crystal.[7] The crystal structure of the salt, $\text{K}_3[\text{MoO}_3(\text{nta})]\cdot\text{H}_2\text{O}$ has been determined which shows that the ligand co-ordinates in a tridentate manner through its nitrogen atom and two of the three carboxylate oxygen atoms.[6] A dinuclear complex $[\text{Hpy}]_2[\text{Mo}_2\text{O}_5(\text{Hnta})_2]$ has been obtained[9] from the reaction of pyridine (py) and nitrilotriacetic acid with MoO_3 in aqueous solution at pH 7–8. The crystal structure determination showed a non-linear oxo bridge (167.0°) between the two molybdenum atoms and with nta co-ordination similar to that in the mononuclear complex.[9]

All these investigations have been carried out at pH > 6 where interference from the protonation and condensation reactions of molybdate is negligible. Apparently no information about the composition and stability of complexes formed at lower pH is available. Previous studies of molybdenum(VI) complexation with other carboxylate ligands have shown that systems of this nature can be unravelled by computer treatment of high-quality potentiometric data provided all the molybdate and ligand side-equilibria are taken into account.[10]

In this paper we report the results of a potentiometric, spectrophotometric and enthalpimetric investigation of molybdenum(VI)–nta complex formation in the range pH 9–1. A number of complexes (including the two mentioned above) have been identified and thermodynamic quantities determined for their formation in aqueous solution.

Experimental

Reagents and Solutions.—All reagents were of analytical grade (Merck, BDH and Aldrich) and solutions were prepared with water obtained from a Millipore Milli-Q system. Sodium molybdate stock solution was prepared from the recrystallized salt $\text{Na}_2[\text{MoO}_4]\cdot 2\text{H}_2\text{O}$ and standardized gravimetrically as described previously.[11] Sodium nitrilotriacetate was used as received and standardized by a potentiometric titration with hydrochloric acid. Hydrochloric acid was standardized indirectly against potassium hydrogenphthalate by titration with sodium hydroxide. Sodium chloride was purified as described previously.[11]

Potentiometric Titrations.—Mixtures of sodium molybdate and sodium nitrilotriacetate (70 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 nitrilotriacetate were as follows: 0.0075, 0.075; 0.01, 0.01; 0.01, 0.05; 0.01, 0.075; 0.025, 0.01; 0.05, 0.05 and 0.075, 0.075, thus obtaining solutions with equal concentrations of molybdate and nitrilotriacetate or an excess of one of these reactants. The pH_c range covered was 9.0–1.0 and 600 data points were collected. The protonation constants of nta were determined by titration of solutions (70 cm^3 0.02 or 0.05 mol dm^{-3}) of the sodium salt with 1.0 mol dm^{-3} hydrochloric acid. All titrations were carried out in duplicate.

The free hydrogen concentration, 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} KCl bridge solution. Equation (1) was used to calculate h from the

$$E = E^\circ + 59.16 \log h + E_\text{j} \qquad (1)$$

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.[12] For brevity $-\log h$ is denoted by pH_c.

Spectrophotometric Titrations.—A Varian Cary 210 spectrophotometer in conjunction with an Apple IIe computer was used for absorption measurements and data collection. Cuvette holders were water-jacketed to maintain the temperature at 25 °C by circulation of water from a thermostat. The ionic medium was 1.0 mol dm^{-3} NaCl and the absorbances were measured against 1.0 mol dm^{-3} NaCl solution in the wavelength range 212–300 nm using a flow-through cell of path length 1.0 cm. The concentrations of molybdate and nta in the reaction vessel (kept in a water-bath at 25 °C) were 2.0×10^{-4} and 2.5×10^{-4} mol dm^{-3} respectively. The titrant solution contained in addition to hydrochloric acid (0.01 mol dm^{-3}) also molybdate and nta at the same concentration as in the test solution. The hydrogen-ion concentration was measured as described for the potentiometric titrations. Thirteen spectra were recorded at pH_c intervals of ≈ 0.25 in the range 5–2.7. A similar titration of nta with hydrochloric was carried out from which the individual spectra of $Hnta^{2-}$ and H_2nta^- were calculated. These spectra were supplied to the program SPECFIT[13] for the treatment of the absorption data pertaining to complexation. In the wavelength range used the absorption of nta species is very small compared to that of molybdate.

Calorimetric Titrations.—An isothermal calorimeter, Tronac model 1250, was used for the enthalpy measurements. Solutions containing molybdate and nta (20.0 cm^3) were titrated with hydrochloric acid from a precision microburette (2.5 cm^3). The data were collected automatically by means of a personal computer using software supplied by Tronac. Two types of titrations were performed. In the first the initial concentration of both molybdate and nta was 0.01 mol dm^{-3} and the pH_c range covered was 9.0–2.0. For the second the initial concentrations of molybdate, nta and hydrochloric acid were 0.04, 0.06 and 0.08 mol dm^{-3} respectively covering the range pH_c 7.5–3.0.

Separate titrations of nta (0.01 mol dm^{-3} nta^{3-} and 0.04 mol dm^{-3} $Hnta^{2-}$) with hydrochloric acid (1.0 mol dm^{-3}) were performed to determine the enthalpy involved in the protonation of nta. 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.[14]

Results and Discussion

Potentiometric Investigation.—The various protonation, condensation and complexation reactions that can take place when a solution containing molybdate and nta is acidified are represented by the general equation (2). For brevity species with

$$p[MoO_4]^{2-} + q\,nta^{3-} + rH^+ \rightleftharpoons [complex]^{(2p+3q-r)-} \qquad (2)$$

overall formation constants β_{pqr} will often be described by the stoichiometric coefficients defining their composition, for example $[1,0,1]^-$ for the hydrogenmolybdate ion $[HMoO_4]^-$.

The results of some representative titrations of nta and of mixtures of molybdate and nta with hydrochloric acid are shown in Fig. 1 as plots of F against pH_c. The function F [equation (3)] represents the fraction of the total negative

$$F = (H - h)/(2B + 3C) \qquad (3)$$

charge neutralized due to protonation where H, B and C are the analytical concentrations of acid, molybdate and nta respectively. An F value of 1.0 therefore indicates an average charge of zero for the species in solution. At pH_c 4.5–6.5 where $Hnta^{2-}$ is the major ligand species a value of 0.33 is indicated by the F *vs.* pH_c curve (*e*) in Fig. 1. A decrease in pH_c causes further protonation of nta until at $pH_c \approx 1$ about 40% is in the form of H_4nta^+. The F curves for equal concentrations of molybdate and nta show an inflexion at pH_c 5 where F has a value of 0.4 which corresponds with the formation of a $[1,1,2]^{3-}$ complex.

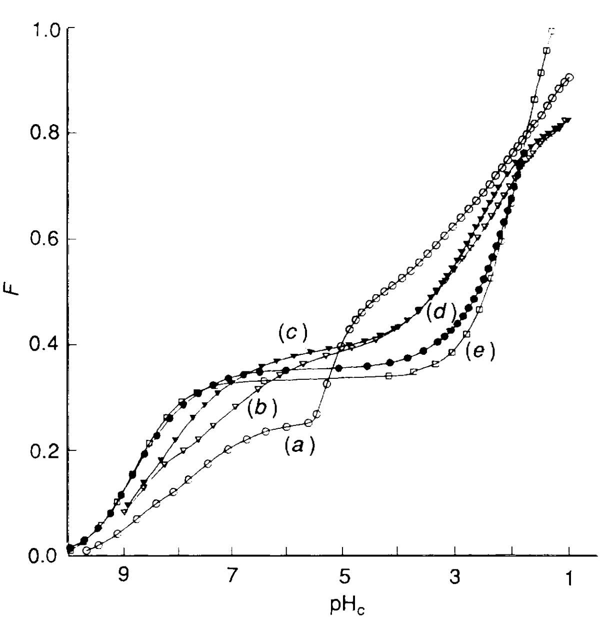


Fig. 1 Plots of function F *versus* pH_c for some representative potentiometric titrations. Initial concentrations (molybdate : nta): (*a*) 0.025 : 0.010, (*b*) 0.010 : 0.010, (*c*) 0.050 : 0.050, (*d*) 0.010 : 0.050, (*e*) 0 : 0.020 mol dm^{-3}

To create conditions that would be favourable for the formation of complexes with stoichiometry other than a 1 : 1 ratio of molybdate to nta an excess of either molybdate or nta was needed. In the treatment of the data it was therefore important to consider all side-reactions of uncomplexed molybdate and nta with protons. The molybdate species $[HMoO_4]^-$, $[MoO_3(OH_2)_3]$, $[MoO_2(OH)(OH_2)_3]^+$, $[HMo_2O_7]^-$, $[Mo_7O_{24}]^{6-}$, $[HMo_7O_{24}]^{5-}$, $[H_2Mo_7O_{24}]^{4-}$, $[H_3Mo_7O_{24}]^{3-}$, $[Mo_8O_{26}]^{4-}$ and $[HMo_2O_6]^+$ were taken into account using previously determined equilibrium constants pertaining to 1.0 mol dm^{-3} NaCl medium at 25 °C.[15–17] For pK_w the previously determined value of 13.71 was used.

The protonation constants of nta in 1.0 mol dm^{-3} NaCl were determined in separate titrations. The values obtained, $\log \beta_{011} = 8.78 \pm 0.01$, $\log \beta_{012} = 11.04 \pm 0.01$, $\log \beta_{013} = 12.73 \pm 0.01$, and $\log \beta_{014} = 13.69 \pm 0.05$, can be compared with those reported[18] for 1.0 mol dm^{-3} $NaClO_4$ namely $\log \beta_{011} = 8.92$, $\log \beta_{012} = 11.33$, $\log \beta_{013} = 13.14$ and $\log \beta_{014} = 14.53$.

The potentiometric data were treated with the program SUPERQUAD[19] to search for the reaction model that would give the best description of the system. The program automatically rejects species for which the relative standard deviation of the formation constant is greater than 33% (or $3\sigma > 0.43$ log units). On account of our previous experience with systems of this type, all possible species with $p = 1$–4 and having reasonable q and r values have been considered in various reaction models. The well characterized $[1,1,2]^{3-}$ complex could easily be identified as the first major complex which forms upon acidification of a mixture of molybdate and nta. With decrease in pH_c this complex is further protonated to form the $[1,1,3]^{2-}$ and $[1,1,4]^-$ species. The other complexes included in the best-fit model are dinuclear, namely $[2,1,5]^{2-}$, $[2,1,6]^-$, $[2,2,7]^{3-}$ and $[2,2,8]^{2-}$. The molybdenum : nta stoichiometry of these complexes is typical of those previously observed for other molybdenum–ligand systems.[14] The

$[2,2,8]^{2-}$ complex has been isolated in the solid state as a pyridinium salt, $[Hpy]_2[Mo_2O_5(Hnta)_2]$, of which the crystal structure has been determined.[9] The only minor species (< 10%) under all conditions investigated, is the $[2,1,5]^{2-}$. The distribution of the complexes as a function of pH_c at equimolar concentrations (0.5 mol dm^{-3}) of molybdate and nta is shown in Fig. 2.

The formation constant obtained for the $[1,1,2]^{3-}$ complex, $\log \beta_{112} = 17.78$, can be compared with the values previously reported for different ionic media namely, 17.90 (0.5 mol dm^{-3} $NaClO_4$),[4] 18.09 (1.0 mol dm^{-3} $NaClO_4$)[7] and 18.60 (3.0 mol dm^{-3} $NaClO_4$).[5]

Spectrophotometric Investigation.—The complexation reactions were investigated by measuring the change in absorption of molybdate with pH_c in the UV region. At the rather low molybdate concentration required for the absorption measurements an excess of nta is essential to promote complex formation, especially at $pH_c < 5$, where the formation of protonated and condensed molybdate species must be counteracted. The excess of nta should be limited, however, because it also absorbs in the UV region, although much more weakly than does molybdate. The spectra of $Hnta^{2-}$ and H_2nta^- were determined in a separate experiment and have been supplied to the program. The titration was started at pH_c 5 where all ligand is already in the form of $Hnta^{2-}$ and ≈50% of the total amount already complexed. Under the conditions chosen for the experiment (2.0×10^{-4} mol dm^{-3} Mo^{VI} and 2.5×10^{-4} mol dm^{-3} nta) all molybdate side-reactions, except the formation of monomeric molybdic acid $[MoO_3(OH_2)_3]$ could be neglected. The percentage concentration of $[MoO_3(OH_2)_3]$, however, was relatively small reaching a maximum of only ≈9% in the solution at the lowest pH_c namely 2.7. The spectrum and formation constant of this species as well as the spectrum of $[MoO_4]^{2-}$ had been determined previously[20] and were supplied to the program as known quantities.

The unknowns to be calculated were therefore the formation constants and spectra of the $[1,1,2]^{3-}$ and $[1,1,3]^{2-}$ complexes. The values for the formation constants obtained, $\log \beta_{112} = 17.84$ and $\log \beta_{113} = 20.90$, agreed very well with those obtained by potentiometry namely $\log \beta_{112} = 17.78$ and $\log \beta_{113} = 21.02$. The slightly greater difference between the constants of the $[1,1,3]^{2-}$ complex (perhaps not significant) can be ascribed to the incipient formation of the $[1,1,4]^-$ complex (3% at pH 2.7) which was neglected in the calculations. The spectra of the species in question are shown in Fig. 3. Although the differences in the absorbances of the $[1,1,2]^{3-}$ and $[1,1,3]^{2-}$ complexes in the wavelength range 212–300 nm are rather small, a quite satisfactory value of β_{113} could be calculated because of the difference in the shapes of the spectral curves and the large number of wavelengths used; obviously high-quality data are also an important requisite. Characterization of the other complexes by spectrophotometry was not attempted mainly because of the great overlap of equilibria and the relatively small change in absorption with pH_c. The good agreement between the spectrophotometric and potentiometric results for the $[1,1,2]^{3-}$ and $[1,1,3]^{2-}$ complexes, however, can be regarded as indirect support for the other species in the model derived from the potentiometric data.

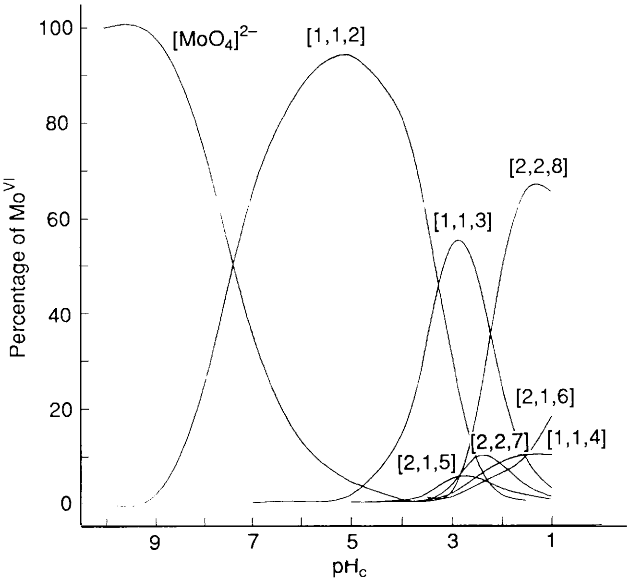


Fig. 2 Distribution of species in the molybdenum(VI)–nitriloacetate system as a function of pH_c for an equimolar solution 0.05 mol dm^{-3}

Enthalpimetric Investigation.—The results obtained in an enthalpimetric titration of an equimolar solution of molybdate and nta (0.01 mol dm^{-3}) with hydrochloric acid are shown in Fig. 4 where the total amount of heat measured, *Q*, is plotted against the molar ratio of acid added to molybdate (or nta).

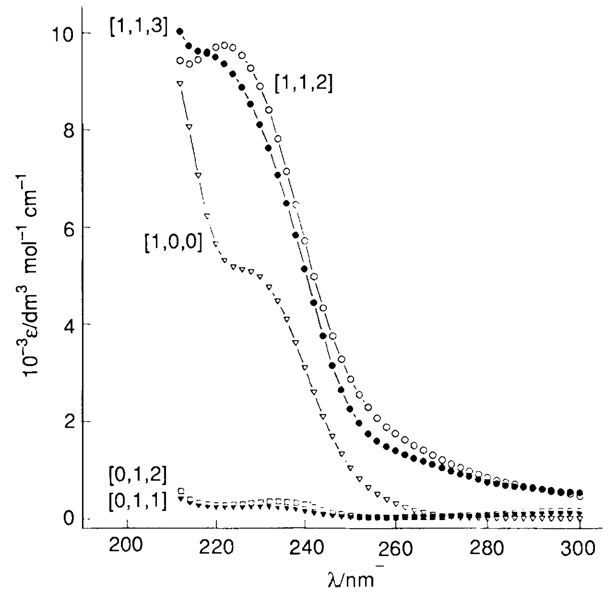


Fig. 3 Absorption spectra of various species

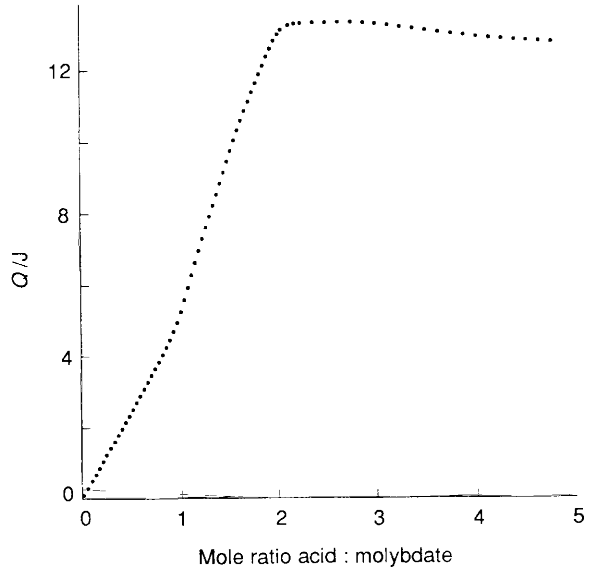


Fig. 4 Measured heat, *Q*, as a function of the molar ratio of acid to molybdate for the titration of an equimolar solution (0.01 mol dm^{-3}) of molybdate and nitrilotriacetate with 1.0 mol dm^{-3} HCl

Two breaks are observed in the curve; the first occurs at a mole ratio where the first protonation of nta is almost complete and complex formation becomes significant. The second break occurs at mole ratio of 2 : 1 indicating that the formation of the first complex $[1,1,2]^{3-}$ has been completed at that point. The enthalpy changes for the formation of the complexes were calculated from the measured heat, Q, corrected for dilution effects [equation (4)], where n_{pqr} is the number of moles formed

$$Q = \Sigma n_{pqr}\Delta H^{\circ}_{pqr} \qquad (4)$$

and ΔH°_{pqr} the molar enthalpy change of a given species $[p,q,r]$ at 25 °C in 1.0 mol dm^{-3} NaCl medium. The set of linear equations obtained from corresponding Q and n_{pqr} values was solved for the unknown ΔH°_{pqr} parameters using a BMDP least-squares program.[21]

The n_{pqr} values at each titration point were calculated, in a subroutine supplied to the BMDP program, from the concentrations of the species obtained by simultaneous solution of the three mass-balance equations (5)–(7) where b, c and h are the

$$B = b + \Sigma p\beta_{pqr}b^{p}c^{q}h^{r} \qquad (5)$$

$$C = c + \Sigma q\beta_{pqr}b^{p}c^{q}h^{r} \qquad (6)$$

$$H = h + \Sigma r\beta_{pqr}b^{p}c^{q}h^{r} \qquad (7)$$

equilibrium concentrations of $[MoO_4]^{2-}$, nta^{3-} and H$^+$ respectively.

The enthalpy changes for the protonation of nta^{3-} in 1 mol dm^{-3} NaCl, $\Delta H^{\circ}_{011} = -24.2$, $\Delta H^{\circ}_{012} = -24.4$ and $\Delta H^{\circ}_{013} = -26.6$ kJ mol^{-1}, were determined in separate titrations and treated as fixed parameters in the calculation of the ΔH°_{pqr} values of the complexes. The relatively large enthalpy change for the first protonation of nta is in agreement with the view that the nitrogen atom accepts the first proton. The small enthalpy changes for the second and third protonations are typical for this type of protonation reaction which is normally entropy driven.[22] The enthalpy changes for the protonation of nta can be compared with the literature values[23] −19.7, −18.4 and −16.7 kJ mol^{-1} pertaining to 0.1 mol dm^{-3} ionic strength.

Evaluation of reliable ΔH° values for all the species in the pH$_c$ region < 4.0 and especially for the minor species is problematical considering the great overlap of the equilibria. Conditions were therefore chosen for which the $[2,1,5]^{2-}$ and $[2,1,6]^{-}$ complexes could be neglected, *i.e.* an excess of ligand was used. Also, by increasing the concentrations of both molybdate and nta the percentage concentrations of the $[2,2,7]^{3-}$ and $[2,2,8]^{2-}$ complexes were increased. However, because the maximum percentage concentration of the $[1,1,4]^{-}$ complex was only about 10.5% and still on the increase at pH$_c$ 1 a realistic value for its enthalpy change could not be evaluated from the data. Rather than neglecting this complex, the quite reasonable approximation, based on results of previous investigations,[11,14] was made that the enthalpy changes for a complex and its protonated form are about the same. The data were therefore treated on the assumption that $\Delta H^{\circ}_{114} = \Delta H^{\circ}_{113}$. Since ΔH°_{113} could be calculated with sufficient accuracy the approximation only affected the value of ΔH°_{114}.

The calculated thermodynamic quantities for the various species are listed in Table 1. Except for a value estimated from the change in log β_{112} with temperature,[8] $\Delta H^{\circ}_{112} = -77$ kJ mol^{-1}, which shows reasonable agreement with that obtained in the present investigation (−69 kJ mol^{-1}) no other enthalpy values for complex formation of molybdate with nta are available.

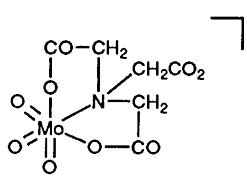
The quite favourable enthalpy change for complexation is typical for molybdate and is the result of an increase in co-ordination number of molybdenum from four to six. The enthalpy change for the formation of mononuclear complexes of the type $[1,1,r]$ with carboxylate or α-hydroxy carboxylate ligands is about −50 to −60 kJ mol^{-1}.[10,11]

It is interesting to compare the thermodynamic quantities of the nta complexes with those of the oxalate complexes[11] because of some structural relationships. The mononuclear complexes $[MoO_3(C_2O_4)(OH_2)]^{2-}$ and $[MoO_3(nta)]^{3-}$ are both *cis*-trioxo systems[6,24] (Fig. 5). The co-ordination of nta, however, is tridentate with nitrogen as one of the donor atoms thus forming two five-membered rings with the central

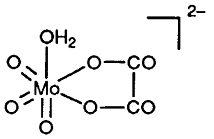
Table 1 Values for the formation constants and thermodynamic quantities (kJ mol^{-1}) for molybdenum(VI) complexes with nta and oxalate[11] in 1 mol dm^{-3} NaCl at 298 K

Complex	(log β_{pqr} ± 3σ)	ΔG°	ΔH°	$T\Delta S^{\circ}$
nta				
$[0,1,1]^{2-}$	8.78 ± 0.01	−50.1	−24.2 ± 0.5	26 ± 1
$[0,1,2]^{-}$	11.04 ± 0.01	−63.0	−24.4 ± 1.0	39 ± 1
$[0,1,3]$	12.73 ± 0.01	−72.7	−26.6 ± 1.0	46 ± 1
$[0,1,4]^{+}$	13.69 ± 0.05	−78.1	—	—
$[1,1,2]^{3-}$	17.78 ± 0.02	−101.5	−69 ± 1	32 ± 1
$[1,1,3]^{2-}$	21.02 ± 0.02	−120.0	−71.2 ± 2	49 ± 2
$[1,1,4]^{-}$	22.57 ± 0.07	−128.8	(−71)*	(58)
$[2,2,7]^{3-}$	45.16 ± 0.05	−257.8	−123 ± 4	135 ± 4
$[2,2,8]^{2-}$	47.95 ± 0.02	−273.7	−132 ± 2	142 ± 2
$[2,1,5]^{2-}$	30.74 ± 0.12	−175.5	—	—
$[2,1,6]^{-}$	33.09 ± 0.04	−188.9	—	—
Oxalate[11]				
$[1,1,2]^{2-}$	13.62	−77.7	−59.5	18.2
$[2,2,5]^{3-}$	31.20	−178.0	−123	55
$[2,2,6]^{2-}$	34.08	−194.5	−117	77.5

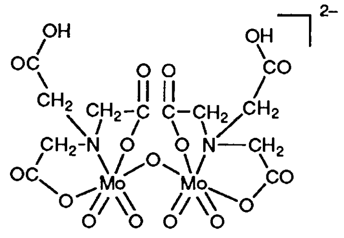
* Values in parentheses are approximate; see text.



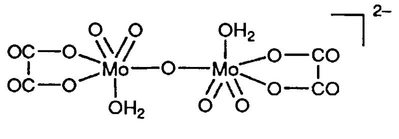
$[MoO_3(nta)]^{3-}$
$[1,1,2]^{3-}$



$[MoO_3(C_2O_4)(OH_2)]^{2-}$
$[1,1,2]^{2-}$



$[Mo_2O_5(Hnta)_2]^{2-}$
$[2,2,8]^{2-}$



$[Mo_2O_5(C_2O_4)_2(OH_2)_2]^{2-}$
$[2,2,6]^{2-}$

Fig. 5 Structures of the mononuclear[6,24] and dinuclear[9,25] complexes of molybdenum(VI) with nitrilotriacetate[6,9] and oxalate[24,25] molybdenum atom. For the two complexation reactions (8) and (9) this difference is seen in the more favourable entropy change

$$[MoO_4]^{2-} + C_2O_4{}^{2-} + 2H^+ \rightleftharpoons [MoO_3(C_2O_4)(OH_2)]^{2-} \quad (8)$$

$$[MoO_4]^{2-} + nta^{3-} + 2H^+ \rightleftharpoons [MoO_3(nta)]^{3-} + H_2O \quad (9)$$

for the formation of the nta complex, illustrating the chelate effect (Table 1). The more favourable enthalpy change for this complex (10 kJ mol^{-1}) reflects the stronger basic character of the triply charged nta compared to that of the doubly charged oxalate. When reaction (10) is considered in which the charges

$$[MoO_3(C_2O_4)(OH_2)]^{2-} + Hnta^{2-} \rightleftharpoons [MoO_3(Hnta)]^{2-} + C_2O_4{}^{2-} + H_2O \quad (10)$$

of the species are comparable the entropy term is still favourable ($T\Delta S^\circ = 4.8$ kJ mol^{-1}) but the enthalpy change ($\Delta H^\circ = 12.7$ kJ mol^{-1}) is so unfavourable that the reaction actually would proceed in the direction of the oxalate complex ($\log K = -1.38$).

The [2,2,*r*] dinuclear complexes of molybdenum(VI) with nta [9] and oxalate [25] have structural characteristics similar to those of the mononuclear complexes discussed above except for the oxygen bridge connecting the two mononuclear units resulting in the *cis*-dioxo moieties which are typical of molybdenum(VI) complexes (Fig. 5). The enthalpy change for the formation of the $[2,2,7]^{3-}$ nta complex (-123 kJ mol^{-1}) is the same as that of the $[2,2,5]^{3-}$ oxalate complex. The chelate effect of the tridentate nta ligand is again shown by a much more favourable entropy change, the difference in the values of $T\Delta S$ being 80 kJ mol^{-1}.

Again, a meaningful comparison of the relative stability of the major dinuclear complexes in terms of the thermodynamic quantities involved can be effected by considering the combined equation (11). Although the entropy change is favourable due to

$$[Mo_2O_5(C_2O_4)_2(OH)_2]^{2-} + 2Hnta^{2-} \rightleftharpoons [Mo_2O_5(Hnta)_2]^{2-} + 2C_2O_4{}^{2-} + 2H_2O \quad (11)$$

the tridentate co-ordination of nta ($T\Delta S^\circ = 12$ kJ mol^{-1}) the enthalpy change ($\Delta H^\circ = 33.2$ kJ mol^{-1}) is the overriding factor which determines the greater stability of the oxalate complex and accordingly the reaction would proceed to the left ($\log K = -3.7$).

Conclusion

Nitrilotriacetate forms both mono- and di-nuclear complexes with molybdenum(VI), of which the latter only occur at relatively low pH$_c$, namely $\leqslant 3.5$. For solutions of equal concentrations of nta and molybdate, and not too dilute, the three most stable complexes are $[MoO_3(nta)]^{3-}$, $[MoO_3(Hnta)]^{2-}$ and $[Mo_2O_5(Hnta)_2]^{2-}$. Protonated or deprotonated products of these complexes namely $[MoO_2(OH)(Hnta)]^{-}$ and $[Mo_2O_5(Hnta)(nta)]^{3-}$ occur as minor species. Two more minor complexes which are dinuclear and have a 2:1 molybdenum to nta stoichiometry have been identified, namely $[Mo_2O_5(nta)(OH)]^{2-}$ and $[Mo_2O_5(nta)(OH_2)]^{-}$. Thermodynamic quantities for the complexes have been determined which show that the chelate behaviour of nta contributes significantly to the stability of some complexes as indicated by the enthalpy and entropy changes.

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