Determination and Comparison of Stability Constants of Vanadium(v), Molybdenum(vi), and Tungsten(vi) Aminocarboxylate Complexes

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The solution structure and equilibria of vanadium(v), molybdenum(vi), and tungsten(vi) complexes formed by ethylenediaminetetra-acetic (H_4edta), ethylenediamine-NN'-diacetic (H_2edda), nitrilotriacetic (H_3nta), and iminodiacetic (H_2ida) acids have been investigated potentiometrically and spectrophotometrically. If Y^{n-} represents the fully dissociated ligand anion, all the 1 : 1 complexes have the formula $[VO_2Y]^{(n-1)-}$, $[MoO_3Y]^{n-}$, and $[WO_3Y]^{n-}$. A 1 : 2 vanadium(v)-ida, a 2 : 1 molybdenum(vi)- or tungsten(vi)-edta and two protonated 1 : 1 vanadium(v)-edta chelate complexes are also formed. The formation constants of the 1 : 1 complexes increase with the number of chelate rings for the same metal and decrease from V^V to Mo^{VI} and W^{VI} for a given ligand. The oxometal ions have a greater affinity for the nitrogen of the amine function than for the acetate oxygen.

THE chemistry of vanadium(v), molybdenum(vi), and tungsten(vi) has been the subject of many investigations, but few quantitative studies on the stability of oxygenated ions ($[VO_2]^+$, $[MoO_4]^{2-}$, and $[WO_4]^{2-}$) with aminopolycarboxylate ligands have been carried out. The stability constants of the complexes of V^V, Mo^{VI}, or W^{VI} with the following ligands have been reported: [1-18] ethylenediaminetetra-acetic acid (H_4edta),[1-5,8-11] ethylenediamine-NN'-diacetic acid (H_2edda),[7] nitrilotriacetic acid (H_3nta),[6,7,11,14,15] N-methyliminodiacetic acid (H_2-mida),[7,11,17] iminodiacetic acid (H_2ida),[11,16] cyclohexanediaminetetra-acetic acid (H_4cdta),[8,9] diethylenetriaminepenta-acetic acid (H_5dtpa),[18] and triethylenetetraminehexa-acetic acid (H_6ttha).[18]
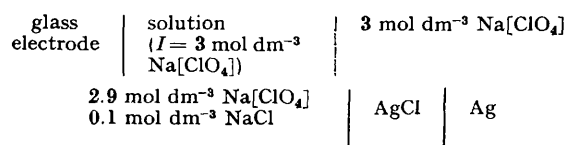
The present paper describes the formation of complexes of V^V, Mo^{VI}, and W^{VI} with ida, nta, edda, and edta. All metal–ligand equilibria were studied at 25 °C with 3 mol dm⁻³ sodium perchlorate as ionic medium. Comparisons are made of chelate stability constants among the ligands and between the metals. These thermodynamic results allow us to speculate on the structures of the complexes obtained. The structures agree with those given by Kula [10,16,17] and Amos and Sawyer [12] for analogous complexes.

EXPERIMENTAL

Reagents.—Sodium perchlorate, sodium monovanadate, sodium molybdate, sodium tungstate, perchloric acid, sodium hydroxide, ethylenediaminetetra-acetic acid, and nitrilotriacetic acid were obtained from E. Merck as analytical reagent grade materials and were used without any purification. Iminodiacetic and ethylenediamine-NN'-diacetic acids, purchased from Fluka, were recrystallised twice from distilled water. Their concentrations were checked by pH titration. Dilute perchloric acid solutions were standardised against $K[HCO_3]$. A 50% sodium hydroxide solution free from carbonate was prepared from the commercial p.a. material filtered through a G4 Jena Glass filter and stored in a polyethylene bottle; dilute solutions were prepared from boiled distilled water and this stock solution and were standardised against $HClO_4$. Vanadium(v) solutions were standardised titrimetrically against a standard iron(ii) sulphate solution.[19]

Measurements.—All measurements were carried out at 25 ± 0.1 °C. The ionic strength was maintained at 3 mol dm⁻³ with sodium perchlorate.

A Tacussel Aries 20 000 pH meter was used for pH measurements. The hydrogen-ion concentration was measured with a Beckman 39099E-3 glass electrode and an Ag–AgCl reference electrode in the cell:

glass electrode	solution ($I = 3$ mol dm⁻³ Na[ClO₄])	3 mol dm⁻³ Na[ClO₄]		
	2.9 mol dm⁻³ Na[ClO₄] 0.1 mol dm⁻³ NaCl		AgCl	Ag

A 1.00×10^{-2} mol dm⁻³ perchloric acid solution containing 2.99 mol dm⁻³ sodium perchlorate was employed as a standard of hydrogen concentration ($-\log[H^+] = 2.000$). Assuming that the activity coefficient of hydrogen ion is constant, then since $pH = -\log[H^+]$, hydrogen-ion concentration $[H^+]$ can be calculated from (1). E_0 was determined for each titration. The change in liquid-junction potential (E_j) was taken into account in acidic medium and was calculated from equation (2). a and b were determined

$$E \text{ mV} = E_0 + 59.16 \log[H^+] + E_j \quad (1)$$

$$pH(\text{real}) = pH(\text{measured}) + a + b[H^+](\text{measured}) \quad (2)$$

mined by measurement of the hydrogen-ion concentration of the two solutions: 0.1 mol dm⁻³ $HClO_4$, 2.9 mol dm⁻³ Na[ClO₄], with pH(real) = 1; 1 mol dm⁻³ $HClO_4$, 2.0 mol dm⁻³ Na[ClO₄], with pH(real) = 0.

Potentiometric titrations were carried out automatically. An automatic Tacussel Electroburex was connected to an Olivetti P652 microcomputer. The order for injection of titration solution was given by the computer when the potential of the measuring electrode was stable with time to a degree which was predetermined by the operator. Spectrophotometric measurements were performed on a Jobin-Yvon Duospac spectrophotometer with thermostatted and matched 10-mm quartz cells. The measurement cell was a flow cell. A Masterflex pump allowed circulation of the solution under study from the potentiometric cell to the spectrophotometric cell and the absorbance and pH of the solution could be measured simultaneously.

RESULTS AND DISCUSSION

(a) *Protonation Equilibria of the Aminocarboxylic Acids.*—Before studying metal–aminocarboxylate chelate complexes, we have to determine the stability constants of the protonation equilibria of edta, edda, nta,

and ida in 3 mol dm^{-3} sodium perchlorate. In particular, we must consider the different cationic species present in an acidic medium of pH <3.5.

The equilibria (3) were studied, where L^{n-} represents

$$H^+ + H_{i-1}L^{(n+1-i)-} \rightleftharpoons H_iL^{(n-i)-} \qquad (3)$$

with $\quad K_{1,i} = \dfrac{[H_iL^{(n-i)-}]}{[H^+][H_{i-1}L^{(n+1-i)-}]}$ and $1 \leqslant i \leqslant n + n'$

the fully dissociated ligand anion, n the number of carboxylic acid functions of the ligand, and n' the number of amine functions of the ligand: $n = 4$, $n' = 2$ for edta; $n = 2$, $n' = 2$ for edda; $n = 3$, $n' = 1$ for nta; and $n = 2$, $n' = 1$ for ida.

Three experimental methods of determination of the $K_{1,i}$ constants of nta and edta were used: potentiometry, spectrophotometry, and solubility measure-

2.5×10^{-2} mol dm^{-3} in perchloric acid were carried out. A non-linear least-squares method of calculation was used for determining the stability constants of the complexes. For a series of estimated equilibrium constants which were varied step by step, the sum of the squares of residuals in pH were calculated from (4) for all experi-

$$S = \Sigma(pH_{calc.} - pH_{expt.})^2 \qquad (4)$$

mental points (40 for each titration). The best values of the equilibrium constants gave $S_{min.}$.

Equilibria (5) were considered with molybdenum (or tungsten). The values of x, y, z, and β_{yxz} giving the best

$$x[MoO_4]^{2-} + yL^{n-} + (z + 2x) H^+ \rightleftharpoons$$
$$[(MoO_3)_xH_zL_y]^{(ny-z)-} + xH_2O \qquad (5)$$
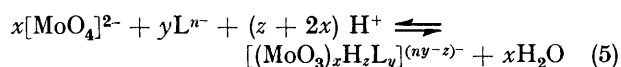
with $\quad \beta_{yxz} = \dfrac{[(MoO_3)_xH_zL_y^{(ny-z)-}]}{[MoO_4^{2-}]^x[L^{n-}]^y[H^+]^{z+2x}}$

TABLE 1

Protonation constants for aminocarboxylate ligands. Uncertainty limits quoted are twice the computed standard deviations

		Potentiometry	Spectrophotometry	Solubility	Refs.
edta	$\log K_{11}$	9.04 ± 0.05	9.02 ± 0.10		5, 20
	$\log K_{12}$	7.00 ± 0.05	7.00 ± 0.02		
	$\log K_{13}$	2.51 ± 0.04			
	$\log K_{14}$	2.13 ± 0.03			
	$\log K_{15}$	1.70 ± 0.03	1.2 ± 0.7	1.75 ± 0.03	
	$\log K_{16}$		0.43 ± 0.15	0.15 ± 0.15	
nta	$\log K_{11}$	9.17 ± 0.04	9.15 ± 0.07		6, 20
	$\log K_{12}$	2.63 ± 0.02		2.61 ± 0.10	
	$\log K_{13}$	2.05 ± 0.05		2.14 ± 0.05	
	$\log K_{14}$	1.42 ± 0.12		1.27 ± 0.03	
edda	$\log K_{11}$	10.06 ± 0.06			This work
	$\log K_{12}$	7.18 ± 0.05			
	$\log K_{13}$	2.98 ± 0.04			
	$\log K_{14}$	1.46 ± 0.03			
ida	$\log K_{11}$	9.68 ± 0.05			This work
	$\log K_{12}$	2.77 ± 0.03			
	$\log K_{13}$	1.92 ± 0.04			

ments. Calculations were performed by non-linear least-squares methods.[5,6,20] The logarithms of the protonation constants kept for the next calculations were: for edta, 9.04, 7.00, 2.51, 2.13, 1.72, 0.29; and for nta, 9.17, 2.63, 2.05, 1.27. The protonation constants of edda and ida have been determined using potentiometric techniques and calculated using the computer program SCOGS [21] which employs a non-linear least-squares method. The values of all the protonation constants are summarised in Table 1.

(b) *Complexes of* V^V, Mo^{VI}, *and* W^{VI} *with Aminocarboxylic Ligands.*—(i) *Potentiometric determination of the stability of molybdenum(VI) and tungsten(VI) chelate complexes.* The occurrence of metal polymerisation in acidic media complicates the study of the molybdenum(VI) and tungsten(VI) systems. Because the stability constants of the polymerisation equilibria are not well known, only the region from pH 7 to 10 is useful for potentiometric determinations. Titrations of solutions 10^{-2}, 1.5×10^{-2}, or 2×10^{-2} mol dm^{-3} in metal and 10^{-3} or 2×10^{-3} mol dm^{-3} in ligand and $n \times 10^{-3}$ or $2n \times 10^{-3}$ mol dm^{-3} in sodium hydroxide by a solution

fit were determined. Complexes present in the solutions investigated were: with edta, $[MoO_3L]^{4-}$, $[(MoO_3)_2L]^{4-}$; with edda, nta, and ida, $[MoO_3L]^{n-}$; and the same in the case of tungsten complexes. The values of the β_{yxz} constants are summarised in Table 2.

TABLE 2

Equilibrium constants of molybdenum and tungsten complexes. Uncertainty limits quoted are twice the computed standard deviations

	Mo^{VI}		W^{VI}	
Ligand	$\log \beta_{110}$	$\log \beta_{120}$	$\log \beta_{110}$	$\log \beta_{120}$
ida	18.48 ± 0.10		18.14 ± 0.10	
nta *	18.60 ± 0.20		19.03 ± 0.15	
edda	19.69 ± 0.05		19.62 ± 0.12	
edta	18.76 ± 0.12	36.06 ± 0.06	19.67 ± 0.10	36.22 ± 0.12

* Values from ref. 15.

(ii) *Spectrophotometric determination of stabilities of* *vanadium(v) chelate complexes.* In acidic solution (pH <2.5), vanadium(v) exists as the $[VO_2]^+$ ion.[22] This ion hydrolyses to $[H_2VO_4]^-$, $[HVO_4]^{2-}$, $[VO_4]^{3-}$,

$[V_3O_9]^{3-}$, and $[HV_2O_7]^{3-}$ in alkaline solutions [23,24] and polymerises in moderately acidic solutions [22] giving an 'instability range.' However, in the presence of a large excess of ligand at pH <7.5 both polymerisation and hydrolysis of $[VO_2]^+$ were found to be negligible. In the pH range of interest (1.5—2.5), absorbance and pH were measured for solutions containing V^V (10^{-4}—5×10^{-4} mol dm^{-3}) with a large excess of ligand (10^{-3}—10^{-1} mol dm^{-3}). In Figure 1 the measured apparent molar absorption coefficients (ε) at 270 nm of some of the solutions are plotted against pH.
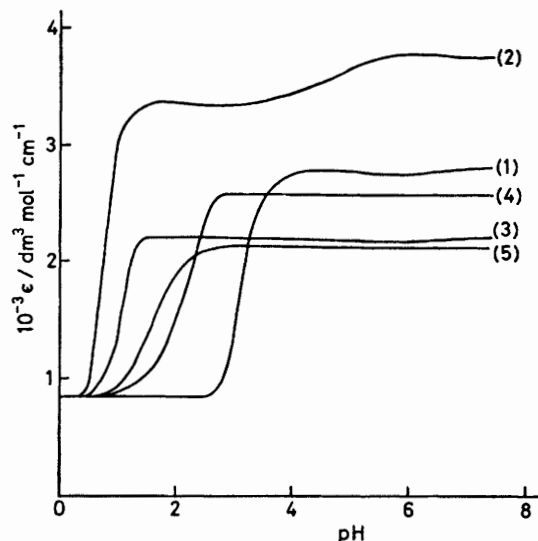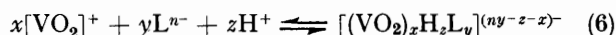

FIGURE 1 Apparent molar absorption coefficient ε as a function of pH of 10^{-4} mol dm^{-3} vanadium(v) solutions: (1) in the absence of aminocarboxylate; (2) [edta] $= 10^{-3}$; (3) [nta] $=10^{-3}$; (4) [edda] $= 6 \times 10^{-3}$; and (5) [ida] $= 10^{-2}$ mol dm^{-3}

Equilibria (6) were considered. The stability constants of the complexes were calculated by a non-linear least-squares method as follows. In the general case, if there are p different species in solution, we have to determine $(p-1)$ equilibrium constants β_{yxz} and p molar absorption coefficients (ε_j) of the p species. The calculated values of the apparent molar absorption coefficient (ε_c) are a function of the $(p-1)$ values of β_{yxz} and of the p values of ε_j. By introducing approximate values of the stability constants β_{yxz} which are varied step by step, ε_c becomes a linear function of ε_j. We can calculate the ε_j values by a linear least-squares method which consists of minimising, for all experimental points, $S' = \Sigma[(\varepsilon_c - \varepsilon)/\varepsilon]^2$. For each series of values of β_{yxz} the same procedure was followed. The best set of values of β_{yxz} give S'_{min}. The following complexes were found: with edta, $[VO_2L]^{3-}$, $[VO_2(HL)]^{2-}$, and $[VO_2(H_2L)]^-$; with nta and edda, $[VO_2L]^{(n-1)-}$; and with ida: $[VO_2L]^-$ and $[VO_2L_2]^{3-}$.

$$x[VO_2]^+ + yL^{n-} + zH^+ \rightleftharpoons [(VO_2)_xH_zL_y]^{(ny-z-x)-} \quad (6)$$

with

$$\beta_{yxz} = \frac{[(VO_2)_xH_zL_y^{(ny-z-x)-}]}{[VO_2^+]^x[L^{n-}]^y[H^+]^z}$$

Molar absorption coefficients of $[VO_2]^+$, $[VO_2L]^{(n-1)-}$ (L = edta, edda, or nta), $[VO_2(H_2L)]^-$ (L = edta), and $[VO_2L_2]^{3-}$ (L = ida) were measured at 270 nm. That of $[VO_2]^+$ was determined by absorbance measurements of solutions of vanadium(v) in an acidic medium (pH <2). In the presence of an excess of ligand (Figure 1), the absorbance remained constant over a range pH 3—7 (edda, nta, or ida). This was due to the $[VO_2L]^{(n-1)-}$ complexes of edda or nta and to the $[VO_2L_2]^{3-}$ complex of ida and the molar absorption coefficients of these species could be directly determined. For edta, the molar absorption coefficients of $[VO_2(H_2L)]^-$ and $[VO_2L]^{3-}$ were measured between pH 1.5 and 2, and between pH 5 and 7 respectively. We then calculated the molar absorption coefficients of the $[VO_2L]^-$ (L = ida) and $[VO_2(HL)]^{2-}$ (L = edta) complexes and their equilibrium constants by the method described above. All the β_{yxz} values giving the best fit are summarised in Table 3.

TABLE 3

Equilibrium constants of vanadium complexes. Uncertainty limits quoted are twice the computed standard deviations

	ida	nta [a]	edda	edta [b]
log β_{110}	11.70 ± 0.20	13.80 ± 0.20	15.98 ± 0.14	15.54 ± 0.30
log β_{210}	22.20 ± 0.30			
log β_{111}				19.64 ± 0.40
log β_{112}				22.94 ± 0.40

[a] Value from ref. 5.   [b] Values from ref. 6.

(c) *Discussion.*—In Figure 2 are the proposed structures of the 1 : 1 aminocarboxylate complexes of V^V, Mo^{VI}, and W^{VI} in aqueous solution as determined by the n.m.r. results of Kula [10,16,17] and Amos and Sawyer.[12] The four available co-ordination sites of the $[VO_2]^+$ ion are occupied by one nitrogen and two acetate oxygen atoms of ida, one nitrogen and three acetate oxygen atoms of nta, or two nitrogen and two acetate oxygen atoms of edda or edta. The former two complexes, whose structures are analogous, have log formation constants of the same order of magnitude (15.98 and 15.54 respectively). For edta complexes the two other acetate groups are not bonded to the metal and are free to rotate around the C–N bond. Protonation of non-bonded acetate groups was shown in the formation of the $[VO_2(HL)]^{2-}$ and the $[VO_2(H_2L)]^-$ complexes in acidic medium [equations (7) and (8)]. These two values of

$$[VO_2L]^{3-} + H^+ \rightleftharpoons [VO_2(HL)]^{2-} \quad (7)$$
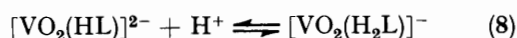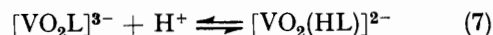
$$[VO_2(HL)]^{2-} + H^+ \rightleftharpoons [VO_2(H_2L)]^- \quad (8)$$

with $K_1 = \dfrac{[VO_2(HL)^{2-}]}{[VO_2L^{3-}][H^+]} = 10^{4.1}$;

$$K_2 = \frac{[VO_2(H_2L)^-]}{[VO_2(HL)^{2-}][H^+]} = 10^{3.3}$$

K_1 and K_2 are those usually found for carboxylic acids. In conclusion, ida reacts with $[VO_2]^+$ as a tridentate ligand whereas nta, edda, and edta react as quadridentate ligands. The three co-ordination sites of the central
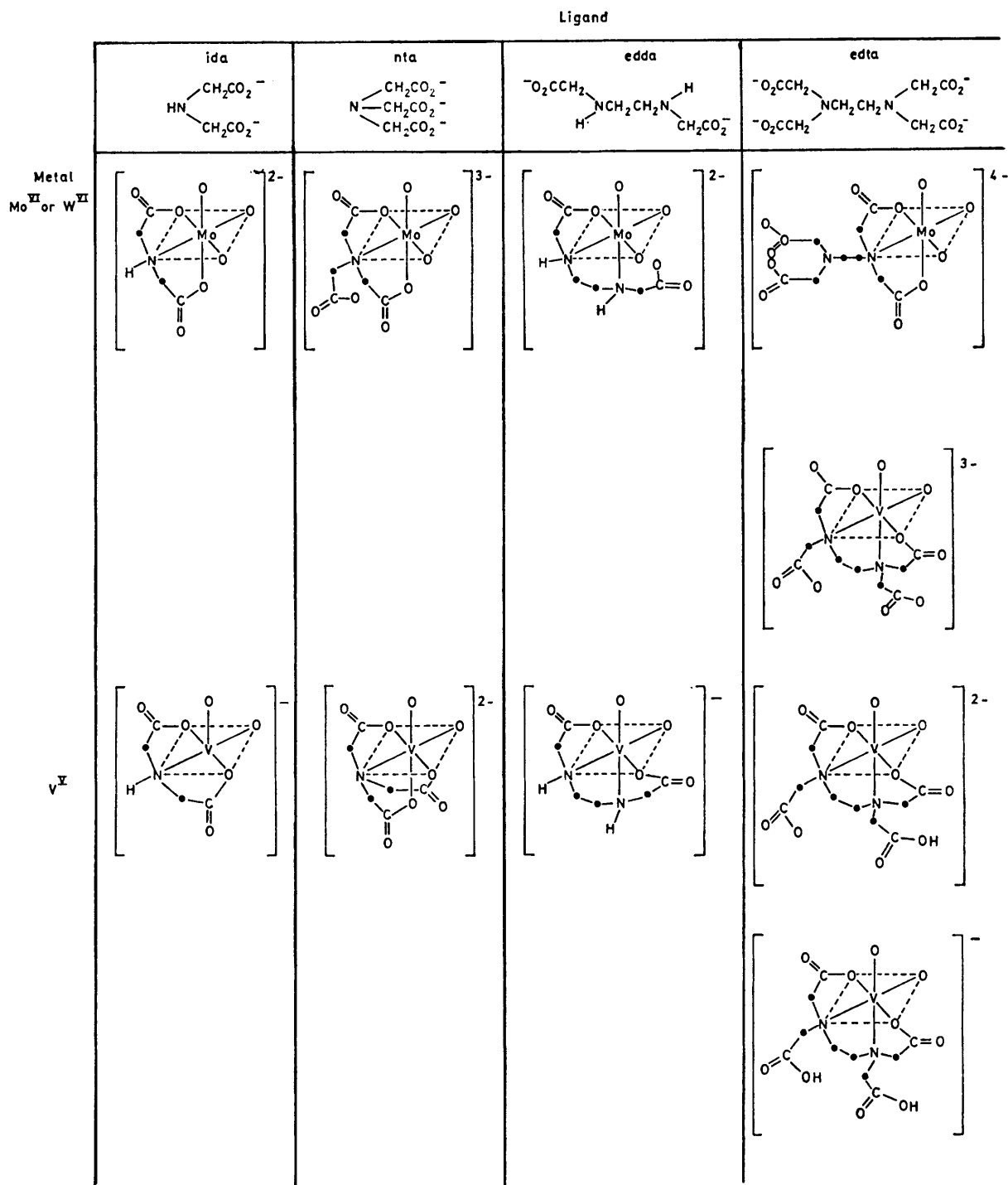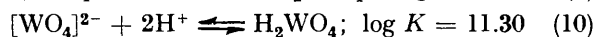
FIGURE 2 Structures of the 1 : 1 chelate complexes

metal co-ordinating unit MoO_3 or WO_3 are occupied by one nitrogen and two acetate oxygen atoms of ida, nta, or edta and by two nitrogen and one acetate oxygen atom of edda. The first three complexes have analogous structures and therefore constants of formation of the same order of magnitude (except the W^{VI}-edta complex). All four ligands should be tridentate when co-ordinated to MoO_3 and WO_3. For nta and edda, one acetate group is

not bonded to the metal. For edta two acetate groups and one amine group are not bonded to the metal; the end of the ligand not co-ordinated to Mo or W behaves much like an iminodiacetate group which can complex another central metal co-ordination unit MoO_3 or WO_3. We expect that the difference between log β_{110} (ida complex) and $\frac{1}{2}$log β_{120} (edta complex) should therefore be small. Our results confirm this hypothesis and the

proposed structures: for Mo^{VI}, $\log \beta_{110} - \frac{1}{2} \log \beta_{120} = 0.45$; for W^{VI}, $\log \beta_{110} - \frac{1}{2} \log \beta_{120} = 0.03$. For nta, edda, and edta complexes, protonation of the non-bonded groups was not observed under our experimental conditions: potentiometric titration with metal in excess and at pH >6.5 for Mo–nta and Mo–edda complexes and at pH >7.5 for Mo–edta, W–nta, W–edda, and W–edta complexes.

The influence of the ligand and of the metal upon the stability constants of 1 : 1 chelate complexes can now be compared. However, the stability constants of vanadium(v) chelate complexes cannot be compared with those of the molybdenum(vi) or tungsten(vi) chelate complexes unless the pH dependence of the formation constants of the latter chelates is eliminated. This may be done using the acid-dissociation constants of molybdic and tungstic acids [equations (9) and (10)] obtained in 3 mol dm^{-3} $Na[ClO_4]$ by Sasaki and co-workers.[25,26]

$$[MoO_4]^{2-} + 2H^+ \rightleftharpoons H_2MoO_4; \quad \log K = 7.5 \quad (9)$$

$$[WO_4]^{2-} + 2H^+ \rightleftharpoons H_2WO_4; \quad \log K = 11.30 \quad (10)$$

Assuming that H_2MoO_4 (or H_2WO_4) is equivalent to $MoO_3 \cdot H_2O$ (or $WO_3 \cdot H_2O$), we can write the molybdenum(vi) [or tungsten(vi)] chelate formation as in (11).

$$MoO_3 + L^{n-} \rightleftharpoons [MoO_3L]^{n-} \quad (11)$$

with $\quad \beta'_{110} = \dfrac{[MoO_3L^{n-}]}{[MoO_3][L^{n-}]} = \dfrac{\beta_{110}}{K}$

These β'_{110} constants are summarised in Table 4 together with the β_{110} constants for the vanadium(v) chelate complexes. We observe the following order of stability for co-ordination to the metals: $W^{VI} < Mo^{VI} < V^V$. Thus stability is related to the reciprocal of the size of the co-ordinating sites.

TABLE 4

Logarithms of pH-independent equilibrium constants for 1 : 1 chelate complexes

| Metal | Ligand | | | |
	ida	nta	edda	edta
V^V	11.70	13.80	15.98	15.54
Mo^{VI}	10.98	11.10	12.19	11.26
W^{VI}	6.84	7.73	8.32	8.37

The stability of complexes of the same metal with different ligands follows the order: ida < nta < edda. The formation constants of edta complexes are of the same order of magnitude as for the corresponding ida complexes (molybdenum) or as for the corresponding edda complexes (vanadium and tungsten). The stability of complexes of multidentate ligands increases with the number of chelate rings formed and, for the same number of rings formed, with the number of nitrogens bound to the metal.

In general, transition metals have a greater affinity for nitrogen than for oxygen, this effect decreasing for the heavier transition metals. Our results are in agreement with this: the stabilities of the M–edda complexes studied were greater than those of the corresponding complexes of nta and the difference in stability decreased from vanadium to tungsten with $\log \beta_{110}(\text{edda}) - \log \beta_{110}(\text{nta}) = 2.18$ for V^V, 1.09 for Mo^{VI}, and 0.59 for W^{VI}.

The thermodynamic studies of these oxometal aminocarboxylate complexes in solution show that the effects of the ligand and of the metal on the stability of the complexes are analogous to the effects observed for the metal ion (non-oxo) complexes usually studied.[27-29]

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