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Reactions of Mo(VI) with (2*R*,3*R*)-Tartaric Acid in Diluted Aqueous Solutions: A Study by Circular Dichroism Spectrophotometry

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Abstract

The reactions between molybdenum(VI) and (2*R*,3*R*)-tartrate in aqueous solutions with $C_L/C_{Mo} \geqslant 1$, pH between 1.5 and 6.0 and metal concentration between 1.0×10^{-4} and 2.5×10^{-2} mol dm^{-3} were studied by circular dichroism and UV spectrophotometry, at room temperature. At least four species were observed, their relative importance in solution varying with the molybdenum concentration, C_L/C_{Mo} relation, pH and ionic medium. Three of them were identified with species previously observed by NMR spectroscopy. The fourth species is probably polymeric, with L/M < 1. The influence of the nature of different electrolytes in solution is reported. The formation constant for the complex $[MoO_2(TH_{-1})_2]^{4-}$, TH_2 = (2*R*,3*R*)-tartaric acid, was determined, the value $\log K = 16.2 \pm 0.2$ being found from solutions with $I = 1$ mol dm^{-3}, NaCl and $T = 18 \pm 1$ °C. Similar reactions between tungsten(VI) and the ligand are also discussed.

Introduction

Although the occurrence of complexation between tartaric acid and molybdenum(VI), in aqueous solution, has been known for more than a century [1], the number and nature of species proposed have been subject to controversy. We have demonstrated in a previous paper [2], using mainly ^1H and ^{13}C NMR techniques, that four main species are present in aqueous solutions of molybdenum(VI) and (2*R*,3*R*)-tartaric acid (TH_2) with $C_L/C_{Mo} \geqslant 1$ (C_L and C_{Mo} being the analytical concentrations of ligand and molybdenum, respectively), over a range of concentrations and pH values, at 298 K. Two of these species are monomers and have ligand to metal ratios, L/M, of 1 and 2, respectively. Another species is a dimer (L/M = 1) [2, 3] and the fourth one is also polymeric. In all these complexes the ligand is either bidentate or bridging bis-bidentate and some of the complexes form stereospecifically. The isolation as solids and characterization of two of the species, a monomer, $[MoO_2T_2]^{2-}$, and a tartrate bridged dimer, $[Mo_2O_4(TH_{-2})_2]^{4-}$, was also described [2].

The X-ray crystal structure determination of the compound $(NMe_4)_2[MoO_2T_2]\cdot EtOH\cdot 1.5H_2O$ has been reported recently [4], providing further evidence for the occurrence of the L/M = 2 complex. Other authors have referred to the preparation of solids containing dimeric species, with oxygen or hydroxyl bridges [5].

The study of dilute solutions (molybdenum concentration below 2.5×10^{-2} mol dm^{-3} and $C_L/C_{Mo} \geqslant 1$) was undertaken using mainly circular dichroism spectrophotometry and is reported in this paper. Comparison of CD and ^1H NMR results was made using solutions with molybdenum concentration above 1.0×10^{-2} mol dm^{-3}. These studies provided evidence for the formation of four different complexes. Three of the complexes were also found in the more concentrated solutions already described [2], namely the dimer with L/M = 1 and the two monomers mentioned above. The formation constant for the complex $[MoO_2(TH_{-1})_2]^{4-}$ was determined in solutions with $I = 1$ mol dm^{-3} (NaCl). The equilibria in solution were found to be affected strongly by the presence of different salts.

Only one earlier report of the circular dichroism spectra of molybdate and natural tartrate in aqueous solutions could be found [6], concerning solutions with an excess of metal. The presence of two species was inferred, but identification was not attempted.

Experimental

Materials and Methods

All reagents were of analytical grade except (2*R*, 3*R*)-tartaric acid that was Sigma reagent grade, and were used without further purification but for occasional drying. Deuterated reagents from Sigma were used. Solutions for CD and UV spectrophotometry were prepared from sodium molybdate and tartaric acid or sodium tartrate solutions. If, in the experiment considered, a set of solutions with the same pH were need, this was adjusted in the made

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up solutions by addition of some drops of HCl or NaOH solutions; if solutions with variable pH were considered, acid or base were added during the preparation. Sodium chloride or any of the used salts (LiCl, $LiClO_4$, KCl, KBr, KNO_3, CsCl, NH_4Cl) was added in the appropriate amount to all solutions in the experiments with I = 1 mol dm^{-3}. The solid compound $K_4[Mo_2O_4(TH_{-2})_2]\cdot 6H_2O$ was prepared as previously described [2], and dissolved in D_2O for ^1H NMR spectra; pD was adjusted with NaOD or DCl solutions and NaCl was added for ionic strength adjustment when necessary.

Circular dichroism spectra were run using either a Jobin-Yvon Dichrographe III or a Jobin-Yvon Dichrographe IV. UV measurements were carried out with a Perkin-Elmer 202 spectrophotometer. ^1H NMR spectra were recorded at 200 MHz using a Varian XL-200 instrument. A Metrohm E520 and a WTW 521 pH meter, fitted with combined glass electrodes, were used for pH and pD measurements.

Deconvolution of the Spectra

A Basic program, able to calculate and represent up to five individual Gaussian curves and compare their resultant with the experimental spectra, was used to deconvolute the spectra. The Y value is calculated as $Y = A \exp\{-0.5((X - M)/S)^2\}$, where X is the wavelength. The value of A may be positive or negative; M represents the wavelength of the maximum of the curve. The parameters were adjusted following visual comparison of the calculated summation curve and the superimposed experimental spectra. To evaluate the resulting fit a standard deviation was determined.

Determination of the Number of Species in Solution

The matrix rank analysis method [7, 8] was used to determine the number of species in solution. The method was originally based on the determination of the rank of an absorption matrix whose element a_{ij} corresponds to the absorbance of a solution j at the wavelength i. Absorbance of n solutions at p wavelength values must be determined, with n and p larger than the number of species in solution. The method can easily be applied to circular dichroism studies.

An adapted version of a computer program previously published [9] was used in our work. As the circular dichroism value, at a given wavelength, is proportional to the deflection of the pen registered in the spectra, that deflection was used to define the CD matrix; an error of ±1 mm in pen deflection was considered.

Determination of Stability Constants

If only one complex of formula ML_n is formed in a solution, with a formation constant $K = [ML_n]/[M][L]^n$, and only that complex originates CD spectra in a considered region, relations (1) and (2) can be deduced.

$$K = [ML_n]/(C_M - [ML_n])(C_L - n[ML_n])^n \tag{1}$$

$$H = [ML_n]\Delta\epsilon \tag{2}$$

In those relations it is considered that

C_M represents the total concentration of metal species in solution;

C_L represents the total concentration of ligand in solution;

H is the intensity of the circular dichroism per unit path length;

$\Delta\epsilon$ is the molar circular dichroism per unit path length of the complex at a certain wavelength.

Assuming that $C_L - n[ML_n] = C_L$ the combination of these equations followed by rearrangements lead to eqns. (3) and (4).

$$H/C_L{}^n = K\Delta\epsilon C_M - KH \tag{3}$$

$$1/v^n = C_M\Delta\epsilon(C_L{}^0/V)^nK(1/H) - K(C_L{}^0/V)^n \tag{4}$$

Equation (4), analogous to Asmus' equation [10], is obtained considering $C_L = C_L{}^0v/V$ (v being the volume of a solution of ligand with concentration $C_L{}^0$ used to prepare the volume V of the studied solution).

The formation constant for the complex studied is given by $K = [MoO_2(TH_{-1})_2{}^{4-}]/[MoO_4{}^{2-}][T^{2-}]^2\cdot[H^+]^2$. A conditional constant $K' = [MoO_2\text{-}(TH_{-1})_2{}^{4-}]/[MoO_4{}^{2-}]^2[T^{2-}]^2$ can be defined, for a certain pH value, such that $K' = K[H^+]^2$. It is easily deduced that eqns. (3) and (4) can be used to determine the conditional constant K' in the case in study and, simultaneously, the value of n, as only with the correct value of n will the plot of $1/v^n$ against $1/H$ correspond to a straight line. The formation constant was then calculated from the relation $\log K = \log K' + 2\text{pH}$.

Results and Discussion

Circular Dichroism Spectra

Aqueous solutions of (2*R*,3*R*)-tartrate and Mo(VI) (C_{Mo} between 1.0×10^{-4} and 2.5×10^{-2} mol dm^{-3}, pH range 1.5–6.0) give positive circular dichroism in the range 220–350 nm. The various spectra show several bands whose relative intensities vary with molybdenum concentration, C_L/C_{Mo}, pH and ionic medium. Between 200–220 nm the circular dichroism may be positive or negative. Spectra of tartaric acid or tartrate solutions exhibit only one negative band in the 200–220 nm region, its position depending on the pH.

In the present study, diluted aqueous solutions containing molybdenum in the range 1.0×10^{-4} to 2.5×10^{-2} mol dm^{-3} and $C_L/C_{Mo} \geqslant 1$ were

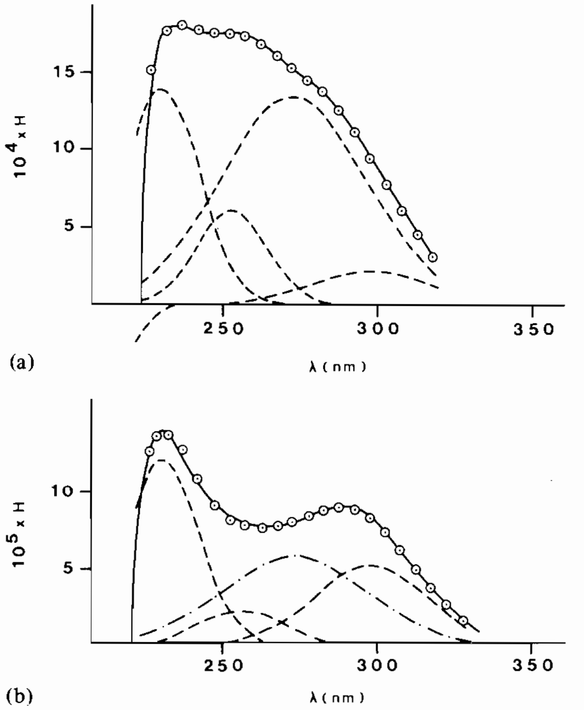

Fig. 1. Circular dichroism spectra of aqueous solutions of sodium molybdate and (2*R*,3*R*)-tartaric acid and their deconvolution in Gauss curves: (a) $C_{Mo} = C_L = 5.0 \times 10^{-4}$ mol dm^{-3}, pH = 3.46, I = 1 mol dm^{-3} (NaCl); (b) $C_{Mo} = C_L = 1.0 \times 10^{-4}$ mol dm^{-3}, pH = 3.65, I = 1 mol dm^{-3} (NaCl); (——) experimental spectrum, (⊙⊙⊙) calculated curve, (– – –) Gauss curves.

considered. In a few experiments solutions with an excess of metal were used. Solutions were prepared either with constant ionic strength (I = 1 mol dm^{-3}) or without any adjustment. Sodium chloride was generally used as supporting electrolyte in ionic strength adjustments, but some solutions were prepared using other salts.

Solutions with $C_L/C_{Mo} \geqslant 1$ and $I = 1$ mol dm^{-3} (NaCl)

To identify the number of species in the title solutions the deconvolution of a large number (around ninety) of CD spectra was performed. These spectra correspond to solutions with C_L/C_{Mo} between 1 and 18 and with pH values between 2.0 and 6.0. A total of four Gaussian curves, centered at 230, 252, 272 and 297 nm, were needed to reproduce the positive part of the spectra, as shown in Fig. 1 for typical situations. As the relative intensities of all these bands vary independently with the parameters studied (C_{Mo}, C_L/C_{Mo} and pH) we consider them to correspond to four different complex species. The number of species in solution was also determined by the matrix rank analysis method [7, 8], agreement being observed in almost all experiments. Not all of these species were present simultaneously in solution, but in most cases at least two complexes were formed.

TABLE 1. Complex species in diluted aqueous solutions[a] of sodium molybdate and (2*R*,3*R*)-tartaric acid and circular dichroism data

Species	Formula	λ_{max}[b] (nm)	Δε[c]
I	$[MoO_2(TH_{-1})_2]^{4-}$	230, 272[c]	2.68
II	$[Mo_2O_4(TH_{-2})_2]^{4-}$	272	
III	$[MoO_3(TH_{-1})(H_2O)]^{3-}$	297	
IV		252, 331	

[a]Solutions with NaCl or without any added electrolyte. [b]Maximum of the Gaussian curves used for deconvolution of the spectra above 220 nm. [c]In mol^{-1} dm^3 cm^{-1}.

Two of these species could be identified comparing the ^1H NMR and CD spectra of appropriate solutions: the monomer $[MoO_2(TH_{-1})_2]^{4-}$ (**I**) and the dimer $[Mo_2O_4(TH_{-2})_2]^{4-}$ (**II**). Two other species, **III** and **IV**, need to be considered to interpret the observed spectra. Table 1 summarizes the results.

The complex $[MoO_2(TH_{-1})_2]^{4-}$ (**I**) was found to be associated with a CD spectrum with two positive bands in the region above 220 nm (Fig. 2). Deconvolution of these spectra was made in terms of the two positive Gaussian curves centered at 230 and 272 nm (with relative intensities approximately 3:1) and one negative curve at lower wavelength.

Complex **I** is the only species formed in solutions of Mo(VI) and (2*R*,3*R*)-tartrate with a large excess of ligand ($C_L/C_{Mo} \geqslant$ 5–10 when C_{Mo} equals 1.0×10^{-3} mol dm^{-3}, pH between 2.5 and 6.0). Graphical methods [10, 11] were used to show that only one complex species, with a ligand to metal ratio L/M = 2, is formed in those solutions. Its formation constant was then determined both from circular dichroism and UV–Vis spectrophotometric data (see below).

The presence of protonated derivatives of complex **I** [2, 4] in solutions with low pH values (below 2.5, when C_{Mo} equals 1.0×10^{-3} mol dm^{-3}) could also be detected from the CD spectra. In these situations the position of the more intense band of the spectra is shifted to higher wavelength and another curve, centered at 243 nm, in addition to the ones already mentioned, is needed to deconvolute the spectra.

The band centered at 272 nm is also considered to be due to complex **II**. In the CD spectrum represented in Fig. 3, as well as in many others, the peak at 272 nm is the most intense or the relative intensities of the bands centered at 230 and 272 nm differ from those observed in the spectra of complex **I** (Fig. 2). These observations can only be explained assuming that the band at 272 nm is not only due to complex **I** but also to another species, that was

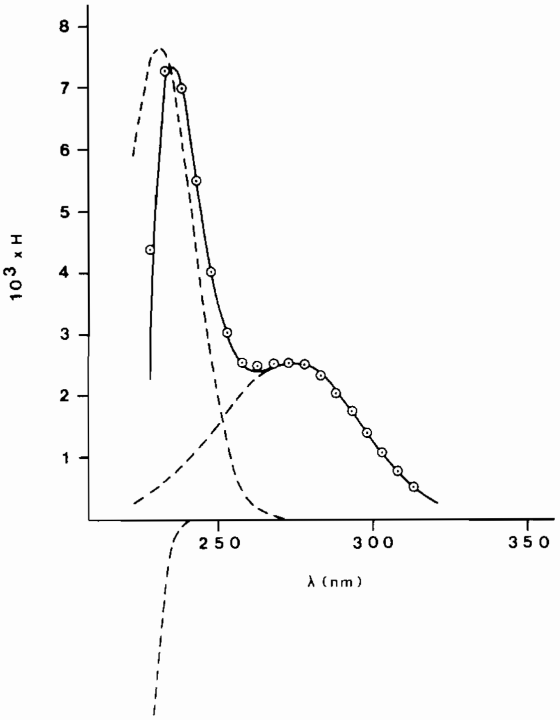

Fig. 2. Circular dichroism spectra of aqueous solutions of sodium molybdate and (2*R*,3*R*)-tartaric acid and their deconvolution in Gauss curves: $C_{Mo} = 1.0 \times 10^{-3}$ mol dm^{-3}, $C_L/C_{Mo} = 18$, pH = 5.80, $I = 1$ mol dm^{-3} (NaCl); (——) experimental spectrum, (⊙⊙⊙) calculated curve, (– – –) Gauss curves.

identified as the complex $[Mo_2O_4(TH_{-2})_2]^{4-}$ (**II**). Comparison of ^1H NMR and CD spectra of a 1×10^{-2} mol dm^{-3} solution of the compound $K_4[Mo_2O_4(TH_{-2})_2]\cdot 6H_2O$, with $I = 1$ mol dm^{-3} (NaCl), confirms this interpretation: the former shows a peak at 3.84 ppm (against tert-butanol) [2] and the latter a band at 272 nm as the predominant features (Fig. 3).

Species **II**, as observed through its CD band, is favoured by pH values around 3.5, as has previously been suggested by the NMR studies [2]. Comparison of spectra of solutions with $C_L/C_{Mo} = 1$ shows that the band centered at 272 nm loses relative intensity with dilution, as expected for a band due to a polymeric species (Fig. 1).

The band centered at 297 nm is considered to be due to a monomeric complex with L/M = 1. It is always a weak band, but its relative intensity increases with dilution (Fig. 1), when C_L/C_{Mo} and pH are kept constant. For a constant molybdenum concentration and pH, the maximum relative intensity is observed in spectra of solutions with C_L/C_{Mo} = 1. The 297 nm band is also observed to decrease in intensity with the lowering of pH. We tentatively assign this band to the monomer with L/M = 1 (**III**)

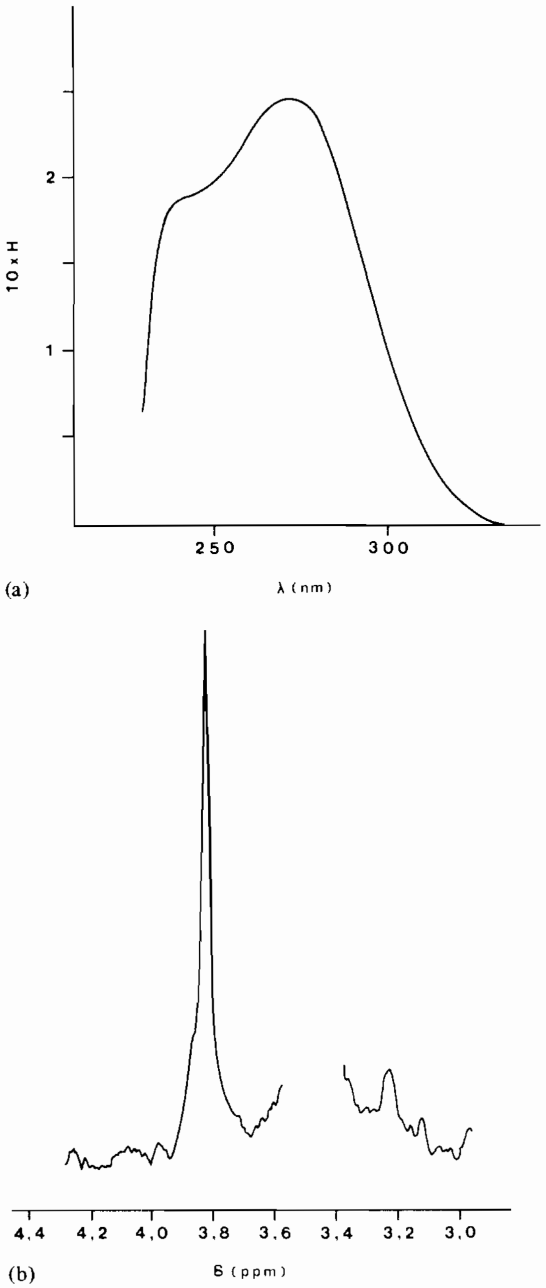

Fig. 3. Spectra of solutions of $K_4[Mo_2O_4(TH_{-2})_2]\cdot 6H_2O$, with $I = 1$ mol dm^{-3} (NaCl): (a) circular dichroism spectrum of an 1.0×10^{-2} mol dm^{-3} aqueous solution; (b) ^1H NMR spectrum of a solution in D_2O, same concentration.

previously identified by NMR spectroscopy in the upper pH range of our studies. This complex seems to be relatively more important in the aqueous solution without ionic strength adjustments than in the ones of the same concentrations and pH but with added NaCl.

The band with λ_{max} = 252 nm is only observed in spectra of solutions with low pH (maximum intensity at pH around 2.5) and low C_L/C_{Mo} ratio (*e.g.* C_L/C_{Mo} = 0.5–1.0). The variation of its intensity with the considered parameters points to a species with $C_L/C_{Mo} < 1$. The species originating this curve will be referred as **IV** and could not be identified.

Based on the assignments described above we can summarize the following facts related to solutions with I = 1 mol dm^{-3} (NaCl) studied by CD spectrophotometry. The main species in solutions with C_L/C_{Mo} = 1, in the upper range of concentrations and pH 3–4, is the dimer $[Mo_2O_4(TH_{-2})_2]^{4-}$ (**II**). This species plus the two monomers **I** and **III** are the predominant complexes at lower concentrations. As the pH of the solutions increase the relative abundance of the dimer decreases in relation to that of the monomers. In solutions with large excess of ligand the main species is the monomer with L/M = 2 in all the pH and concentration range studied.

The Effect of Changes in the Ionic Strength and Influence of Various Electrolytes

Circular dichroism spectra of solutions prepared with I = 1 mol dm^{-3}, adjusted with NaCl, are always different from those spectra of similar solutions (same C_{Mo}, C_L/C_{Mo} and pH values) prepared without sodium chloride. Deconvolution of the spectra of solutions without supporting electrolyte, in the 220–350 nm region, was, however, performed using the same Gaussian curves as before, plus a new curve, centered at 331 nm. This new curve was found to be associated with the previously mentioned curve at 252 nm (the ratio of the intensities of these two curves was constant in all spectra analysed).

The evidence gathered so far points to the existence of the same species in the solutions with I = 1 mol dm^{-3}, adjusted with NaCl, and in the ones with low ionic strength. The differences observed in the spectra of solutions with C_L/C_{Mo} = 1 and low concentrations ($C_{Mo} \leqslant 2.5 \times 10^{-3}$ mol dm^{-3}) are, however, particularly noticeable. In the spectra of solutions with low ionic strength, the most intense band is the one centered at 252 nm or this one plus that centered at 297 nm, if the pH is higher than about 4 (Fig. 4). The band centered at 272 nm, corresponding to the complex **II**, is always weak. Spectra of similar solutions with I = 1 mol dm^{-3} are shown in Fig. 1.

It is worth noting that solutions with I = 1 mol dm^{-3} (adjusted with NaCl) and similar solutions without any added support electrolyte have not only different CD and ^{1}H NMR spectra but also different pH values. This difference is of the order of 0.8–1.0 pH units for solutions with $C_L = C_{Mo}$ between 10^{-3} and 10^{-2} mol dm^{-3}, with those with NaCl having lower pH values than the others.

The influence of the supporting electrolyte in the equilibria in solution cannot be attributed only to ionic strength effects. Solutions with I = 1 mol dm^{-3} prepared with distinct chlorides (alkali metal and ammonium chlorides) gave different spectra, as shown in Fig. 5 for a typical example. The substitution of the chloride anion by bromide, nitrate or perchlorate had only a small influence in the spectra in the cases studied (solutions with C_L/C_{Mo} = 1, $C_{Mo} = 10^{-3}$ mol dm^{-3} and pH = 3–4).

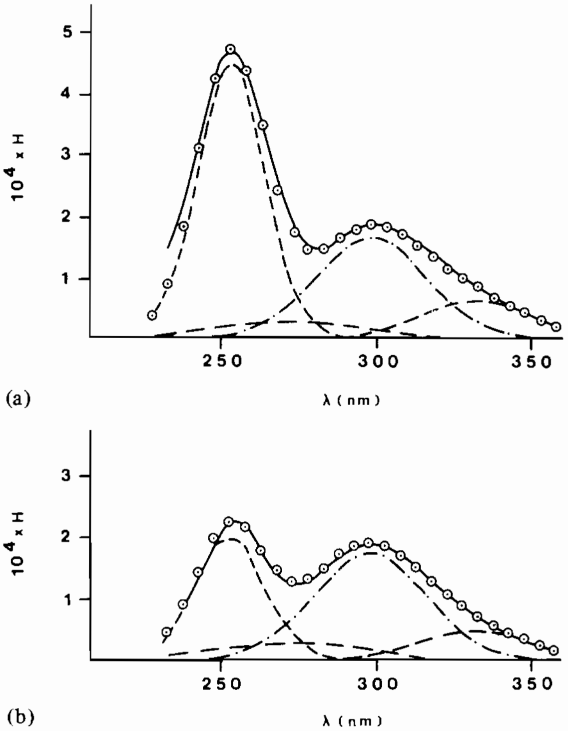

Fig. 4. Circular dichroism spectra of aqueous solutions of sodium molybdate and (2*R*,3*R*)-tartaric acid and their deconvolution in Gauss curves: (a) $C_{Mo} = C_L = 2.5 \times 10^{-4}$ mol dm^{-3}, pH = 3.60; (b) $C_{Mo} = C_L = 2.5 \times 10^{-4}$ mol dm^{-3}, pH = 4.21; (——) experimental spectrum, (⊙⊙⊙) calculated curve, (– – –) Gauss curves.

The described observations can be interpreted in terms of ion pairing between the cation and one or more species in solution. This effect may influence the resulting spectra in two ways: (a) the relative concentration of the species in solution is altered by the presence of different cations, (b) the spectrum of a particular species may be dependent on the formation of the ion pairs. Preliminary experiments seem to indicate that the size of the cation is important.

In an early report, Brown and McLellan [12] reported a very pronounced increase in the optical rotation of a 0.002 mol dm^{-3} molybdenum solution (C_L/C_{Mo} = 1 and pH = 4), at 313 nm, as the cations change along the series Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$. To our knowledge this influence hasn't yet been studied in detail and we are now continuing to investigate the effects observed on the circular dichroism spectra.

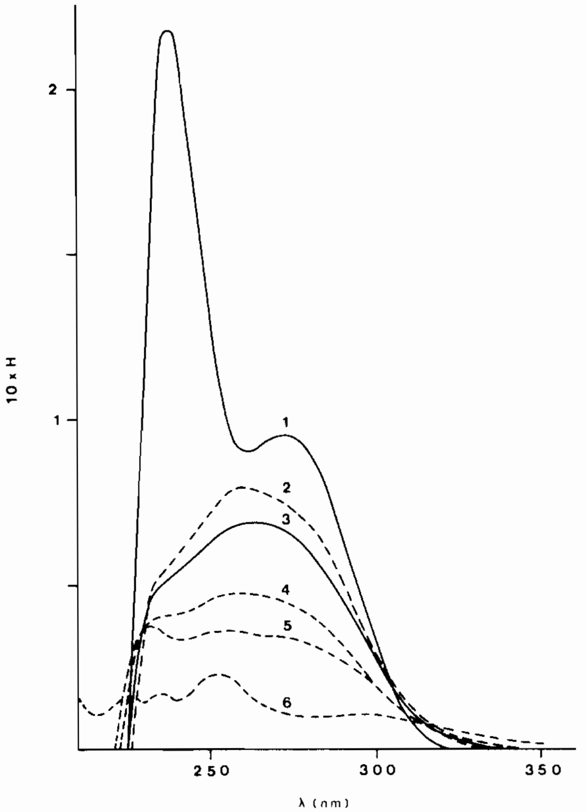

Fig. 5. Circular dichroism spectra of aqueous solutions of sodium molybdate and (2*R*,3*R*)-tartaric acid, $C_{Mo} = C_L = 1.0 \times 10^{-3}$ mol dm^{-3}, pH = 3.6, in the presence of different support electrolytes: 1, CsCl; 2, KCl; 3, NH$_4$Cl; 4, NaCl; 5, LiCl; 6, without electrolyte.

Determination of the Formation Constant of $[MoO_2(TH_{-1})_2]^{4-}$ at $I = 1$ mol dm^{-3} (NaCl)

The determination of the formation constant of the title complex was performed using circular dichroism values from solutions with high excess of ligand, pH values 5.8–5.9 and ionic strength adjusted to I = 1 mol dm^{-3} with NaCl. The high excess of ligand is necessary to ensure that only the considered complex is present in solution. The value of pH was chosen so that only reaction (5) takes place, the formation of isopolymolybdates occurring at lower pH values for the range of concentrations studied. In these conditions we can determine the formation constant using very simple graphical methods whose possible application is limited by the need to ensure that only one reaction envolving the metal (or the ligand) is occurring in solution.

$$MoO_4^{2-} + 2T^{2-} + 2H^+ \rightleftharpoons [MoO_2(TH_{-1})_2]^{4-} + 2H_2O \qquad (5)$$

In the chosen conditions the value of the circular dichroism intensity, at constant wavelength, of a series of solutions with constant pH and molybdenum(VI) concentration and variable ligand concentration increases regularly with C_L, corresponding to the formation of a complex with a small conditional formation constant [13]. The method of Asmus *et al.* [10], originally developed to apply to UV–Vis absorption measurements, was adapted to CD data. A straight line (Fig. 6) was obtained when $n = 2$ was considered in eqn. (4), indicating the proposed stoichiometry. Equations (3) and (4) were used for the determination of the conditional equilibrium constant, the formation constant and $\Delta\epsilon$ at the chosen wavelengh. The results can be seen in Table 2.

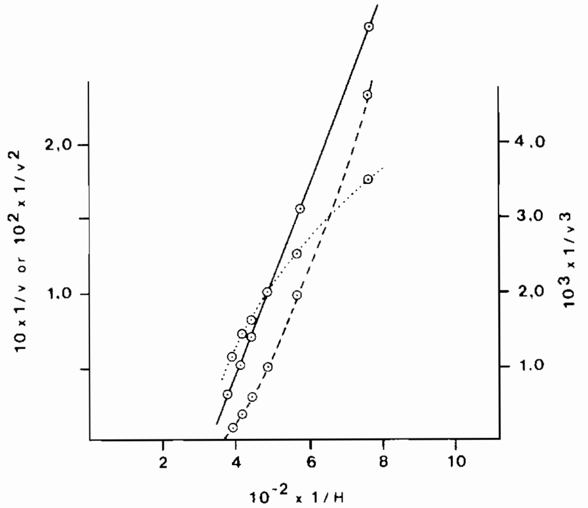

Fig. 6. Application of Asmus' eqn. (4) to the determination of the L/M ratio of the complex formed in the reaction of molybdate and (2*R*,3*R*)-tartrate in solutions with excess ligand: $C_{Mo} = 1.0 \times 10^{-3}$ mol dm^{-3}, C_L/C_{Mo} = 6–18, pH = 5.83, I = 1 mol dm^{-3}, λ = 272 nm. (·······) $n = 1$; (——) $n = 2$; (– – –) $n = 3$.

Values for the formation constant, in agreement with the results in Table 2, were obtained from spectrophotometric determinations in the 330–350 nm range, using analogous methods. In these cases solutions with $C_{Mo} = 1.0 \times 10^{-2}$ mol dm^{-3} and pH = 7 were considered. The UV spectra in the referred region is virtually featureless, as it corresponds to the tail of lower wavelength bands. These are due to the complexes and to molybdate itself. The lower precision associated with measurements in a region of the spectra with a steep slope plus the fact that visual inspection of the spectra doesn't give evidence for the formation of only one complex in solution (as the CD spectra generally do) make, in this case, the use of CD measurements more attractive than the UV absorption ones.

Circular dichroism and NMR spectroscopy have shown that, depending on concentration and pH, more than one species may be present in solution even when there is excess of ligand. We believe that

TABLE 2. Determination of the formation constant of the complex $[MoO_2(C_4H_3O_6)_2]^{4-}$ in solutions with I = 1 mol dm^{-3} (NaCl)[a]

Exp	C_{Mo}[c]	C_L/C_{Mo}	pH	K'[d]	log K	$\Delta\epsilon$[f]	K'[e]	log K	$\Delta\epsilon$[f]
1	4.05×10^{-4}	6–18	5.81	3.4×10^4	16.15	2.45	3.1×10^4	16.11	2.61
2	1.01×10^{-3}	6–18	5.83	2.2×10^4	16.00	2.92	2.1×10^4	15.98	2.90
3	1.01×10^{-3}	6–20	5.98	2.5×10^4	16.34	2.53	1.8×10^4	16.22	2.66
4[b]	1.00×10^{-3}	4–9	5.90	2.4×10^4	16.19		1.8×10^4	16.23	

$K = 1.49(0.42) \times 10^{16}$
$\log K = 16.2 \pm 0.2$

[a] Average values, obtained from CD determinations at 272 and 287 nm. [b] Values obtained from 267 nm CD determinations. [c] In mol dm^{-3}. [d] Application of eqn. (4). [e] Application of eqn. (3). [f] In mol^{-1} dm^3 cm^{-1}, corresponding to λ = 272 nm.

the value presented by Cadiot and Viossat [14] for the constant for a L/M = 2 monomeric molybdenum(VI) complex with tartrate, log K = 17.8, is higher than our value due to its determination having been done in the presence of other unaccounted species. These authors used potentiometric measurements of solutions with a small excess of ligand ($C_{Mo} = 2.5 \times 10^{-2}$ mol dm^{-3}, $C_L/C_{Mo} = 3.2$) and I = 1 mol dm^{-3}, adjusted with NaCl. Yet another determination of the apparent formation constant [15] of a L/M = 2 monomeric complex, at pH = 6.75, cannot be compared with our results as no experimental details were given by the authors [15].

Reactions of Tungsten(VI) and (2R,3R)-Tartaric Acid

Positive circular dichroism in the 200–280 nm region is generally observed in the spectra of solutions with $C_L/C_W = 1$ ($C_W = 1.0 \times 10^{-4}$ to 1.0×10^{-3} mol dm^{-3}), pH = 1.9–5.5 and I = 1 mol dm^{-3} (NaCl). Overall the spectra are not much different from those of similar molybdenum solutions, but are comparatively shifted to lower wavelengths. This fact introduces serious instrumental limitations to the study of the number and type of complexes formed. On the other hand, interference from the negative circular dichroism of the free ligand, in the lower wavelength region, prevents the complete assessment of the spectra of complexes formed in solutions with excess ligand, or when the pH is such as to lead to incomplete reaction. The existence of complexation could be detected, however, in solutions with tungsten concentrations as low as 5×10^{-5} mol dm^{-3} ($C_L = C_W$, pH 3–4, I = 1 mol dm^{-3}).

The influence of pH and concentration of the solutions on the shape of the spectra, when $C_L/C_W = 1$, can be easily recognized, suggesting the simultaneous presence of several species in solution. No systematic study was undertaken, however, as the method used for the study of molybdenum(VI) solutions could not be applied in this case, due to the limitations referred to above. But the general information gathered so far seems to point to a similarity between the two systems, in the lower concentration range studied by circular dichroism spectrophotometry, analogous to the observed by NMR spectroscopy, in the higher concentration studies previously reported [3].

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