Complexes of D-, L-, DL-, and *meso*-Tartaric Acid with Hydrogen and Oxovanadium(IV) Cations †

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The formation constants of the complexes of D-, L-, DL-, and *meso*-tartaric acid (H_2L) with the hydrogen ion and the oxovanadium(IV) cation, $[VO]^{2+}$, have been measured potentiometrically at 25.0 °C and $I = 0.10$ mol dm^{-3} ($K[NO_3]$). The enthalpy changes on formation of the protonated tartaric acids have been measured calorimetrically under identical conditions. The existence of binuclear complexes of both optically active and, to a lesser extent, *meso*-tartaric acids with $[VO]^{2+}$ has been confirmed. With active tartaric acids the major species at pH >6 is $[(VO)_2\{D(\text{or } L)\text{-}L\}_2H_{-4}]^{4-}$, but with *meso*-tartaric acid this species is of minor importance as a result of conformational differences. The binuclear complex $[(VO)_2(D\text{-}L)(L\text{-}L)H_{-4}]^{4-}$ is significantly more stable than $[(VO)_2(D\text{-}L)_2H_{-4}]^{4-}$. This may be explained as resulting from conformational differences.

TARTARIC ACID, $(CHOH\cdot CO_2H)_2$, contains two carboxyl groups and two hydroxyl groups. In solution it generally behaves, therefore, as a dibasic acid, H_2L, with both the carboxyl protons being ionized by pH 5. The hydroxyl groups, on the other hand, are not ionized under normal conditions. However, in strongly alkaline solutions dissociation can take place to give the anions $[H_{-1}L]^{3-}$ (pK 14.0) and $[H_{-2}L]^{4-}$ (pK 15.6).[1] In the absence of metal ions these dissociations can therefore be ignored. In the presence of metal ions, however, stable five-membered chelate rings can be formed if these hydroxyl protons are ionized. In the presence of Cu^{2+} and the oxovanadium(IV) cation, $[VO]^{2+}$, this ionization takes place at pH *ca.* 5. Since the tetranegative tartrate anion, $[H_{-2}L]^{4-}$, can form two such five-membered chelate rings, polynuclear complex formation at 1 : 1 ligand : metal ratios is to be expected. The possibility of polynuclear complex formation was anticipated as early as 1932,[2] but has been considered seriously only recently.

The spectral properties and potentiometric-titration curves for the Cu^{2+}– and $[VO]^{2+}$–tartrate systems show the equilibria to be complicated,[3-5] and polynuclear complex formation has been proposed. Racemic and optically active tartaric acid solutions behave very differently in the presence of these metal ions. Dunlop *et al.*[3] demonstrated the occurrence of much larger stereoselective effects in these polynuclear species than are observed in any mononuclear complexes. The formation of polynuclear tartrate complexes with Cu^{2+} appears to be more complicated than with $[VO]^{2+}$. Since the chemistry of $[VO]^{2+}$ (a d^1 cation) shows many similarities so that of Cu^{2+} (a d^9 cation) we have carried out a detailed potentiometric study of the complexes of $[VO]^{2+}$ with D-, L-, DL-, and *meso*-tartaric acids in an attempt to elucidate the species taking part in the equilibria and detect the origins of the stereoselectivity found.

The crystal structures of ammonium oxovanadium(IV) D-tartrate[6] and the analogous DL-tartrate[7] have been determined. Both show a binuclear structure. The optically active solid has a *trans* geometry for the tartrate ligands, while the racemic complex has a *cis* geometry. Electronic and Cotton-effect spectra of the solid and solutions of oxovanadium(IV) D-tartrate in the pH 7—8 region are identical,[8] as are the i.r. spectrum of the solutions and the reflectance spectrum of the solid.[6] This provides good evidence that the structure of the dimeric species in solution is the same as that found in the crystals. The e.s.r. spectrum also indicates weak intermetallic coupling between the vanadium atoms of the dimer, presumably through some bridging atoms.[5]

Solutions of oxovanadium(IV) tartrate absorb molecular oxygen at a rate which is pH dependent. The rate of oxygen uptake is also stereoselective.[9] Hence early attempts to carry out potentiometric titrations gave unreproducible results,[5] and the potentiometric data could not be analyzed quantitatively. In spite of this, clear differences between D-, DL-, and *meso*-tartaric acid in the presence of $[VO]^{2+}$ were apparent. We have carried out these titrations under suitable oxygen-free conditions so that reproducible curves could be obtained and the data have been treated quantitatively in an attempt to explain the equilibria present.

EXPERIMENTAL

D-, L- and *meso*-tartaric acids were obtained from the Sigma Chemical Co. and were checked for optical purity. Racemic tartaric acid was prepared by mixing equal quantities of solutions of D- and L-tartaric acid. Solutions of oxovanadium(IV) sulphate were analyzed by redox titration with ammonium cerium(IV) sulphate using platinum indicator electrodes. Arsenic(III) oxide was the primary standard used for the redox titrations. Oxovanadium(IV) sulphate crystals contain a little free acid. This was estimated by the addition of 2 equivalents of sodium oxalate followed by potentiometric titration with a standard base.[10]

All the solutions were prepared using deoxygenated deionized water in a glove-box under oxygen-free nitrogen. Solutions were stored under argon in flasks sealed with

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† No reprints available.

[1] M. T. Beck, B. Csaszar, and P. Szarvas, *Nature*, 1960, **188**, 846.

[2] J. P. Mathieu, *Compt. rend.*, 1932, **195**, 1017; 1933, **196**, 1222.

[3] J. H. Dunlop, D. F. Evans, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1260.

[4] R. E. Tapscott, R. L. Belford, and I. C. Paul, *Co-ordination Chem. Rev.*, 1969, **4**, 323.

[5] R. E. Tapscott and R. L. Belford, *Inorg. Chem.*, 1967, **6**, 735.

[6] J. G. Forrest and C. K. Prout, *J. Chem. Soc.* (*A*), 1967, 1312.

[7] R. E. Tapscott, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, 1968, **7**, 356.

[8] R. D. Gillard and S. H. Laurie, *J. Chem. Soc.* (*A*), 1970, 59.

[9] R. D. Gillard and R. A. Wiggins, *J.C.S. Dalton*, 1973, 125.

[10] P. Ducret, *Ann. Chim.* (*France*), 1951, **6**, 705.

serum caps and were transferred to the titration vessel by syringe. All the titrations were carried out under oxygen-free nitrogen. Changes in pH were followed with a glass electrode calibrated in terms of hydrogen-ion concentrations using the Radiometer pHM 64 pH meter. Titrations were carried out using 1 : 1 and 1 : 2 metal : ligand ratios and concentrations between 10^{-3} and 4×10^{-3} mol dm^{-3}. Formation constants were calculated from the experimental data with the aid of the MINIQUAD computer program.[11] The standard deviations given do not include systematic errors. They, therefore, give only an indication of the relative precision of the results, and the importance of the species (large deviations generally indicate only minor species in the equilibrium). When a choice had to be made between various possible models the R factor and χ^2 values were used as a basis for selection. Hydrolysis of $[VO]^{2+}$ is known to take place to form the comparatively stable species $[VO(OH)]^{+}$. Inclusion of the formation constant for this species [12] had no significant influence on the calculated formation constants since, in all cases, the concentration of free oxovanadium ions was insignificant at pH >4.2.

The stepwise enthalpy changes for the ionization of the carboxyl protons for both DL- and *meso*-tartaric acid were determined calorimetrically under the same experimental conditions {25.0 °C and I = 0.10 mol dm^{-3} (K[NO$_3$])} as the potentiometric titrations. Results were calculated from series of nine calorimetric experiments using an LKB 8700 solution calorimeter, in which the acid was neutralized with between 0.9 and 2.0 equivalents of sodium hydroxide. Measured heats of reaction were corrected for changes in pH and heats of dilution.

RESULTS AND DISCUSSION

Hydrogen-ion Complex-formation Constants.—These constants, corresponding to the protonation of the two carbonyl groups, are given in Table 1. The precision of log K_{H_2L} (corresponding to pK_1) is not high since its value is low (log $K_{H_2L} \sim 2.8$), the diprotonated form always being a minor species except in the presence of excess of free acid. The value for log K_{HL} was measured much more precisely and the values for D- and L-tartaric acid did not differ significantly from one another or from the value for DL-tartaric acid. This confirmed the purity since no differences were expected.[13] In general, asymmetric ligands show no stereoselectivity in their proton-ionization reactions.

TABLE 1

Thermodynamic quantities for the formation of hydrogen-ion complexes of D-, L-, DL-, and *meso*-tartaric acids at 25.0 °C and I = 0.10 mol dm^{-3} (K[NO$_3$]). Standard deviations are given in parentheses

(*a*) Formation constants

	Tartaric acid			
	D [a]	L	DL	*meso*
logK_{HL}	3.972(2)	3.962(2)	3.968(2)	4.456(1)
logK_{H_2L}	2.87(1)	2.83(1)	2.85(1)	2.95(1)
logβ_{H_2L}	6.84(1)	6.79(1)	6.82(1)	7.41(1)

(*b*) Thermodyamic quantities (kJ mol^{-1})

	DL			*meso*		
Process	ΔG	ΔH [b]	$T\Delta S$	ΔG	ΔH	$T\Delta S$
$H + L \longrightarrow HL$	−22.6	−1.5(2)	21	−25.4	−5.7(4)	20
$H + HL \longrightarrow H_2L$	−16.0	−3.3(2)	13	−16.85	−4.3(6)	12
$2H + L \longrightarrow H_2L$	−38.5	−4.7(1)	34	−42.25	−10.0(5)	32

[a] From ref. 13: D-tartaric acid, logK_{HL} = 3.94, logK_{H_2L} = 2.82; *meso*-tartaric acid, logK_{HL} = 4.44, logK_{H_2L} = 2.99.
[b] From ref. 14: $\Delta H_{HL} = -1.0$, $\Delta H_{H_2L} = -3.1$ kJ mol^{-1}.

There is a large difference in the measured values for both β_{HL} and β_{H_2L} between DL- and *meso*-tartaric acids. Similar differences (0.50 and 0.67 log units) were recorded in the only previous determination of the hydrogen-ion complexes of optically active and *meso*-tartaric acids under similar conditions of temperature and ionic strength.[13] The previous workers did not comment on this large free-energy difference between the diastereoisomers.

Table 1 also gives the measured enthalpy changes accompanying proton complex formation, together with calculated entropy changes. From these results the driving force for protonation of A^{2-} is largely derived from the entropy changes. The enthalpy changes are small and therefore the percentage errors are high. However, the results for DL-tartaric acid agree tolerably with those obtained by Bates and Canham,[14] which were obtained from the temperature coefficient of the proton complex-formation constants and relate to zero ionic strength. From our results the differences in the free-energy changes between the protonation of *meso*- and DL-tartaric acids are certainly accompanied by parallel differences in the enthalpy changes, and may be entirely due to the enthalpy term. Thus the formation of the monoprotonated anion $[HL]^-$ from L^{2-} is more favourable for the *meso* isomer, by 2.8 kJ mol^{-1} in ΔG and 4.2 ± 0.5 kJ mol^{-1} in ΔH.

The free energies of acyclic diastereoisomers usually differ, although not generally by very much. In general the *meso* form is more stable than the DL or optically active forms. Provided that the interactions between the groups are purely steric in origin, the most stable conformation is the centrosymmetric *anti* conformer, in which all the similar groups are fully staggered about the central C–C axis. This conformation can only be adopted by the *meso* form; the optically active forms necessarily contain sterically unfavourable *gauche* interactions (Figure 1). For the tartaric acid diastereoisomers such a simple steric argument for the free-energy differences is invalidated by the possibility of hydrogen-bond formation.

Crystal-structure analyses have shown that all the three crystalline forms of *meso*-tartaric acid (one anhydrous, and two of the monohydrate),[15] and also of the dianion in its potassium and rubidium salts,[16] do not in

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[11] P. Gans, A. Sabatini, and A. Vacca, *Inorg. Chim. Acta*, 1976, **18**, 237.

[12] F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, 1955, **9**, 1177.

[13] I. Feldman, C. North, and M. B. Hunter, *J. Phys. Chem.*, 1960, **64**, 1224.

[14] R. G. Bates and R. G. Canham, *J. Res. Nat. Bur. Stand.*, 1951, **47**, 343.

[15] G. A. Bootsma and J. C. Schoone, *Acta Cryst.*, 1967, **22**, 522.

[16] J. Kroon, A. F. Peerdeman, and J. M. Bijvoet, *Acta Cryst.*, 1965, **19**, 293.

fact adopt the centrosymmetric conformation, but are in a supposedly less stable conformation in which the carboxyl and hydroxyl groups are mutually *gauche*.

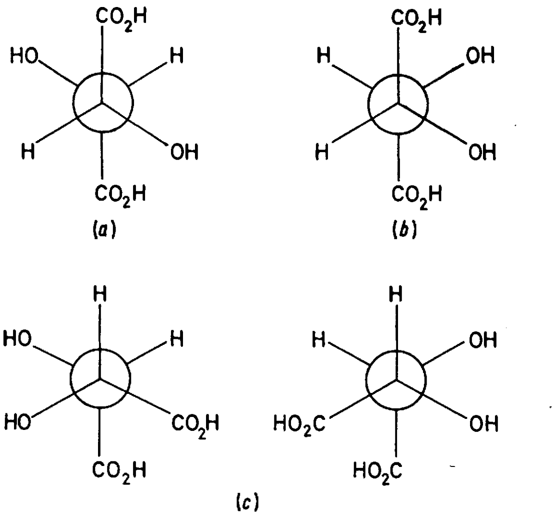

FIGURE 1 Conformations of D- and *meso*-tartaric acids: (*a*) centrosymmetric *anti* conformation of *meso*-tartaric acid; (*b*) *gauche* conformation of D-tartaric acid; and (*c*) conformations of *meso*-tartaric acid (or tartrates) found in the solid state

Since this conformer is asymmetric the *meso* form exists as an equal mixture of optical enantiomers, both of which are detected in the crystals. It was reasoned [16] that, since the hydrated and anhydrous *meso* acid and its dianion all exhibit the same conformation, then *meso*-tartaric acid in solution also exists in this conformation and therefore should be resolvable. In contrast, DL- and D-tartaric acid and tartrates all adopt the expected conformation in which the carboxyl groups are fully staggered and the hydroxyl groups are *gauche*. [17,18]

The optical rotary dispersion (o.r.d.) spectra of solutions of D-tartaric acid have been explained by Hargreaves and Richardson [19] in terms of hydrogen-bridged molecular conformations of a more or less rigid nature. They did not, however, consider the possible conformations of *meso*-tartaric acid in solution.

If indeed the conformations of the crystalline tartrates are also predominant in aqueous solution, then the origin of the large differences in free-energy and enthalpy changes, particularly for the first protonation, $L^{2-} + H^+ \longrightarrow [HL]^-$, are readily understood. It is noted that the repulsion between the two negatively charged carboxylate groups in the *gauche* conformation of the *meso*-tartrate dianion is particularly unfavourable; therefore, formation of the monoprotonated anion of *meso*-tartaric acid has a larger driving force than for protonation of the DL-tartrate. For the second stepwise protonation, $[HL]^- + H^+ \longrightarrow H_2L$, the energy difference between the diastereoisomers is smaller, since the major electrostatic repulsion between the two carboxyl groups is eliminated by the first stepwise protonation reaction. The *meso*-tartrate anion probably adopts its observed conformation in order to maximize hydrogen bonding, either intramolecular or with the solvent. Intramolecular hydrogen bonding of the hydroxyl groups requires their *gauche* disposition.

Formation Constants of the Tartrate Complexes of Oxovanadium(IV).—These constants are given in Table 2. The titration curves for 1 : 1 mixtures of $[VO][SO_4]$ with the various isomers of tartaric acid are shown in Figure 2, together with the curves for the acids alone and for the free mineral acid in $[VO][SO_4]$. These curves are qualitatively similar to those reported previously although, in these earlier reports, oxygen absorption prevented reliable reproducibility.[5,10]

TABLE 2

Formation constants (log β_{xyz}) for the complexes of $[VO]^{2+}$ with D-, L-, DL-, and *meso*-tartaric acids at 25.0 °C and I = 0.10 mol dm^{-3} ($K[NO_3]$). Standard deviations are given in parentheses

			Tartaric acid			
x	*y*	*z*	D	L	DL	*meso*
1	1	0		4.0(1)	3.86(3)	4.42(2)
1	1	−1	1.33(8)	1.50(7)	1.20(3)	
1	1	−2			−4.31(1)	
2	2	−1	9.78(1)	9.84(1)	9.527(4)	7.75(1)
2	2	−2	5.98(6)	6.21(5)	6.11(1)	4.46(1)
2	2	−3	−0.9(1)	−0.3(1)		−0.41(3)
2	2	−4	−6.26(2)	−6.04(1)	−5.30(1)	

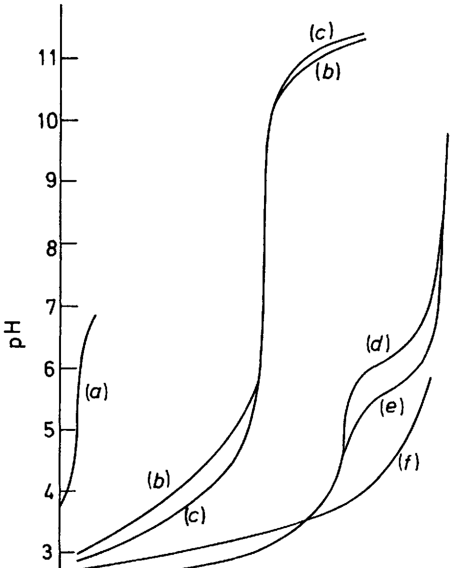

FIGURE 2 Titration curves for 1 : 1 mixtures of $[VO]^{2+}$ and various tartaric acids: (*a*) $[VO][SO_4]$ + sodium oxalate; (*b*) *meso*-tartaric acid; (*c*) D-, L-, or DL-tartaric acid; (*d*) $[VO][SO_4]$ + D- or L-tartaric acid; (*e*) $[VO][SO_4]$ + DL-tartaric acid; and (*f*) $[VO][SO_4]$ + *meso*-tartaric acid

The titration curves of $[VO]^{2+}$ with optically active and DL-tartaric acid exhibit two plateaux. The first,

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[17] G. S. Parry, *Acta Cryst.*, 1951, **4**, 131.

[18] Y. Okaya, N. R. Stemple, and M. I. Kay, *Acta Cryst.*, 1966, **32**, 237.

[19] M. K. Hargreaves and P. J. Richardson, *J. Chem. Soc.*, 1957, 2260.

from pH 2 to 5, corresponds to the addition of 3 equivalents of base over and above that required to neutralize any initial excess of free acid. In this pH region the curves obtained with D-, L-, and DL-tartaric acid are superimposable within experimental error (less than 0.01 pH unit). The second plateau (pH 5—7) corresponds to the addition of a fourth equivalent of base. Here there is a marked divergence of the curves for optically pure and DL-tartaric acid, the latter being depressed by 0.6 log units from that of the optically pure form. It may be deduced that up to the addition of the fourth equivalent similar complexes of equal stability are formed from the optically pure and DL ligands, but that on addition of a fourth equivalent a more stable complex is formed from the DL mixture. Ionization of hydroxyl protons must be involved on the addition of 3—4 equivalents of base, presumably together with formation of the dimers found in the crystals.[6,7]

The titration curve of $[VO]^{2+}$ with *meso*-tartaric acid does not show an end-point corresponding to the addition of 3 equivalents of base or a second plateau at high pH. However, it is considerably depressed during addition of the third and fourth equivalents of base, indicating the formation of stable complexes in this region which involve ionization of the hydroxyl protons of *meso*-tartaric acid.

Various model equilibrium systems were used in an attempt to satisfy the experimental data. In view of the excellent evidence that the dimeric species of formula $[(VO)_2L_2H_{-4}]^{4-}$ is the ultimate complex formed at pH 7—8 in the 1 : 1 mixtures of $[VO]^{2+}$ with D- and DL-tartaric acids, this species was included in all the models, and initially also with *meso*-tartaric acid. Various possible precursors to this dimer were then included to explain the stepwise formation of the dimer starting at pH 2.7.

Overall formation constants, β values, are expressed in the usual way, *e.g.* for the species $[(VO)_2L_2H_{-4}]^{4-}$ (the 22—4 species) the formation constant is expressed as $\beta_{22\text{-}4}$. With D-, L-, and DL-tartaric acids the formation constants of the dimers 22—4, 22—2, and 22—1 were refined consistently as major species. The only mononuclear complexes essential for a good statistical fit over the range pH 2.7—8 were the 11—1 and, to a lesser extent, the 110. With *meso*-tartaric acid the 22—4 dimer was always rejected, as was the 11—1 complex. Agreement between constants calculated from titrations carried out in 1 : 1 metal : ligand mixtures, of strength 10^{-3}—4×10^{-3} mol dm^{-3}, was excellent and the results, together with computed errors, given in Table 2 were calculated from combined experimental data. Calculations on titration data using 1 : 2 metal : ligand ratios gave identical major species to those found in 1 : 1 mixtures. Agreement between calculated formation constants for 1 : 1 and 1 : 2 mixtures with optically active tartaric acids was good. For example, with L-tartaric acid, $\Delta\log \beta_{22\text{-}4} = 0.12(7)$, $\Delta\log \beta_{22\text{-}2} = 0.21(6)$, and $\Delta\log \beta_{22\text{-}1} = 0.02(7)$. With *meso*-tartaric acid the agreement was a little less satisfactory [*e.g.* $\Delta\log \beta_{22\text{-}3}$ 0.23(4)] and possibly indicates some further polymerization. Table 2 therefore contains the constants calculated from the combined 1 : 1 titrations. Calculated species-distribution curves for 1 : 1 mixtures of $[VO]^{2+}$ and D- and *meso*-tartaric acids are given in Figure 3.

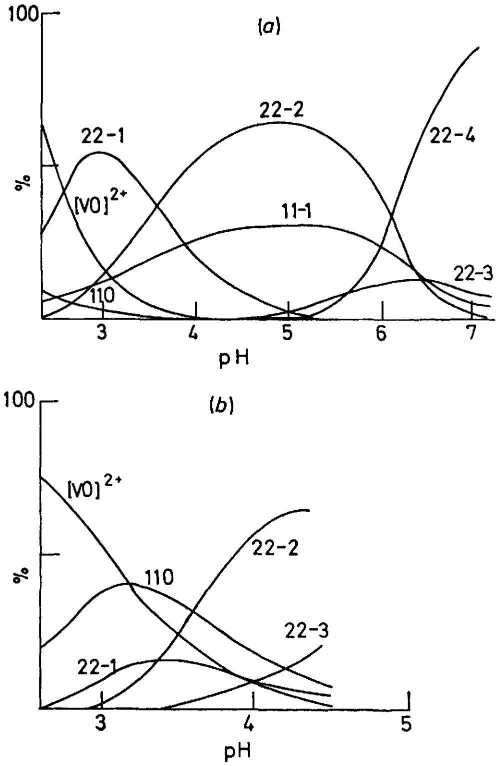

FIGURE 3 Species-distribution curves for 1 : 1 mixtures of $[VO]^{2+}$ and (*a*) D-tartaric acid and (*b*) *meso*-tartaric acid

The sharp end-point observed when 3 equivalents of base is added to the 1 : 1 $[VO]^{2+}$–D- or DL-tartrate solutions corresponds to the replacement of the dimer 22—2 by the species 22—4 and to a lesser extent 22—3 as the major complexed species in solution. Tapscott and Belford [5] concluded that only monomeric species formed below the equivalence point, and above it there existed a monomer $\rightleftharpoons$ dimer equilibrium by which the dimer of fully deprotonated tartaric acid was formed exclusively. Results reported here show that the dimer is formed by successive deprotonation of dimeric species which exist at below pH 3. Several other published results give indirect support to this conclusion. (*a*) Cotton effect and electronic spectra of $[VO]^{2+}$–D- and DL-tartrate solutions begin to diverge when only 2 equivalents of base have been added,[3] not when 3 have been added as do the titration curves. This observation of stereoselectivity below the third equivalence point supports the conclusion that dimers are formed in this pH region. (*b*) Simple mononuclear complexes have been reported at the very low pH of <2.[20] Hence ionization of the carboxyl groups is strongly encouraged.

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[20] K. Kustin and R. Pizer, *Inorg. Chem.*, 1970, **9**, 1536.

It is reasonable, therefore, that species involving ionization of hydroxyl groups should also form at low pH. (*c*) From kinetic studies, tartrate(2—)-bridged binuclear complexes of Ni^{2+} have been proposed at pH <5.[21] Such complexes are also likely with other bivalent transition-metal ions.

There is a small or zero difference between optically active and DL-tartaric acid in the values of the stability constants refined for the species which form below the third equivalence point. However, the observed stability constant for the species 22—4 using the DL isomer ($\log \beta = -5.30$) is significantly different from the mean value (−6.15) obtained for the D and L forms of the acid. Therefore the observed stereoselectivity in the titration curves can be ascribed entirely to the stereoselective formation of the tartrate(4—)-bridged binuclear complex in agreement with previous work.[4,5]

The observed formation constant, $\beta_{22\text{-}4}$, using the DL acid is a mixed or apparent constant and may be corrected to give a true constant for reaction (1) by

$$2[\mathrm{VO}]^{2+} + \mathrm{D\text{-}L}^{2-} + \mathrm{L\text{-}L}^{2-} \longrightarrow [(\mathrm{VO})_2(\mathrm{D\text{-}L})(\mathrm{L\text{-}L})\mathrm{H}_{-4}]^{4-} + 4\mathrm{H}^+ \quad (1)$$

using the relation described previously for the correction of $\log \beta_{(\mathrm{DL})}$.[22] From this the corrected value for the overall formation constants of $[(\mathrm{VO})_2(\mathrm{D\text{-}L})(\mathrm{L\text{-}L})\mathrm{H}_{-4}]^{4-}$ is found to be $\log \beta'_{22\text{-}4} = -4.95$. The equilibrium constant, K_e, for reaction (2) (which is a measure of the

$$\tfrac{1}{2}[(\mathrm{VO})_2(\mathrm{D\text{-}L})_2\mathrm{H}_{-4}]^{4-} + \tfrac{1}{2}[(\mathrm{VO})_2(\mathrm{L\text{-}L})_2\mathrm{H}_{-4}]^{4-} \rightleftharpoons [(\mathrm{VO})_2(\mathrm{D\text{-}L})(\mathrm{L\text{-}L})\mathrm{H}_{-4}]^{4-} \quad (2)$$

stereoselectivity) follows from the relation $\log K_e = \log \beta'_{22\text{-}4} - \log \bar{\beta}_{22\text{-}4}$ where $\log \bar{\beta}_{22\text{-}4}$ is the mean value for the formation constants for the D and L forms of the ligand. Hence $\log K_e = 1.20$. This is a large stereoselectivity and leads to the following distribution of complexes in the DL mixture: $[(\mathrm{VO})_2(\mathrm{L\text{-}L})(\mathrm{D\text{-}L})\mathrm{H}_{-4}]^{4-}$ (90), $[(\mathrm{VO})_2(\mathrm{L\text{-}L})_2\mathrm{H}_{-4}]^{4-}$ (5), and $[(\mathrm{VO})_2(\mathrm{D\text{-}L})_2\mathrm{H}_{-4}]^{4-}$ (5%).

With *meso*-tartaric acid the 22—4 species with $[\mathrm{VO}]^{2+}$ is either very unstable or non-existent in solution before the fourth equivalence point since, when included in the model, the constant for this species was consistently rejected. This behaviour is expected from the shapes of the titration curves shown in Figure 2. Curve (*f*) (*meso*-tartaric acid) shows a sharp end-point at 4 equivalents of base while the D, L, and DL ligands show a buffer region between pH 5 and 6 between the third and fourth equivalence points. The dimer 22—2 is, however, found to be an important species and, with the *meso* ligand, formation of the monomer [VO(*meso*-L)] assumes great importance (Figure 2). This can be understood by reference to Figure 4, which shows that in the most stable conformation of *meso*-tartaric acid the two carboxylate groups occupy spatial positions which would allow chelation as a dicarboxylic acid complex of formula ML, although this will result in the formation of a comparatively unstable seven-membered chelate ring. With the optically active form, chelation as an α-hydroxycarboxylic acid is favoured provided the hydroxyl proton is ionized (*e.g.* MLH_{-1} or $\mathrm{M}_2\mathrm{L}_2\mathrm{H}_{-4}$).

The observed order of stability of the tartrate(4—)-bridged oxovanadium binuclear species, DL > optically active > *meso*, can be explained in terms of the ligand conformations in the complexes. Comparison of the crystal structures of optically active tartaric acid[17,18] reveals that in order to act as a quadridentate bridging ligand the ligand does not need to change from its preferred conformation (Figures 1 and 4). In the free optically pure ligand and its binuclear complexes the carbonyl groups are fully staggered with respect to the C(α)–C(β) axis. In the DL complex, $[(\mathrm{VO})_2(\mathrm{D\text{-}L})(\mathrm{L\text{-}L})\mathrm{H}_{-4}]^{4-}$, formed from DL-tartaric acid, the carboxyl groups are *cis* with respect to each $[\mathrm{VO}]^{2+}$ square plane, and the complex is centrosymmetric. In the complexes formed from optically pure tartaric acid, *e.g.* $[(\mathrm{VO})_2(\mathrm{D\text{-}L})_2\mathrm{H}_{-4}]^{4-}$, the co-ordination must be *trans*, resulting in D_2 symmetry. Thus the observed stereoselectivity can be rationalized by ascribing enhanced stability to *cis* co-ordination of CO_2^- and O^- groups around the $[\mathrm{VO}]^{2+}$ square plane. Another difference between the structures is that in the complex formed from optically active ligands the vanadium atoms are staggered. This difference in structure would be expected to lead to a difference in stability of the complexes.

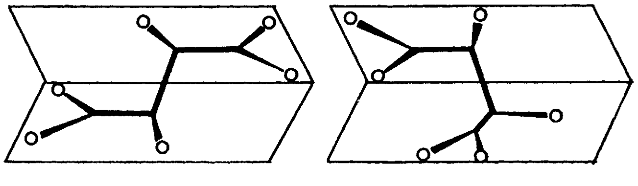
(*a*) (*b*)

FIGURE 4 Preferred conformations of tartaric acid and tartrate in the solid state, and probably in solution also: (*a*) active tartaric acid; (*b*) *meso*-tartaric acid

Hypothetical structures for *cis*- and *trans*-$[(\mathrm{VO})_2(meso\text{-}\mathrm{L}_2)\mathrm{H}_{-4}]^{4-}$ can only be formed by the total eclipsing of the groups about the C(α)–C(β) axis and the complexes would therefore be less stable. This is confirmed by the failure to refine a stability constant in this work, and the failure of attempted preparations of such a complex.[4] However, stable dimeric species in which the bridging tartrate ligands are not quadridentate are formed in $[\mathrm{VO}]^{2+}$–*meso*-tartaric acid solutions. These species are responsible for the depression of the pH-titration curve after the addition of more than 2 equivalents of base. The species 22—2 which probably involves two tridentate tartrate(3—) anions is especially stable, and presumably tridentate *meso*-tartrate(3—) bridging ligands have a greater degree of conformational freedom than their hypothetical quadridentate analogues.

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