Thermodynamics of Complexing between (+)-Tartaric Acid and Lanthanum(III) Ion in Aqueous Solution

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The stability constants of the lanthanum–tartrate complexes $LaTar^+$, $LaTar_2^-$, and $LaHTar^{2+}$ have been determined in 0·1, 0·2, and 0·4M $(Me_4N)Cl$ media † by potentiometric titration by use of a glass electrode. Thermodynamic constants have been determined at 15, 25, and 35 °C by the same method and standard enthalpy and entropy changes obtained from the temperature variation of the constants. Some structural implications of the results are discussed.

THE closeness of the two dissociation constants of tartaric acid makes the determination of the stability constants of tartrate complexes difficult, since protonated and unprotonated species may coexist in acidic conditions and this greatly complicates the calculations. Previous work on the lanthanum–tartaric acid system has usually considered only two complexes at a time, and no attempt has been made to obtain thermodynamic values. Moreover, the background media have usually contained considerable amounts of sodium or potassium ion, which have been shown [1,2] to form complexes with tartrate ion.

TABLE 1

Stability constants of lanthanum–tartrate complexes

Medium (M) *	log β_1	log β_2	log β_{11}	Method *	Ref.†
0·0597 ($NaClO_4$)	3·75	6·02		A	*a*
0·1 (KNO_3)	3·46	5·52		B	*b*
1 ($NaClO_4$)	2·08			A	*c*
C			2·5	D	*d*
C	3·68	6·37		D	*e*
	3·06	4·25		E	*f*
0·2 (KCl)	3·10			B	*g*
G	2·36	6·10		F	*h*
0·2	3·06		1·19	B	*i*
0·1 ($NaClO_4$)	3·21		2·43	H	*j*
0·1 ($KClO_4$)		6·72		A	*k*

* A, Distribution; B, glass electrode; C, uncontrolled; D, hydrogen electrode; E, e.m.f.; F, solubility; G, saturated solution; H, pH titration. † [a] P. G. Manning, *Canad. J. Chem.*, 1963, **41**, 2566. [b] N. A. Dobrynina, L. I. Martinenko, and V. I. Spitsin, *Izvest. Akad. Nauk S.S.S.R. Ser. khim.*, 1968, 2203. [c] K. L. Mattern, UCRL–1407, U.S.A.E.C., 1964. [d] F. Brězina and J. Rosický, *Monatsh.*, 1963, **96**, 1025. [e] R. Pastorek and F. Brězina, *Monatsh.*, 1966, **97**, 1095. [f] U-Czin-Guan and Sjuj Guan-sjan, *Kesue Tunbao*, 1959, No. 10, 330. [g] N. K. Davidenko and V. F. Deribon, *Zhur. neorg. Khim.*, 1966, **11**, 99. [h] N. K. Davidenko, *Redkozem. Elementy. Akad. Nauk S.S.S.R., Inst. Geokhim. i analit. Khim.*, 1963 (*Chem. Abs.*, 1964, **61**, 5011g). [i] Wu Chin-Kwang and Hsu Kwang-Hsien, *Acta Chim. Sinica*, 1965, **31**, 58. [j] V. N. Kumok and N. A. Skorik, *Zhur. neorg. Khim.*, 1970, **15**, 291. [k] J. Starý, *Analyt. Chim. Acta*, 1963, **28**, 132.

Pastorek [3] has reported i.r. spectra and thermal analyses for a number of solid lanthanum–tartrate complexes prepared from alkaline solution and finds a large number of species in existence. Zvayagintsov and Tikhonov [4] and Katzin and Barnett [5] have made spectroscopic studies of lanthanide tartrates in alkaline solution and find only one complex present. Gallett and Pâris [6] have studied cerous and dysprosium tartrates by means of thermometric titration and found three complexes of the type $MTar^+$, M_2Tar_3, and $MTar_2^-$.

We have carried out titrations at three different ionic strengths, using background media containing tetramethylammonium ion, which does not form complexes with tartrate ion. We have also performed titrations in dilute solutions at three temperatures, activity coefficients being calculated by means of equation (3). Constants are defined as in equations (A)—(E).

$$\beta_1 = [LaTar^+]/([La^{3+}][Tar^{2-}]) \quad (A)$$

$$\beta_2 = [LaTar_2^-]/([La^{3+}][Tar^{2-}]^2) \quad (B)$$

$$\beta_{11} = [LaHTar^{2+}]/([La^{3+}][H^+][Tar^{2-}]) \quad (C)$$

$$\beta_{12} = [LaHTar_2]/([La^{3+}][H^+][Tar^{2-}]^2) \quad (D)$$

$$K_{11} = [LaHTar^{2+}]/([La^{3+}][HTar^-]) \quad (E)$$

EXPERIMENTAL

Reagents.—Distilled water was obtained from an all-glass still. Potassium chloride, potassium nitrate, potassium

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† The nomenclature of A. E. Martell and L. G. Sillén (' Stability Constants,' Chem. Soc. Special Publ., No. 17, 1964) has been adopted.

[1] H. S. Dunsmore and D. Midgley, *J. Chem. Soc.* (*A*), 1971, 3238.

[2] H. S. Dunsmore and D. Midgley, *J.C.S. Dalton*, 1972, 64.

[3] R. Pastorek, *Monatsh.*, 1968, **99**, 676.

[4] O. E. Zvayagintsov and V. P. Tikhonov, *Zhur. neorg. Khim.*, 1964, **9**, 2789.

[5] L. I. Katzin and M. L. Barnett, *J. Phys. Chem.*, 1964, **68**, 3779.

[6] J.-P. Gallet and R. A. Pâris, *Analyt. Chim. Acta*, 1968, **40**, 321.

hydrogen phthalate, and (+)-tartaric acid (AnalaR) were recrystallised from distilled water. Tetramethylammonium chloride (B.D.H., Reagent Grade) was recrystallised from methanol–acetone [7] or methanol. Hydrochloric acid solutions were made up by dilution of the constant-boiling acid.[8] Sodium carbonate was prepared by decomposition of sodium hydrogen carbonate (AnalaR). Tetramethylammonium hydroxide solutions were prepared by treating tetramethylammonium chloride solutions with freshly precipitated hydrated silver oxide and filtering the solution. Sodium hydroxide solutions were prepared by dilution of a saturated solution made up from pellets (AnalaR). Hydroxide solutions were stored in, and dispensed from, the usual syphon arrangement. The concentrations of the hydroxide solutions were determined by titration against potassium hydrogen phthalate, with phenolphthalein as indicator, and by potentiometric titration against standard hydrochloric acid solutions. Lanthanum chloride solutions were prepared by dissolving lanthanum oxide (Johnson, Matthey and Co. Ltd., Specpure) in a small excess of diluted constant-boiling hydrochloric acid. The chloride concentration of the solution was determined gravimetrically as silver chloride and the excess of acid by potentiometric titration with standard tetramethylammonium hydroxide solution. The lanthanum concentration was obtained by difference. The results for a batch are given in Table 2.

TABLE 2

Analysis of lanthanum chloride stock solution

	$[Cl^-]$/M	$[H^+]$/M	[La]/M
Theoretical	0·1084	0·0085	0·0333
Observed	0·1084	0·0085	0·0333

Potentiometric Measurements.—Potentials were measured on a Pye 7565 potentiometer, with use of an Electronic Instruments Ltd. Vibron 33B electrometer as a null detector. The glass electrodes were of the type GC33 made by Electronic Instruments Ltd. The reference half-cell consisted of a Wilhelm bridge [9] containing a silver–silver chloride electrode in either a tetramethylammonium chloride solution of the same ionic strength as the test solution or an equimolar solution (0·15M each) of potassium chloride and potassium nitrate. The latter was chosen to reduce liquid junction potentials [10] with measurements made in dilute solution.

The glass electrodes were calibrated with solutions of hydrochloric acid and by titration of hydrochloric acid solutions with standard sodium hydroxide or sodium carbonate solutions. When the ionic strength was maintained with tetramethylammonium chloride, Biedermann and Sillén's [11] empirical liquid-junction potential correction was applied and a linear-relationship was obtained between the corrected e.m.f. and $-\log\,[H^+]$. Since no linear calibration was obtained when the ionic strength was not maintained, and no suitable liquid-junction correction was available, the observed e.m.f., *E*, and the pH were fitted to equation (1) by the method of least squares. Here we define

$$E = a_0 + a_1(\mathrm{pH}) + a_2(\mathrm{pH})^2 + a_3(\mathrm{pH})^3 + a_4(\mathrm{pH})^4 \quad (1)$$

$\mathrm{pH} = -\log\,[H^+] - \log f$, where f is the univalent ion activity coefficient calculated by means of the Davies equation.[12] The validity of this calibration in the presence of other ions was checked by repeating the calibrations with potassium chloride added. No significant difference was observed. Calibrations and experiments were normalised by reference to the e.m.f. observed with 0·05 mol kg^{-1} potassium hydrogen phthalate buffer before and after every run. The sensitivity of the electrodes was checked periodically and found to be constant.

Titration Procedure.—Series (I). Tetramethylammonium hydroxide solution was added from a burette to solutions containing tartaric acid, lanthanum chloride, and tetramethylammonium chloride. Tetramethylammonium chloride solution was added from a second burette to maintain the chloride concentration at the desired level (0·1, 0·2, or 0·4M). Alternatively, lanthanum chloride solution was added to a partially neutralised solution of tartaric acid, the ionic strength being maintained as before. The temperature was 25 °C for all these titrations.

Series (II). Tetramethylammonium hydroxide solution was added from a weight burette to solutions of tartaric acid and lanthanum chloride made up by weight. In some runs the lanthanum chloride solution was added to a tartaric acid solution partially neutralised with tetramethylammonium hydroxide. All weights were corrected for the buoyancy of air. Titrations were performed at 15, 25, and 35 °C.

Nitrogen from a cylinder was passed successively through solutions of hydrochloric acid, sodium hydroxide, and tetramethylammonium chloride (twice) before being bubbled through the test solutions in order to mix them and to prevent the absorption of carbon dioxide. The saturators were at the temperature and ionic strength of the test solutions, except in Series (II), where distilled water replaced the tetramethylammonium chloride solutions.

The titration cell and Wilhelm bridge were immersed in a water-bath whose temperature was controlled to ±0·01 °C by a mercury–toluene regulator operating a heating element through a Sunvic relay (A.E.I. Ltd.). A Frigidaire refrigerator unit with its coil in the water enabled measurements to be made at temperatures below ambient. All operations were carried out in a room maintained at 25 ± 1 °C.

Volumetric glassware was of Grade A and its calibration had been checked.

CALCULATION AND RESULTS

In order to keep the calculations simple it is desirable that no hydroxy-complex is formed. Biedermann and Ciavatta [13] reported that hydrolysis of La^{3+} ion does not occur below pH 6·5. Since the titrations in this work do not reach pH 5, hydrolysis of the metal ion presents no problem. The dissociation constants of tartaric acid were determined in the same conditions as the lanthanum titrations, and have been reported.[2]

Series (I).—The data were first treated as an $LaTar^+$–$LaTar_2^-$ system by the method of Gelles and Nancollas,[14]

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[7] B. E. Conway, R. E. Verrall, and J. E. Desnoyers, *Trans. Faraday Soc.*, 1966, **62**, 2738.

[8] C. W. Foulk and M. Hollingsworth, *J. Amer. Chem. Soc.*, 1923, **45**, 1220; J. A. Shaw, *Ind. Eng. Chem.*, 1926, **18**, 1065; A. C. Titus and D. E. Smith, *J. Amer. Chem. Soc.*, 1941, **63**, 3266.

[9] W. Forsling, S. Hietanen, and L. G. Sillén, *Acta Chem. Scand.*, 1952, **6**, 901.

[10] K. V. Grove-Rasmussen, *Acta Chem. Scand.*, 1949, **3**, 445; 1951, **5**, 442.

[11] G. Biedermann and L. G. Sillén, *Arkiv Kemi*, 1953, **5**, 425.

[12] C. W. Davies, 'Ion Association,' Butterworths, London, 1962.

[13] G. Biedermann and L. Ciavatta, *Acta Chem. Scand.*, 1961, **15**, 1347.

[14] E. Gelles and G. H. Nancollas, *Trans. Faraday Soc.*, 1956, **52**, 98.

but the resultant plots showed a pronounced upward curvature in the low pH region, indicating that protonated complexes were also present. An estimate of β_1 was obtained from data at higher pH's and used to calculate β_{11} from data in the low pH region.[15] β_1 and β_2 were then determined by a modification of Gelles and Nancollas' method which allowed for the effect of the (known) β_{11}. Starting from the estimate obtained above, β_{11} was varied systematically until a good straight line was obtained. The values of β_1 and β_2 given by this line, together with the corresponding value of β_{11}, were taken as the 'best'. Linear plots were obtained for all runs and, at a given ionic strength, gave good agreement between runs, except for one run in 0·2M medium when there was a large ligand–metal ratio at low pH.

Since the data cover a wide range of pH, metal–ligand ratios, and absolute metal and ligand concentrations, and good agreement was found between the various runs, with the exception noted above, it is concluded that the system can be treated as consisting of three complexes, $LaTar^+$, $LaTar_2^-$, and $LaHTar^{2+}$, in most of the conditions studied. Further checks were made to see if the system could be explained in terms of any other combination of complexes.

Treatment of the data by Leden's method[16] gave no evidence for the formation of a $(LaTar)_2^{2+}$ dimer. The assumption of an $LaTar^+$–$LaTar_2^-$–$LaTar_3^{3-}$ system produced only negative stability constants. Allowance for an La_2Tar_3 complex also produced negative constants. The possible existence of the neutral species $LaHTar_2$ was also investigated. There was no evidence for the presence of this complex, except in Run 9, in which the conditions were particularly favourable.

TABLE 3

The stability constants of lanthanum–tartrate complexes

Run	log β_1	$10^3\sigma_1$	log β_2	$10^2\sigma_2$	log β_{11}	$10^2\sigma_{11}$	No. of points
0·1M Medium							
1	3·733	3·9	6·376	4·4	6·533	2·0	21
2	3·649	2·9	6·120	0·8	6·380	1·0	18
3	3·658	6·5	6·266	7·8	6·395	5·5	15
Mean	3·676	2·2	6·128	0·7	6·409	0·9	
0·2M Medium							
4	3·399	7·8	5·729	10·4	6·240	3·3	18
5	3·367	33·8	5·054	69·2	5·923	32·4	15
6	3·403	10·4	5·546	5·9	6·139	53·3	16
7	3·419	7·2	5·675	6·3	6·203	2·7	23
8	3·414	4·9	5·648	4·6	6·149	4·7	42
10	3·420	108·5	5·716	10·2	6·123	38·4	27
Mean	3·410	3·4	5·640	2·9	6·206	1·9	
9 †	(3·410)		(5·640)		6·22	5·9	36
0·4M Medium							
11	3·090	2·4	5·486	2·6	5·848	1·0	22
12	3·157	6·4	5·764	3·2	6·005	5·5	15
13	3·119	6·3	5·541	1·4	(5·820)		11
14	3·116	2·3	(5·559)		5·769	1·3	13
Mean	3·108	1·6	5·559	1·1	5·820	0·8	

† log $\beta_{12} = 9·0$, $\sigma_{12} = 3·5 \times 10^{-2}$.

TABLE 4

Data for lanthanum–tartrate complexing at constant ionic strengths

Run	$10^3[H_2Tar]$/M	$10^3[LaCl_3]$/M	$-\log [H^+]$	$10^3[Me_4NOH]$/M	$10^4[HCl]$/M
1	3·917	3·468	2·511	0·000	5·543
	3·672	3·251	2·789	2·217	5·196
	3·525	3·121	3·013	3·544	4·988
	3·436	3·041	3·190	4·354	4·861
	3·370	2·983	3·354	4·949	4·768
	3·264	2·889	3·739	5·908	4·618
2	4·148	1·838	2·586	0·000	2·938
	3·918	1·736	2·852	1·966	2·775
	3·750	1·662	3·114	3·396	2·656
	3·597	1·594	3·452	4·705	2·548
	3·422	1·517	4·138	6·194	2·424
3	2·076	1·835	2·739	0·000	2·933
	2·005	1·772	2·980	1·211	2·832
	1·939	1·714	3·311	2·340	2·739
	1·877	1·659	3·909	3·395	2·651
4	3·705	3·700	2·514	0·000	9·444
	3·585	3·580	2·666	1·290	9·139
	3·510	3·505	2·780	2·101	8·947
	3·428	3·433	2·904	2·881	8·762
	3·369	3·364	3·043	3·624	8·586
	3·302	3·297	3·203	4·338	8·417
	3·238	3·233	3·393	5·029	8·253
	3·176	3·172	3·645	5·693	8·096
	3·117	3·112	4·026	6·335	7·944
	3·088	3·083	4·306	6·648	7·870
5	1·750	1·755	2·777	0·000	4·479
	1·679	1·684	3·176	1·618	4·297
	1·645	1·650	3·491	2·378	4·212
	1·614	1·618	4·024	3·104	4·130
	1·598	1·603	4·753	3·458	4·090
6	3·914	1·961	2·587	0·000	5·005
	3·692	1·850	2·916	2·258	4·722
	3·538	1·773	3·226	3·827	4·525
	3·394	1·700	3·684	5·297	4·340
	3·293	1·650	4·280	6·324	4·211
7	7·391	3·702	2·379	0·000	9·448
	6·932	3·472	2·592	2·477	8·861
	6·653	3·332	2·751	3·978	8·506
	6·398	3·204	2·920	5·357	8·179
	6·162	3·086	3·104	6·629	7·878
	5·942	2·976	3·320	7·818	7·596
	5·837	2·924	3·430	8·381	7·463
8	5·735	1·916	2·555	0·510	4·891
	5·484	1·823	2·664	1·451	4·677
	5·253	1·755	2·780	2·319	4·480
	5·040	1·684	2·902	3·119	4·298
	4·844	1·618	3·032	3·855	4·131
	4·663	1·558	3·176	4·535	3·977
	4·495	1·502	3·331	5·167	3·833
	4·331	1·447	3·515	5·782	3·694
	4·186	1·399	3·719	6·327	3·570
	4·050	1·353	3·967	6·839	3·454
	3·892	1·300	4·421	7·433	3·319
9	3·655	0·372	3·021	0·9737	0·949
	3·576	1·079	2·938	0·9528	2·755
	3·501	1·758	2·875	0·9327	4·488
	3·429	2·405	2·823	0·9136	6·140
	3·360	3·030	2·781	0·8951	7·733
	3·293	3·633	2·744	0·8773	9·272
	3·299	4·208	2·713	0·8603	10·74
	3·167	4·763	2·685	0·8439	12·16
	3·074	5·607	2·646	0·8189	14·31
	2·993	6·059	2·668	0·9758	15·47
10	4·008	0·403	3·880	5·858	1·030
	3·914	1·173	3·692	5·721	2·993
	3·824	1·911	3·534	5·589	4·879
	3·596	2·339	3·738	6·211	5·970
	3·520	2·996	3·606	6·079	7·648
	3·447	3·624	3·496	5·953	9·250
	3·360	4·374	3·406	5·803	11·16
	3·326	4·663	3·350	5·745	11·90
11	3·497	4·591	2·550	0·000	9·251
	3·335	4·379	2·758	1·599	8·823
	3·257	4·275	2·881	2·379	8·615
	3·163	4·153	3·053	3·300	8·368
	3·076	4·037	3·252	4·170	8·136
	2·940	3·859	3·733	5·515	7·776
12	7·826	2·569	2·778	4·068	5·177
	7·474	2·454	2·936	5·441	4·944
	7·152	2·348	3·101	6·695	4·732
	6·721	2·207	3·373	8·377	4·446
	6·460	2·121	3·580	9·395	4·273
13	3·872	1·018	3·729	5·638	2·050
	3·784	1·987	3·571	5·510	4·005
	3·680	3·139	3·423	5·358	6·325
	3·620	3·799	3·354	5·270	7·655
14	11·61	10·14	2·428	4·424	20·43
	11·09	9·687	2·527	5·765	19·52
	10·40	9·083	2·671	7·562	18·30
	9·985	8·721	2·769	8·649	17·57

The computer program GAUSS G[17] was used to refine the stability constants for each run in turn. Three constants, β_1, β_2, and β_{11} were refined simultaneously. When a

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[15] G. H. Nancollas, 'Interactions in Electrolyte Solutions,' Elsevier, Amsterdam, 1966.

[16] I. Leden, *Svensk kem. Tidskr.*, 1946, **58**, 129.

[17] R. S. Tobias and M. Yasuda, *Inorg. Chem.*, 1963, **2**, 1307.

fourth constant, β_{12}, calculated from the data of Run 9, was included in the runs at 0·2M neither all four constants, nor any three of them, could be refined simultaneously. Two of the four could be refined, but the agreement between different runs was poor and the standard errors larger than when only three complexes were taken into account. The same was true at the other ionic strengths when an estimate of β_{12} was made. The results for the individual runs, together with the weighted means of results at the same ionic strength, are in Table 3. By σ_i is meant the standard deviation in the logarithm of the ith constant. The parentheses in Table 3 indicate that the particular constant was not refined simultaneously with the others, but was given the mean value from the other runs at that ionic strength.

The results were extrapolated to infinite dilution by plotting E_c from equation (2) against I, where I is the ionic

$$E_c = \log \beta_c + r \, . \, A \, . \, I^{\frac{1}{2}}/(1 + B \, . \, a \, . \, I^{\frac{1}{2}}) = \log \beta_c^0 + r \, . \, A \, . \, b \, . \, I \quad (2)$$

strength. A and B are the Debye–Hückel parameters, a and b are adjustable parameters, β_c and β_c^0 are the stability constants at the particular ionic strength, c, and at infinite dilution respectively, and r is an integer characteristic of the equilibrium. The value of r for the constant β_1 is 12. As a was varied systematically, values of E_c were calculated and fitted to the equation $E_c = p \, . \, I + q$ by the method of least squares. The a value which led to the best straight line for the plot of E_c against I was assumed to be correct. The most precisely known constant, β_1, was used in the calculation of E_c for obtaining the best value of a, which was subsequently used in the extrapolation of the other two constants. The best fit resulted from $a = 7$ and gave $\log \beta_1^0 = 4{\cdot}84$. The corresponding values of $\log \beta_2^0$ and $\log \beta_{11}^0$ were $7{\cdot}5 \pm 0{\cdot}2$ and $7{\cdot}45 \pm 0{\cdot}06$ respectively. A selection of the data from which the constants were calculated is given in Table 4. The first and last points for each run are given, together with every fourth point. Run 4 is given in greater detail (alternate points).

Series (II).—Activity coefficients were calculated from equation (3) for an ion of charge z. Activity coefficients

$$-\log f_z = A \, . \, z^2 \, [I^{\frac{1}{2}}/(1 + B \, . \, a \, . \, I^{\frac{1}{2}}) - b \, . \, I] \quad (3)$$

had to be calculated iteratively and since the results in constant ionic media indicate that only three complexes are significant in the conditions under study, the modified Gelles–Nancollas method was used rather than add yet another iterative stage to the GAUSS G program. At constant ionic strength GAUSS G produced only small refinements in the constants obtained by the former method. The values $a = 7$ [from Series (I)] and $b = 0{\cdot}3$ were used in calculating the activity coefficients. The runs were first treated individually and the average value of K_{11}^0 found at the particular temperature. This value was then used to calculate β_1^0 and β_2^0 from the combined data at that temperature. The stability constants, in molal units, are summarised in Table 5.

TABLE 5

Thermodynamic stability constants of lanthanum–tartrate complexes

t/°C	$\log \beta_1^0$	$10^3\sigma_1$ *	$\log \beta_2^0$	$10^2\sigma_2$ *	$\log K_{11}^0$	No. of points
15	4·852	3	7·41	12	3·10	33
25	4·604	3	7·59	4	2·48	40
35	4·876	4	7·93	5	2·70	19

* σ_i is the standard deviation in the logarithm of the ith constant.

TABLE 6

Coefficients of the temperature variation of thermodynamic stability constants

	a	b	10^3c
$\log \beta_1^0$	235·06	−1·547	2·597
$\log \beta_2^0$	74·39	−0·474	0·840
$\log K_{11}^0$	382·65	−2·530	4·210

TABLE 7

Thermodynamic quantities for lanthanum–tartrate complexing at 25 °C

Reaction	$-10^{-4}\Delta G^0$ J mol^{-1}	$10^{-4}\Delta H^0$ J mol^{-1}	ΔS^0 J K^{-1} mol^{-1}
$La^{3+} + Tar^{2-} \rightleftharpoons LaTar^+$	2·63	0·0	95
$La^{3+} + 2Tar^{2-} \rightleftharpoons LaTar_2^-$	4·33	4·47	295
$La^{3+} + HTar^- \rightleftharpoons LaHTar^{2+}$	1·41	0·56	66

TABLE 8

Data for lanthanum–tartrate complexing at low ionic strengths

Run	t/°C	$10^3[H_2Tar]$ mol kg^{-1}	$10^3[LaCl_3]$ mol kg^{-1}	pH	$10^3[Me_4NOH]$ mol kg^{-1}	$10^4[HCl]$ mol kg^{-1}	$10^6[Me_4NCl]$ mol kg^{-1}
15	15	1·324	1·450	3·411	1·993	4·482	1679
		1·314	1·439	3·680	2·400	4·448	2021
		1·310	1·435	3·816	2·544	4·436	2143
16	15	0·8482	1·015	3·040	0·228	3·138	192·4
		0·8432	1·009	3·150	0·551	3·120	464·4
		0·8394	1·005	3·254	0·794	3·106	668·9
		0·8352	0·999	3·397	1·067	3·090	898·2
		0·8316	0·995	3·557	1·302	3·077	1096
		0·8275	0·990	3·827	1·565	3·062	1318
		0·8243	0·986	4·195	1·770	3·050	1490
		0·8233	0·985	4·387	1·833	3·046	1543
17	15	1·663	0·1372	3·964	2·076	0·424	1749
		1·649	0·3059	3·840	2·058	0·946	1733
		1·632	0·5056	3·695	2·037	1·563	1716
		1·611	0·7488	3·544	2·011	2·315	1694
		1·587	1·025	3·419	1·982	3·169	1669
		1·561	1·336	3·319	1·949	4·130	1641
		1·543	1·547	3·260	1·926	4·783	1622
18	25	2·428	0·6419	2·833	0·0690	1·985	1·057
		2·416	0·6386	2·901	0·4356	1·975	6·675
19	25	1·905	0·7698	2·856	0·000	2·380	0·000
		1·895	0·7658	2·934	0·372	2·368	5·704
		1·889	0·7635	2·977	0·587	2·361	9·003
		1·880	0·7599	3·054	0·922	2·349	14·12
		1·876	0·7582	3·098	1·078	2·344	16·52
		1·871	0·7562	3·145	1·261	2·338	19·32
		1·861	0·7521	3·265	1·643	2·325	25·17
		1·844	0·7451	3·528	2·299	2·304	35·23
		1·831	0·7399	3·795	2·777	2·288	42·56
		1·821	0·7358	4·067	3·157	2·275	48·38
20	25	0·8672	0·1855	3·485	0·6274	0·574	9·614
		0·8638	0·2615	3·434	0·6249	0·809	9·576
		0·8575	0·4040	3·355	0·6203	1·249	9·506
		0·8540	0·4828	3·323	0·6178	1·493	9·467
21	25	0·6972	1·025	3·027	0·000	3·170	0·000
		0·6946	1·022	3·114	0·267	3·158	4·098
		0·6915	1·017	3·242	0·581	3·145	8·909
		0·6889	1·013	3·377	0·847	3·133	12·98
		0·6853	1·008	3·665	1·218	3·116	18·66
		0·6834	1·005	3·923	1·413	3·108	21·65
22	35	1·676	1·152	2·822	0·000	3·561	0·000
		1·647	1·132	3·021	0·941	3·500	792·2
		1·635	1·124	3·124	1·338	3·474	1127
		1·614	1·109	3·369	2·032	3·430	1712
		1·599	1·099	3·613	2·514	3·398	2117
		1·585	1·089	4·053	2·998	3·367	2525
23	35	1·618	0·9423	2·892	0·198	2·913	166·6
		1·591	0·9263	3·125	1·127	2·864	948·8
		1·578	0·9188	3·269	1·565	2·841	1318
		1·562	0·9097	3·505	2·093	2·813	1763
		1·551	0·9034	3·733	2·460	2·793	2071
		1·535	0·8941	4·257	2·999	2·764	2525
24	35	0·8545	1·693	3·151	0·918	5·235	772·9
		0·8449	1·674	3·445	1·523	5·177	1283
		0·8412	1·667	3·633	1·758	5·154	1400
25	35	1·865	0·6509	3·427	2·017	2·013	1690
		1·843	0·6434	3·752	2·626	1·989	2201
		1·832	0·6395	3·972	2·947	1·977	2470

The stability constants were related to the absolute temperature by means of equation (4). The coefficients

$$\log \beta = a + b\,.\,T + c\,.\,T^2 \qquad (4)$$

are listed for the three constants in Table 6. The standard entropy change for each reaction was calculated from equation (5) and the enthalpy change from equation (6).

$$\Delta S^0 = R(a + 2b\,.\,T + 3c\,.\,T^2) \qquad (5)$$

$$\Delta G^0 = \Delta H^0 + T\,.\,\Delta S^0 \qquad (6)$$

Table 7 summarises these thermodynamic quantities for the three equilibria at 25 °C.

Table 8 contains a selection of the data from which the results of Series (II) were calculated. The first and last points in each run are given, and alternate points between.

DISCUSSION

Measurements made over a considerable range of pH, metal–ligand ratio, and total metal and total ligand concentrations at a number of ionic strengths and temperatures show that the existence of three complexes, $LaTar^+$, $LaTar_2^-$, and $LaHTar^{2+}$ must be invoked to account for the data. No other complex was significant, except in Run 9, where in conditions of low pH and low metal–ligand ratios there was evidence for $LaHTar_2$. Previous determinations of stability constants may be in error through neglect of one or other of the three main complexes. For example, in Run 4, in which the total metal and ligand concentrations are virtually equal, the approximate relationships (7)—(10) hold. In a titration of this sort neglect of one of the complexes cannot be justified.

$$\text{pH } 2{\cdot}5\text{: } [La^{3+}] \simeq 10[LaTar^+] \simeq 1000[LaTar_2^-] \simeq 5[LaHTar^{2+}] \qquad (7)$$

$$\text{pH } 3{\cdot}0\text{: } [La^{3+}] \simeq 3[LaTar^+] \simeq 120[LaTar_2^-] \simeq 4[LaHTar^{2+}] \qquad (8)$$

$$\text{pH } 3{\cdot}5\text{: } [La^{3+}] \simeq [LaTar^+] \simeq 10[LaTar_2^-] \simeq 5[LaHTar^{2+}] \qquad (9)$$

$$\text{pH } 4{\cdot}0\text{: } [La^{3+}] \simeq [LaTar^+] \simeq 5[LaTar_2^-] \simeq 10[LaHTar^{2+}] \qquad (10)$$

Comparison of the stability constant of lanthanum tartrate at 25 °C and infinite dilution with that for lanthanum succinate in the same conditions,[18] $\log \beta_1{}^0 = 3{\cdot}96$, shows the increased stability of the tartrate complex caused by the co-ordination of the α-hydroxy-groups of the tartrate ion. Shevchenko [19] has studied the i.r. absorption spectrum of solid $La_2(C_4H_4O_6)_3,9H_2O$ and found that some of the hydroxyl groups were co-ordinated and some not. Shevchenko found that lead(II), cadmium(II), and cobalt(II) tartrates exhibited the same behaviour. Grdenic and Kamenar [20] studied $(NH_4)_2Sb_2(C_4H_4O_6)_2,4H_2O$ by *X*-ray diffraction and found that both hydroxyl groups co-ordinate the antimony ion. For aqueous solution, Larsson [21] has reported the coexistence of three types of complexing of the uranyl ion by glycollate ion: (*a*) by the carboxylate group alone, (*b*) by both the carboxylate and hydroxyl groups, and (*c*) directly by the carboxylate group and indirectly by the hydroxyl group, which is hydrogen-bonded to a water molecule in the first co-ordination sphere. The possibilities in the lanthanum–tartrate system, where the ligand has two of each type of co-ordinating group, are even more varied.

Attempts have been made [22] to find the denticity of ligands from Bjerrum's formula [23] (11) where P is the

$$P = S\,.\,R\,.\,T \qquad (11)$$

ratio, k_n/k_{n+1}, of two successive stepwise thermodynamic stability constants, S is a statistical term depending on the co-ordination number of the cation and the denticity of the ligand, T is an electrostatic term, and R is the 'rest effect,' a catch-all for any unconsidered factors. T has been calculated to be *ca.* 6·5 for bivalent ligands in lanthanide complexes.[24] The rest effect is commonly taken to be equal to unity,[25] although Bjerrum found that this need not be so. For lanthanum tartrate at 25 °C, we have found $P = 41$, giving $S\,.\,R = 6{\cdot}2$, which is large enough to indicate that tartrate is more than bidentate.

Compilations of enthalpy and entropy changes for lanthanide complexing have been published,[26] comprising two main bodies: aminopolycarboxylate complexes in 0·1M potassium nitrate or chloride media and monocarboxylate complexes in 2M-sodium perchlorate medium. A few studies have been made at infinite dilution. Of these, lanthanum malonate [27] has a similar standard Gibbs energy change at 25 °C ($-2{\cdot}8 \times 10^4$ J mol^{-1}) to lanthanum tartrate, but the enthalpy change is more positive ($2{\cdot}0 \times 10^4$ J mol^{-1}). The more favourable enthalpy change of the tartrate complex may be ascribed to the effects of the co-ordination of one or both hydroxyl groups. The standard entropy change (160 J K^{-1} mol^{-1}) of the malonate complex is more favourable than for the tartrate. The same trends in the enthalpy and entropy changes have been observed in the rare-earth monocarboxylates and their α-hydroxy-derivatives,[28,29] where it has been suggested that the more favourable enthalpy changes found with the hydroxy-acids arise from the

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participation of the hydroxyl group in the complexing and that the reason for the smaller entropy changes, contrary to what is expected on chelation, lies in the co-ordination of the hydroxyl group *via* a water molecule in the first co-ordination sphere of the cation. In this case the normal entropy gain on chelation, caused by the release of extra particles into the system, does not occur, although the loss of configurational entropy of the ligand still does, resulting in a net lower entropy gain for the hydroxy-acid complexes than for unsubstituted ligands.

The above interpretation ignores the contribution to the entropy changes made by the release of water molecules from the hydration sphere of the anion. The compilation by Christensen, Oscarson, and Izatt[30] shows that the entropy change of dissociation is more negative for a monocarboxylic acid than for its α-hydroxy-derivative, where hydrogen bonding between the hydroxyl group and the carboxylate group may reduce the number of water molecules entering the anion's co-sphere, thus making the entropy change less negative, in spite of any loss of configurational entropy caused by the hydrogen bonding. The same phenomenon is observed in the first dissociation of a dicarboxylic acid when either there is a hydroxyl group available for hydrogen bonding or the second carboxyl group is in a position to do the same. The magnitudes of ΔS_1^0(diss) for various acids are in the order maleic $\sim$ oxalic $>$ tartaric $\sim$ malonic $>$ malic $>$ succinic $>$ glutaric $\simeq$ adipic $\simeq$ pimelic $\simeq$ suberic. The values of ΔS_2^0(diss) are much the same for all the acids except tartaric, which has a second hydroxyl group available and a less negative value of ΔS_2^0(diss) also. It is interesting to compare the difference in ΔS_1^0(diss) for acetic and glycollic acids at infinite dilution, 20 J K^{-1} mol^{-1}, with the difference reported by Grenthe[28] between the entropy changes on complexing of lanthanum acetate and glycollate, 28 J K^{-1} mol^{-1}, in a 2M-sodium perchlorate medium. Comparison of literature values for lanthanum malonate and ours for the tartrate gives a difference in ΔS^0 of 65 J K^{-1} mol^{-1}, perhaps reflecting a double effect from the two hydroxyl groups of the tartrate anion.

The evidence from ratios of successive stability constants and from the thermodynamic data is not strong enough to confirm that α-hydroxy-acids chelate only indirectly *via* a bound water molecule, or even that such co-ordination is the most important of Larsson's three possible types.

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