

Thermodynamic Properties of Rare Earth Complexes

XIX. Free Energy, Enthalpy, and Entropy Changes for the Formation of Some Lanthanoid Maleate Complexes

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The changes in free energy, enthalpy, and entropy for the formation of Pr, Sm, Gd, Ho, and Yb maleate complexes with the composition MA and MA₂ have been determined. The changes in free energy were calculated from stability constants, determined by a standard potentiometric method, *viz.* the determination of the concentration of free hydrogen ion, using a glass electrode. The enthalpy changes were measured calorimetrically. All data refer to a temperature of 25.0°C and 1 M Na(ClO₄) medium.

A fairly small number of investigations of the complex formation of trivalent lanthanoids with bidentate ligands containing oxygen donors have been published. In most of these investigations only the stability constants have been determined, but in some cases, *e.g.* for the glycolate,¹ malonate,^{2,3} kojate,⁴ tropolonate,⁵ and acetylacetonate⁶ systems, both free energy and enthalpy data for the complexation reactions have been obtained. The limited number of data is undoubtedly connected with the ease of formation of solid phases with this type of bidentate ligands.

Our series of investigations on lanthanoid dicarboxylate complexes has been extended to the maleate complexes in order to permit a further discussion of the following points:

a. We have been interested in the variation of thermodynamic quantities within the lanthanoid series. For the five ligands mentioned above, a regular and near linear variation of ΔG_j° , ΔH_j° and ΔS_j° with the ionic radius or the atomic number is found. This is at variance with the trends observed for a number of other ligands, *e.g.* oxydiacetate⁷ and iminodiacetate,⁸ where $\Delta H^\circ(Z)$ and $\Delta S^\circ(Z)$ increase rapidly in the region Sm–Tb. As the malonate ion is the only dicarboxylate in the group of bidentate ligands studied so far,⁹ it seems motivated to investigate the complexation reactions of another bidentate ligand, *viz.* the maleate ion.

b. When the ligand is the anion of a polyprotic acid, there is a possibility for the formation of acid complexes of the type MH_qA_r , $q > 0$. Such acid complexes have been detected, *e.g.* in the malonate and thiodiacetate¹⁰ systems. X-Ray studies of solid maleic acid have shown that there is a strong intramolecular hydrogen bond in the hydrogen maleate ion.¹¹ This bond must be broken when the hydrogen maleate ion forms a complex with a metal ion, thus rendering the formation of an acid complex energetically unfavoured. Hence, the corresponding stability constants ought to be small. It is of interest to investigate whether this is true or not.

c. A well-established structural effect in chelate complexes is the enhanced stability of five-membered rings as compared to six-membered ones. The lanthanoid complexes with oxalate ion,¹² which forms a five-membered ring, are much stronger than those formed with malonate ion⁹ where a six-membered ring is formed. We have been interested to see, if a further decrease in stability is observed when a chelate containing a seven-membered ring is formed. When this comparison is made, one has to be aware of the difference in ligand geometry of the maleate ion as compared to oxalate and malonate, due to the presence of a double bond in the maleate ion.

There are some earlier investigations on rare earth maleate complexes. Roulet *et al.*¹³ have determined stability constants for the 1:1 and 1:2 complexes at 25°C and ionic strength 0.1 M (NaClO_4).

Paramonova *et al.*¹⁴ described the results of an ion-exchange study on the europium system by assuming that both maleate ion and hydrogen maleate ion formed 1:1 complexes with the metal ion.

Choppin *et al.*²² have determined ΔH°_1 for the lanthanoid maleate complexes at ionic strength 0.1 M.

This paper describes the determination of the changes in free energy, enthalpy and entropy for the formation of the Pr^{3+} , Sm^{3+} , Gd^{3+} , Ho^{3+} , and Yb^{3+} maleates. The changes in free energy were calculated from the stability constants, which were determined from potentiometric measurements of the hydrogen ion concentration in solutions, containing metal perchlorate, maleic acid and disodium maleate. The enthalpy values were obtained in a direct calorimetric determination. The solvent was an aqueous sodium perchlorate medium with the total sodium ion concentration equal to 1.00 M. The temperature was $25.0 \pm 0.1^\circ\text{C}$.

NOTATIONS AND CALCULATIONS

The notations have been defined earlier.^{8,9}

The stability constants and enthalpy values have been calculated by least-squares programs in the "Letagrop" series.^{15,16} Different error-carrying variables, *viz.* E/mV and \bar{n}_H , respectively, have been used in the calculation of the stability constants from (v/ml , E/mV)-data. A least-squares program, using weighted (a/M , \bar{n})-data has also been used.¹⁷ The weighting scheme assumes that the relative error in the determination of the concentration of free ligand is constant.

In addition, standard graphical procedures have been used for some systems.

EXPERIMENTAL

Chemicals used. The preparation and standardisation of the lanthanoid perchlorate and sodium perchlorate solutions have been described earlier.⁹

The formula weight of the maleic acid (Fluka, *p.a.*) was determined by alkalimetric titration as 116.3 (calc. 116.1). However, neither this method nor any electrometric titration with the equipment used here can be used to decide whether small amounts of fumaric acid are present or not. The presence of about 1 % fumaric acid in the Fluka sample was shown by thin layer chromatography.¹⁸ Maleic acid can be separated from fumaric acid by using the fact that only maleic acid can form an anhydride, which can be distilled.¹⁹ Thus, a 0.5 M stock solution of maleic acid was prepared after distilling the solid acid under reduced pressure, adding water to the anhydride obtained and standardising the solution with sodium hydroxide.

The potentiometric measurements on the proton and lanthanoid maleate systems were performed as titrations in the same way and with the same equipment as used before.⁹ Contamination of the solutions with carbon dioxide was prevented by bubbling nitrogen through the solution in the titration vessel. The experimental emf-values were corrected for a hydrogen ion and a perchlorate ion dependent liquid junction potential in the same way as was described for the malonates.^{9,p-1398} The perchlorate ion dependent liquid junction potential is a linear function of the perchlorate ion concentration with the slope 6.4 mV/M.

The stabilities of the proton maleate complexes were determined in solutions with $C_M = 0$ and with different constant values of the total maleate concentration, *viz.* $C_A = 25$ mM, 50 mM, 100 mM, and 200 mM. With C_A -values greater than 125 mM, a precipitate with the composition $\text{NaHA} \cdot \frac{1}{2}\text{H}_2\text{O}$ (after air-drying) is formed in solutions with \bar{n}_H approximately equal to 1.

In order to get precise values of the stability constants of the various complexes, a wide concentration range must be covered in the titrations. The ratio C_H/C_A varies from 1 to about 1/5, and the total metal ion concentration is in the range 15 mM to 40 mM. In solutions with $C_M > 20$ mM, a precipitate is formed when the value of \bar{n} in the solution is close to 1.5.

The calorimetric measurements were made with the calorimeter developed by Grenthe, Ots and Ginstrup,²⁰ using the same titrimetric technique as described for the malonates.³

The enthalpy values for the protonation of the maleate ion were determined by titrating disodium maleate solution with perchloric acid.

The heats of formation of the metal maleates were determined by titrating a metal solution with maleate buffers. The initial total metal ion concentration was about 20 mM, and two different buffer solutions with the ratio C_H/C_A equal to 2/5 and 1/3, respectively, were used. For each system, about 25 experimental points were measured.

RESULTS

Determination of the stability constants

The proton maleate system. The potentiometric measurements were described by assuming the existence of two proton maleate complexes, HA and H_2A , with the following stability constants:

$$\begin{aligned}\beta_{0,1,1} &= (4.15 \pm 0.04) \times 10^5 \text{ M}^{-1} \\ \beta_{0,2,1} &= (1.65 \pm 0.03) \times 10^7 \text{ M}^{-2}\end{aligned}$$

These values were calculated in a "Letagrop" least-squares treatment of 182 experimental (v/ml , E/mV)-values. The standard deviation in C_H/C_A was equal to 6.3×10^{-3} . The experimental values are satisfactorily described by the calculated constants, except for some points with high \bar{n}_H -values ($\bar{n}_H > 1.35$), where the values of $\bar{n}_{H, \text{calc}}$ exceed the $\bar{n}_{H, \text{exp}}$ -values with at most

1.5 %. This deviation might in part be due to an error in the correction for the hydrogen ion dependent liquid junction potential in the very acid solutions used here.

The lanthanoid maleate systems. Fig. 1 shows calculated \bar{n} vs. $-\log(a/M)$ curves for the samarium and ytterbium systems, together with some experi-

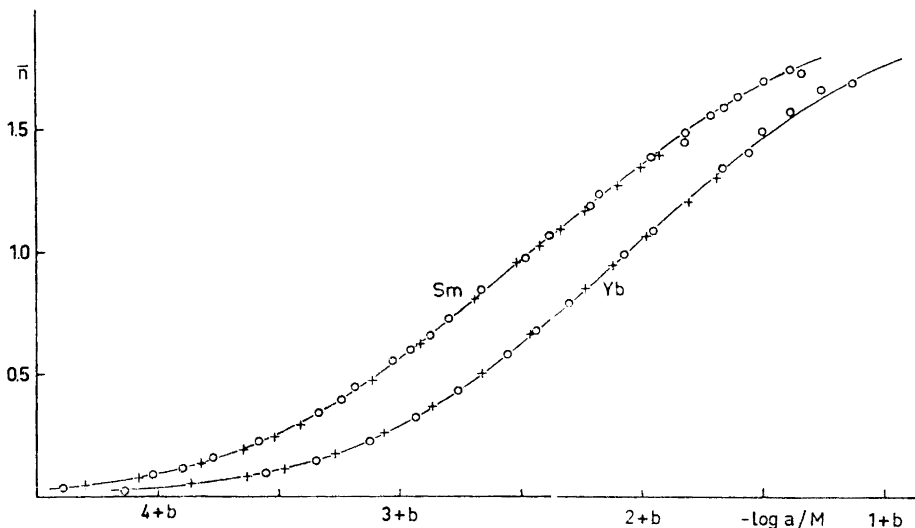


Fig. 1. Experimental \bar{n} vs. $-\log(a/M)$ data for the samarium and ytterbium systems. The curves have been calculated with the constants in Table 2. The value of b is zero for the Sm system and 0.25 for the Yb system. Titrations with $C_M = 20$ mM and 40 mM are denoted with \circ and $+$, respectively.

mental points. Primary data for the praseodymium system are given in Table 1, and the calculated stability constants for the systems investigated are given in Table 2.

The stability constants have been calculated with the least-squares procedures using different error-carrying variables, *viz.* the measured emf E and C_H/C_A , respectively, in the "Letagrop" calculations. The same experimental points were used but the different choices of the error-carrying variable correspond to a different weighting of the data. The calculated values of the stability constants are the same in the two procedures, as they should be, but not the estimates of the corresponding standard deviations. Table 3 shows that the "Letagrop" procedure with the emf E as error-carrying variable gives the lowest values of the errors, especially for the stability constant $\beta_{1,1,1}$ of the acid complex MHA. The largest estimates are obtained by using weighted $(a/M, \bar{n})$ -data in the calculations. The limits of error for the constants, quoted in Table 2, have been calculated by multiplying these estimates of the standard deviations with three.

Table 1. Experimental results of the potentiometric measurements on the praseodymium maleate system. Values of v/ml and E/mV are given. The sodium ion concentration is 1.00 M in all solutions.

- Series 1.* S: $C_{\text{H}}=0.00091$ M, $C_{\text{M}}=0.01941$ M, $C_{\text{A}}=0$;
 T: $C_{\text{H}}=0.06254$ M, $C_{\text{M}}=0.01941$ M, $C_{\text{A}}=0.1807$ M;
 $V_0=19.96$ ml; $E_0=497.7$ mV.
 0.250, 253.8; 0.500, 233.4; 0.750, 226.0; 1.000, 221.5; 1.500, 215.8; 2.000, 211.5;
 3.000, 205.2; 4.000, 200.1; 5.000, 195.4; 7.000, 187.7; 9.000, 182.3; 12.00, 176.7.
- Series 2.* S: $C_{\text{H}}=0.00148$ M, $C_{\text{M}}=0.03115$ M, $C_{\text{A}}=0$;
 T: $C_{\text{H}}=0.08322$ M, $C_{\text{M}}=0.03115$ M, $C_{\text{A}}=0.1908$ M;
 $V_0=19.96$ ml; $E_0=497.3$ mV.
 0.500, 265.0; 0.750, 254.0; 1.000, 248.6; 1.500, 242.1; 2.000, 238.3; 2.500, 235.2;
 3.000, 233.3; 4.000, 229.7; 5.000, 226.9; 7.000, 221.5; 10.00, 214.6; 12.00, 210.7;
 15.00, 205.7; 17.00, 203.0.
- Series 3.* S: $C_{\text{H}}=0.05072$ M, $C_{\text{M}}=0.02009$ M, $C_{\text{A}}=0.02500$ M;
 T: $C_{\text{H}}=0.00081$ M, $C_{\text{M}}=0.02009$ M, $C_{\text{A}}=0.02500$ M;
 $V_0=20.01$ ml; $E_0=389.5$ mV.
 3.000, 275.2; 5.000, 269.3; 7.000, 263.3; 9.000, 257.1; 11.00, 250.5; 14.00, 239.5;
 17.00, 226.1; 20.00, 208.8; 25.00, 178.8; 30.00, 159.9.
- Series 4.* S: $C_{\text{H}}=0.02078$ M, $C_{\text{M}}=0.02009$ M, $C_{\text{A}}=0.02500$ M;
 T: $C_{\text{H}}=0.00081$ M, $C_{\text{M}}=0.02009$ M, $C_{\text{A}}=0.02500$ M;
 $V_0=30.00$ ml; $E_0=389.3$ mV.
 5.000, 140.8; 10.00, 129.1; 15.00, 120.4; 20.00, 113.9; 25.00, 108.5; 30.00, 103.7.
- Series 5.* S: $C_{\text{H}}=0.0108$ M, $C_{\text{M}}=0.02009$ M, $C_{\text{A}}=0.02500$ M;
 T: $C_{\text{H}}=0.00081$ M, $C_{\text{M}}=0.02009$ M, $C_{\text{A}}=0.02500$ M;
 $V_0=20.01$ ml; $E_0=389.3$ mV.
 5.000, 93.1; 10.00, 85.7; 15.00, 79.8; 20.00, 75.2.
- Series 6.* S: $C_{\text{H}}=0.00581$ M, $C_{\text{M}}=0.02009$ M, $C_{\text{A}}=0.02500$ M;
 T: $C_{\text{H}}=0.00081$ M, $C_{\text{M}}=0.02009$ M, $C_{\text{A}}=0.02500$ M;
 $V_0=20.00$ ml; $E_0=389.2$ mV.
 5.000, 68.1; 10.00, 63.0.
- Series 7.* S: $C_{\text{H}}=0.1007$ M, $C_{\text{M}}=0.02009$ M, $C_{\text{A}}=0.05000$ M;
 T: $C_{\text{H}}=0.00090$ M, $C_{\text{M}}=0.02009$ M, $C_{\text{A}}=0.05000$ M;
 $V_0=20.01$ ml; $E_0=389.4$ mV.
 5.000, 279.3; 7.000, 272.4; 9.000, 265.4; 11.00, 258.2; 14.00, 245.8; 17.00, 230.4;
 20.00, 209.7; 25.00, 174.2; 30.00, 153.2.
- Series 8.* S: $C_{\text{H}}=0.04083$ M, $C_{\text{M}}=0.02009$ M, $C_{\text{A}}=0.05000$ M;
 T: $C_{\text{H}}=0.00090$ M, $C_{\text{M}}=0.02009$ M, $C_{\text{A}}=0.05000$ M;
 $V_0=30.00$ ml; $E_0=389.0$ mV.
 5.000, 131.7; 10.00, 117.8; 15.00, 107.5; 20.00, 99.4; 25.00, 92.8; 30.00, 87.3.
- Series 9.* S: $C_{\text{H}}=0.02087$ M, $C_{\text{M}}=0.02009$ M, $C_{\text{A}}=0.05000$ M;
 T: $C_{\text{H}}=0.00090$ M, $C_{\text{M}}=0.02009$ M, $C_{\text{A}}=0.05000$ M;
 $V_0=20.00$ ml; $E_0=388.9$ mV.
 5.000, 75.0; 10.00, 66.4; 15.00, 59.9; 20.00, 54.7.

Table 2. The overall stability constants for the maleate complexes, calculated from $([A], \bar{n})$ -data. The errors are equal to three standard deviations.

Metal ion	Number of experimental points	$\beta_{1,0,1} \times 10^{-2} \text{ M}$	$\beta_{1,0,2} \times 10^{-4} \text{ M}^2$
Pr	56	6.50 ± 0.22	4.96 ± 0.36
Sm	143	9.98 ± 0.09	8.00 ± 0.15
Gd	73	9.24 ± 0.10	6.10 ± 0.14
Ho	59	7.73 ± 0.34	4.73 ± 0.50
Yb	60	6.39 ± 0.13	4.44 ± 0.18

Table 3. "Letagrop" calculations of the stability constants for the Pr, Sm, and Gd maleate complexes with different error-carrying variable y , and with two different assumptions as to which complexes are formed. The number of experimental points is also given.

Metal ion	Assumed complexes	$y = C_H/C_A$		$y = E$	
		sig $y \times 10^3$	Calculated stability constants	sig y/mV	Calculated stability constants
Pr (67 p).	MA	3.81	$(6.22 \pm 0.10) \times 10^2$	0.44	$(6.27 \pm 0.10) \times 10^2$
	MA ₂		$(5.05 \pm 0.21) \times 10^4$		$(5.01 \pm 0.17) \times 10^4$
	MA	3.33	$(6.42 \pm 0.16) \times 10^2$	0.45	$(6.36 \pm 0.10) \times 10^2$
	MA ₂ MHA		5.1×10^4 $(3.9 \pm 2.9) \times 10^4$		5.1×10^4 $(1.75 \pm 0.80) \times 10^5$
Sm (239 p).	MA	3.62	$(10.02 \pm 0.08) \times 10^2$	0.64	$(10.28 \pm 0.08) \times 10^2$
	MA ₂		$(8.09 \pm 0.20) \times 10^5$		$(8.27 \pm 0.17) \times 10^4$
	MA	4.33	$(10.09 \pm 0.09) \times 10^2$		The calculations did not converge.
	MA ₂ MHA		8.1×10^4 $(0 \pm 2.4) \times 10^5$		
Gd (132 p).	MA	2.67	$(9.14 \pm 0.09) \times 10^2$	0.41	$(9.02 \pm 0.04) \times 10^2$
	MA ₂		$(5.97 \pm 0.13) \times 10^4$		$(6.00 \pm 0.01) \times 10^4$
	MA	2.43	$(9.31 \pm 0.12) \times 10^2$	0.37	$(9.17 \pm 0.09) \times 10^2$
	MA ₂ MHA		6.0×10^4 $(2.5 \pm 1.3) \times 10^5$		6.0×10^4 $(1.3 \pm 0.14) \times 10^5$

In the Pr, Sm, and Gd systems measurements were made with solutions containing a high concentration of hydrogen maleate ion, in order to obtain information on the possible formation and the stability of an acid complex MHA. (These points have not been used for the calculations presented in Table 2.) Table 3 shows that the calculated $\beta_{1,1,1}$ -values are significantly positive for the praseodymium and gadolinium systems, though the estimated errors are fairly large. However, this fact is not sufficient to justify a claim as to the existence of this species; the effects of experimental errors must also be considered. For the acid solutions used, small concentration errors or small errors in the measured emf give large errors in the constant $\beta_{1,1,1}$. In fact,

the positive values found for the Pr and Gd systems disappear if the total concentrations and E_0 -values are changed in a few titration series with at most 0.5 % or 0.2 mV. The equilibrium constant $K_{M, HA}$ for the reaction $M + HA \rightleftharpoons MHA$ is about 1 M^{-1} , according to the $\beta_{1,1,1}$ -values found, and the experimental technique used here thus gives an upper limit for $K_{M, HA}$ of about 2 M^{-1} . This is the value found by Paramonova *et al.*¹⁴ for the europium system in 0.5 M NaNO_3 .

The accuracy of the calculated stability constants depends on the uncertainties in the protonation constants; an error of 1 % in $\beta_{0,1,1}$ thus corresponds to an error of 1 % in $\beta_{1,0,1}$ and 3 % in $\beta_{1,0,2}$.

Determination of the enthalpy values

The heats of protonation of the maleate ion were determined from 25 experimental points, and the following values were obtained:

$$\Delta H_{0,1,1}^{\circ} = (0.75 \pm 0.12) \text{ kJ mol}^{-1}$$

$$\Delta H_{0,2,1}^{\circ} = (1.38 \pm 0.25) \text{ kJ mol}^{-1}$$

Table 4. Experimental results of the calorimetric measurements on the praseodymium maleate system. Corresponding values of v/ml , $Q_{\text{corr,exp}}/J$ and $(Q_{\text{corr,calc}} - Q_{\text{corr,exp}})/J$ are given.

- Series 1.* S: $C_{\text{H}} = 0.00116 \text{ M}$, $C_{\text{M}} = 0.02108 \text{ M}$, $C_{\text{A}} = 0.001194 \text{ M}$;
 T: $C_{\text{H}} = 0.1042 \text{ M}$, $C_{\text{M}} = 0$, $C_{\text{A}} = 0.3004 \text{ M}$;
 $V_0 = 100.60 \text{ ml}$.
 3.000, 5.700, 0.088; 6.000, 5.420, 0.074; 9.000, 5.093, -0.072; 12.00, 4.519, -0.105; 15.00, 3.760, -0.030; 18.00, 2.899, 0.150.
- Series 2.* S: $C_{\text{H}} = 0.00116 \text{ M}$, $C_{\text{M}} = 0.02108 \text{ M}$, $C_{\text{A}} = 0.001194 \text{ M}$;
 T: $C_{\text{H}} = 0.1042 \text{ M}$, $C_{\text{M}} = 0$, $C_{\text{A}} = 0.3004 \text{ M}$;
 $V_0 = 100.60 \text{ ml}$.
 3.000, 5.688, 0.100; 6.000, 5.542, -0.048; 9.00, 5.172, -0.151; 12.00, 4.544, -0.130; 15.00, 3.710, 0.020; 18.00, 2.877, 0.172.
- Series 3a.* S: $C_{\text{H}} = 0.000436 \text{ M}$, $C_{\text{M}} = 0.01837 \text{ M}$, $C_{\text{A}} = 0$;
 T: $C_{\text{H}} = 0.1032 \text{ M}$, $C_{\text{M}} = 0$, $C_{\text{A}} = 0.3011 \text{ M}$;
 $V_0 = 79.93 \text{ ml}$.
 3.000, 5.188, 0.163; 6.000, 4.975, -0.033; 9.000, 4.092, -0.121; 12.00, 3.084, -0.134; 15.00, 2.067, 0.038; 18.00, 1.351, 0.125; 21.00, 0.937, 0.113.
- Series 3b.* S: $C_{\text{H}} = 0.02181 \text{ M}$, $C_{\text{M}} = 0.01455 \text{ M}$, $C_{\text{A}} = 0.06266 \text{ M}$;
 T: $C_{\text{H}} = 0.1032 \text{ M}$, $C_{\text{M}} = 0$, $C_{\text{A}} = 0.3011 \text{ M}$;
 $V_0 = 81.93 \text{ ml}$.
 3.000, 0.686, 0.054; 6.000, 0.448, 0.075.
- Series 4a.* S: $C_{\text{H}} = 0.000436 \text{ M}$, $C_{\text{M}} = 0.01837 \text{ M}$, $C_{\text{A}} = 0$;
 T: $C_{\text{H}} = 0.1032 \text{ M}$, $C_{\text{M}} = 0$, $C_{\text{A}} = 0.3011 \text{ M}$;
 $V_0 = 79.93 \text{ ml}$.
 2.000, 3.410, 0.117; 5.000, 5.192, 0.021; 8.000, 4.481, -0.167; 11.00, 3.431, -0.151; 14.00, 2.393, -0.033; 17.00, 1.573, 0.088; 20.00, 1.063, 0.113.
- Series 4b.* S: $C_{\text{H}} = 0.02100 \text{ M}$, $C_{\text{M}} = 0.01469 \text{ M}$, $C_{\text{A}} = 0.06027 \text{ M}$;
 T: $C_{\text{H}} = 0.1032 \text{ M}$, $C_{\text{M}} = 0$, $C_{\text{A}} = 0.3011 \text{ M}$;
 $V_0 = 84.93 \text{ ml}$.
 3.000, 0.628, 0.201; 6.000, 0.519, 0.063; 9.000, 0.347, 0.079.

Table 5. The changes in enthalpy, free energy and entropy for the formation of lanthanoid maleate complexes. The errors in the enthalpy values are equal to three standard deviations.

Metal ion	Standard deviation in Q_{corr}/J	$\Delta H^\circ_{1,0,1}$ kJ mol ⁻¹	$\Delta G^\circ_{1,0,1}$ kJ mol ⁻¹	$\Delta S^\circ_{1,0,1}$ J mol ⁻¹ K ⁻¹	$\Delta H^\circ_{1,0,2}$ kJ mol ⁻¹	$\Delta G^\circ_{1,0,2}$ kJ mol ⁻¹	$\Delta S^\circ_{1,0,3}$ J mol ⁻¹ K ⁻¹
Pr	0.116	10.80 ± 0.45	-16.06	90.1	20.0 ± 0.8	-26.80	157
Sm	0.044	10.67 ± 0.13	-17.12	93.2	17.74 ± 0.23	-28.00	153
Gd	0.043	12.51 ± 0.12	-16.94	98.8	19.83 ± 0.23	-27.32	158
Ho	0.076	15.44 ± 0.23	-16.47	107.0	24.1 ± 0.5	-26.60	170
Yb	0.055	16.32 ± 0.16	-16.01	108.4	27.03 ± 0.29	-26.53	179

The standard deviation in Q_{corr} was 0.20 J. The errors are fairly large, but as this does not affect the further calculations on the metal complexes very much, no further work has been done on this system.

The values of the changes in free energy and entropy for the formation of proton maleate complexes at 25°C are:

$$\begin{aligned}\Delta G^\circ_{0,1,1} &= -32.14 \text{ kJ mol}^{-1} \\ \Delta G^\circ_{0,2,1} &= -40.69 \text{ kJ mol}^{-1} \\ \Delta S^\circ_{0,1,1} &= 110.3 \text{ J K}^{-1} \text{ mol}^{-1} \\ \Delta S^\circ_{0,2,1} &= 141.1 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

Experimental data for the determination of the heats of formation of the praseodymium maleate complexes are given in Table 4. The Q_{corr} -values include the small correction for the heats of dilution of the titrant. The overall enthalpy changes for the formation of the complexes are given in Table 5, together with the corresponding free energy and entropy changes. The standard deviation in the individual measurements, denoted *sig* Q_{corr} , is of the magnitude expected from the precision of the calorimetric equipment. The large error for the praseodymium system is an exception which cannot be explained, either as due to errors in the calorimetric procedure or to reasonable errors in the concentrations of the solutions.

DISCUSSION

The entropy of formation of lanthanoid maleate complexes is an approximately linear function of the atomic number, as is also the case for the malonates and other bidentate ligands with oxygen donors. The ΔH°_1 -values are nearly the same for the malonates³ and the maleates; the small differences are, however, larger than the experimental errors.

The non-monotonous, "normal" variation pattern of thermodynamic properties across the lanthanoid series as shown by, *e.g.*, the oxydiacetates,⁷ has been interpreted as due to a release of different numbers of water molecules in the complex formation reactions. This in turn might be a result of different hydration numbers for the lanthanoid ions. According to Choppin *et al.*,⁴ the

approximately linear behaviour of the ΔS° vs. Z function is a reflection of the fact that the mono-ligand complexes consist of species of different hydration in equilibrium. It is in principle possible to check this hypothesis, *e.g.* by measuring the temperature variation of ΔH° . This will be difficult to do experimentally with this type of ligand, as solid phases are easily formed. Measurements of this type on some malonate systems are, however, in progress at this laboratory.

In some cases, when the ligand is the anion of a polyprotic acid, protonated forms of the ligand also form complexes with lanthanoid ions. Stability constants $K_{M, HA}$ for the formation of some such ternary complexes are given in Table 6. The correlation between $K_{M, HA}$ and the protonation constant

Table 6. The protonation constants ($K_{H, HA}$) and stability constants for europium (or samarium) complexes ($K_{M, HA}$) with some protonated ligands.

Ligand	$\log(K_{H, HA} M)$	$\log(K_{M, HA} M)$	Ref.
Hydrogen oxalate ion ($M = Eu^{3+}$)	0.91	1.50	14
Hydrogen maleate ion ($M = Eu^{3+}$)	1.53	0.3	14
Hydrogen maleate ion	1.60	< 0.3	This study
Iminodiacetic acid ($M = Eu^{3+}$)	1.88	0.97	8
Hydrogen malonate ion ($M = Eu^{3+}$)	2.55	1.42	9
Hydrogen iminodiacetate ion ($M = Eu^{3+}$)	2.58	1.48	8
Hydrogen thiodiacetate ion ($M = Sm^{3+}$)	3.13	1.60	10
Hydrogen succinate ion ($M = Eu^{3+}$)	4.2	2.0	23

of the ligand HA is poor. According to experiments, the value of $K_{M, HA}$ is less than $2 M^{-1}$ for the maleates, *i.e.* hydrogen maleate ion forms the least stable complexes of the ligands quoted in Table 6. The formation of an acid maleate complex MHA with a chelated lanthanoid ion is energetically unfavoured, as a strong hydrogen bond in the hydrogen maleate ion has then to be broken. The large electrostatic repulsion from a chelated lanthanoid ion will also prevent a hydrogen ion from coordinating to any carboxylate oxygen.

The stability constants decrease in the order oxalates > malonates > maleates, *i.e.* the stability constants decrease when the size of the chelate ring increases. The enhanced stability of the malonates as compared to the maleates is almost entirely due to the more positive entropy change for the malonates. Nancollas *et al.*²¹ have calculated thermodynamic functions for the formation of oxalate and malonate complexes of some transition metal ions. The lower stabilities of the malonates was nearly entirely an enthalpy effect. There are no determinations of enthalpy values for lanthanoid oxalate complexes, due to their low solubilities.

The effect on thermodynamic properties of changing the ionic medium can be assessed for the malonates and maleates, as complexes with both these ligands have been studied in different ionic media.²² When the medium

is changed from 0.1 M NaClO₄ to 1.00 M Na(ClO₄), there is a change in the ΔG°_1 -values with about +5 kJ mol⁻¹, both for the malonates and maleates.¹³ This is mainly due to a corresponding decrease in ΔS°_1 , whereas the enthalpy changes, ΔH°_1 , are less sensitive to changes in the ionic medium.

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