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Thermodynamic Properties of Rare Earth Complexes

XIV. Free Energy, Enthalpy and Entropy Changes for the Formation of Lanthanoid Malonate and Hydrogen Malonate Complexes

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The changes in free energy, enthalpy and entropy for the formation of lanthanoid (III) malonate and hydrogen malonate complexes have been determined. The free energy changes were computed from the previously determined stability constants. The enthalpy changes were obtained from a direct calorimetric determination of the heats of complex formation. All data refer to a temperature of 25.0°C and a sodium perchlorate medium with the sodium ion concentration equal to 1.00 M.

Earlier in this series of investigations on the thermodynamic properties of lanthanoid (III) carboxylate complexes, the stability constants for the formation of malonate and hydrogen malonate complexes have been determined.[1] This paper describes a calorimetric determination of the corresponding enthalpy changes.

Values of the changes in free energy, entropy and enthalpy for the formation of the first malonate complex with lanthanum (3+), gadolinium (3+), and lutetium (3+) have been reported by Gelles and Nancollas.[2] The enthalpy changes were determined from the temperature dependence of the stability constants; a method which will give enthalpy values with low precision.

Grenthe and Hansson have determined ΔG_i°, ΔH_i° and ΔS_i° for the formation of scandium (III) malonate, diglycolate and dipicolinate complexes.[3] The values of the enthalpy change (ΔH_1°) and entropy change (ΔS_1°) for the formation of the first scandium diglycolate and dipicolinate complexes are of the expected magnitude, as estimated from the general trends in the variation of ΔH_1° and ΔS_1° with respect to the ionic radius within the lanthanoid series. This is not the case for the entropy change for the formation of the second scandium diglycolate (and dipicolinate) complex.

The formation of the diglycolate and dipicolinate complexes is exothermic, while the formation of the malonate complexes is endothermic. The values of ΔS_1° is about the same for the formation of the malonate, diglycolate and dipi-

colinate complexes, whereas ΔS_2° for the malonate complex is much larger than for the other two complexes. With data for the corresponding lanthanoid complexes available, it might be possible to decide whether this "anomalous" behaviour is due to the small radius of the scandium ion or to some property of the ligand.

The calorimeter described by Grenthe *et al.*[4] has been used in this work. The measurements were performed at 25.00°C in an aqueous sodium perchlorate medium with the total sodium ion concentration equal to 1.00 M.

NOTATIONS AND CALCULATIONS

The notations used here have been defined in Refs. 1 and 5. The enthalpy changes have been calculated from the experimental data by the least-squares method LETAGROP KALLE, developed by Arnek and Sillén.[6] Only the heats of the malonate ion have been calculated by standard graphical methods.[7]

EXPERIMENTAL

Chemicals used. Stock solutions of the various rare earth perchlorates, malonic acid, disodium malonate and sodium perchlorate were prepared and analyzed as described before.[1]

Procedure. The titration calorimeter developed by Grenthe *et al.* was used for these measurements. Two different inner vessels have been used, one containing about 120 ml and the other about 103 ml. The inner vessel is filled with a solution S with an initial volume V_0 equal to 100.0 ml or 80.0 ml. When the S solution has the same temperature as the outer thermostat bath, a portion (at most 3 ml) of the titrant solution T is added from a piston burette. Additions were made at a constant rate, 1 ml/min. When the inner vessel is filled, a suitable volume is withdrawn through the outlet tube, which is connected to a second piston burette.

The system was electrically calibrated and in general two calibrations were made during each run.

The heats of dilution of the T solutions were determined by successive additions of T solution to an S solution consisting of 1.00 M $NaClO_4$. It was assumed that the heats of dilution of the metal ions and the various complexes could be neglected.[8]

The compositions of the S and T solutions have been chosen in order to cover a wide concentration range during the titrations. The different compositions are mainly of the following three types: The S solution contains only metal ion, while T is a solution with the ratio C_H/C_A approximately equal to 1/1 (type I) or 1/3 (type II).

For type III, the S solution contains metal ion and perchloric acid (or malonic acid) and T is a buffer with the ratio C_H/C_A less than 1/3.

Fig. 1 a and b show the concentrations of the various species during titrations of types II and III in the lutetium system. Titrations of type I give concentrations of the acid complexes intermediate to those in titrations of types II and III.

The formation of a slightly soluble compound of the composition $M_2A_3.nH_2O$ complicates the measurements. Thus, for the lighter elements (La – Tb), $\Delta H^\circ_{1,0,3}$ could not be determined and the precision in the determinations of $\Delta H^\circ_{1,0,1}$ and $\Delta H^\circ_{1,0,2}$ is low. In the potentiometric measurements some information on $\beta_{1,0,3}$ could be obtained by making titration series "backwards", using an S solution with a high free ligand concentration and an acid titrator solution. This method cannot be used in the calorimetric measurements, which are considerably more time-consuming than the potentiometric ones. A precipitate is formed in the S solution before the titration series is started.

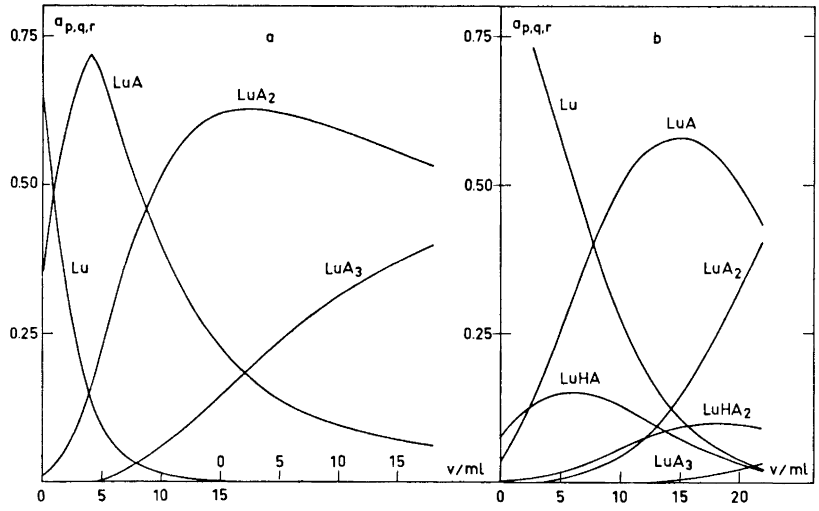

Fig. 1. The relative amounts of the different complexes in the lutetium malonate system during two titration series. *a.* Titration series of type II. Data refer to series 5a (lower volume scale) and 5b (upper volume scale) in Table 1. *b.* Titration series of type III, series 2 in Table 1.

RESULTS

The heat equivalent ε_V was the same for all experiments with the rare earths, and a linear relationship was established between ε_V and the total volume V of the system. The estimated maximum error in ε_V is ± 0.3 %.

a. The proton-malonate system. The titrations were performed by adding perchloric acid to a solution of disodium malonate. The initial total concentrations of malonate ion were 50 mM and 100 mM, respectively.

Graphical calculation of the overall entropy changes for the formation of the two proton-malonate complexes gave the values:

$$\Delta H^\circ_{0,1,1} = (2.00 \pm 0.02) \text{ kJ/mol}$$
$$\Delta H^\circ_{0,2,1} = (0.46 \pm 0.02) \text{ kJ/mol}$$

(The errors are estimated maximum errors.) These values agree with those given in Ref. 3.

Using the stability constants in Ref. 1, the following values are obtained for the changes in free energy and enthalpy for the formation of proton-malonate complexes at 25°C:

$$\Delta G^\circ_{0,1,1} = (-28.90 \pm 0.02) \text{ kJ/mol}$$
$$\Delta G^\circ_{0,2,1} = (-43.68 \pm 0.04) \text{ kJ/mol}$$
$$\Delta S^\circ_{0,1,1} = (103.6 \pm 0.2) \text{ J K}^{-1} \text{ mol}^{-1}$$
$$\Delta S^\circ_{0,2,1} = (148.0 \pm 0.2) \text{ J K}^{-1} \text{ mol}^{-1}$$

Table 1. Experimental results for the lutetium malonate system. Corresponding values of v/ml, $Q_{corr,\,exp}$/J and $(Q_{corr,\,calc} - Q_{corr,\,exp})$/J are given. The withdrawal of solution from the inner vessel during a titration series is indicated by small letters, *e.g.* Series 1a, . . . Series 1b.

Series 1a. S: $C_H = 0.05543$ M, $C_M = 0.01963$ M, $C_A = 0.02737$ M, $C_{NaClO_4} = 1.000$ M;
T: $C_H = 0.1056$ M, $C_M = 0$, $C_A = 0.3018$ M, $C_{NaClO_4} = 0.502$ M;
$V_0 = 99.95$ ml;

3.000, 4.050, −0.054; 6.000, 5.586, −0.264;

Series 1b. S: $C_H = 0.05827$ M, $C_M = 0.01852$ M, $C_A = 0.04291$ M, $C_{NaClO_4} = 0.972$ M;
T: $C_H = 0.1056$ M, $C_M = 0$, $C_A = 0.3018$ M, $C_{NaClO_4} = 0.502$ M;
$V_0 = 97.95$ ml;

2.000, 3.799 −0.029; 4.000, 3.753, 0.004;
6.000, 3.607, 0.046; 8.000, 3.514, −0.021;
11.00, 4.975, −0.059; 14.00, 4.527, −0.004;
17.00, 4.146, 0.012;

Series 2. S: $C_H = 0.05543$ M, $C_M = 0.01963$ M, $C_A = 0.02737$ M, $C_{NaClO_4} = 1.000$ M;
T: $C_H = 0.1037$ M, $C_M = 0$, $C_A = 0.3016$ M, $C_{NaClO_4} = 0.500$ M;
$V_0 = 79.93$ ml;

2.000, 2.531, 0.046; 4.000, 3.473, −0.033;
6.000, 3.807, −0.046; 8.000, 3.778, 0.017;
10.00, 3.686, −0.004; 12.00, 3.498, 0.004;
14.00, 3.289, 0.008; 16.00, 3.054, 0.038;
18.00, 2.866, 0.033; 20.00, 2.690, 0.021;
22.00, 2.468, 0.046;

Series 3. S: $C_H = 0.000479$ M, $C_M = 0.01475$ M, $C_A = 0$, $C_{NaClO_4} = 1.000$ M;
T: $C_H = 0.05723$ M, $C_M = 0$, $C_A = 0.1953$ M, $C_{NaClO_4} = 0.667$ M;
$V_0 = 100.00$ ml;

3.000, 6.054, −0.079; 6.000, 5.887, −0.046;
9.000, 5.443, −0.046; 12.00, 4.678, 0.004;
15.00, 3.849, 0.025; 18.00, 3.117, 0.067;

Series 4. S: $C_H = 0.000479$ M, $C_M = 0.01475$ M, $C_A = 0$ M, $C_{NaClO_4} = 1.000$ M;
T: $C_H = 0.05723$ M, $C_M = 0$, $C_A = 0.1953$ M, $C_{NaClO_4} = 0.667$ M;
$V_0 = 100.00$ ml;

2.000, 3.958, 0.004; 5.000, 6.008, −0.067;
8.000, 5.623, −0.046; 11.00, 4.803, 0.142;
14.00, 4.071, 0.063; 17.00, 3.330, 0.071;

Series 5a. S: $C_H = 0.001357$ M, $C_M = 0.007230$ M, $C_A = 0.003829$ M, $C_{NaClO_4} = 0.994$ M;
T: $C_H = 0.05723$ M, $C_M = 0$, $C_A = 0.1953$ M, $C_{NaClO_4} = 0.667$ M;
$V_0 = 102.00$ ml;

3.000, 4.996, 0.251; 6.000, 4.012, −0.322;
9.000, 2.577, −0.197; 12.00, 1.669, −0.071;
15.00, 1.142, −0.025;

Table 1. Continued.

Series 5b. S: $C_H = 0.00852$ M, $C_M = 0.006303$ M, $C_A = 0.02838$ M, $C_{NaClO_4} = 0.952$ M;
T: $C_H = 0.05723$ M, $C_M = 0$, $C_A = 0.1953$ M, $C_{NaClO} = 0.667$ M;
$V_0 = 100.00$ ml;

3.000, 0.766, 0.038;	6.000, 0.548, 0.046;
9.000, 0.422, 0.038;	12.00, 0.402, −0.033;
15.00, 0.293, 0.008;	18.00, 0.213, 0.038;

Series 6. S: $C_H = 0.000691$ M, $C_M = 0.01963$ M, $C_A = 0$, $C_{NaClO_4} = 1.000$ M;
T: $C_H = 0.3033$ M, $C_M = 0$, $C_A = 0.3024$ M, $C_{NaClO_4} = 0.698$ M;
$V_0 = 79.93$ ml;

2.000, 2.456, 0.117;	4.000, 1.966, 0.050;
6.000, 1.791, 0.042;	8.000, 1.607, 0.054;
10.00, 1.452, 0.067;	12.00, 1.289, 0.088;
14.00, 1.180, 0.067;	16.00, 1.063, 0.067;
18.00, 0.937, 0.084;	

Series 7. S: $C_H = 0.000691$ M, $C_M = 0.01963$ M, $C_A = 0$, $C_{NaClO_4} = 1.000$ M;
T: $C_H = 0.3033$ M, $C_M = 0$, $C_A = 0.3024$ M, $C_{NaClO_4} = 0.698$ M;
$V_0 = 79.93$ ml;

2.000, 2.456, 0.117;	4.000, 1.996, 0.021;
6.000, 1.807, 0.025;	8.000, 1.640, 0.022;
10.00, 1.477, 0.042;	

Table 2. The overall enthalpy values for the formation of lanthanoid malonate complexes. The errors are equal to three standard deviations.

Metal ion	Number of experimental points	Standard deviation in Q_{corr}/J	$\Delta H^\circ_{1,0,1}$ kJ mol^{-1}	$\Delta H^\circ_{1,0,2}$ kJ mol^{-1}	$\Delta H^\circ_{1,0,3}$ kJ mol^{-1}	$\Delta H^\circ_{1,1,1}$ kJ mol^{-1}	$\Delta H^\circ_{1,1,2}$ kJ mol^{-1}
La	29	0.082	12.1 ±0.7	20.4±2.6	–	5.2±0.7	17.8±1.7
Ce	31	0.082	12.2 ±0.8	19 ±10	–	5.3±0.8	20.0±2.5
Pr	39	0.111	12.7 ±0.7	21.5±1.8	–	5.3±0.9	19.0±4.2
Nd	33	0.086	13.1 ±0.7	21.1±3.3	–	5.0±0.7	19.2±2.2
Sm	43	0.094	12.5 ±0.5	21.3±2.0	–	5.6±0.7	18.3±1.4
Eu	42	0.085	12.8 ±0.5	20.0±3.8	–	5.9±0.8	16.8±1.0
Gd	47	0.087	12.6 ±0.5	20.1±2.1	–	6.5±0.8	18.1±1.5
Tb	42	0.072	12.61±0.33	22.0±0.7	–	7.6±0.7	17.2±0.8
Dy	49	0.086	12.83±0.36	22.3±0.9	23 ±11	8.2±1.2	18.0±1.7
Ho	53	0.080	13.51±0.32	22.1±0.6	30 ± 4	6.9±1.2	18.0±1.2
Er	49	0.110	13.4 ±0.5	22.5±1.0	28 ±11	6.3±1.5	20.5±2.0
Tm	52	0.077	14.46±0.34	23.2±0.5	33.9±2.5	5.8±1.8	17.0±2.2
Yb	74	0.061	14.24±0.20	24.40±0.24	33.1±0.9	7.9±1.0	21.6±1.6
Lu	57	0.091	14.59±0.37	25.4±0.6	35.2±3.3	8.0±1.5	24.6±3.9

b. The lanthanoid-malonate systems. The data for the lutetium malonate system are given in Table 1. The corrections for the dilution of the various titrator solutions have not been tabulated. These corrections are small and do not exceed 0.03 J/per ml added T solution.

Table 3. — $\Delta G°$ and $\Delta S°$ for the formation of lanthanoid malonate complexes at 25.0°C. (The entropy unit, J K^{-1} mol^{-1}, is written e.u.)

Metal ion	$-\Delta G°_{1,0,1}$ kJ mol^{-1}	$-\Delta G°_{1,0,2}$ kJ mol^{-1}	$-\Delta G°_{1,0,3}$ kJ mol^{-1}	$-\Delta G°_{1,1,1}$ kJ mol^{-1}	$-\Delta G°_{1,1,2}$ kJ mol^{-1}	$\Delta S°_{1,0,1}$ e.u.	$\Delta S°_{1,0,2}$ e.u.	$\Delta S°_{1,0,3}$ e.u.	$\Delta S°_{1,1,1}$ e.u.	$\Delta S°_{1,1,2}$ e.u.
La	17.51	29.4	–	36.0	52.4	99	167	–	138	235
Ce	18.6	29.9	–	36.4	53.1	103	170	–	140	245
Pr	18.8	32	–	36.9	53	106	179	–	142	240
Nd	19.29	33.8	–	37.0	53.9	109	184	–	141	245
Sm	20.98	34.7	–	37.6	56.3	112	188	–	145	250
Eu	21.24	35.6	–	37.0	57.0	114	186	–	144	248
Gd	21.30	35.6	–	37.1	55.8	114	187	–	146	248
Tb	21.78	36.4	–	36.3	57.6	115	196	–	147	251
Dy	21.97	36.2	43	36.0	56.0	117	196	220	148	248
Ho	21.87	36.4	43.8	36.0	56.8	119	196	250	144	251
Er	21.98	36.5	43.5	36.2	56.7	119	198	240	143	259
Tm	21.95	36.7	43.5	35.8	57.0	122	201	260	140	248
Yb	22.09	36.6	44.4	35.5	55.7	122	205	260	146	259
Lu	22.14	36.6	45.0	35.7	54	123	208	269	147	260

The overall enthalpy changes for the formation of the various complexes are given in Table 2. All values have been calculated by the least-squares procedure. Table 3 gives the corresponding free energy and entropy changes.

Table 2 also gives the standard deviation in the individual measurements. There are several sources for these errors and some of them will be discussed.

(i) An error of about 0.04 J in Q_{corr} can be attributed to errors in the calorimetric procedure, *e.g.* uncertainties in the graphical evaluation of the thermistor resistance change at the addition of titrant, and to temperature changes in the thermostat bath or in the calorimeter room during the measurements.

(ii) The data in Table 1 show the presence of systematic errors in some titration series. If the enthalpy values are calculated for some of these series separately, results which differ slightly will be obtained. This is exemplified in Table 4, where data from Table 1 have been used.

Table 4. Enthalpy values for the lutetium malonate system, calculated from different titration series in Table 1.

Series used	Standard deviation in Q_{corr}/J	$\Delta H°_{1,0,1}$ kJ mol^{-1}	$\Delta H°_{1,0,2}$ kJ mol^{-1}	$\Delta H°_{1,0,3}$ kJ mol^{-1}	$\Delta H°_{1,1,1}$ kJ mol^{-1}	$\Delta H°_{1,1,2}$ kJ mol^{-1}
1 – 7	0.0913	14.59 ± 0.37	25.4 ± 0.6	35.2 ± 3.3	8.0 ± 1.5	24.6 ± 3.9
1 – 5	0.0933	14.56 ± 0.38	25.5 ± 0.6	35.3 ± 3.4	8.9 ± 1.9	26.2 ± 4.5
3 – 7	0.0937	14.67 ± 0.40	25.6 ± 0.7	35.2 ± 3.4	7.1 ± 2.8	19.6 ± 8.7

The effects of concentration errors vary with the different types of compositions. The order of magnitude of these errors has been estimated for the various types of titrations. The figures given below refer to titrations performed with $(C_M)_S = 20$ mM and $(C_A)_T = 300$ mM, which corresponds to the conditions for the lutetium and most of the other systems. Only concentration errors which cause a large error in the measured heat are discussed.

Type I. An error of 1 % in the ratio $(C_H/C_A)_T$ gives a corresponding change on Q_{corr} of 0.05 J/3 ml addition.

Type II. An error of 1 % in $(C_M)_S$ or $(C_A)_T$ each gives a change in Q_{corr} of about 0.04 J/3 ml addition.

Type III. An error of 1 % in $(C_A)_T$ gives a change in Q_{corr} of $0.10 - 0.04$ J/3 ml addition.

(iii) The heats of formation of the malonate complexes, which were determined in separate measurements, could be regarded as two additional unknown parameters to be determined from the measurements on the metal systems. When this was done in the ytterbium system, the following values were calculated

$$\Delta H^\circ_{0,1,1} = (1.80 \pm 0.25) \text{ kJ/mol}$$
$$\Delta H^\circ_{0,2,1} = (0.3 \pm 0.6) \text{ kJ/mol}$$

The other enthalpy values and the standard deviation in Q_{corr} remained the same. Thus, reasonable errors in $\Delta H^\circ_{0,1,1}$ and $\Delta H^\circ_{0,2,1}$ do not influence the other enthalpy values.

(iv) The complexes of the type MA_j are rather strong and the enthalpy values are thus not sensitive to errors in $\beta_{1,0,j}$. For the equilibrium $M + HA \rightleftharpoons MHA$ the equilibrium constant has a value of about 20 M^{-1}, and the concentration of MHA thus strongly depends on the value of $\beta_{1,1,1}$. Table 5 shows values of the error square sum U and $\Delta H^\circ_{1,1,1}$, calculated for three different values of $\beta_{1,1,1}$, with data from the ytterbium system.

Table 5. The error square sum U and $\Delta H_{1,1,1}$ calculated for three different values of $\beta_{1,1,1}$. The calculation refers to the ytterbium system with 74 experimental points.

$\beta_{1,1,1} \times 10^6$ / M^{-2}	$\Delta H^\circ_{1,1,1}$ / KJ mol^{-1}	U / J^2
1.41	8.4 ± 1.0	0.2715
1.63	8.1 ± 0.9	0.2678
1.85	7.8 ± 0.8	0.2666

The shifts in $\beta_{1,1,1}$, which correspond to three standard deviations, have a very small effect on the error square sum. Only Q_{corr}-values from titration series of types I and III are affected, and this with 0.025 J at most. The changes in the concentration of the complex MHA are compensated by opposite concentration changes in MA, and as all the enthalpy values are of the same order or magnitude, the resulting change in Q_{corr} is small.

Calorimetric measurements on solutions with a low C_H/C_A ratio can be described by the same set of "false" equilibrium constants that described the potentiometric measurements on this type of solutions, and a set of enthalpy values, which are nearly the same as the correct enthalpy values. The discussion in Ref. 1 showed that in these systems the erroneously calculated value of the concentration of free ligand, a^*, is greatly in error, whereas the error in $\bar{n}^*$ is small. This means that the error in the concentration of MA is small. Thus, if the measurements had been performed by using only solution with the ratio C_H/C_A less than ½, neither the potentiometric nor the calorimetric measurements would have shown the existence of acid complexes in these solutions.

The calorimetric measurements do not give any check on the stability constants in these systems.

DISCUSSION

The enthalpy and entropy changes of the complex formation reactions of lanthanoid ions with charged bases as ligands are often described by using a simple electrostatic model in connection with the Frank and Evans "iceberg" concept. Species in water solution are surrounded by a cloud of water molecules with a geometry different from that of the bulk water. The extension of this cloud depends on the size and charge of the central ion. As the complex formed has a greater radius and reduced charge as compared to the reactants, water molecules will be released in the association reaction. Thus, as regards the stepwise reactions, the entropy changes are expected to decrease in the order $\Delta S_1^\circ > \Delta S_2^\circ > \Delta S_3^\circ$. This is in acordance with experiments for the malonates and a number of other complexes.[9] The values in Table 3 also permit a calculation of the entropy changes for the reactions

$$MA^+ + A^{2-} \rightarrow MA_2^- \qquad \text{I}$$

$$MHA^{2+} + A^{2-} \rightarrow MHA_2 \qquad \text{II}$$

and the expected relationship $\Delta S^\circ_{II} > \Delta S^\circ_{I}$ is found.

Also, a ligand forming a chelate is expected to give a more positive entropy change than a unidentate ligand. The results for the reactions

$$MA^+ + A^{2-} \rightarrow MA_2^- \qquad \text{I}$$

$$M^{3+} + HA^- \rightarrow MHA^{2+} \qquad \text{IV}$$

for which $\Delta S^\circ_{I} > \Delta S^\circ_{IV}$, are in accordance with this. As arguments based on radius and charge would have given the opposite relationship, this result indicates that malonate ion acts as a bidentate ligand. However, the model cannot be used to make any quantitative estimates of the thermodynamic properties.

This same model also predicts that the function ΔH° *vs.* $1/r$ (or ΔH° *vs.* Z, as $1/r$ is an approximately linear function of Z for the lanthanoid ions), where r is the radius of the lanthanoid ion, should be linear. This is not the case, as is shown in Fig. 2a. The similar shape of ΔH° *vs.* Z plots (and also ΔS° *vs.* Z) for the complex formation with many different ligands is an in-

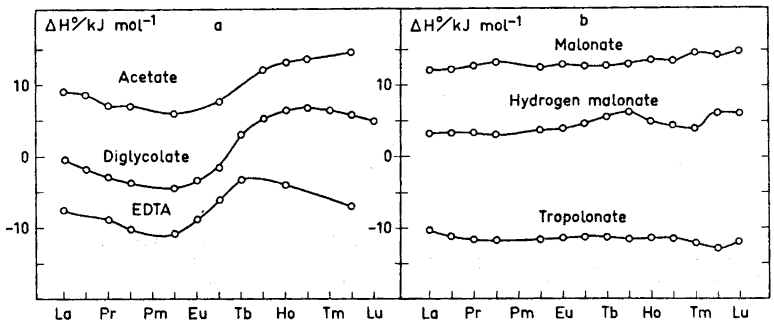

Fig. 2. The enthalpy changes for the formation of (*a*) the first acetate,[16] diglycolate,[8] and EDTA [18] lanthanoid complexes, and (*b*) for the formation of the first malonate, hydrogen malonate, and tropolonate [17] complexes.

dication that the variation is due to some property of the metal ions, *i.e.* there is in the lanthanoid series a change of the structure of the solvation sphere or of the coordination number. A host of thermodynamic and other data have as yet not given any clear picture regarding these structural changes.[10–13] However, the thermodynamic investigation on diglycolate complexes by Grenthe and Ots [14] gave evidence for the presence of a hydration equilibrium

$$M(diglyc)_2(H_2O)_x \rightleftharpoons M(diglyc)_2(H_2O)_y + (x-y)H_2O$$

for the second complex.

For the malonate complexes, the variation in $\Delta H^\circ_{1,0,1}$ is small (Fig. 2b) and a plot of $\Delta S^\circ_{1,0,1}$ *vs.* Z is approximately linear, increasing with decreasing metal ion size. The value of $\Delta H^\circ_{1,0,1}$ for the formation of the scandium complex is the same as for the heavy lanthanoids, whereas $\Delta S^\circ_{1,0,1}$ is about 30 J K^{-1} mol^{-1} more positive than one might expect from the value of the ionic radius of scandium. This behaviour might be compared with that of some other ligands of bidentate character, with oxygen as donor atoms.

Choppin and Friedman have determined the changes in free energy, enthalpy and entropy for the formation of lanthanoid lactate and α-hydroxyisobutyrate complexes.[15] The ΔH_1° -values are negative and vary little across the lanthanoid series and the ΔS_1°-values have a small positive value, 15 to 40 J K^{-1} mol^{-1} throughout the series. For the corresponding complexes with propionate and isobutyrate, respectively, the enthalpy changes are positive and the entropy changes are greater, 60 to 100 J K^{-1} mol^{-1}. An interpretation of this behaviour has been discussed by Grenthe.[16]

For the tropolonate systems,[17] a plot of ΔH°_1 *vs.* Z is given in Fig. 2b. The behaviour of ΔS_1° *vs.* Z is similar to that of the malonate systems. Campbell and Moeller propose that a change in the hydration structure of the metal ions is compensated by a parallel structural change in the hydration spheres of the 1:1 complexes. This suggestion has as yet no experimental basis. In this connection, precise values of the thermodynamic parameters for the higher tropolonato complexes would be of interest. Due to experimental difficulties, such data have not been determined, neither for the malonate nor for the tropolonate systems.

Entropy data for bidentate dicarboxylate complexes are scarce. One reason for this is the formation of sparingly soluble solids with this type of ligand. However, measurements on some maleate systems are in progress at this laboratory and will be reported in a following publication.

Note added in proof. Degischer and Choppin have recently reported (*J. Inorg. Nucl. Chem.* **34** (1972) 2823) the changes in free energy, enthalpy and entropy for the formation of the 1:1 lanthanoid-malonate complexes at ionic strength 0.10 M.

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