

Thermodynamic Properties of Rare Earth Complexes

III. Free Energy, Enthalpy, and Entropy Changes for the Formation of Rare Earth Acetate, Glycolate and Thioglycolate Complexes at 25.00° C

INGMAR GRENTHE

Department of Inorganic and Physical Chemistry, Chemical Institute, University of Lund, Lund, Sweden

The changes in free energy, enthalpy and entropy for the formation of certain rare earth acetate, glycolate and thioglycolate complexes have been determined. All data refer to a sodium perchlorate medium of an ionic strength of 2.00 M and a temperature of 25.00°C. The changes in the various thermodynamic functions were obtained from previously determined stability constants and by a direct calorimetric determination of the heats of complex formation. A comparison of the magnitude of the enthalpy changes for the various systems gives additional support of the view that the thioglycolate ion acts as a unidentate ligand while the glycolate ion forms chelates.

In Part II of this series¹ the changes in free energy, enthalpy and entropy for the formation of rare earth diglycolate and dipicolinate complexes were determined. In this communication the corresponding changes for a number of rare earth acetate, glycolate and thioglycolate complexes will be reported.

The variation of the enthalpy and entropy changes for the formation of carboxylate complexes in the rare earth series has been studied previously only for polycarboxylates. It is of interest to extend these investigations to include a monodentate carboxylate ligand, and for this reason acetate was chosen. The glycolate and thioglycolate ions have, apart from the hydroxo and thio groups, the same constitution as the acetate ion. The magnitude of the free energy changes for the formation of rare earth complexes with these ligands indicates that the glycolate ion forms chelates,² while the thioglycolate ion acts as a monodentate ligand in the same way as acetate.³ A study of the enthalpy and entropy changes will give additional information of the properties of these systems and it will thus be easier to decide whether the ligands are mono or bidentate. The stability constants necessary for computing the enthalpy values were those of Sonesson for the acetate^{4,5} and glycolate²

systems and those of Bear, Choppin and Quagliano for the thioglycolate systems.³ The corresponding enthalpy changes were obtained by the calorimetric titration procedure described before.⁶ All free energy, enthalpy and entropy changes refer to 25.00°C and an ionic strength of 2.00 M. No enthalpy and entropy quantities, except for the cerium and gadolinium glycolate systems,⁷ have been reported before.

CALCULATION OF ENTHALPY CHANGES FROM CALORIMETRIC DATA

The same notation as in Parts I and II of this series has been used. All calorimetric titrations were performed by the use of a titrant composed of NaA and HA, where A denotes the various ligands. As the complexes are formed, the hydrogen ion concentration of the solution will change and the heat effect caused by ionization of HA must be taken into account. Eqn. (1) in Part II has in this case to be modified as follows:

$$h_v = \sum \Delta \mathcal{H}_i^\circ \cdot \alpha_j + \frac{\Delta \mathcal{H}^\circ \cdot [A]_*}{C_M}, \quad (1)$$

where $\Delta \mathcal{H}^\circ$ is the heat of ionization of HA and $[A]_*$ the concentration of acid protolyzed during the reaction. The heats of ionization of acetic acid and glycolic acid are 0.721 ± 0.006 kcal·mole⁻¹,⁸ respectively 0.56 ± 0.02 kcal·mole⁻¹.⁹ The heat of reaction between excess perchloric acid in the metal perchlorate solutions and the ligands has also to be taken into account. This heat of reaction has been neglected in this investigation because of the very low concentration of excess acid.

For the acetate systems the change in the hydrogen ion concentration during the titration is very small (~ 0.05 mM) and the heat effect caused by ionization of the acid is thus negligible. The amount of dissociated HA is larger in the glycolate systems because of the stronger rare earth-glycolate complexity and the larger dissociation constant of HA. The maximum concentration of $[A]_*$ in the glycolate solutions is approximately 0.3 mM, which corresponds to 0.017 calories or less than a change of 0.01 Ω in the resistance of the thermistor. This is below the experimental random errors and no corrections of the experimental Q_{corr} values have been made. No value of the heat of ionization of thioglycolic acid was available. The $\Delta \mathcal{H}^\circ$ -value will certainly be of the same magnitude as for the other two acids, and no corrections of the measured Q_{corr} values are thus necessary.

Sonesson^{4, p. 171} made corrections for the decrease in ionic strength of the solutions caused by the complex formation. This could not be done with the titration procedure used here. The titrations had instead to be interrupted at C_A -values, where these errors were small. The largest error in \bar{n} is approximately 2 % for the acetate and 1 % for the glycolate systems. In the calculations it is assumed that only mononuclear complexes are formed and that the amount of hydrolysis products is negligible. Sonesson's measurements indicate that small amounts of polynuclear acetate complexes are formed by the heavy lanthanides.⁵ These elements are also slightly hydrolysed in the buffer solutions used here. The effects are small and are of importance only for low values of \bar{n} .

It was, nevertheless experimentally verified that these effects did not affect the measured $\Delta\mathcal{H}_j^\circ$ -values (*vide infra* p. 286).

From the corresponding values of Q_{corr} , v , V and β_j the enthalpy changes $\Delta\mathcal{H}_j^\circ$ were computed by the use of the least-square procedure "Leta Grop" as described before.¹, p. 2489

EXPERIMENTAL

Chemicals used. Stock solutions of the various rare earth perchlorates were prepared and standardized as described before.¹⁰, p.2103 All rare earths (Lindsay Chemical Co.) had a purity > 99.9 %. Stock solutions of sodium perchlorate, sodium acetate (Merck p.a.) and acetic acid (Merck p.a.) were prepared and standardized as described before.¹¹, p.1497 The acetate buffers were prepared by mixing appropriate amounts of sodium acetate, acetic acid and sodium perchlorate solutions. Glycolic acid (Fluka, purum) was used without further purification while thioglycolic acid (Fluka, puriss) was purified by a vacuum distillation. Glycolate and thioglycolate buffers were prepared and standardized as described in an earlier paper.¹¹, p.1497

Procedure. The calorimeter and the titration procedure were the same as described before.⁶ As the complexes investigated here were much weaker than those investigated in the preceding communication, the titration procedure had to be modified. Two titrants with different concentrations had to be used in order to get a sufficiently high ligand concentration and in order to avoid too small additions of titrant for the low values of C_A . The change from titrant I to titrant II was usually made in the middle of each titration series (after the fifth addition). For the thioglycolate systems, where only two stability constants have been reported a sufficiently wide C_A -range could be obtained by the use of one titrant.

The glycolate titrations had to be interrupted at a rather low concentration of free ligand because of precipitation of the neutral complex.

RESULTS

The M^{3+} -acetate systems. All systems were titrated with a buffer of NaAc and HAc with the concentration ratio 2:1. The solutions S, T₁ and T₂ had the following composition:

$$S \begin{cases} C_M (\sim 30 \text{ mM}) \\ C_{\text{HClO}_4} (\sim 0.3 \text{ mM}) \\ I = 2.00 \text{ (M)} \end{cases} \quad T_{1,2} \begin{cases} C_{\text{NaAc}} (0.804 \text{ or } 1.810 \text{ M}) \\ C_{\text{HAc}} (0.398 \text{ or } 0.896 \text{ M}) \\ I = 2.00 \text{ (M)} \end{cases}$$

The neodymium and holmium acetate systems were also titrated at $C_M \sim 10$ mM by the use of the 2:1 acetate buffer. The same systems were also investigated at $C_M \sim 30$ mM by the use of a 1:2 buffer.

The heat of dilution of the titrants was determined as described before.¹, p.2490 The result for the solutions T₁ and T₂ is given in Table 1. The heat equivalents, ϵ_V , of the systems were also determined as before⁶, p.2193 and were the same for all the investigated systems. The following values were obtained for $v = 0$, 10.5 and 18.5 ml.

$$\begin{aligned} \epsilon_{100} &= 2.08 \text{ cal.ohm}^{-1} \\ \epsilon_{110.5} &= 2.29 \text{ cal.ohm}^{-1} \\ \epsilon_{118.5} &= 2.46 \text{ cal.ohm}^{-1} \end{aligned}$$

The experimental values of Q_{corr} and C_A for the systems, titrated with the 2:1 buffers at $C_M \sim 30$ mM, are given in Table 2. Only half the experimental

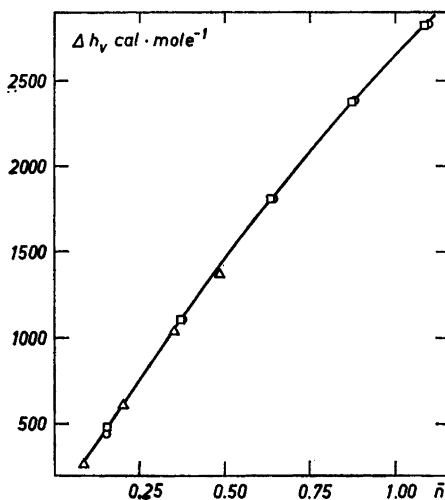


Fig. 1 Δh_v versus \bar{n} for the holmium acetate system. \square denotes $C_M = 31.94$ mM titrated with the 2:1 buffer. \triangle denotes $C_M = 10.35$ mM titrated with the 2:1 buffer and \circ denotes $C_M = 31.94$ mM titrated with the 1:2 buffer. The curve has been computed from the values of $\Delta \mathcal{H}_i^\circ$ and $\Delta \mathcal{G}_i^\circ$ in Table 3.

material has been tabulated. The calculated $\Delta \mathcal{H}_i^\circ$ -values with their corresponding standard deviations are given in Table 3. The values of $\Delta \mathcal{G}_i^\circ$, $\Delta \mathcal{S}_i^\circ$ and the standard deviation $\sigma_{Q_{\text{corr}}}$ in the measured Q_{corr} values have also been included in this table.

In Fig. 1 Δh_v has been plotted versus \bar{n} for the holmium acetate system investigated at different values of C_M and by the use of buffer solutions of different acidity. The curve has been computed from the $\Delta \mathcal{H}_i^\circ$ -values given in Table 3. The experimental values of Δh_v versus \bar{n} for the various titrations are in good agreement with the calculated curve. There is no systematic variation of the $\Delta h_v - \bar{n}$ values either with C_M or with the acidity of the buffer. This shows that the small amounts of polynuclear complexes and hydrolysis products have no influence on the measured $\Delta \mathcal{H}_i^\circ$ -values. The neodymium acetate system showed the same behaviour as the holmium system. These two elements were supposed to be representative of the other rare earths and we conclude that all the tabulated $\Delta \mathcal{H}_i^\circ$ -values are unaffected by the polynuclear and hydrolytic reactions occurring in the solutions used here.

Sonesson was not able to determine the third stability constant for the acetate complexes very accurately. It is thus important to investigate how much the $\Delta \mathcal{H}_i^\circ$ -values are affected by a change in the values of β_j . One example is given in Table 4 where the values of $\Delta \mathcal{H}_i^\circ$ for the samarium acetate system have been tabulated for three different sets of β_j -values. A significant deviation is only obtained for the value of $\Delta \mathcal{H}_3^\circ$. Because of the low value of A no considerable amount of the fourth complex is present in the solutions, and it is not possible to determine a heat of reaction for this step.

The accuracy of the $\Delta \mathcal{S}_i^\circ$ -values is within ± 0.1 , ± 0.5 and ± 1.0 e.u. for j equal to 1, 2 and 3, respectively. The largest contribution to this uncertainty is given by the uncertainty in the stability constants.

The value of $\Delta \mathcal{H}_2^\circ$ for the praseodymium acetate system is larger and the value of $\Delta \mathcal{H}_3^\circ$ smaller than expected. The effect may be real but can also be

Table 1. Molar heats of dilution of the acetate, glycolate and thioglycolate buffers used. The heats of dilution are constant within the C_A -range used.

Buffer solution	T_1	T_2
Ligand	$-Q_{DH}$ (cal. mole $^{-1}$)	
acetate	22	24
glycolate	48	63
thioglycolate	-13	-

Table 2. Corresponding values of Q_{corr} and C_A for the rare earth acetate systems. The titrations have been made by the use of buffer solutions with $C_{NaAc} : C_{HAc} = 2:1$. In the first five additions $C_{NaAc} = 0.804$ M and in the last five $C_{NaAc} = 1.810$ M. C_M is the initial concentration of metal ion in the solutions S.

C_A (mM)		8.00	19.71	34.79	49.90	63.28	95.02	115.6	155.2	183.7	211.3
Metal ion	C_M (mM)	Q_{corr} (cal)									
La	30.66	0.90	1.18	1.32	1.10	0.91	1.59	1.13	0.84	0.63	0.49
Ce	30.30	0.99	1.28	1.37	1.11	0.93	1.60	1.07	0.79	0.56	0.44
Pr	30.16	0.88	1.30	1.40	1.10	0.89	1.48	1.03	0.71	0.52	0.41
Nd	29.84	0.94	1.26	1.38	1.09	0.88	1.43	0.95	0.70	0.53	0.40
Sm	29.81	0.87	1.18	1.29	1.01	0.77	1.29	0.82	0.57	0.40	0.31
Gd	30.22	0.98	1.35	1.48	1.14	0.88	1.40	0.87	0.55	0.37	0.26
Dy	30.00	1.36	1.85	2.00	1.57	1.27	1.94	1.09	0.64	0.37	0.26
Ho	31.04	1.48	1.97	2.19	1.76	1.41	2.24	1.28	0.71	0.44	0.26
Er	29.63	1.42	2.00	2.24	1.84	1.52	2.40	1.48	0.88	0.54	0.33
Yb	30.11	1.60	2.19	2.50	2.07	1.69	2.79	1.74	1.15	0.78	0.52
Y	30.71	1.37	1.83	2.14	1.75	1.46	2.42	1.58	1.01	0.67	0.44

caused by errors in the stability constants or by an error in the titration procedure. This system will be reinvestigated.

The M^{3+} -glycolate systems. For the rare earth glycolate systems there are no polynuclear reactions to take into account for the values of C_M used in this investigation. The hydrolytic reactions are also without importance for the buffer solutions used here. For this reason only one value of C_M and one acidity of the buffer solutions were used in the titrations. The titration procedure was in this case complicated by precipitation of the neutral complex. It was not possible to avoid the precipitation by decreasing the value of C_M because of the corresponding loss in accuracy of the Q_{corr} -values. Instead the titrations had to be interrupted when precipitation occurred, *i.e.* for values of $\bar{n} < 3$. Because

Table 3. The overall values of $\Delta\mathcal{H}_j^\circ$, $\Delta\mathcal{G}_j^\circ$ and ΔS_j° for the formation of rare earth acetate complexes. The data refer to a temperature of 25.00° C and an ionic strength of 2.00 M. The values of $\Delta\mathcal{H}_j^\circ$ are tabulated with their corresponding standard deviations.

Metal ion	$\Delta\mathcal{H}_1^\circ \pm \sigma\Delta\mathcal{H}_1^\circ$ (kcal.mole ⁻¹)	$-\Delta\mathcal{G}_1^\circ$ (kcal.mole ⁻¹)	ΔS_1° (e.u.)	$\Delta\mathcal{H}_2^\circ \pm \sigma\Delta\mathcal{H}_2^\circ$ (kcal.mole ⁻¹)	$-\Delta\mathcal{G}_2^\circ$ (kcal.mole ⁻¹)	ΔS_2° (e.u.)	$\Delta\mathcal{H}_3^\circ \pm \sigma\Delta\mathcal{H}_3^\circ$ (kcal.mole ⁻¹)	$-\Delta\mathcal{G}_3^\circ$ (kcal.mole ⁻¹)	ΔS_3° (e.u.)	σ_Q corr (cal)
La	2.181 ± 0.010	2.16	14.6	3.786 ± 0.059	3.44	24.2	4.62 ± 0.14	4.14	29.4	0.011
Ce	2.092 ± 0.011	2.33	14.8	3.664 ± 0.059	3.73	24.8	5.11 ± 0.17	4.36	31.8	0.037
Pr	1.719 ± 0.012	2.50	14.2	4.154 ± 0.071	3.91	27.0	3.61 ± 0.20	4.54	27.3	0.033
Nd	1.708 ± 0.008	2.63	14.6	3.486 ± 0.038	4.17	25.7	4.36 ± 0.11	4.80	30.7	0.017
Sm	1.453 ± 0.014	2.77	14.2	2.876 ± 0.028	4.49	24.7	3.773 ± 0.050	5.32	30.5	0.016
Gd	1.898 ± 0.009	2.54	14.8	3.245 ± 0.032	4.31	25.3	3.543 ± 0.070	5.13	29.1	0.020
Dy	2.925 ± 0.011	2.33	17.6	4.439 ± 0.036	4.13	28.7	4.309 ± 0.052	5.24	32.0	0.030
Ho	3.167 ± 0.022	2.28	18.3	5.009 ± 0.037	3.99	30.2	4.583 ± 0.039	5.19	32.6	0.023
Er	3.276 ± 0.027	2.24	18.5	5.509 ± 0.034	3.96	31.8	5.166 ± 0.041	5.07	34.3	0.025
Yb	3.507 ± 0.018	2.30	19.5	6.065 ± 0.071	3.97	33.7	6.58 ± 0.12	4.95	38.7	0.030
Y	3.262 ± 0.016	2.14	18.1	5.390 ± 0.025	3.73	30.6	5.243 ± 0.027	4.70	33.3	0.013

Table 4. $\Delta\mathcal{H}_j^\circ$ -values for rare earth acetate and glycolate systems using different sets of β_j -values.

The acetate system				The glycolate system										
Metal ion	j	β_j	$\Delta\mathcal{H}_j^\circ \pm \sigma\Delta\mathcal{H}_j^\circ$ (kcal.mole ⁻¹)	σ_Q corr (cal)	Metal ion	j	β_j	$-\Delta\mathcal{H}_j^\circ \pm \sigma\Delta\mathcal{H}_j^\circ$ (kcal.mole ⁻¹)	σ_Q corr (cal)	Metal ion	j	β_j	$-\Delta\mathcal{H}_j^\circ \pm \sigma\Delta\mathcal{H}_j^\circ$ (kcal.mole ⁻¹)	σ_Q corr (cal)
	1	106	1.459 ± 0.017	0.020			1	3.09·10 ²	0.016	Gd	1	2.94·10 ²	0.019	
	2	2150	2.801 ± 0.032				2	2.07·10 ⁴			2	2.57·10 ⁴		
	3	6750	4.047 ± 0.071				3	3.35·10 ⁵			3	5.60·10 ⁵		
Sm	1	108	1.453 ± 0.014	0.016	Nd	4	9.80·10 ⁵	0.080	0.016	2	2.21·10 ⁶	0.063		
	2	1970	2.876 ± 0.028			1	3.29·10 ²			1	2.80·10 ²			
	3	7950	3.773 ± 0.050			2	1.87·10 ⁴			2	2.77·10 ⁴			
	1	111	1.445 ± 0.013	0.015		3	3.85·10 ⁵	0.034	0.016	3	5.00·10 ⁵	0.048		
	2	1790	2.976 ± 0.028			4	6.00·10 ⁵			4	2.60·10 ⁶			
	3	9150	3.564 ± 0.041			4	4.87 ± 0.13			4	4.263 ± 0.063			

Table 5. Corresponding values of Q_{corr} and C_A for the investigated rare earth glycolate complexes. The first five experimental points were obtained by the use of a buffer T_1 while the remaining points were obtained by the use of buffer T_2 .

C_A (mM)		8.33	16.51	24.52	40.08	55.07	70.15	99.48	127.8	155.1	181.4
Metal ion	C_M (mM)	- Q_{corr} (cal)									
La	20.44	0.39	0.30	0.27	0.47	0.31	0.29	0.41	0.28	0.21	
Ce	20.20	0.55	0.47	0.41	0.69	0.51	0.40	0.51	0.31	0.21	
Nd	19.90	0.80	0.77	0.62	1.02	0.75	0.59	0.76	0.50	0.31	0.25
Sm	19.88	0.83	0.74	0.70	1.25	0.94	0.70	0.92	0.53	0.30	
Gd	20.15	0.48	0.50	0.56	1.10	0.94	0.79	1.08	0.66	0.43	0.33
Dy	20.00	0.13	0.14	0.18	0.49	0.48	0.44	0.64	0.45	0.32	
Er	19.75	0.15	0.16	0.20	0.41	0.34	0.28	0.37	0.23	0.15	
Yb	20.08	0.25	0.24	0.27	0.53	0.44	0.28	0.32	0.14		
Y	20.50	0.04	0.04	0.06	0.22	0.19	0.21	0.30	0.21	0.17	

of this the accuracy of $\Delta\mathcal{H}_4^\circ$ will be low, and it will be impossible to determine the heat of reaction for the formation of the fifth complex.

The solutions S, T_1 and T_2 had the composition:

$$S \begin{cases} C_M (\sim 20 \text{ mM}) \\ C_{\text{HClO}_4} (\sim 0.2 \text{ mM}) \\ I = 2.00 \text{ (M)} \end{cases} \quad T_{1,2} \begin{cases} C_{\text{NaA}} (0.838 \text{ or } 1.676 \text{ M}) \\ C_{\text{HA}} (0.292 \text{ or } 0.584 \text{ M}) \\ I = 2.00 \text{ (M)} \end{cases}$$

The heats of dilution of the titrants are tabulated in Table 1. The heat equivalents of the systems were the same as for the acetate systems. The experimental values of Q_{corr} and C_A have been tabulated in Table 5. The calculated constants $\Delta\mathcal{H}_j^\circ$ are given in Table 6. The values of $\Delta\mathcal{G}_j^\circ$, $\Delta\mathcal{S}_j^\circ$ and $\sigma_{Q_{\text{corr}}}$ have been included in the same table.

The values of $\Delta\mathcal{H}_j^\circ$ for the neodymium and gadolinium glycolate systems have been computed by the use of other sets of β_j -values. The result is given in Table 4. As expected the largest change is observed for the value of $\Delta\mathcal{H}_4^\circ$. The uncertainty in the values of $\Delta\mathcal{S}_j^\circ$ is for $j = 1-4$, 0.2, 0.3, 0.8 and 2.0 e.u. respectively. The largest errors are also in this case caused by the uncertainty of the stability constants.

The M^{3+} -thioglycolate systems. Only the lanthanum, samarium and erbium thioglycolate complexes were investigated. According to Bear, Choppin and Quagliano only two complexes MA and MA₂ are formed. A sufficiently large C_A -range could be obtained by the use of only one buffer solution. The solutions S and T had the composition:

$$S \begin{cases} C_M (\sim 21 \text{ mM}) \\ C_{\text{HClO}_4} (\sim 0.2 \text{ mM}) \\ I = 2.00 \text{ (M)} \end{cases} \quad T \begin{cases} C_{\text{NaA}} (0.800 \text{ M}) \\ C_{\text{HA}} (0.400 \text{ M}) \\ I = 2.00 \text{ (M)} \end{cases}$$

Table 6. The overall values of $\Delta\mathcal{H}_j^\circ$, $\Delta\mathcal{G}_j^\circ$ and $\Delta\mathcal{S}_j^\circ$ for the formation of rare earth glycolate complexes at the ionic strength of 2.00 M and a temperature of 25.00° C. The $\Delta\mathcal{H}_j^\circ$ -values are given with their corresponding standard deviations. The standard deviation in the measured Q_{corr} values are given in the last column of the table. The erbium system is calculated by the graphical method.

Metal ion	$\Delta\mathcal{H}_j^\circ$ (kcal.mole ⁻¹)	$\Delta\mathcal{S}_j^\circ$ (e.u.)	$\Delta\mathcal{G}_j^\circ$ (kcal.mole ⁻¹)	$\Delta\mathcal{H}_j^\circ$ (kcal.mole ⁻¹)	$\Delta\mathcal{S}_j^\circ$ (e.u.)	$\Delta\mathcal{G}_j^\circ$ (kcal.mole ⁻¹)	$\Delta\mathcal{H}_j^\circ$ (kcal.mole ⁻¹)	$\Delta\mathcal{S}_j^\circ$ (e.u.)	$\Delta\mathcal{G}_j^\circ$ (kcal.mole ⁻¹)	Q_{corr} (cal)	
La	0.633 ± 0.021	7.9	1.055 ± 0.035	5.11	13.6	1.680 ± 0.085	6.54	16.3	2.19 ± 0.39	6.90	0.019
Ce	0.810 ± 0.017	8.0	1.599 ± 0.030	5.46	12.9	2.268 ± 0.037	6.98	15.8	2.99 ± 0.11	7.51	0.021
Nd	1.193 ± 0.016	7.4	2.188 ± 0.021	5.89	12.4	3.479 ± 0.037	7.54	13.6	4.00 ± 0.08	8.18	0.016
Sm	1.039 ± 0.031	8.1	2.404 ± 0.045	6.14	12.5	3.686 ± 0.055	7.93	14.2	4.94 ± 0.12	8.71	0.030
Gd	0.614 ± 0.020	9.3	1.734 ± 0.034	6.02	14.4	3.515 ± 0.045	7.84	14.5	4.27 ± 0.07	8.68	0.019
Dy	0.164 ± 0.034	11.0	0.608 ± 0.069	6.10	18.4	1.737 ± 0.086	8.02	21.1	2.58 ± 0.17	8.80	0.036
Er	0.19 ± 0.04	11.3	0.60 ± 0.02	6.25	18.9	1.28 ± 0.05	8.18	23.1	1.43 ± 0.15	8.84	0.018
Yb	0.288 ± 0.045	11.4	0.768 ± 0.080	6.56	19.4	1.66 ± 0.12	8.60	23.3	0.59 ± 0.29	9.24	0.042
Y	0.073 ± 0.022	11.1	0.173 ± 0.034	6.00	19.6	0.895 ± 0.042	7.76	23.0	0.92 ± 0.08	8.52	0.020

Table 7. Corresponding values of Q_{corr} and C_A for the La^{3+} , Sm^{3+} and Er^{3+} thioglycolate systems. The tabulated Q_{corr} values are the average of three titrations. The titrations have been made by the use of buffer solution with $C_{\text{NaA}} = 0.800$ M and $C_{\text{HA}} = 0.400$ M. The ionic strength of the buffer solution is equal to 2.00 M.

C_A (mM)		7.96	19.60	34.60	49.03	62.93
Metal ion	C_M (mM)	Q_{corr} (cal)				
La	21.00	0.40	0.53	0.60	0.51	0.42
Sm	21.40	0.59	0.69	0.73	0.57	0.46
Er	22.10	0.53	0.85	0.99	0.86	0.77

Table 8. The overall values of $\Delta\mathcal{H}_i^\circ$, $\Delta\mathcal{G}_i^\circ$ and $\Delta\mathcal{S}_i^\circ$ for the formation of rare earth thioglycolate complexes at the ionic strength of 2.00 M and a temperature of 25.00 C. The $\Delta\mathcal{H}_i^\circ$ -values are given with their corresponding standard deviations. The standard deviation σQ_{corr} is given in the last column of the table.

Metal ion	$\Delta\mathcal{H}_1^\circ \pm \sigma\Delta\mathcal{H}_1^\circ$ (kcal-mole ⁻¹)	$-\Delta\mathcal{G}_1^\circ$ (kcal-mole ⁻¹)	$\Delta\mathcal{S}_1^\circ$ (e.u.)	$\Delta\mathcal{H}_2^\circ \pm \sigma\Delta\mathcal{H}_2^\circ$ (kcal-mole ⁻¹)	$-\Delta\mathcal{G}_2^\circ$ (kcal-mole ⁻¹)	$\Delta\mathcal{S}_2^\circ$ (e.u.)	σQ_{corr} (cal)
La	1.486 ± 0.023	1.93	11.5	3.89 ± 0.09	2.88	22.7	0.019
Sm	1.335 ± 0.032	2.46	12.7	3.31 ± 0.10	3.70	23.5	0.031
Er	2.380 ± 0.085	1.75	13.8	5.44 ± 0.22	2.98	28.2	0.042

The buffer solution T is so acidic that hydrolytic reactions will not occur. The reproducibility of the measurements was much lower than for the other systems. This may be caused by the slight oxidation of the ligand noticed before.^{11, p.1700}

The measured heat of dilution of the titrant is given in Table 1. The heat equivalents of the systems were also in this case the same as for the acetate systems. Corresponding values of Q_{corr} and C_A are given in Table 7. The tabulated Q_{corr} -values are averages of three titrations. The values of $\Delta\mathcal{S}_i^\circ$, $\Delta\mathcal{H}_i^\circ$, $\Delta\mathcal{G}_i^\circ$ and σQ_{corr} are given in Table 8.

The standard deviations in Q_{corr} and $\Delta\mathcal{H}_i^\circ$ are both fairly large. Part of this is certainly caused by the low accuracy of the measurements but errors in the stability constants cannot be ruled out.

DISCUSSION

From Tables 3, 6 and 8 it is obvious that all the investigated complexes are entropy stabilized. This effect is specially noticeable for the acetate and thioglycolate systems where the enthalpy change is positive and thus opposes the formation of complexes.

The difference in $\Delta \mathcal{H}_j^\circ$ between the acetate and the glycolate systems is large, approx. $3\text{kcal}\cdot\text{mole}^{-1}$ for the formation of the first complex and $6.5\text{kcal}\cdot\text{mole}^{-1}$ for the formation of the third one. The entropy change is also smaller for the glycolate systems than for the corresponding acetate systems. The introduction of a hydroxyl groups in the carboxylate ligand will thus have a large effect both on the free energy, enthalpy and entropy changes. It is reasonable to assume that this is caused by bonding of the hydroxyl group to the central ion, *i.e.* the formation of a chelate. This chelate can be formed in different ways: *i.* Water may be replaced and a direct metal oxygen bond formed between the central ion and the hydroxyl oxygen *ii.* The bond may be formed *via* a water molecule. The carboxylate group is presumably bonded in the same way in both these cases and, furthermore, in the same way as for the simple acetates. The changes in the enthalpy and entropy terms are expected to be different for the two reactions. In Part IV of this series¹² it has been pointed out that the entropy term is mainly influenced by the release of water from the hydration sphere of the central ion and that the corresponding enthalpy change is determined by the difference in bond energy between coordinated water and the ligand. With this model in mind it is tempting to interpret the small ΔS_j° and the fairly large $-\Delta \mathcal{H}_j^\circ$ values for the glycolate systems as due to a predomination of the scheme *ii.* above. The same model can be used for the thioglycolate systems. However, the magnitude of $\Delta \mathcal{H}_j^\circ$ implies in this case that the ligand acts in much the same way as acetate, *i.e.* as a monodentate ligand.

All systems in this investigation show variations of the $\Delta \mathcal{H}_j^\circ$ values that are similar to the ones observed for the rare earth diglycolate and dipicolinate systems. There is a close similarity in the variation of ΔS_2° for the acetate systems and ΔS_1° for the diglycolate and dipicolinate systems. The systems will be further discussed in Part IV of this series.

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