

Thermodynamic Properties of Rare Earth Complexes

VI. Stability Constants for the Oxalate Complexes of Ce(III), Eu(III), Tb(III), and Lu(III)

INGMAR GRENTHE, GÖRAN GÄRDHAMMAR and
ESKIL RUNCRAANTZ

Division of Physical Chemistry, Chemical Center, University of Lund, Box 740, S-220 07 Lund 7, Sweden

The solubilities of different sparingly soluble oxalates of tervalent cerium, europium, terbium, and lutetium have been determined at various oxalate concentrations. The solid phases were $M_2A_3 \cdot xH_2O$, $NaMA_2 \cdot xH_2O$, and $Na_4M_2A_6 \cdot xH_2O$ where A denotes the oxalate ion and M one of the lanthanoids. Solubility products and stability constants for four mono-nuclear oxalate complexes of each lanthanoid were determined from the solubility data. The constants refer to a temperature of 20.0° and a medium containing 1 M $Na^+(ClO_4^-)$ as neutral salt.

The lanthanoid complexes for which the most solution chemistry information is available contain polydentate carboxylates as ligands. The experiments have shown that all rare earth elements form complexes of the same type with a given ligand. If the ratios of the stepwise stability constants are considered, individual differences are noticed. *E.g.* for the tridentate ligands oxydiacetate¹ and 2,6-pyridino-dicarboxylate² one can notice that the ratio between the second and third stepwise stability constant is increasing rapidly from erbium to lutetium. In other words, there is an increased difficulty for the third complex to be formed for the last elements in the lanthanoid series. This "steric effect" is probably caused by a combination of a decrease in the ionic radius of the central ion and the special geometric requirements of the ligand.

The present work is part of a systematic investigation of lanthanoid dicarboxylate complexes from which we hope to get a better understanding of the various factors of importance for complex formation in solution. We have chosen oxalate as a ligand because it is the simplest of the dicarboxylate ions and we want to determine:

a. The composition and the concentrations of the various oxalate complexes formed in solution.

X-Ray structure determinations of various rare-earth compounds have shown that the coordination number of these elements is always larger than six in the solid state.³ Several investigations strongly suggest that this is also the case in solution. In this connection it is of special interest to investigate if a fourth oxalate complex is formed in solution.

b. The possible occurrence of individual variations of the stepwise stability constants which can be interpreted as due to "steric effects" of the type discussed before.

Lanthanoide oxalate complexes have been studied by experimental methods such as solubility,⁴⁻⁶ ion-exchange,⁷ and solvent-extraction.⁸ All investigators agree that strong oxalate complexes are formed but the opinions differ about the maximum number of coordinated oxalate groups.

The most reliable of these investigations is a solvent-extraction study by Sekine,⁸ whose results will be compared with our own in the discussion.

The results of the solubility measurements published so far are questionable in two ways:

a. The authors have not used a medium with constant ionic strength. Therefore the activity coefficients of all the species participating in the equilibria have to be determined. The practical impossibility of this task has been pointed out several times, *e.g.* by Rossotti and Rossotti.⁹

b. When interpreting the solubility data the possibility of the formation of a solid solution or a phase transition must always be kept in mind. Phase transitions occur (*vide infra* p. 101) in the rare earth oxalate systems, a fact which escaped the earlier investigators.

In this study we have investigated the complex formation in solution by means of the solubility method, and using in most cases more than one solid phase. For two elements, europium and terbium, we have also made a solvent-extraction study of solutions with high oxalate concentrations and in this way extended the measurements of Sekine.⁸ All measurements have been performed in a medium with constant sodium-ion concentration, *viz.* 1.00 M, and a temperature of 20.0°C.

SOLUBILITY MEASUREMENTS

The lanthanoide elements form several sparingly soluble oxalates. All of these can be described by the general formula $N_pM_qA_r \cdot xH_2O$, where N is one of H, Na, K, or NH_4 , M is a trivalent lanthanoide and A is oxalate. The best known compounds have the composition $M_2A_3 \cdot xH_2O$, where the most common value of x is 10. Solid phases with this general composition are in the following referred to as phase I. Solids with the general formula $NaMA_2 \cdot xH_2O$ are referred to as phase II. In the course of this investigation we have discovered a third oxalate phase (phase III) of the composition $Na_4Ce_2A_5 \cdot 11H_2O$.

In contact with an aqueous solution, the various phases are thermodynamically stable in different ranges of oxalate concentrations. Phase I is stable

at the lowest oxalate concentrations and is in equilibrium with phase II at a first transition point where the oxalate concentration equals $[A]_t$. In the case of cerium a second transition point, where phase II is in equilibrium with phase III, occurs at a still higher oxalate concentration, $[A]_T$. All solid phases have constant composition as far as we have been able to judge.

In many cases the phase-transitions are so slow that the solubility of a phase can be determined even in solutions where the phase is metastable (*cf.* p. 101).

Calculation of stability constants from solubility data

In the solutions, complexes of the general composition M_iA_j are formed between the rare-earth elements and the oxalate ion. The stability constants are denoted $\beta_{i,j}$ where:

$$\beta_{i,j} = \frac{[M_iA_j]}{[M]^i[A]^j} \quad (i \geq 1; j \geq 0; \beta_{1,0} \equiv 1) \quad (1)$$

If $[M]$ and $[A]$ refer to the concentration of lanthanoide ion and oxalate ion in a saturated solution, the solubility, S , and the solubility product, K , may be written:

$$S = \sum_{i=1}^I \sum_{j=0}^J i \beta_{i,j} [M]^i [A]^j \quad (2)$$

$$K = [Na]^p [M]^q [A]^r \quad (3)$$

Hence

$$S = \sum_{i=1}^I \sum_{j=0}^J i \beta_{i,j} K^{i/q} [Na]^{-pi/q} [A]^{j-(ri/q)} \quad (4)$$

If the sodium ion concentration is kept constant throughout the series of measurements we obtain

$$S = \sum_{i=1}^I \sum_{j=0}^J i \beta_{i,j} K^{i/q} [A]^{j-(ri/q)} \quad (5)$$

where:

$$K = K[Na]^p$$

It is obvious from eqn. (5) that several sets of i, j can give the same value of the exponent $[j - (ri/q)]$. Hence it is not possible to distinguish between mono- and polynuclear complexes from solubility measurements using only *one* solid phase. This dilemma disappears if solubility data are available from at least two solid phases with different values of r/q . Eqn. (5) takes the following forms for the three phases

$$S_1[A]^{3/2} \cdot K_1^{-3/2} = 1 + (\beta_{1,1} + 3\beta_{3,4} \cdot K_1 + \dots)[A] + (\beta_{1,2} + \dots)[A]^2 + \dots + (2\beta_{2,1}K_1^2 + 4\beta_{4,4}K_1^4 + \dots)[A]^{-3/2} + \dots \quad (5,I)$$

$$S_{\text{II}}[A]^2 \cdot K_{\text{II}}^{-1} = (1 + 3\beta_{3,4}K_{\text{II}}^2 + \dots) + (\beta_{1,1} + 3\beta_{3,5}K_{\text{II}}^2 + \dots)[A] + (\beta_{1,2} + \dots)[A]^2 + \dots \quad (5, \text{II})$$

$$S_{\text{III}}[A]^{5/2} \cdot K_{\text{III}}^{-3} = 1 + (\beta_{1,1} + 3\beta_{3,6}K_{\text{III}} + \dots)[A] + (\beta_{1,2} + \dots)[A]^2 + \dots + (2\beta_{2,1}K_{\text{III}}^2 + \dots)[A]^{-3/2} + \dots \quad (5, \text{III})$$

The coefficients for $[A]^i$ can be determined from these expressions, *e.g.* by the extrapolation methods of Leden and Fronæus^{9, p. 102} or by some least-squares method (Letagrop) using a high-speed digital computer. If the various coefficients turn out to have the same value for different solid phases it has been proved that the system is mononuclear.

In order to calculate the concentration of free oxalate ions in the saturated solutions the following method was adopted: The total concentration of ligand, C_A , in equilibrium with the solid phase is equal to

$$C_A = C_A' + (r/q)S \quad (6)$$

where C_A' is the total ligand concentration before any solid phase has been added. The oxalate ion is a fairly strong base with protonation constants δ_1 and δ_2 . Taking the protonated species into account we can write eqn. (6) for the mononuclear case as

$$C_A = [A](1 + \delta_1 h + \delta_2 h^2) + \sum_{j=1}^J j[\text{MA}_j] \quad (7)$$

The free oxalate concentration can now be calculated from the relation

$$[A] = \{C_A' - (\bar{n} - r/q)S\}(1 + \delta_1 h + \delta_2 h^2)^{-1} \quad (8)$$

obtained from eqns. (6), (7) and the definition of the average ligand number, \bar{n} .

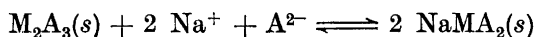
\bar{n} is obtained from the solubility curve ($\log S$ vs. $\log[A]$) using the expression

$$\frac{d \log S}{d \log [A]} = \bar{n} - \frac{r}{q} \quad (9)$$

An iterative procedure has to be used in the calculation of the free oxalate concentration. As a first approximation the term $(\bar{n} - r/q)S$ may be neglected in comparison with C_A' . A preliminary solubility curve is plotted from which values of \bar{n} can be obtained using eqn. (9). Using this set of \bar{n} -values a new and more accurate value of $[A]$ is calculated. Further iteration did not improve this value.

It is necessary to have solubility data at low oxalate concentrations in order to determine that various solubility products. This is not always possible for phase II and III as they are thermodynamically unstable at small oxalate concentrations. The solubility products must then be calculated from the experimental values of the oxalate concentration at the phase transition point and the solubility product of the phase I (resp. II).

The transition I \longrightarrow II may be described by

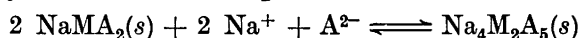


At the point of transition where the two solid phases both are in equilibrium with the solution we have

$$S_I = S_{II} \text{ and } K_I^{\frac{1}{2}}[A]_t^{-3/2} = K_{II}[A]_t^{-2}$$

$$i.e. \quad K_{II} = (K_I[A]_t)^{\frac{1}{2}} \quad (10)$$

In the same way we obtain for the phase transition II \longrightarrow III:



$$\text{and} \quad K_{III} = K_{II}^2[A]_T \quad (11)$$

Experimental

Chemicals used. Stock solutions of the various lanthanoide perchlorates and sodium perchlorate were prepared and analysed as described before.^{10,11} Stock solutions of oxalic acid and sodium oxalate (Merck *p.a.*) were analysed by cerimetric titrations. All radioactive tracers (¹⁴⁴Ce, ¹⁵²⁺¹⁵⁴Eu, ¹⁶⁰Tb, and ¹⁷⁷Lu) were obtained from the Radiochemical Centre, Amersham, U.K.

The rare earth oxalates were prepared in the following way: $\text{M}_2\text{A}_3 \cdot x\text{H}_2\text{O}$ were obtained by precipitating the rare-earth perchlorate solutions with oxalic acid. $\text{NaMA}_2 \cdot x\text{H}_2\text{O}$ was prepared by shaking phase I with a 75 mM sodium oxalate solution, with the sodium concentration equal to 1 M, or by precipitating the rare-earth solution with an excess of sodium oxalate. In the cerium case the oxalate concentration must be kept smaller than 14 mM because $\text{Na}_4\text{Ce}_2\text{A}_5 \cdot 11\text{H}_2\text{O}$ is formed if higher oxalate concentrations are used. This phase was prepared by shaking phase II with a solution containing a sodium oxalate concentration of 75 mM and a sodium perchlorate concentration of 1.00 M. Radioactive oxalates were prepared in the same way from lanthanoide stock-solutions of known specific activity.

Analyses of solid phases. The Eu, Tb, and Lu contents of the various oxalates was determined by burning the solids in a platinum crucible, dissolving the oxide in hydrochloric acid and titrating with EDTA after evaporation of the excess acid. The cerium contents of the various cerium oxalates was determined by direct oxidation of the oxalates with peroxodisulphate followed by a titration with Fe(II). The oxalate content was

Table 1. Analyses of the various rare earth oxalate phases.

Solid phase	% lanthanoide		% oxalate		% sodium		% carbon		% hydrogen	
	exptl.	calc.	exptl.	calc.	exptl.	calc.	exptl.	calc.	exptl.	calc.
$\text{Ce}_2\text{A}_3 \cdot 10\text{H}_2\text{O}$	38.7	38.7	36.3	36.4	—	—	10.2	10.0	3.3	2.8
$\text{NaCeA}_2 \cdot 6\text{H}_2\text{O}$	31.1	31.3	39.0	39.4	5.01	5.14	10.9	10.7	3.0	2.7
$\text{Na}_4\text{Ce}_2\text{A}_5 \cdot 11\text{H}_2\text{O}$	27.6	27.7	43.3	43.6	9.5	9.1	12.4	11.9	2.3	2.2
$\text{Eu}_2\text{A}_3 \cdot 10\text{H}_2\text{O}$	35.0	35.3	40.6	40.6	—	—	9.8	9.6	2.8	2.7
$\text{NaEuA}_2 \cdot 3.5\text{H}_2\text{O}$	42.6	42.5	36.9	36.7	5.52	5.55				
$\text{Tb}_2\text{A}_3 \cdot 10\text{H}_2\text{O}$	34.6	34.6	41.9	41.7	—	—	9.6	9.5	2.9	2.7
$\text{NaTbA}_2 \cdot 3\text{H}_2\text{O}$	43.0	42.7	38.9	38.6	5.61	5.58	11.9	11.7	1.7	1.5
$\text{Lu}_2\text{A}_3 \cdot 7\text{H}_2\text{O}$	47.3	47.3	35.6	35.7	—	—	10.0	9.7	1.8	1.9
$\text{NaLuA}_2 \cdot 4\text{H}_2\text{O}$	38.9	39.2	39.4	39.5		5.15	10.9	10.8	2.3	1.8

Table 2. Experimental data for the determination of the protonation constants of the oxalate ion. The results are given as $C_{\text{H}_2\text{A}}$ (mM); $E - E_{\text{d}}$ (mV); $(h - h_{\text{calc}}) \times 10^4$ (M). The total oxalate concentration is constant, and equal to 50.00 mM. E is the measured emf and E_{d} the diffusion potential.^{1,p.2107}

$C_{\text{H}_2\text{A}}, E - E_{\text{d}}, h - h_{\text{calc}}$: 5.00, 125.6, -0.004; 10.00, 100.8, 0.005; 20.00, 59.0, 0.14; 25.40, 28.9, -0.5; 26.95, 19.9, -0.2; 28.05, 14.3, -0.3; 28.90, 10.7, -1.1; 29.60, 7.3, 0.4; 30.00, 6.1, -1.2; 30.55, 4.4, -2.3; 36.30, -11.9, -3.2; 40.00, -19.4, 0.00; 45.00, -27.0, -0.3; 50.00, -32.9, 0.00.

Table 3. Experimental data for the determination of the protonation constants for the oxalate ion at different total concentrations. The results are given as C_{A} (mM), $E - E_{\text{d}}$ (mV), $(h - h_{\text{calc}}) \times 10^4$ (M).

Series 1. $C_{\text{H}_2\text{A}}/C_{\text{Na}_2\text{A}} = 9:1$. $C_{\text{A}}, E - E_{\text{d}}, (h - h_{\text{calc}}) \times 10^4$: 5.00, 22.8, -0.6; 10.00, 6.9, -0.1; 20.00, -8.5, 0.8; 50.00, -27.0, -0.3; 100.0, -39.3, -3.0.
Series 2. $C_{\text{H}_2\text{A}}/C_{\text{Na}_2\text{A}} = 1:9$. $C_{\text{A}}, E - E_{\text{d}}, (h - h_{\text{calc}}) \times 10^6$: 5.00, 126.9, 0.9; 10.00, 126.6, -1.0; 20.00, 126.5, -2.5; 50.00, 125.6, -0.4; 100.0, 125.6, -1.0.

determined by cerimetric titrations. Carbon and hydrogen were determined by elemental analyses, and sodium was analysed using a flame photometer. All phases were also characterised by their X-ray powder patterns. An X-ray structure investigation of the various solid oxalates is in progress.¹² The results of the analyses are collected in Table 1.

Solubility measurements. The solubility was investigated using two different methods. In the first method a small amount of active lanthanoide oxalate was equilibrated with 20 ml oxalate solution in a 100 ml glass flask. Equilibrium was attained by slow agitation in a thermostatted bath. The two phases were separated by filtration through a filter stick and the solubility was determined by measuring the activity of a 5.00 ml sample of the oxalate solution in a γ -scintillation detector (Landis & Gyr, EQP 3.1). Equilibrium was attained after 10–30 min but an equilibration time of 24 h was nevertheless used in most cases.

In the second method we used a solubility column of the Brønsted type.¹³ This is a more handy method to work with and has been used for obtaining most of our solubility data. The height of the oxalate column was approximately 1 cm and equilibrium was established after one passage of the oxalate solution through the column. The composition of the various oxalate solutions used in the solubility experiments are given in Tables 5 and 6. The sodium ion concentration is constant at 1.00 M in all solutions.

Table 4. Experimental determinations of the various phase transition points. The "best" values are given in the last column. The errors are estimated maximum errors.

Metal	Type of phase transition	Graphical determination	Two-phase determination	Determination from solubility prod.	"Best" value of transition points
		[A] (M)	[A] (M)	[A] (M)	[A] (M)
Ce	I → II	$(2.5 \pm 0.1) \times 10^{-4}$	$(1.0 \pm 0.1) \times 10^{-4}$		$(2.5 \pm 0.1) \times 10^{-4}$
	II → III	$(1.4 \pm 0.1) \times 10^{-2}$	$(1.6 \pm 0.2) \times 10^{-2}$		$(1.5 \pm 0.1) \times 10^{-2}$
Eu	I → II	$(7.6 \pm 1.2) \times 10^{-6}$	$(5.9 \pm 0.5) \times 10^{-6}$	$(8 \pm 2) \times 10^{-6}$	$(6.7 \pm 0.7) \times 10^{-6}$
Tb	I → II	$(1.45 \pm 0.1) \times 10^{-6}$	$(1.29 \pm 0.06) \times 10^{-6}$	$(1.45 \pm 0.25) \times 10^{-6}$	$(1.45 \pm 0.10) \times 10^{-6}$

Table 5. Experimental values of log S and log[A] for the cerium and lutetium oxalate systems. log S_{calc} is calculated with the final solubility products and stability constants of Table 8.

Lu(III), phase II C _A ⁰ = 1.000 mM					Ce(III), phase I C _A ⁰ = 10.00 mM				
-log h	-log [A]	-log S	log $\frac{S}{S_{calc}}$	\bar{n}	-log h	-log [A]	-log S	log $\frac{S}{S_{calc}}$	\bar{n}
0.921	5.820	3.608	-0.024	0.24	1.377	4.330	5.128	0.011	0.69
0.921	5.819	3.605	-0.020	0.24	1.377	4.330	5.140	-0.001	0.69
Lu(III), phase II C _A ⁰ = 10.00 mM					Ce(III), phase I C _A ⁰ = 10.00 mM				
0.495	5.674	3.820	0.016	0.31	1.495	4.180	5.240	0.011	0.81
0.495	5.674	3.811	0.025	0.31	1.495	4.180	5.249	0.002	0.81
0.602	5.493	4.120	0.012	0.42	1.620	4.029	5.361	-0.016	0.94
0.602	5.493	4.119	0.013	0.42	1.620	4.029	5.356	-0.011	0.94
0.721	5.295	4.431	0.006	0.56	1.770	3.855	5.424	0.005	1.10
0.721	5.295	4.425	0.008	0.56	1.770	3.855	5.424	0.005	1.10
0.824	5.129	4.668	-0.006	0.69	1.886	3.726	5.509	-0.036	1.22
0.824	5.129	4.671	-0.009	0.69	1.886	3.726	5.492	-0.019	1.22
0.921	4.976	4.852	-0.001	0.82	1.886	3.726	5.505	-0.002	1.22
0.921	4.976	4.853	-0.002	0.82	2.026	3.576	5.513	-0.008	1.36
1.000	4.856	4.994	-0.007	0.93	2.026	3.576	5.500	0.000	1.36
1.000	4.856	4.990	-0.003	0.93	2.097	3.501	5.520	-0.007	1.43
1.097	4.713	5.127	0.003	1.06	2.097	3.501	5.509	0.004	1.43
1.097	4.713	5.129	0.001	1.06	2.222	3.373	5.553	-0.039	1.55
1.180	4.594	5.239	-0.004	1.17	2.222	3.373	5.517	-0.033	1.55
1.180	4.594	5.245	-0.011	1.17	2.398	3.198	5.524	-0.033	1.72
1.268	4.474	5.334	-0.006	1.28	2.398	3.198	5.508	-0.018	1.72
1.268	4.474	5.324	0.004	1.28	2.523	3.078	5.487	-0.032	1.84
1.377	4.330	5.412	0.010	1.42	2.523	3.078	5.472	-0.017	1.84
1.377	4.330	5.412	0.010	1.42	2.921	2.725	5.293	-0.015	2.18
1.495	4.181	5.485	0.012	1.57	2.921	2.725	5.306	-0.028	2.18
1.495	4.181	5.489	0.008	1.57	2.921	2.725	5.301	-0.023	2.18
1.770	3.856	5.595	-0.007	1.88	3.222	2.497	5.197	-0.099	2.41
1.770	3.856	5.595	-0.007	1.88	3.222	2.497	5.210	-0.112	2.41
1.886	3.726	5.599	-0.003	2.00	3.523	2.315	5.024	-0.106	2.59
1.886	3.726	5.602	-0.006	2.00	3.523	2.315	5.029	-0.111	2.59
2.026	3.575	5.596	-0.010	2.14	Ce(III), phase II C _A ⁰ = 10.00 mM				
2.026	3.575	5.597	-0.011	2.14	2.026	3.576	5.524	-0.001	1.36
2.097	3.501	5.582	-0.009	2.21	2.026	3.576	5.530	-0.007	1.36
2.097	3.501	5.582	-0.009	2.21	2.097	3.501	5.580	-0.013	1.43
2.222	3.373	5.537	0.002	2.32	2.097	3.501	5.583	-0.016	1.43
2.222	3.373	5.540	-0.001	2.32	2.222	3.373	5.658	-0.025	1.55
2.398	3.198	5.551	0.018	2.48	2.222	3.373	5.640	-0.007	1.55
2.398	3.198	5.451	0.018	2.48	2.398	3.198	5.702	-0.005	1.72
2.523	3.078	5.374	0.030	2.59	2.398	3.198	5.713	-0.016	1.72
2.523	3.078	5.374	0.030	2.59	2.523	3.078	5.727	-0.004	1.84
2.803	2.825	5.221	0.007	2.80	2.523	3.078	5.730	-0.007	1.84
2.803	2.825	5.221	0.007	2.80	2.745	2.875	5.733	0.003	2.03
2.863	2.699	5.129	-0.007	2.90	2.745	2.875	5.738	-0.002	2.03
2.863	2.699	5.151	-0.009	2.90	2.921	2.725	5.718	0.003	2.18
3.184	2.524	4.965	-0.012	3.03	2.921	2.725	5.711	0.000	2.18
3.184	2.524	4.965	-0.012	3.03	3.222	2.497	5.650	0.004	2.41
3.523	2.316	4.757	-0.035	3.19	3.222	2.497	5.646	0.008	2.41
3.551	2.302	4.683	0.022	3.20	3.523	2.315	5.550	0.013	2.59
4.398	2.060	4.355	0.039	3.36	3.523	2.315	5.558	0.005	2.59
Lu(III), phase I C _A ⁰ varying -log h = 6.000					Ce(III), phase II C _A ⁰ varying -log h = 6.000				
C _A ⁰ · 10 ³ (M)	-log [A]	-log S	log $\frac{S}{S_{calc}}$	\bar{n}	C _A ⁰ · 10 ³ (M)	-log [A]	-log S	log $\frac{S}{S_{calc}}$	\bar{n}
14.00	1.859	4.072	0.031	3.52	14.00	1.856	5.180	0.006	3.05
28.00	1.561	3.600	0.022	3.70	14.00	1.856	5.181	0.005	3.05
28.00	1.561	3.611	0.011	3.70	20.00	1.701	5.008	0.004	3.20
37.50	1.436	3.402	0.000	3.76	20.00	1.701	5.007	0.005	3.20
37.50	1.436	3.401	0.005	3.76	28.00	1.555	4.821	0.007	3.33
50.00	1.312	3.203	-0.017	3.81	28.00	1.555	4.821	0.007	3.33
50.00	1.312	3.199	-0.012	3.81	37.50	1.428	4.648	0.004	3.43
Ce(III), phase I C _A ⁰ = 1.000 mM					Ce(III), phase II C _A ⁰ = 10.00 mM				
-log h	-log [A]	-log S	log $\frac{S}{S_{calc}}$	\bar{n}	-log h	-log [A]	-log S	log $\frac{S}{S_{calc}}$	\bar{n}
0.921	5.773	3.385	-0.013	0.05	0.495	5.665	3.490	0.033	0.06
0.921	5.781	3.407	-0.046	0.05	0.495	5.667	3.538	-0.013	0.06
Ce(III), phase I C _A ⁰ = 10.00 mM					Ce(III), phase II C _A ⁰ = 10.00 mM				
0.495	5.665	3.490	0.033	0.06	0.602	5.489	3.782	-0.004	0.09
0.495	5.667	3.538	-0.013	0.06	0.602	5.488	3.770	0.010	0.09
0.602	5.489	3.782	-0.004	0.09	0.721	5.292	4.031	0.020	0.14
0.602	5.488	3.770	0.010	0.09	0.721	5.292	4.045	0.006	0.14
0.721	5.292	4.031	0.020	0.14	0.721	5.293	4.055	-0.005	0.14
0.721	5.293	4.045	0.006	0.14	0.824	5.127	4.279	-0.008	0.19
0.824	5.127	4.279	-0.008	0.19	0.824	5.127	4.273	-0.002	0.19
0.824	5.127	4.273	-0.002	0.19	0.921	4.975	4.454	0.011	0.26
0.921	4.975	4.454	0.011	0.26	0.921	4.975	4.457	0.008	0.26
1.000	4.855	4.622	-0.012	0.32	1.000	4.855	4.611	-0.001	0.32
1.000	4.855	4.611	-0.001	0.32	1.097	4.712	4.758	0.015	0.40
1.097	4.712	4.758	0.015	0.40	1.097	4.712	4.760	0.013	0.40
1.180	4.594	4.891	0.007	0.48	1.180	4.594	4.905	-0.007	0.48
1.180	4.594	4.905	-0.007	0.48	1.268	4.474	5.013	0.001	0.57
1.268	4.474	5.013	0.001	0.57	1.268	4.474	5.002	0.012	0.57
1.268	4.474	5.002	0.012	0.57	Ce(III), phase II C _A ⁰ = 10.00 mM				
Ce(III), phase II C _A ⁰ = 10.00 mM					-log h	-log [A]	-log S	log $\frac{S}{S_{calc}}$	\bar{n}
0.495	5.665	3.490	0.033	0.06	3.222	2.497	5.333	-0.009	2.41
0.495	5.667	3.538	-0.013	0.06	3.222	2.497	5.341	-0.017	2.41
0.602	5.489	3.782	-0.004	0.09	3.523	2.315	5.320	0.004	2.59
0.602	5.488	3.770	0.010	0.09	3.523	2.315	5.316	0.008	2.59
0.721	5.292	4.031	0.020	0.14	3.523	2.315	5.324	0.000	2.59
0.721	5.293	4.045	0.006	0.14	4.398	2.058	5.277	-0.009	2.85
0.824	5.127	4.279	-0.008	0.19	4.398	2.058	5.276	-0.008	2.85
0.824	5.127	4.273	-0.002	0.19	Ce(III), phase II C _A ⁰ = 10.00 mM				
0.921	4.975	4.454	0.011	0.26	-log h	-log [A]	-log S	log $\frac{S}{S_{calc}}$	\bar{n}
0.921	4.975	4.457	0.008	0.26	3.222	2.497	5.333	-0.009	2.41
1.000	4.855	4.622	-0.012	0.32	3.222	2.497	5.341	-0.017	2.41
1.000	4.855	4.611	-0.001	0.32	3.523	2.315	5.320	0.004	2.59
1.097	4.712	4.758	0.015	0.40	3.523	2.315	5.316	0.008	2.59
1.097	4.712	4.760	0.013	0.40	3.523	2.315	5.324	0.000	2.59
1.180	4.594	4.891	0.007	0.48	4.398	2.058	5.277	-0.009	2.85
1.180	4.594	4.905	-0.007	0.48	4.398	2.058	5.276	-0.008	2.85
1.268	4.474	5.013	0.001	0.57	Ce(III), phase II C _A ⁰ = 10.00 mM				
1.268	4.474	5.002	0.012	0.57	-log h	-log [A]	-log S	log $\frac{S}{S_{calc}}$	\bar{n}
Ce(III), phase II C _A ⁰ = 10.00 mM					3.222	2.497	5.333	-0.009	2.41
Ce(III), phase II C _A ⁰ = 10.00 mM					3.222	2.497	5.341	-0.017	2.41
Ce(III), phase II C _A ⁰ = 10.00 mM					3.523	2.315	5.320	0.004	2.59
Ce(III), phase II C _A ⁰ = 10.00 mM					3.523	2.315	5.316	0.008	2.59
Ce(III), phase II C _A ⁰ = 10.00 mM					3.523	2.315	5.324	0.000	2.59
Ce(III), phase II C _A ⁰ = 10.00 mM					4.398	2.058	5.277	-0.009	2.85
Ce(III), phase II C _A ⁰ = 10.00 mM					4.398	2.058	5.276	-0.008	2.85

Table 6. Continued.

Tb(III), phase II -log[H ⁺] = 6.00					Eu(III), phase II -log[H ⁺] = 6.00					
C _A · 10 ³ (M)	-log[A]	-log S	log $\frac{S}{S_{Scale}}$	\bar{n}	C _A · 10 ² (M)	-log[A]	-log S	log $\frac{S}{S_{Scale}}$	\bar{n}	
0.500	3.303	6.52	$\begin{matrix} -0.08 \\ +0.06 \end{matrix}$	-0.11	2.09	1.400	1.855	5.654	-0.010	3.23
1.000	3.002	6.36	$\begin{matrix} -0.10 \\ +0.18 \end{matrix}$	-0.02	2.40	2.000	1.701	5.394	0.052	3.24
1.500	2.926	6.21	$\begin{matrix} +0.07 \\ +0.09 \end{matrix}$	0.04	2.57	2.000	1.701	5.388	0.058	3.34
2.000	2.701	6.12	$\begin{matrix} -0.09 \\ +0.09 \end{matrix}$	0.05	2.68	2.800	1.555	5.232	0.010	3.45
3.00	2.525	6.036		0.005	2.81	2.800	1.555	5.224	0.018	3.45
5.00	2.303	5.851		-0.008	2.98	3.75	1.428	5.054	-0.001	3.53
5.00	2.303	5.862		-0.019	2.98	3.75	1.428	5.055	-0.002	3.53
10.00	2.002	5.44		0.08	3.18	5.00	1.303	4.857	+0.000	3.61
10.00	2.002	5.39		0.14	3.18	5.00	1.303	4.860	-0.003	3.61
20.00	1.701	5.155		-0.021	3.38	6.30	1.202	4.692	+0.000	3.67
20.00	1.701	5.162		-0.028	3.38	6.30	1.202	4.688	0.004	3.67
37.5	1.428	4.735		-0.003	3.56					
37.5	1.428	4.741		-0.009	3.56					
50.0	1.303	4.532		-0.002	3.64					
50.0	1.303	4.526		0.004	3.64					
75.0	1.127	4.230		0.006	3.72					
75.0	1.127	4.217		0.019	3.72					

Perchloric acid has to be added to the solutions containing the lowest oxalate concentrations and this will cause small variations in the ionic strength of the solutions. The variations are usually small and can be calculated from the data in Tables 5 and 6.

Determination of the phase transition points. The phase transition points have been determined by the following three methods:

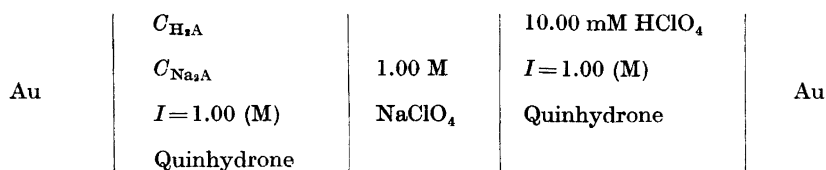
a. The point of intersection between the two solubility curves have been determined graphically. The difference in slope between the two curves was in all cases sufficiently large for an accurate determination.

b. Approximately 0.2 g of the phases I and II (or II and III) were added to a solution with an oxalate concentration close to the expected transition point. As equilibrium was approached the relative amounts of the two phases changed. The oxalate concentration of the solution in equilibrium with two solid phases present is equal to [A]_t resp. [A]_T and was determined by a potentiometric determination of the concentration of free hydrogen ions, *h*, followed by a cerimetric determination of the total oxalate concentration.

c. The phase-transition points can also be calculated from the experimental values of the two solubility products.

Rate of phase transitions. The rate for the transformation phase I → phase II is rather slow, especially in the vicinity of the transition point. The oxalate concentration can usually be increased by a factor two to three above the value at the transition point without any noticeable changes in the composition of the solid during an equilibration time of 1 h. If the oxalate concentration is increased beyond this limit a rapid phase transition occurs. The phase-transition phase II → phase I always proceeds much faster than the reverse transition and for the determination of the solubility when the solid was metastable much shorter equilibration times had to be used. In the cerium and terbium systems the transition II → I occurred so fast that no solubilities of phase II could be determined to the left of the first transition point. The transition phase II → phase III and its reverse are both fairly slow and it is possible to study the meta-stable phases over a large range of oxalate concentrations.

Determination of the protonation constants for the oxalate ion. The protonation constants δ₁ and δ₂ were determined by potentiometric *h*-determinations in different buffers of oxalic acid and sodium oxalate. The method has been described before.¹ The galvanic elements used were of the type:



Results

Protonation constants of the oxalate ion. The stability constants δ_1 and δ_2 were determined by standard methods (graphical) from the experimental material in Table 2. The following values were obtained:

$$\delta_1 = (3.55 \pm 0.04) \times 10^3 \text{ (M}^{-1}\text{)}$$

$$\delta_2 = (3.62 \pm 0.11) \times 10^4 \text{ (M}^{-2}\text{)}$$

The errors quoted are estimated maximum errors. The acidity constants do not vary with the total buffer concentration in the range investigated (5 mM–100 mM), cf. Table 3.

Values of the various phase-transition points. The experimental values of the different phase-transition points are given in Table 4. The final values are given in the last column of the table and have been obtained by taking into account the results of all the different methods of determination. The two-phase method gives erroneous results for the first transition point in the cerium case — a reason for this might be that some other solid phase is formed in this experiment. In this connection it may be mentioned that $\text{Ce}_2\text{A}_3 \cdot x\text{H}_2\text{O}$ has been reported to contain between nine and twelve water molecules.¹⁴

Solubility measurements. The solubility data for the various phases of the investigated rare earths are collected in Tables 5 and 6, the corresponding solubility curves are shown in Figs. 1 and 2.

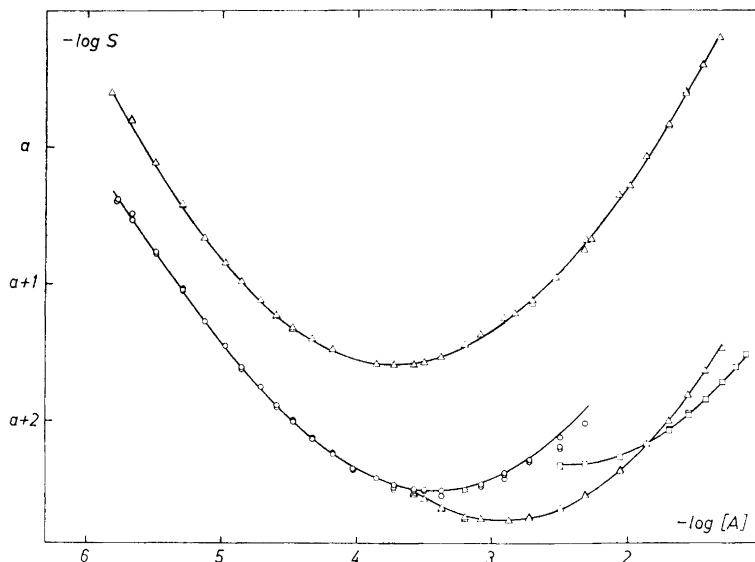


Fig. 1. Experimental solubility curves for the cerium and lutetium oxalate systems. The value of a is equal to 3 for the cerium system (the lower curves) and equal to 4 for the lutetium system (the upper curve). The full-drawn curves have been calculated with the final set of solubility products and stability constants given in Table 8.

In the cerium-oxalate system we could only determine one solubility product directly from solubility measurements at low oxalate concentrations and had to determine the other two from the phase-transition points. A direct determination of the two solubility products was possible for europium and terbium even if the second solubility product is more uncertain than the first. The "best" solubility product was also based on the results obtained from the phase-transition point. For lutetium, $\text{NaLuA}_2 \cdot 4\text{H}_2\text{O}$ was the only stable solid in the oxalate range investigated.

The constants $\beta_{i,j}K^{i/q}$ were determined for each phase and the result is given in Table 7. The errors quoted are equal to three standard deviations. From the different values in Table 7 a final "best" set of stability constants, $\beta_{i,j}$, was chosen and the errors in these constants were estimated from the 3σ -values of Table 7. The final values of the various solubility products and stability constants are given in Table 8.

The full-drawn curves in Figs. 1 and 2 have been calculated using these sets of constants. The agreement between experimental and calculated solubility is satisfactory.

The fact that the different phases for each of the investigated systems give the same stability constants proves that the complexes formed are mononuclear. A maximum of four oxalate groups are coordinated to the various central ions in the oxalate range investigated, and it is not likely that complexes higher than the fourth can be formed in aqueous solution (*vide* the values of \bar{n} for Lu in Table 5).

The possible occurrence of acid complexes must also be investigated. For the europium-oxalate system, we have measured the solubility of phase I in solutions with the same free oxalate concentration but with different

Table 7. Values of the constants $\beta_{i,j}K^{i/q}$ for the various lanthanoide oxalate phases. The errors quoted are equal to three standard deviations.

Constant	Ce(III)	Eu(III)	Tb(III)	Lu(III)
$K_I^{1/2} \times 10^{14} (\text{M}^{1/2})$	88.5 \pm 3.7	10.1 \pm 0.8	24.5 \pm 1.8	
$\beta_1 \cdot K_I^{1/2} \times 10^8 (\text{M}^{3/2})$	2.72 \pm 0.20	1.34 \pm 0.22	2.56 \pm 0.40	
$\beta_2 \cdot K_I^{1/2} \times 10^5 (\text{M}^{1/2})$	7.12 \pm 0.74	5.7 \pm 1.7	18.7 \pm 5.4	
$\beta_3 \cdot K_I^{1/2} \times 10^2 (\text{M}^{-1/2})$	1.24 \pm 0.30	3.7 \pm 1.1	13.5 \pm 8.1	
$K_{II} \times 10^{16} (\text{M}^4)$	138 \pm 10	2.86 \pm 0.30	2.95 \pm 0.72	4.60 \pm 0.36
$\beta_1 \cdot K_{II} \times 10^{11} (\text{M}^3)$	39.4 \pm 2.1	3.19 \pm 0.33	3.45 \pm 1.2	8.85 \pm 0.66
$\beta_2 \cdot K_{II} \times 10^6 (\text{M}^2)$	1.12 \pm 0.05	12.1 \pm 2.1	24.6 \pm 9.6	1.57 \pm 0.12
$\beta_3 \cdot K_{II} \times 10^4 (\text{M})$	2.84 \pm 0.17	1.10 \pm 0.13	2.20 \pm 0.66	25.3 \pm 1.7
$\beta_4 \cdot K_{II} \times 10^3$	7.46 \pm 0.82	3.39 \pm 0.54	7.4 \pm 2.5	222 \pm 10
$K_{III}^{1/2} \times 10^{15} (\text{M}^{11/2})$	1.67 \pm 0.15			
$\beta_3 \cdot K_{III}^{1/2} \times 10^5 (\text{M}^{1/2})$	3.35 \pm 0.25			
$\beta_4 \cdot K_{III}^{1/2} \times 10^4 (\text{M}^{9/2})$	9.7 \pm 1.2			

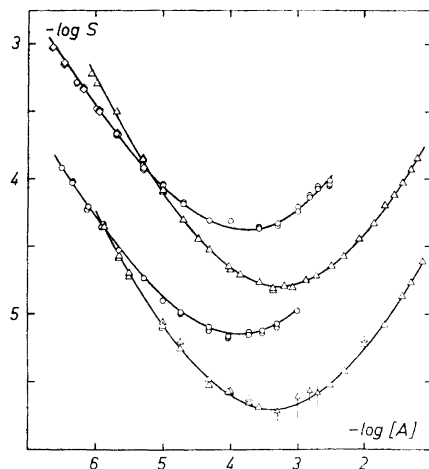


Fig. 2. Experimental solubility curves for the europium and terbium oxalate systems. The upper curve denote the europium system and the lower curve the terbium system. The full-drawn curves have been calculated with the constants in Table 8.

hydrogen ion concentrations. We found that the solubility curve in the range $5.3 < \text{pA} < 6.3$ was independent of the hydrogen-ion concentration and thus conclude that no acid complexes are formed in our range of measurement. This conclusion is supported by the investigation of Sekine.⁸

SOLVENT EXTRACTION MEASUREMENTS

Solvent extraction measurements have only been made for the europium and terbium oxalate systems in order to confirm the presence of a fourth complex. For this reason, we have made the largest part of the experimental distribution measurements at an oxalate range where the highest complexes

Table 8. Final solubility products and stability constants for the investigated lanthanoid oxalate systems with their estimated maximum errors. The ratio between the various stepwise stability constants are also given.

Constant	Ce(III)	Eu(III)	Tb(III)	Lu(III)
$K_{\text{I}} \times 10^{26} (\text{M}^5)$	78 ± 5	1.17 ± 0.15	5.9 ± 0.7	
$K_{\text{II}} \times 10^{16} (\text{M}^4)$	138 ± 10	2.8 ± 0.3	2.9 ± 0.3	4.60 ± 0.05
$K_{\text{III}} \times 10^{30} (\text{M}^{13})$	2.8 ± 0.5			
$\beta_1 \times 10^{-4} (\text{M}^{-1})$	3.1 ± 0.3	11.0 ± 1.5	12.0 ± 2.0	19.0 ± 1.0
$\beta_2 \times 10^{-8} (\text{M}^{-2})$	0.81 ± 0.10	5.0 ± 0.7	7.2 ± 1.7	34 ± 2
$\beta_3 \times 10^{-11} (\text{M}^{-3})$	0.20 ± 0.02	3.7 ± 0.6	7.1 ± 1.5	55 ± 3
$\beta_4 \times 10^{-13} (\text{M}^{-4})$	0.56 ± 0.06	12.4 ± 1.6	26 ± 6	480 ± 30
K_1/K_2	12 ± 2	24 ± 6	20 ± 6	11 ± 2
K_2/K_3	11 ± 2	6 ± 4	6 ± 4	11 ± 2
K_3/K_4	9 ± 2	22 ± 8	27 ± 10	18 ± 4

are present in largest amounts. The experimental method used is the same as described by Sekine⁸ using TTA and hexone as extracting agents and carbon tetrachloride as the solvent.

Notations. The general equations used have been given by Sekine. The function X can be determined from measurements of the distribution of metal between organic and aqueous phase and

$$X = D_0/D \quad (12)$$

where D_0 is the distribution coefficient when $C_A=0$. The following expression may be derived from eqn. (12)

$$\frac{d \log D^{-1}}{d \log [A]} = \bar{n} \quad (13)$$

Experimental

Chemicals used. TTA (Columbia Organic Chemical Co) was used without further purification. Hexone (Merck) and carbon tetrachloride (Merck) were both of analytical grade. All other solutions were the same as described in the preceding section.

Distribution measurements. The experimental conditions had to be optimized in order to get as accurate distribution coefficients as possible ($-2 < \log D < 2$). Since the value of D is dependent on the hydrogen-ion concentration it was practical to keep h as constant as possible. The hydrogen ion concentration had to be rather low ($-\log h > 4.0$) in order to prevent precipitation of NaHA at the high oxalate concentrations used in this investigation. The hydrogen-ion concentration changed slightly during the equilibration with the organic phase and was therefore measured with a Radiometer PhM 4 c pH-meter. All the measured distribution coefficients were then recalculated to a "normalized" hydrogen-ion concentration equal to $10^{-4.254}$ M, and were then denoted D .

The distribution coefficients were determined in the following way: 5.00 ml of a ligand solution and 0.0500–0.300 ml of a radioactive rare-earth solution were equilibrated with 5.00 ml of an organic phase containing 0.400 M TTA and ten volume percent hexone. Equilibrium was attained by agitation for two hours at 20.0°C. The total lanthanoid concentration in the two phases was then determined by γ -activity measurements as described before (p. 98). The total metal concentration in the aqueous phase was in all cases so low that no rare earth oxalate could precipitate.

Results

The experimental values of D are given in Table 9 and have been plotted in Fig. 3 as $(\log D^{-1} + \text{const})$ versus pA . The slope of this curve is equal to \bar{n} and it is obvious from the figure that the slope is larger than three at the highest oxalate concentrations. The fact that more than three complexes are formed is more obvious from Fig. 4 where we have used the relation:

$$\frac{1}{D[A]^4} = \frac{\beta_4}{D_0} + \frac{\beta_3}{D_0} \cdot \frac{1}{[A]} + \dots$$

and plotted $1/D[A]^4$ versus $1/[A]$. The result is a straight line from which a value of K_4 can be determined. The following values were obtained for the two systems investigated:

extr.	Eu(III) $K_4 = 39 \pm 4$ (M ⁻¹)	sol.	$K_4 = 34 \pm 5$ (M ⁻¹)
	Tb(III) $K_4 = 41 \pm 5$ (M ⁻¹)		$K_4 = 37 \pm 10$ (M ⁻¹)

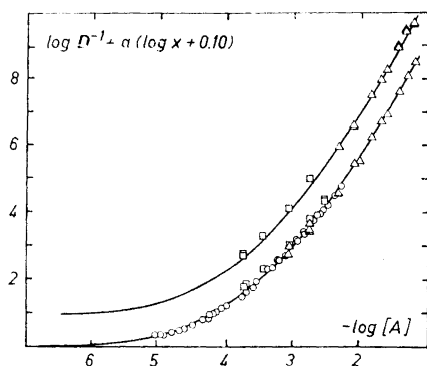


Fig. 3. $\log D^{-1} + \text{const}$ as a function of $-\log [A]$ for the europium and terbium oxalate system. a equals 5.68 for the europium system (the lower curve) and 6.91 for the terbium system. The full-drawn curves have been calculated from the values of $\log X$ obtained from the solubility measurements. The circles denote the values of $(\log X + 0.10)$ where $\log X$ have been determined by Sekine.⁸

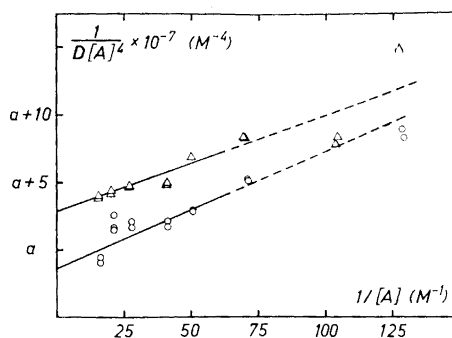


Fig. 4. Graphical evaluation of the constant K_4 from solvent-extraction data for the europium and terbium oxalate systems. The lower curve refers to the terbium system where the value of a equals 5 and the upper curve to the europium system where a equals 0.

These results are in good agreement with the values found from the solubility data.

We did not make any attempt to determine D_0 experimentally. This constant was calculated from eqn. (12) and the values of X obtained from the solubility data instead. The full-drawn curves in Fig. 3 have been calculated using the final constants given in Table 8. The extraction data are well described by this curve and we have thus confirmed the existence of a fourth complex and also the value of the fourth consecutive stability constant.

For the europium-oxalate system, we could directly compare our results with those of Sekine. His $\log X$ -values are systematically lower than ours. We have therefore in Fig. 3 added 0.10 to Sekine's $\log X$ -values and denoted the result with circles. One can now notice a good agreement between the two sets of extraction data and the values of $\log X$ -obtained from the solubility measurements. The systematic displacement might be caused by a systematic error in the determination of D_0 . Some support for this conclusion is given by the fact that a plot of Sekine's values of $(X - \beta_2[A]^2)$ versus $[A]$ gives an extrapolated value of $X = 0.8 \pm 0.2$ when $[A] = 0$, i.e. his value of $\log D_0$ should be increased with approximately 0.10 units.

DISCUSSION

This investigation has shown that the lanthanoide ions form stable mononuclear oxalate complexes in solution. A maximum of four oxalate groups are coordinated to the central ion probably forming a complex with a coordina-

Table 9. Corresponding values of $-\log [A]$, $-\log h$, $\log D^{-1}$ and $\log D^{-1}$ for the europium and terbium oxalate systems.

$-\log [A]$	$-\log h$	$\log D^{-1}$	$\log D^{-1}$	$-\log [A]$	$-\log h$	$\log D^{-1}$	$\log D^{-1}$
3.737	3.442	-1.767	-3.91	3.768	3.388	-1.286	-4.18
3.709	3.493	-1.250	-3.83	3.769	3.386	-1.230	-4.13
3.441	3.503	-0.822	-3.38	3.479	3.434	-0.852	-3.61
3.441	3.503	-0.814	-3.37	3.480	3.430	-0.836	-3.61
3.062	3.464	-0.023	-2.69	3.083	3.424	0.001	-2.79
3.055	3.478	-0.039	-2.67	3.083	3.424	0.005	-2.79
2.760	3.507	0.652	-1.89	2.769	3.486	0.685	-1.92
2.760	3.507	0.660	-1.88	2.769	3.486	0.690	-1.92
2.544	3.510	1.210	-1.32	2.330	4.207	-0.516	-0.96
2.540	3.519	1.158	-1.35	2.111	4.233	0.044	-0.32
3.081	3.975	-1.803	-2.94	2.109	4.248	0.028	-0.29
3.081	3.975	-1.800	-2.94	1.852	4.287	0.798	0.60
3.068	4.026	-1.730	-2.71	1.850	4.292	0.792	0.61
2.774	3.995	-1.179	-2.26	1.704	4.321	1.173	1.08
2.768	4.021	-1.226	-2.23	1.704	4.316	1.192	1.08
2.755	4.073	-1.209	-2.05	1.616	4.336	1.419	1.37
2.337	4.170	-0.582	-1.13	1.616	4.334	1.448	1.39
2.337	4.170	-0.578	-1.13	1.446	4.345	2.063	2.04
2.105	4.271	0.002	-0.25	1.445	4.353	2.073	2.07
2.105	4.271	0.005	-0.25	1.328	4.354	2.496	2.50
2.019	4.262	0.122	-0.16	1.328	4.353	2.513	2.51
2.015	4.285	0.041	-0.17	1.329	4.349	2.578	2.56
1.844	4.307	0.684	0.54	1.214	4.358	2.737	2.75
1.841	4.327	0.639	0.56	1.214	4.361	2.770	2.79
1.700	4.320	1.139	1.04				
1.698	4.330	1.117	1.05				
1.612	4.320	1.341	1.24				
1.612	4.320	1.349	1.25				
1.434	4.344	1.964	1.93				
1.434	4.344	1.967	1.93				
1.310	4.337	2.432	2.38				
1.310	4.337	2.452	2.40				
1.193	4.354	2.812	2.81				
1.193	4.354	2.830	2.83				

tion number of at least eight. Such a high coordination number is not unexpected¹⁵ because of the high charge and fairly large ionic radius of the lanthanoid elements.

From the variations of the stepwise stability constants, *cf.* Table 8, one can see that there is no difficulty for the fourth complex to be formed. This fact indicates that the steric effects noticed previously for the oxydiacetato and 2,6-pyridinodicarboxylato ligands, to the largest part are caused by the geometrical requirements of the ligands.

The results of this investigation are also supported by the work of Sekine.⁸ The results of the earlier solubility measurements⁴⁻⁶ are probably more or less in error.

Acknowledgements. This investigation has in part been supported by a grant from Statens Naturvetenskapliga Forskningsråd (Swedish Natural Science Research Council).

REFERENCES

1. Grenthe, I. and Tobiasson, I. *Acta Chem. Scand.* **17** (1963) 2101.
2. Grenthe, I. *J. Am. Chem. Soc.* **83** (1961) 360.
3. Cotton, A., Ed., *Progress in Inorganic Chemistry*, Interscience 1967, Vol. 8, p. 109.
4. Crouthamel, C. E. and Martin, D. S., Jr. *J. Am. Chem. Soc.* **72** (1950) 1382.
5. Crouthamel, C. E. and Martin, D. S., Jr. *J. Am. Chem. Soc.* **73** (1951) 569.
6. Feibush, A. M., Rowley, K. and Gordon, L. *Anal. Chem.* **30** (1958) 1610.
7. Zaborenko, K. B., Zaval'skaya, A. V. and Fomin, V. V. *Radiokhimiya* **1** (1959) 387.
8. Sekine, T. *Acta Chem. Scand.* **19** (1965) 1476.
9. Rossotti, F. J. C. and Rossotti, H. *The Determination of Stability Constants*, McGraw, New York, Toronto, London 1961.
10. Grenthe, I. *Acta Chem. Scand.* **16** (1962) 1695.
11. Grenthe, I. and Williams, D. R. *Acta Chem. Scand.* **21** (1967) 341.
12. Hansson, E. and Albertsson, J. *Acta Chem. Scand.* **22** (1968) 1682.
13. Ahrland, S. and Johansson, L. *Acta Chem. Scand.* **18** (1964) 2125.
14. Gmelin-Kraut, *Handbuch der anorganischen Chemie*, Heidelberg 1932, Band VI, Abteilung 2, p. 223.
15. Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, Ithaca, New York 1969, p. 220.

Received June 5, 1968.