Thermodynamic Parameters on the Complexation of Trivalent Lanthanide Ions by Cyclopentanecarboxylate in an Aqueous Solution

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Received February 14, 2001

Previously, we determined the thermodynamic parameters for the formation of trivalent lanthanide cations with L-proline[1] and its derivatives.[2-4] We found that both the nitrogen atom and the carboxylate group in the ligands are involved in the chelates formed by lanthanide cations. However, the thermodynamic parameters contributed by the nitrogen atom or the carboxylate group to the chelate formation have not been separately investigated. In this study, we selected the cyclopentanecarboxylate ligand to examine the contribution of the carboxylate group in the ligand to the complexation reaction with lanthanide cations in an aqueous solution. The results can provide the informations on the role of the carboxylate group in the saturated heterocyclic carboxylate ligand when it forms the chelate with lanthanide cations. The results were also compared with those of other carboxylate ligands, and an attempt was made to discover the effect of the cyclopentane ring in the ligand in the complexation process.

Experimental Section

Lanthanide perchrolate solutions were prepared by dissolving the lanthanide oxides in perchloric acid, and the solutions were standardized by EDTA titration using xylenol orange as an indicator in a buffer solution. The concentration of cyclopentanecarboxylic acid was determined by using the standard NaOH solution. $NaClO_4$ was used to adjust the total ionic strength of all of the working solutions to 0.10 M.

A Fisher 520 digital pH meter in conjunction with a Fisher standard combination electrode was used for the pH titrations. The calorimetric titrations were performed by using a Tronac model 450 solution calorimeter. The calorimeter was tested by measuring the amount of the heat of the protonation of THAM (trishydroxymethylaminomethane).

The acid constant and the heat of the protonation of cyclopentanecarboxylic acid were determined respectively by pH and calorimetric titration using a standard NaOH solution. The stability constants of the lanthanide cyclopentanecarboxylate complexes were determined at 25.0 ± 0.1 °C using a jacked titration vessel. The initial pH of the lanthanide and the cyclopentanecarboxlylate solutions were adjusted to approximately the value of pKa of the ligand, and the lanthanide solutions were titrated with a cyclopentanecarboxylate buffer solution. The amount of the heat pro-

duced in the formation of lanthanide cyclopentanecarboxylate complexes were examined by the incremental addition of the cyclopentanecarboxylate buffer solution (2.0 mL) into the lanthanide solutions (50.0 mL). The procedure for calorimetric titration has been described in the literature.[5] The heat of dilution was measured by adding the ligand solution into the 0.10 M $NaClO_4$ solution.

Results and Discussion

The acid constant and the thermodynamic parameters for the protonation of cyclopentanecarboxylic acid were determined in an aqueous medium of 0.1 M $NaClO_4$ ionic strength at 25.0 °C. The results are summarized in Table 1. Table 2 lists a typical set of pH titration data of the europium(III) cyclopentanecarboxylate complex. The average number of ligands per cation, n, was calculated based on the pH titration data. A linear-least square analysis of the equation of $n/1-n=\beta_1 [L]$ (where [L] is a free ligand concentration) produced the value of β_1. Under the experimental conditions, 1 : 1 lanthanide cyclopentanecarboxylate complexes were formed. The calorimetric titration data for the complexation of europium(III) by a cyclopentanecarboxylate ligand are listed in Table 3, and the thermodynamic parameters for the complexation reaction were calculated based on the data. The amounts of the heat measured were corrected for the dilution and the deprotonation of the ligand. Table 4 shows the thermodynamic parameters for the formation of some 1 : 1 lanthanide cyclopentanecarboxylate complexes in an aqueous solution.

The correlation between the sum of the acid constants (ΣpKa) and the stability constants ($\log \beta_1$) of the europium(III) complexes with some bidentate (line a) and monodentate (line b) ligands are shown in Figure 1. The cyclopentanecarboxylate complex is in the monodentate group, and the observed linear relationship between the sum of the acid constants and the stability constants indicates that the inter-

Table 1. Thermodynamic parameters of cyclopentanecarboxylic acid at 25.0 °C and at 0.1 M $NaClO_4$ ionic strength

pKa	$-\Delta Gp$ (kJmol^{-1})	ΔHp (kJmol^{-1})	ΔSp (JK^{-1}mol^{-1})
4.94 ± 0.01	28.19 ± 0.06	42.85 ± 0.01	238.4 ± 0.2

Table 2. pH titration data for Eu^{3+}-cyclopentanecarboxylic acid at 25.0 °C and at 0.1 M NaClO$_4$ ionic strength

Volume of titrant (mL)	pH	[L] × 10^4 (M)	$\bar{n}$
0.5	4.875	0.65	0.000
1.0	4.747	0.96	0.005
1.5	4.690	1.27	0.009
2.0	4.653	1.55	0.014
2.5	4.631	1.83	0.018
3.0	4.613	2.10	0.022
3.5	4.605	2.39	0.026
4.0	4.598	2.67	0.030
4.5	4.594	2.96	0.034
5.0	4.580	3.16	0.040
5.5	4.575	3.41	0.044
6.0	4.572	3.66	0.048
6.5	4.569	3.91	0.052
7.0	4.568	4.17	0.056
7.5	4.567	4.42	0.060
8.0	4.567	4.68	0.064
8.5	4.565	4.91	0.068
9.0	4.562	5.12	0.072
9.5	4.562	5.36	0.076
10.0	4.560	5.57	0.080

initial volume=48.431 mL, initial pH=5.115. [Eu^{3+}]=6.6322 × 10^{-3} M, [HL]=7.9351 × 10^{-3} M. [L$^-$]$_T$ =1.3624 × 10^{-2} M, [L$^-$]=5.6886 × 10^{-3} M

Table 3. Enthalpy titration data for the complexations of Eu^{3+}-cyclopentanecarboxylic acid at 25.0 °C and at 0.1 M NaClO$_4$ ionic strength

Volume of titrant (mL)	-Q$_{Total}$ (mJ)	-Q$_{corrected}$ (mJ)	[L]$_T$ × 10^3 (M)
1.00	141.4	180.0	1.691
1.10	155.6	198.0	1.861
1.20	169.7	216.0	2.030
1.30	183.8	234.0	2.199
1.40	198.0	252.0	2.368
1.50	212.1	270.0	2.537
1.60	226.3	288.0	2.706
1.70	240.4	306.0	2.875
1.80	254.5	324.0	3.045

initial volume=50.42 mL, [M]$_T$=6.328 × 10^{-3} M. initial [H$^+$]=2.851 × 10^{-6} M final [H$^+$]=3.673 × 10^{-5} M

action between the metal and the ligand is primarily electrostatic in lanthanide series.[6] The stability constants increase form La(III) to Gd(III), showing maxmum value in the Gd(III) complex. The stability constants also increase from Dy(III) to Er(III) as decreasing ionic radius or increasing atomic number. These results also support the ionic nature of the metal-ligand interaction in the lighter lanthanide series (La^{+3} through Gd^{+3}) and the heavier lanthanide series (Tb^{+3} through Lu^{+3}). This so-called "gadolinium break" between the lighter lanthanide series and the heavier lanthanide series has been observed in lanthanide series. The break has been interpreted to be the different hydration sphere structure for

Table 4. Thermodynamic parameter for the formation of lanthanide-cyclopentanecarboxylic acid at 25.0 °C and at 0.1 M NaClO$_4$ ionic strength

Metal	-ΔG$_1$ (kJmol^{-1})	ΔH$_1$ (kJmol^{-1})	ΔS$_1$ (JK^{-1}mol^{-1})
La	11.68 ± 0.15	5.86 ± 0.03	58.9 ± 0.6
Nd	13.10 ± 0.33	4.63 ± 0.08	59.5 ± 1.3
Sm	13.83 ± 0.25	5.54 ± 0.06	65.0 ± 1.0
Eu	12.83 ± 0.19	4.42 ± 0.08	57.9 ± 0.9
Gd	16.31 ± 0.18	9.75 ± 0.08	87.4 ± 0.9
Dy	12.60 ± 0.37	6.46 ± 0.08	63.9 ± 1.5
Ho	12.79 ± 0.46	8.68 ± 0.10	72.1 ± 1.9
Er	13.60 ± 0.28	4.01 ± 0.05	59.1 ± 1.1
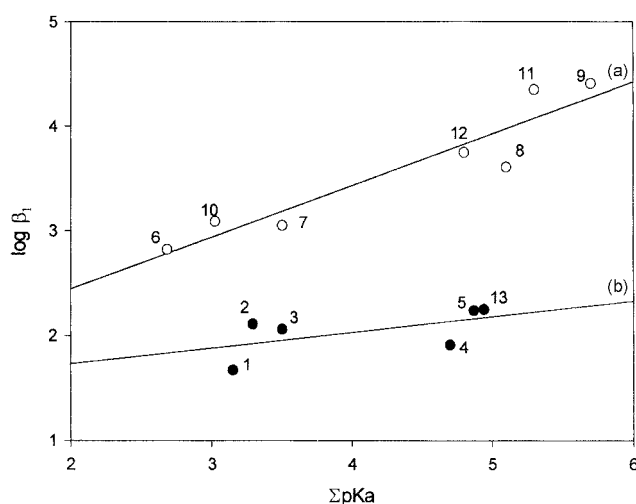
Figure 1. Correlation of logβ_1 of the Eu^{3+} complexes and ΣpKa of the ligand, (a) bidendate (b) monodendate; 1. furoic acid, 2. thioglycolate, 3. methoxyacetate, 4. acetate, 5. propionate, 6. pyrazine carboxylate, 7. α-picolinated N-oxide, 8. α-picolinate, 9. 1,4-cyclohexanedicarboxylate, 10. croconate, 11. malonate, 12. glutarate, 13. cyclopentanecarboxylate

the two series in an aqueous solution.[7]

As seen in Table 4, the positive values of enthalpy and entropy change during the complexation reaction clearly indicate that the driving force for the complexation is an entropy effect, and that the inner-sphere complexes are formed in an aqueous solution.[8] The thermodynamic parameters for some europium(III) complexes are shown in Table 5. The europium complexes with monocarboxylic acids are stabilized by the positive entropy effect, whereas amino acid complexes are stabilized both by the exothermic enthalpy effect and by the entropy effect.

It can be seen from Table 5 that the europium(III) cyclopentanecarboxylate complex is more stable than the corresponding furoate complex. This can be explained by the fact that cyclopentanecarboxylic acid is more basic than furoic acid (pKa=3.11).[9] The europium(III) cyclopentanecarboxylate complex is more stable than its corresponding acetate complex, even though the basicity of the two carboxylic acids are quite similar (pKa=4.94 for cyclopentanecarboxy-

Table 5. Thermodynamic paramaters of some europium complexes

ligand	$-\Delta G_1$ (kJmol)	ΔH_1 (kJmol^{-1})	ΔS_1 (JK^{-1}mol^{-1})	Ref.
cyclopentane-carboxylic acid	12.83	4.42	57.9	this work
acetic acid	10.92	5.9	62	10
furoic acid	9.54	6.32	53.1	9
benzoic acid	12.33	7.9	68	11
α-picolinic acid	20.58	-6.4	48	10
pyrazine carboxylate	16.09	-0.29	56	12
L-proline	13.23	11.7	84	1

lic acid, and pKa=4.8 for acetic acid).[10] The opposite result is anticipated if the steric hindrance caused by the bulky cyclopentane ring in the cyclopentanecarboxylate ligand reduces the bonding interaction between europium(III) and the cyclopentanecarboxylate ion, thereby resulting in greater endothermic enthalpy change in the formation of the cyclopentanecarboxylate complex. Actually, the value of the enthalpy change for samarium(III) complexes with acetate (ΔH_1=6.07 kJmol^{-1}), propionate (ΔH_1=6.53 kJmol^{-1}), and isobutatonate (ΔH_1=11.13 kJmol^{-1}) ligands increases as the steric hindrance caused by the bulky alkyl group in the ligand is increased, and this steric hindrance is responsible for the greater endothermic enthalpy change.[10]

In this study, however, we found that the enthalpy changes for the formation of europium(III) cyclopentanecarboxylate complexes are less endothermic than those of the corresponding acetate complexes. The overall complexation reaction is believed to consist of two steps: first, the dehydration step, and second, the complexation step. The dehydration step reflects the disruption of the solvent structure of the reactants in an aqueous solution, and the complexation step combines the ions to form the bonds. In terms of the enthalpy changes, the disrupton of the hydration structure is an endothermic contribution, while the ionic combination is an exothermic one. Based on the results of the relatively smaller endothermic enthalpy changes in the cyclopentanecarboxlate complexes, it is thought that the hydration structure of the cyclopentanecarboxlate ion is probably disrupted to a less extent than that of the acetate ion before the com-

plexation reaction actually occurs in an aqueous solution. This suggetion is also supported by the fact that the entropy changes in cyclopentanecarboxylate complexes are less than those of acetate complexes.

In conclusion, the cyclopentanecarboxylate ligand forms quite stable complexes by the trivalent lanthanide cations in an aqueous solution, and the driving force for the complexation reaction is an entropy effect. The increased stability in the cyclopentanecarboxylate complexes as compared to that in the acetate complexes is attributable to a smaller endothermic enthalpy change. The less disruption in the hydration structure of the cyclopentanecarboxylate ion occurs before the complexation step in an aqueous solution.

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