of **2**, **4**, **5**, and **7**, tables of rms amplitudes of thermal vibration for **2**, **4**, and **5**, and figures showing the special position and general equivalent position region for **4** (23 pages); tables of structure factors (58 pages). Ordering information is given on any current masthead page.

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Thermodynamics of Complexation of Lanthanides by 3-Fluoro-, 4-Fluoro-, and 3-Nitrobenzoic Acids

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The thermodynamic parameters (log β_{101}, ΔH_{101}, and ΔS_{101}) for the formation of the LnL^{2+} complexes between lanthanide cations and 3-fluoro-, 4-fluoro-, and 3-nitrobenzoate anions (L^-) were determined by potentiometric and calorimetric titrations in 0.10 M ($NaClO_4$) ionic strength aqueous solution at 25 °C. The stabilities of the present complexes agreed with the relationship for monocarboxylate complexation (e.g. log β_{101} vs. log K_{011}).

Introduction

The complexation of trivalent lanthanide cations has been studied with a relatively large number of aliphatic monocarboxylic acid ligands. The stability constants show a linear correlation with the acidity constants of the ligands. The enthalpy and entropy of complexation are positive and largely compensatory, reflecting the major effect that dehydration has in the overall complexation reaction. Recently, complexation by benzoate ligand has been reported,[1] and the same trends in β_{101}, ΔH_{101}, and ΔS_{101} have been observed. The subscripts refer to the coefficients of the reaction

$$p\text{Ln}^{3+} + q\text{H}^+ + r\text{L}^- = \text{Ln}_p\text{H}_q\text{L}_r \quad \beta_{pqr}, \text{ etc.}$$

In this paper we report the results of complexation studies of lanthanides by three additional aromatic monocarboxylate ligands. Our primary goal was to extend the data base for such systems and to compare these data with corresponding values of lanthanide–aliphatic monocarboxylate interaction.

Experimental Section

Reagents. Stock solutions of lanthanide perchlorates were prepared and analyzed as described previously.[1] Commercially available 3-fluoro-, 4-fluoro-, and 3-nitrobenzoic acids (Aldrich) were used without further purification. The concentrations of aqueous solutions of the ligand acids were determined by titration with a standard sodium hydroxide solution. The buffer solutions of the ligands were prepared by dissolving the acids in known amounts of 1 M NaOH and adjusting the $[HL]/[L^-]$ ratios with standardized $HClO_4$, followed by dilution to the desired concentrations (0.02–0.04 M). A stock solution of perchloric acid was prepared by dilution of concentrated perchloric acid (Baker) with deionized water and analysis by titration with NaOH solution. The other chemicals were reagent grade. The metal and ligand solutions used in the titrations were adjusted to 0.10 M ionic strength with $NaClO_4$.

Procedures. In potentiometric measurements a Corning Model 130 pH meter was used with a combination electrode. The potentiometer allowed pH readings to ±0.001 pH unit accuracy. The titrations were performed in the pH region between 2 and 4, where the liquid-junction potential due to the free hydrogen ions of the test solution is significant. Therefore, the $-\log [H^+]$ values after each titrant addition were determined from a plot of $-\log [H^+]$ (calculated) vs. pH (experimental). This calibration plot was developed by titration of 0.10 M $NaClO_4$ solution with standardized $HClO_4$ solution.

Because of the limited solubilities of the ligand acids (especially 4-fluorobenzoic acid), the stability constants were evaluated by titration of mixtures of lanthanide perchlorates and sodium salts of the ligand anions with standardized (about 0.1 M) $HClO_4$ solution. The stability constants of the 3-fluoro- and 3-nitrobenzoate complexes were determined by other titrations of lanthanide perchlorate solutions with buffered ligand solutions. In all titrations, the total metal concentrations, C_M, were varied between 0.008 and 0.02 M. In the first type of titrations, the C_L/C_M ratios (C_L = the total concentration of the ligand) varied between 0.5 and 2. In the second type of titrations, the total ligand concentrations in the titrant were 0.02–0.04 M, and about two-thirds of the ligand acids was neutralized with NaOH.

The protonation constants were determined by titration of the ligand acid solutions with CO_2-free NaOH solution.

Calorimetric titrations were performed on a Peltier-cooled calorimeter with use of titration techniques described elsewhere.[2,3] For a particular experiment, 50 mL of a lanthanide perchlorate solution ($0.008 < C_M < 0.018$ M) was titrated with 0.5-mL aliquots of the neutralized ligand solution (C_L = 0.025, 0.04, and 0.04 M for 4-fluoro-, 3-fluoro-, and 3-nitrobenzoic acids, respectively). The heats of dilution of the ligands and lanthanide solutions were also determined as described earlier.[1]

Under the experimental conditions the effect of the heats of protonation should be minimal. Nevertheless, they were included in the calculations. For the protonation heats of 3-fluoro- and 3-nitrobenzoic acids the values −0.92 and −1.55 kJ/mol respectively were used[4] while for 4-fluorobenzoic acid the estimated value of −0.85 kJ/mol was used.

The protonation constants, stability constants, and ΔH_{101} values were calculated with Simplex algorhythm programs written by Dr. William B. Cacheris.

Results and Discussion

Typical sets of potentiometric and calorimetric data are listed in Tables I–III. The "calcd" columns are the values calculated for each titration point with the final constants of Table V. The protonation constants are given in Table IV, and the thermodynamic parameters (log β_{101}, $-\Delta G_{101}$, ΔH_{101}, and ΔS_{101}) are presented in Table V. The standard deviations in individual titrations for log K_{011}, log β_{101}, and ΔH_{101} were estimated to be 0.001–0.005, 0.005–0.020, and 0.03–0.10, respectively. However, the errors given in Tables IV and V are based on the agreement in repetitive titrations. Both potentiometric and calorimetric measurements have some evidence of the formation of the second complex, LnL_2^+, but no values of log β_{102} or ΔH_{102} are reported as the maximum $\bar{n}$ values were too small to allow a valid estimate. The protonation constants agree well with the literature values[4] when the difference in the ionic strengths is taken into account.

Figure 1 shows the relationship between the value of log β_{101} for a number of Sm(III) complexes with monocarboxylate ligands and the acidity, pK_a, of the ligand acid. The values for the Sm(III)–benzoate system are taken from ref 1 and the remaining data from ref 5. The values have been adjusted when necessary

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Table I. Potentiometric Data for the Yb(III)–3-Fluorobenzoic Acid System (I = 0.10 M ($NaClO_4$); T = 25 °C)[a]

titrant vol, mL	$10^4[H^+]$(exptl), M	$10^4[H^+]$(calcd), M	10^3[M], M	10^3[L], M	$\bar{n}$(calcd)
6.0	1.220	1.214	2.055	1.219	0.069
7.0	1.237	1.234	1.999	1.392	0.078
8.0	1.248	1.249	1.947	1.560	0.087
9.0	1.254	1.261	1.897	1.723	0.095
10.0	1.266	1.271	1.849	1.881	0.103
11.0	1.280	1.279	1.804	2.034	0.111
12.0	1.283	1.285	1.761	2.183	0.118
13.0	1.289	1.290	1.720	2.328	0.125
14.0	1.295	1.294	1.680	2.469	0.131
15.0	1.301	1.297	1.643	2.606	0.137

[a] Initial conditions: cup solutions, volume 50.5 mL, $C_M = 2.470 \times 10^{-3}$ M, $C_H = 3.610 \times 10^{-5}$ M; titrant, $C_L = 1.951 \times 10^{-2}$ M, $C_H = 7.429 \times 10^{-3}$ M.

Table II. Potentiometric Titration Data for the Gd(III)–3-Nitrobenzoic Acid System (I = 0.10 M ($NaClO_4$); T = 25 °C)[a]

titrant vol, mL	$10^4[H^+]$(exptl), M	$10^4[H^+]$(calcd), M	10^3[M], M	10^3[L], M	$\bar{n}$(calcd)
0.7	0.974	1.009	2.641	1.155	0.384
0.8	1.078	1.112	2.653	1.135	0.380
0.9	1.191	1.218	2.665	1.116	0.376
1.0	1.327	1.326	2.677	1.097	0.372
1.1	1.445	1.439	2.689	1.078	0.368
1.2	1.530	1.554	2.702	1.059	0.364
1.3	1.647	1.673	2.714	1.040	0.360
1.4	1.773	1.796	2.726	1.021	0.356
1.5	1.931	1.922	2.739	1.003	0.352
1.6	2.035	2.052	2.751	0.984	0.347
1.7	2.176	2.186	2.764	0.966	0.343
1.8	2.315	2.325	2.776	0.948	0.339
1.9	2.464	2.468	2.789	0.930	0.334
2.0	2.621	2.615	2.802	0.912	0.330
2.1	2.757	2.768	2.815	0.894	0.326
2.2	2.942	2.925	2.827	0.876	0.321
2.3	3.116	3.088	2.840	0.859	0.317
2.4	3.273	3.256	2.853	0.841	0.312
2.5	3.442	3.430	2.866	0.824	0.308

[a] Initial conditions: cup solution, volume 50.0 mL, $C_M = 4.350 \times 10^{-3}$ M, $C_L = 1.563 \times 10^{-2}$ M, $C_H = 9.270 \times 10^{-4}$ M; titrant, C_H = 0.1014 M.

Table III. Calorimetric Titration Data for the Ho(III)–4-Fluorobenzoic Acid System (I = 0.10 M ($NaClO_4$); T = 25 °C)[a]

titrant vol, M	Q(corr),[b] mJ	Q(calcd), mJ	10^2[M], M	10^3[L], M	$-\log [H^+]$
0.5	64	59	1.223	0.1193	4.687
1.0	130	121	1.200	0.2431	4.812
1.5	189	182	1.177	0.3677	4.890
2.0	246	243	1.155	0.4922	4.944
2.5	306	303	1.133	0.6163	4.984
3.0	358	363	1.112	0.7400	5.016
3.5	414	421	1.092	0.8629	5.041
4.0	474	479	1.072	0.9854	5.062
4.5	542	535	1.053	1.107	5.080
5.0	590	591	1.035	1.228	5.092
5.5	643	646	1.016	1.349	5.109
6.0	699	700	9.99	1.468	5.121
6.5	755	754	9.82	1.587	5.132
7.0	807	806	9.65	1.706	5.142
7.5	863	858	9.49	1.823	5.150
8.0	905	909	9.33	1.940	5.158
8.5	960	959	9.17	2.056	5.166
9.0	1016	1008	9.02	2.172	5.173
9.5	1056	1057	8.88	2.287	5.180
10.0	1105	1106	8.73	2.401	5.185

[a] Initial conditions: cup solution, volume 50.0 mL, $C_M = 1.246 \times 10^{-2}$ M, $C_H = 3.60 \times 10^{-5}$ M; titrant, $C_L = 2.550 \times 10^{-2}$ M, $C_H = 7.00 \times 10^{-4}$ M; constants used, $\beta_{011} = 8957$, $\beta_{101} = 76$, $\beta_{102} = 1150$. [b] Corrected for dilution effects.

Table IV. Protonation Constants of Different Benzoate Anions (T = 25 °C)

anion	medium concn, M	$\log K_{011}$	ref
benzoate	0.10 ($NaClO_4$)	3.99 ± 0.05	1
4-fluorobenzoate	0	4.14	4
4-fluorobenzoate	0.10 ($NaClO_4$)	3.95 ± 0.01	this work
3-fluorobenzoate	0	3.87	4
3-fluorobenzoate	0.10 ($NaClO_4$)	3.68 ± 0.05	this work
3-nitrobenzoate	0	3.45	4
3-nitrobenzoate	0.10 ($NaClO_4$)	3.28 ± 0.02	this work

to an ionic strength of 0.10 M in $NaClO_4$ solution as described earlier.[1] The correlation of $\log \beta_{101}$ and pK_a is expected to be linear for metal–ligand equilibria in which the metal–ligand bond is strongly ionic and in which no variation in steric effects occurs.[6]

Table V. Thermodynamic Parameters for Complexation of Lanthanides by 3-Fluoro-, 4-Fluoro-, and 3-Nitrobenzoic Acids (I = 0.10 M ($NaClO_4$); T = 25 °C)

metal ion	$\log \beta_{101}$	$-\Delta G_{101}$, kJ/mol	ΔH_{101}, kJ/mol	ΔS_{101}, J/(mol K)
		(a) 3-Fluorobenzoic Acid		
La	1.65 (±0.05)	9.42 (±0.28)	6.7 (±0.3)	54 (±2)
Pr	1.78	10.12	5.5	52
Nd	1.90	10.82	6.3	57
Sm	1.95	11.11	6.1	58
Eu	1.88	10.71	7.5	61
Gd	1.80	10.25	8.1	62
Tb	1.76	10.02	8.3	61
Dy	1.73	9.85	8.5	62
Ho	1.70	9.68	9.0	63
Er	1.76	10.02	8.9	63
Tm	1.73	9.85	9.0	63
Yb	1.79	10.20	8.3	62
Lu	1.80	10.25	9.2	65
		(b) 4-Fluorobenzoic Acid		
La	1.88 (±0.04)	10.71 (±0.23)	8.1 (±0.2)	63 (±1)
Pr	2.02	11.51	7.6	64
Nd	2.06	11.73	7.9	66
Sm	2.12	12.08	8.0	67
Eu	2.08	11.85	8.3	68
Gd	2.00	11.39	8.0	65
Tb	1.89	10.77	9.6	68
Dy	1.89	10.65	10.1	70
Ho	1.87	10.71	10.7	72
Er	1.88	10.77	9.6	68
Tm	1.85	10.54	11.0	72
Yb	1.88	10.71	12.0	76
Lu	1.89	10.77	11.8	76
		(c) 3-Nitrobenzoic Acid		
La	1.57 (±0.06)	9.00 (±0.34)	5.5 (±0.5)	49 (±2)
Pr	1.64	9.34	6.5	53
Nd	1.75	9.96	5.9	53
Sm	1.85	10.51	5.7	54
Eu	1.76	10.02	6.6	56
Gd	1.68	9.57	7.3	57
Tb	1.61	9.17	7.9	57
Dy	1.62	9.23	8.1	58
Ho	1.61	9.17	7.6	56
Er	1.64	9.34	9.5	63
Tm	1.60	9.11	9.3	62
Yb	1.65	9.40	8.7	61
Lu	1.64	9.34	9.0	62

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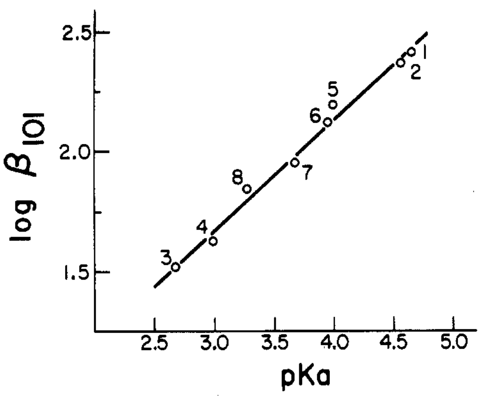

Figure 1. Relationship between the stability constant, β_{101}, for formation of SmL^{2+} and the acid constant, pK_a, of HL: (1) propionic acid; (2) acetic acid; (3) iodoacetic acid; (4) chloroacetic acid; (5) benzoic acid; (6) 4-fluorobenzoic acid; (7) 3-fluorobenzoic acid; (8) 3-nitrobenzoic acid.

The correlation in Figure 1 for the alkyl and aryl monocarboxylates reflects the validity of these interpretations in lanthanide–monocarboxylate complexation.

Figure 2 presents the thermodynamic parameters for different lanthanide–benzoate equilibrium systems. From the similar shapes of the curves for each complexed system we can infer that the complexation involves similar dehydration and bonding effects in all four systems (including the benzoate complexes). Unfortunately, enthalpy and entropy data are not reported[5] for the lanthanide complexation with aliphatic monocarboxylate ligands at an ionic stength of 0.1 M, so no comparison of enthalpy and entropy changes can be made. We can note in Figure 2 that there is some grouping in that, for both ΔH and ΔS, the benzoate and 4-fluorobenzoate curves fall closer together as do the 3-fluorobenzoate and 3-nitrobenzoate curves. Moreover, the relative values indicate slightly more dehydration in benzoate and 4-fluorobenzoate complexation than in the case of the other two ligands.

Smith et al.[7] have proposed values for predicting stability constants of lanthanide complexes. For saturated alkyl monocarboxylate ligands, they propose addition of a correction to the successive log β's of La(III). For example, for Nd(III) complexation, +0.33 is added to the log β_{101} value of La(III); for Sm(III), the correction is +0.45 for Dy(III), it is +0.10, and for Lu(III), it is +0.11. For the aromatic ligand systems of this study, the corrections result in log β_{101} values that are larger than the experimental values in all cases. For the Nd(III) complexes, for our ligands plus benzoate, the predicted log β_{101} value is 0.08–0.15 unit larger than the experimental value. For Sm(III), the average of the differences between predicted and experimental log β_{101} values for the four ligands is 0.17, while for Dy(III) complexation, it is 0.06, and for Lu(III), it is 0.07. For many purposes, such a deviation would not be troublesome.

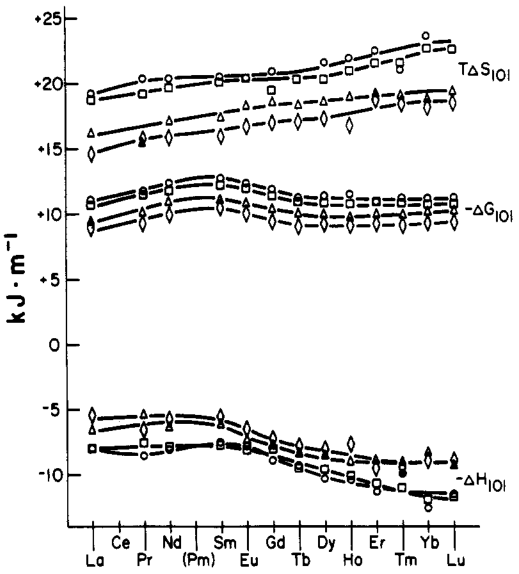

Figure 2. Thermodynamic parameters ($-\Delta G_{101}$, $-\Delta H_{101}$, and $T(\Delta S_{101})$) for formation of LnL^{2+} complexes: (○) benzoic acid; (□) 4-fluorobenzoic acid; (△) 3-fluorobenzoic acid; (◇) 3-nitrobenzoic acid.

Previously the complexation of lanthanides by *o*-, *m*-, and *p*-methoxybenzoates was reported. The stability constants were larger than predicted from the log β_{101} vs. pK_a correlation in Figure 1. This enhanced stability was attributed to an increased negative charge on the carboxylate group when bound to the lanthanide cation. Such increased charge could be explained by inductive and/or resonance effects. In the ligands studied in this work, resonance effects are unlikely and both F and NO_2 are such strong electron-withdrawing groups that the lanthanide cations cannot achieve the charge polarization that seemingly occurs with the methoxy group.

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Registry No. 3-Fluorobenzoic acid, 455-38-9; 4-fluorobenzoic acid, 456-22-4; 3-nitrobenzoic acid, 121-92-6.

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Notes

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Studies Relating to the Specificity of the Hemerythrin Active Site

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Hemerythrin from sipunculid marine worms consists of an octamer form (M_r 108 000) present in the coelomic fluid, each subunit of which contains a binuclear Fe active site capable of binding a single O_2 molecule.[1-4] A monomer form is present in the retractor muscle, and the situation appears closely analogous to that of hemoglobin and myoglobin. The active site of deoxyHr A has two Fe(II)'s, one of which is six-coordinate and the other five-coordinate.[5] Uptake of O_2 at the vacant position is accompanied by a 2e redox change to give two Fe(III)'s, and peroxide, which is bound in an unusual manner (B).[7-9] The metHr form

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