

Thermodynamics of Complexation of Lanthanides by Benzoic and Isophthalic Acids

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The thermodynamic parameters (ΔG , ΔH , and ΔS) of formation of the 1:1 complexes between lanthanide cations and benzoate and isophthalate anions were determined by potentiometric and calorimetric titrations in aqueous solutions of 0.10 M (NaClO_4) ionic strength. The values for the benzoate complexes agreed with the general relationships for alkyl monocarboxylate complexation (e.g., $\log \beta_{101}$ vs. $\text{p}K_a$). Even though the isophthalate complexes must also involve interaction between the metal and a single carboxylate group, the thermodynamic parameters differ from those for benzoate complexing. It is proposed that the enhanced stability of the isophthalate complexes is related to polarization of electronic charge from the unbound carboxylate group through the π system of the phenyl ring to the bonding carboxylate.

Introduction

The formation in aqueous solution of lanthanide complexes with many aliphatic carboxylic acids has been studied in a number of laboratories over the past 20 years.^{2a} By comparison, less attention has been given to the complexation of lanthanides with aromatic acids. Partially, this reflects some problems with the solubilities of the species involved, and partially, it can be attributed to greater interest in the use of the aliphatic acids in separations of the lanthanide and actinide elements.

Many of the organic substances that can affect the biological and ecological behavior of the lanthanide and actinide ions have aromatic carboxylate binding sites. For example, results from this laboratory show that hard-acid cations such as Ca(II), Eu(III), Am(III), Th(IV), and U(VI) are bound by the aromatic carboxylate sites in humic and fulvic acids.^{2b} The binding in these systems is enhanced by the "polyelectrolyte" effect.³ To study the effect of nonbinding carboxylate groups on the complexation, we have studied lanthanide complexation by benzoic acid and by isophthalic acid. In the latter ligand, steric effects prevent simultaneous binding to both carboxylate sites. Potentiometry and calorimetry were used to obtain the thermodynamic parameters of complexation.

Experimental Section

Reagents. Perchlorate stock solutions of the lanthanides were prepared from the reagent grade metal oxides. Working solutions were prepared from the stock solutions by dilution (usually between 0.5 and 15 mM). Lanthanide concentrations were determined by titration with EDTA using xylenol orange as the indicator and either acetate or hexamethylenetetramine as the buffer.

Commercially available benzoic acid was used as purchased while isophthalic acid (benzene-1,3-dicarboxylic acid) was recrystallized from ethanol. The purity of the acids was checked by titration with CO_2 -free NaOH solution. Buffer solutions of these ligands were prepared by dissolving the appropriate weights in sodium hydroxide and diluting as required. The initial pH values of the ligand and the lanthanide solutions ranged from 3.7 to 4.9. Ionic strength was kept constant by adjusting the solutions to 0.10 M NaClO_4 . Prior to the stability constant measurements, the exact acid concentrations of the metal and ligand buffer solutions were obtained by potentiometry.

Procedures. To determine the stability constants, we titrated aliquots of metal solution with ligand buffer solution and measured the pH after each titrant addition. The titrations were conducted in a jacketed vessel maintained at 298 K by circulating water from a constant-temperature bath. The hydrogen ion concentration at each titrant addition was measured on a research pH meter using a glass

Table I. Potentiometric Titration Data
($T = 298 \text{ K}$, $I = 0.10 \text{ M}$ (NaClO_4))

(a) Europium-Benzoate ^a					
vol of titrant, mL	pH	$10^3 [L^-]$, M	\bar{n}		
4.0	3.846	1.00	0.141		
5.0	3.846	1.237	0.171		
6.0	3.848	1.471	0.199		
7.0	3.850	1.700	0.226		
8.0	3.852	1.922	0.252		
9.0	3.853	2.140	0.278		
10.0	3.855	2.353	0.303		
11.0	3.858	2.573	0.323		
12.0	3.858	2.766	0.350		
14.0	2.863	3.169	0.392		
15.0	3.865	3.368	0.410		
16.0	3.868	3.572	0.424		
17.0	3.87	3.759	0.443		
18.0	3.872	3.942	0.461		
19.0	3.874	3.122	0.479		
(b) Samarium-Isophthalate					
vol of titrant, mL	Q_i , mJ ^c	\bar{n}	vol of titrant, mL	Q_i , mJ ^c	\bar{n}
1.00	104.8	0.033	7.00	757.6	0.236
2.00	208.3	0.067	8.00	869.0	0.269
3.00	327.8	0.101	9.00	972.5	0.302
4.00	430.0	0.135	10.00	1080.8	0.336
5.00	538.9	0.169	11.00	1193.0	0.369
6.00	654.4	0.202	12.00	1293.6	0.401

^a Conditions: for Eu(III) $[\text{Eu(III)}]_i = 3.105 \times 10^{-3} \text{ M}$, pH 3.978, 55.0 mL of solution; for L $[\text{L}]_i = 4.121 \times 10^{-2} \text{ M}$, pH 3.990. The subscript i refers to the initial concentration, and L denotes the free ligand. ^b Conditions: for Sm(III) $[\text{Sm(III)}]_i = 1.300 \times 10^{-2} \text{ M}$, pH 4.464, 50.0 mL of solution; for L $[\text{L}]_i = 2.370 \times 10^{-2} \text{ M}$.

^c Corrected for dilution effects.

electrode and an Ag-AgCl reference electrode. The acid constants of benzoic acid and isophthalic acid in 0.10 M ionic strength (NaClO_4) were measured potentiometrically by titration with CO_2 -free NaOH solution.

Calorimetric titrations were performed on a Peltier-cooled calorimeter with use of titration techniques described previously.^{4,5} For a particular experiment, 50-55 mL of a lanthanide solution was titrated with approximately 1-mL aliquots of the ligand solution. The heats of dilution of the ligands and lanthanide solutions were also determined, the former by titration of the ligand solution into 0.1 M NaClO_4 and the latter by titration of 0.1 M NaClO_4 into metal solution. The enthalpy of protonation of benzoic acid was determined calorimetrically by titration of the ligand solution with perchloric acid. Since isophthalic acid has a very limited solubility in water, the heats of protonation of this ligand could not be obtained by calorimetric techniques; however, Purdie et al.⁶ have reported these values from

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Table II. Thermodynamic Values of Protonation ($T = 298 \text{ K}$, $I = 0.10 \text{ M}$ (NaClO_4))

anion	$\log K_{011}$	$\log K_{021}$	ΔH_{011}^a	ΔH_{021}^a	ΔS_{011}^b	ΔS_{021}^b
benzoate	3.99 ± 0.05		-0.87 ± 0.05		74 ± 5	
isophthalate ^c	4.38 ± 0.01	3.30 ± 0.02	$+2.00$	0.0	92	67

^a In kJ/mol. ^b In J/(mol K). ^c ΔH and ΔS values from ref 7.

Table III. Thermodynamic Parameters ($T = 298 \text{ K}$, $I = 0.10 \text{ M}$ (NaClO_4))

ion	$\log \beta_{101}$	$\log \beta_{102}$	$-\Delta G_{101}$, kJ/mol	ΔH_{101} , kJ/mol	ΔS_{101} , J/(mol K)
(a) Lanthanide-Benzoate					
La	1.92 (± 0.04)	3.56 (± 0.10)	11.01 (± 0.20)	8.0 (± 0.6)	64 (± 2)
Pr	2.06	3.60	11.76	8.5	68
Nd	2.15	3.83	12.27	8.0	68
Sm	2.21	3.92	12.61	7.6	68
Eu	2.16	3.79	12.33	7.9	68
Gd	2.08	3.70	11.87	9.0	70
Tb	1.95	3.65	11.01	9.3	68
Dy	1.96	3.64	11.19	10.3	72
Ho	2.01	3.77	11.41	10.4	73
Er	1.92	3.63	10.90	11.3	75
Tm	1.94	3.63	11.07	9.9	70
Yb	1.94	3.72	11.01	12.6	79
Lu	1.92	3.77	11.01	11.5	76
(b) Lanthanide-Isophthalate					
La	2.15 (± 0.05)		12.27 (± 0.20)	14.57 (± 0.20)	90 (± 1)
Pr	2.55		14.52	13.47	94
Nd	2.65		15.10	11.94	91
Sm	2.82		16.08	10.71	90
Eu	2.77		15.82	11.89	93
Gd	2.73		15.56	12.20	93
Tb	2.64		15.07	12.77	93
Dy	2.67		14.93	13.11	94
Ho	2.55		14.56	15.56	101
Er	2.58		14.69	16.22	104
Tm	2.57		14.67	17.15	107
Yb	2.59		14.79	17.71	109
Lu	2.58		14.74	19.23	114
Y	2.51		14.31	15.04	99

temperature coefficient measurements.

Most titrations were repeated two or three times with, in all cases, the repetitive runs agreeing satisfactorily. The data from both the potentiometric and the calorimetric titrations were treated by linear least-squares analysis (program LINW, modified⁷). Calculations were performed on the CDC Cyber 730 computer at Florida State University. The equations used have been described in earlier publications.^{4,7} The errors in the reported β_{101} values are estimated to be in the range of 2–10%, with the errors in β_{102} being slightly larger. ΔH_{101} values for duplicate calorimetric runs agree to within $\pm 0.63 \text{ kJ/mol}$ in the case of benzoate and $\pm 0.24 \text{ kJ/mol}$ in the case of isophthalate. Errors in the reported enthalpy values are therefore estimated to be ca. 6 and 2%, respectively.

Results and Discussion

Table I provides sample sets of the potentiometric and calorimetric data. Table II reports the thermodynamic data used in our calculations for stepwise protonation. Table III is a summary of the thermodynamic values calculated for the formation of the complexes in 0.10 M NaClO_4 medium.

In both systems, the calorimetric data gave evidence of the formation of a second complex, also with positive enthalpy of complexation. A linear least-squares fit of the data, using the potentiometric β_{101} and β_{102} values, was used to obtain ΔH_{101} and ΔH_{102} . Due to the low values of \bar{n} in the calorimetric experiments, ΔH_{102} could not be determined with accuracy for either system although it appears to be roughly of the same

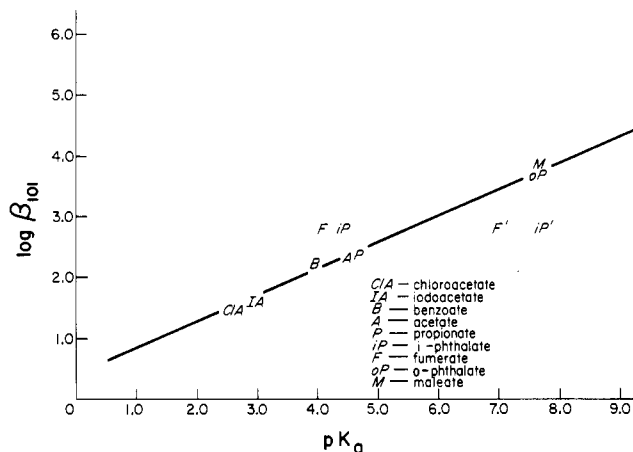


Figure 1. Relationship between the stability constant, β_{101} , for formation of SmL and the acid constant, $\sum pK_{a_i}$, of H_nL .

magnitude as ΔH_{101} . It should be noted that the calculated value of ΔH_{101} was found to be relatively insensitive to moderate variations in the value of β_{102} used in the enthalpy calculations. However, completely ignoring formation of the 1:2 complex leads to calculated ΔH_{101} values approximately 10% larger than those in Table III if all the data points of the titrations are included. The uncertainties in β_{102} for the isophthalate complexing were rather large, so no values are reported.

The values for the lanthanide-benzoate complexes in Table III are consistent with those measured for complexing by alkyl monocarboxylate ligands.^{2a} However, even though the isophthalate complexes must also involve complexation through a single carboxylate group, the thermodynamic parameters differ significantly from those for benzoate complexing.

In Figure 1 the value of $\log \beta_{101}$ for a number of Sm(III) complexes with monocarboxylate ligands is plotted as a function of the pK_a of the ligand. The data are taken from ref 2a. All the values have been adjusted to an ionic strength of 0.10 M in NaClO_4 solution since the measurements in several systems were conducted in 0.10 M KNO_3 medium. The correction was calculated from $\beta(\text{cor}) = \beta(\text{exptl}) (1 + \beta_{\text{SmNO}_3^{2+}}[\text{NO}_3^-])$, which corresponds to $\beta(\text{cor}) = 1.6\beta(\text{exptl})$ for $[\text{NO}_3^-] = 0.10$.⁸ The correlation of $\log \beta_{101}$ and pK_a is expected to be linear for systems in which the interaction is strongly ionic and no variations in steric effects occur with different ligands.⁹ These conditions are present in these lanthanide-monocarboxylate systems. As expected, the SmB^{2+} ($\text{B} = \text{benzoate}$) data fit the correlation well.

Data for Sm(III) complexation by maleate and *o*-phthalate, dicarboxylate chelating ligands, also fit the correlation when $pK_a = pK_{a_1} + pK_{a_2}$. This reflects that the ionic character of the interaction is the dominant feature of these complexes. The isophthalate complex cannot be a chelate due to steric hindrance, and the $\log \beta_{101}$ for the Sm(iP)^+ ($\text{iP} = \text{isophthalate}$) formation fails to fit the correlation either when pK_{a_2} (iP) or when $pK_{a_1} + pK_{a_2}$ (iP') are plotted.

A similar nonchelating dicarboxylate ligand, fumarate (F), had been studied previously.¹⁰ The $\log \beta_{101}$ for SmF^+ has been

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plotted in Figure 1 vs. pK_{a_2} (F) and $pK_{a_1} + pK_{a_2}$ (F'). As in the isophthalate case, no correlation with the other data is found. The enhanced stability for $\log \beta_{101}$ over that expected from the pK_{a_2} value ($\Delta \log \beta_{101} \approx 0.6$) was attributed to an increased negative charge of the binding carboxylate as a result of transmission of electron density through the ligand π system from the unbonded carboxylate group. Similar charge transmission in the isophthalate ligand would account for its enhanced bonding ($\Delta \log \beta_{101} \approx 0.5$).

It is noteworthy that SmF^+ and Sn(iP)^+ have the same value of $\log \beta_{101}$. Moreover, this value corresponds to a pK_a of ca. 5.5 for the correlation fit. This value also corresponds to the upper limit observed for pK_a values of monocarboxylic acids, both aliphatic and aromatic.^{11,12} A simple explanation is that the saturation negative charge density for carboxylate groups correlates with a value of pK_a slightly greater than 5. Therefore, the amount of charge transmitted to the binding carboxylate in the fumarate and the isophthalate complexes

is limited by this saturation value, leading to similar stability constants in both cases.

If the increased binding of lanthanides to isophthalate (relative to benzoate) is due to polarization of electronic charge density to the binding carboxylate, the hydration of the unbonded carboxylate should decrease. This would result in an increased positive entropy, in accord with the experimental values (e.g., $\Delta S_{101} = 68 \text{ J/(mol K)}$ for SmB^{2+} and 90 J/(mol K) for Sm(iP)^+). It would also cause the enthalpy change for the isophthalate to be more endothermic, which is also observed.

In summary, the thermodynamic parameters for lanthanide benzoate complexation are similar to those measured for analogous alkyl monocarboxylates. The stability constants fit the correlation with pK_a of the alkyl ligand, indicating no effect due to the phenyl ring. However, the isophthalate complexes are stronger than expected, which can be explained by an increase in the electronic charge density at the binding carboxylate. This increased charge transmitted via the π system from the nonbonding carboxylate results in a decrease of hydration, which increases (positively) both the entropy and enthalpy of complexation when compared to the case for the benzoate complexation.

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Preparation and Characterization of Mixed-Oxidation-State Tin Carboxylates and Related Tin(IV) Carboxylates

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The solvolysis of hexaphenylditin by carboxylic acids leads to the formation of compounds with empirical formula $\text{Sn}(\text{O}_2\text{CR})_3$. ^{119}Sn Mössbauer spectroscopy shows that these compounds contain tin in both the II and IV oxidation states. The Mössbauer data taken together with the vibrational data, IR and Raman, lead to the conclusion that these compounds are best formulated as $[\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}\text{O}(\text{O}_2\text{CR})_4\text{O}(\text{OCR})_2]_2$. The four tin atom cluster is held together by two μ_3 -oxo bridges and bridging acetato ligands, which result in the Sn(IV) atoms being in octahedral environments, while the Sn(II) atoms have pentagonal-bipyramidal geometry in which the μ_3 -oxo bridge occupies one axial position and the Sn(II) nonbonding electron pair the other axial position. The equatorial positions accommodate four acetato oxygens and an anhydride oxygen atom. ^{119}Sn Mössbauer data for $\text{Sn}(\text{O}_2\text{CR})_4$ are also presented for the first time.

Introduction

It is well-known that the solvolysis of tetraalkyltin(IV) compounds in acidic solvents leads to the successive loss of alkyl groups to produce first trialkyltin(IV) and finally dialkyltin(IV) species. These have been characterized by a variety of techniques.¹⁻⁴ Similar products can be obtained from the solvolysis of hexamethylditin through cleavage of the tin-tin bond. However, by careful control of the reaction conditions the tin-tin bond can be retained and tetramethylditin(IV) compounds can be isolated.⁴ Solvolysis of hexaphenylditin might have been expected to lead to analogous products since tetraphenylditin dicarboxylates are known.⁵ Reaction of hexaphenylditin with acetic acid results in the cleavage of all of the tin-carbon bonds to give a compound formulated as $\text{Sn}_2(\text{O}_2\text{CCH}_3)_6$.⁶ It was suggested that this

compound was a ditin species in which the tin-tin bond was stabilized by bridging acetato ligands. However, little spectroscopic evidence was presented to support this contention, which was based upon the consumption of 1 mol of bromine to give $\text{BrSn}(\text{O}_2\text{CCH}_3)_3$. This latter reaction is normally taken as evidence for the presence of a tin-tin bond.

We have repeated this solvolysis of hexaphenylditin using seven different carboxylic acids, and in all cases we have been able to isolate compounds with the empirical formula $\text{Sn}(\text{O}_2\text{CR})_3$. The acetato compound ($\text{R} = \text{CH}_3$) appears to be identical with that of $\text{Sn}_2(\text{O}_2\text{CCH}_3)_6$ reported earlier by Wiberg and Behringer.⁶ However, ^{119}Sn Mössbauer spectroscopic results presented in this paper clearly establish that these compounds contain tin atoms in both the II and the IV oxidation states and should be formulated as mixed-oxidation-state compounds of tin rather than as ditin species. Raman and infrared spectroscopic data are also presented, which, taken with the Mössbauer evidence, establish that these compounds have structures very similar to two previously reported mixed-oxidation-state tin carboxylates.^{7,8} We also

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