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Calorimetric Studies of Americium(III) Complexation by Amino Carboxylates

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The enthalpies of formation of the 1:1 complexes of Am(III) with acetate and a series of amino carboxylate ligands were determined by titration calorimetry. The estimated ΔH_{101} values are −6.8, 4.5, 12.6, 23.9, 10.8, 39.5, and −13.3 kJ mol^{-1} for complexation by acetate, IDA, NTA, EDTA, DCTA, DTPA, and TMDTA, respectively. Comparison of these values with those for the Eu(III) and Cm(III) complexation provides no evidence of significant differences in the bonding of these three metal ions with the ligands studied.

Introduction

Studies on the complexation of trivalent lanthanide and actinide cations with borderline or soft ligands such as *o*-phenanthroline and diethyl hexyl dithiophosphate[1] and azide[1,2] showed an enhanced stability of the actinide complexes compared to that of the corresponding lanthanide complexes. It has been proposed[1] that the difference in stability reflects a greater degree of covalency for the actinide–ligand bonding.

Enhanced covalency can be expected to be reflected by a more exothermic enthalpy of complexation with little effect on the entropy change. To delineate such interactions, we conducted a calorimetric study of curium(III) complexation by a series of amino carboxylate ligands.[3,4] The "hard" carboxylate interactions would not be expected to show covalent effects between the lanthanides and actinides. However, the metal–nitrogen interactions are strong in these complexes[5,6] and differences in covalency could be present in these bonds. The results were interpreted to possibly reflect a small enhancement in covalency for the Cm(III) complexes compared to those of Eu(III).

In the present paper, we report similar calorimetric measurements of americium(III)–amino carboxylate systems. Among the considerations that prompted the present investigation was the expectation that a comparison of Am(III) data with those of Cm(III) and Ln(III) systems would provide a better defined data base for evaluating the possible differences in covalency between lanthanides and actinides as well as between Am(III) and Cm(III).

Experimental Section

Reagents and Solutions. A stock solution of $Eu(ClO_4)_3$ was prepared by dissolving the oxide (Aldrich, 99.99%) in perchloric acid. The molarity was determined by complexometric titration using Na_2H_2EDTA (J. T. Baker) in the presence of xylenol orange indicator. Amino carboxylate buffers of ethylenediaminetetraacetate (EDTA), 1,2-cyclohexanedinitrilotetraacetate (DCTA), nitrilotriacetate (NTA), and diethylenetrinitrilopentaacetate (DTPA, doubly recrystallized) were prepared by partial neutralization of the free acid (Aldrich) solutions. The disodium salt of iminodiacetic acid (IDA) was used as such. Trimethylenedinitrilotetraacetic acid (H_4 = TMDTA) was synthesized by the method of Tanaka and Ogino[7] and recrystallized from 25% ethanol. Sodium acetate (NaOAc) buffer solution was prepared from acetic acid by partial neutralization with NaOH solution. The ionic strength of the solutions was adjusted to 0.50 M (except for the acetate measurements, where the ionic strength was 2.00 M) with sodium perchlorate.

$^{243}AmCl_3$ was obtained from Argonne National Laboratory. The solid was dissolved in 0.1 M HCl and the solution passed through a column of cation-exchange resin in the acid form. After elution of the daughter ^{239}Np with dilute acid, americium(III) was removed with 7 M HCl solution. This eluate was evaporated to near dryness, fumed with perchloric acid, diluted to volume, and adjusted to a pH between 4 and 5. The exact concentration of this solution was determined by calorimetric titration using EDTA titrant.

Procedure. The enthalpies of complexation of americium by various ligands were determined by a calorimetric technique using the semiadiabatic minicalorimeter at Florida State University[8] interfaced to an Ohio Scientific computer.[9] The 4 mL volume calorimeter cup allowed the use of ca. 8–10 mg of ^{243}Am per experiment. Complexation of Eu(III) with these ligands was measured by using both the mini and large (60 mL) calorimeter cups. Agreement between both sets of data confirmed the accuracy of the values from the minicalorimeter. The corrections for the heats of dilution were determined in separate runs. The AmEDTA titration was repeated three times and that of AmNTA and AmDTPA twice, while only a single titration was performed for AmIDA, AmDCTA, and AmTMDTA due to the limited quantity of ^{243}Am available. The radioactive decay over the duration of the experiments was not great enough to require corrections for heating.

Table I. Thermodynamics of the Stepwise Protonation of IDA and DTPA Ligands[a]

ligand	species	log *K*	$-\Delta H$, kJ mol^{-1}
IDA[b]	HL	9.17	38.0 ± 1.6
	H_2L	2.56	4.9 ± 1.0
	H_3L	1.76	−1.0 ± 1.0
DTPA[c]	HL	9.86	29.0 ± 0.5
	H_2L	8.32	24.9 ± 1.0
	H_3L	4.12	8.2 ± 0.3
	H_4L	2.85	4.8 ± 1.2

[a] I = 0.50 M ($NaClO_4$); T = 298 K. [b] Reference 10. [c] Reference 6.

The pK_a values for acetate and IDA were taken from ref 10, for NTA, DCTA, EDTA, and DTPA from ref 6, and for TMDTA from ref 4. Enthalpies of protonation of acetate, IDA, and DTPA ligands were obtained by titrating the sodium salts with 0.10 M $HClO_4$. The results obtained are summarized in Table I. Other protonation enthalpies were obtained from ref 4 and 6.

Results

The general reaction studied in this research was

$$Am^{3+} + L^{z-} \rightleftharpoons AmL^{3-z}$$

with a stability constant defined by

$$\beta_{101} = [AmL^{3-z}]/[Am^{3+}][L^{z-}]$$

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Table II. Calorimetric Titration Data for Am^{3+} with EDTA[a]

vol,[b] mL	$-\sum Q_{obsd}$,[c] mJ	$\sum Q_{ML}$,[d] mJ	$[M^{3+}]$,[e] mM	$[L^{4-}]$, 10^{17} M	$[H^+]$, mM	$-\Delta H_{101}$, kJ mol^{-1}
Run 1						
0.1	26.0	92.4	8.872	0.187	0.996	22.9
0.2	49.0	187.5	7.699	0.421	1.943	23.2
0.3	73.7	280.9	6.583	0.721	2.842	23.2
0.4	98.1	373.7	5.520	1.119	3.695	23.2
0.5	120.8	466.9	4.510	1.671	4.498	23.2
0.6	142.5	558.8	3.554	2.481	5.247	23.2
0.7	161.9	648.6	2.656	3.771	5.929	23.2
Run 2						
0.1	18.6	99.8	4.929	0.337	0.996	24.7
0.2	37.4	199.1	3.851	0.842	1.941	24.7
0.3	53.5	300.1	2.827	1.676	2.834	24.8
0.4	66.1	401.9	1.862	3.302	3.661	25.0
0.5	82.8	490.0	0.981	7.570	4.371	24.7
0.6	92.3	541.1	0.324	25.732	4.678	23.8
Run 3						
0.1	22.8	95.6	7.886	0.211	1.004	23.7
0.2	43.6	193.1	6.737	0.481	1.951	23.9
0.3	63.3	291.2	5.643	0.841	2.849	24.0
0.4	82.5	388.9	4.603	1.341	3.699	24.1
0.5	102.6	484.0	3.617	2.081	4.496	24.1
0.6	119.2	579.2	2.687	3.274	5.230	24.1
0.7	134.0	668.8	1.828	5.450	5.872	24.1
0.8	147.1	741.9	1.077	10.169	6.341	23.8
0.9	158.1	774.0	0.528	22.027	6.451	22.9

[a] I = 0.50 M ($NaClO_4$); T = 298 K. [b] The titrant was 40.41 mM EDTA; C_H = 40.83 mM. [c] Corrected for dilution. [d] Corrected for ligand protonation changes. [e] The cup contents of $[Am^{3+}]$ and C_H, respectively, were as follows: run 1, 10.10 mM, 5.97×10^{-7} M; run 2, 6.06 mM, 5.97×10^{-7} M; run 3, 9.09 mM, 8.95×10^{-6} M.

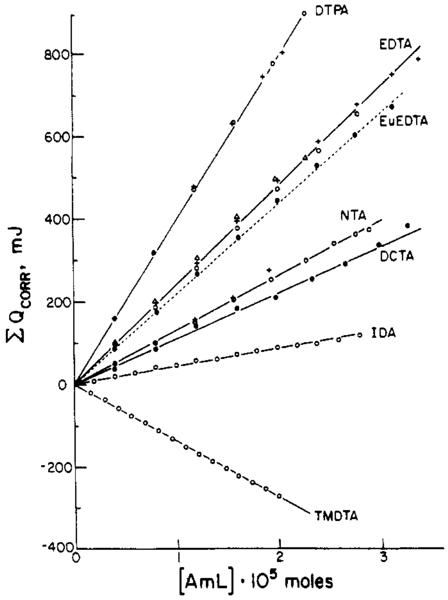

Figure 1. Relation between the observed heat (corrected for protonation) and the calculated concentration of AmL (solid lines) and EuL (dotted line) during the titrations.

The enthalpies of complexation, ΔH_{101}, for the above reaction were computed by fitting the observed heat changes, corrected for heats of dilution and ligand protonation, to the equation

$$\begin{aligned} Q_{AmL} &= Q_{obs} - \sum_{n=1}^{N} Q_{HnL} \\ &= Q_{obs} + \sum_{n=1}^{N} (\Delta n_{0n1}) \Delta H_{0n1} \\ &= -(\Delta n_{AmL}) \Delta H_{101} \end{aligned}$$

and minimizing

$$E = \sum_{x=1}^{X} [Q_{x,calcd} - Q_{x,AmL}]^2$$

Table III. Thermodynamic Parameters of Complexation of Am(III), Cm(III), and Eu(III) with Acetate and Polyamino Carboxylate Ligands[a]

ligand	Am(III)	Cm(III)	Eu(III)
	(A) ΔG_{101} (kJ mol^{-1})		
acetate[b]	11.2 ± 0.1[c]	11.6 ± 0.1[c]	10.9 ± 0.1[c]
IDA	44.9 ± 0.3[d]		35.9 ± 0.3[e]
NTA	63.9 ± 0.3[d]	64.4 ± 0.4[d]	63.6 ± 0.5[f]
EDTA	95.7 ± 0.6[d]	96.2 ± 0.5[d]	92.6 ± 0.4[f]
DCTA	103.9 ± 0.6	103.3 ± 0.6	103.3 ± 0.3[f]
DTPA	120.6 ± 0.6[d]		119.1 ± 0.4[f]
TMDTA	73.7 ± 0.3	74.5 ± 0.3	74.7 ± 0.6
	(B) ΔH_{101} (kJ mol^{-1})		
acetate[b]	−6.8 ± 0.3	−6.0 ± 0.4[g]	−7.1 ± 0.8
IDA	4.5 ± 0.7		4.0 ± 0.9
NTA	12.6 ± 0.6	11.5 ± 2.2[h]	7.5 ± 1.7
EDTA	23.9 ± 1.0	29.3 ± 1.3[g]	21.6 ± 0.8
DCTA	10.8 ± 0.8	9.7 ± 1.9[h]	6.2 ± 0.9
DTPA	39.5 ± 1.0		39.8 ± 1.5
TMDTA	−13.3 ± 1.0	−12.7 ± 1.5[h]	−13.6 ± 0.7
	(C) ΔS_{101} (J K^{-1} mol^{-1})		
acetate[b]	60 ± 1	59 ± 1[g]	60 ± 3
IDA	136 ± 3		107 ± 3
NTA	172 ± 2	178 ± 8[h]	188 ± 6
EDTA	241 ± 4	225 ± 5[h]	238 ± 3
DCTA	312 ± 3	314 ± 7[h]	326 ± 3
DTPA	272 ± 5		266 ± 5
TMDTA	292 ± 4	293 ± 5[h]	296 ± 3

[a] I = 0.50 M ($NaClO_4$); T = 298 K. [b] 2.00 M ($NaClO_4$). [c] Reference 10. [d] Reference 11. [e] Reference 8. [f] Reference 9. [g] Reference 3. [h] Reference 4.

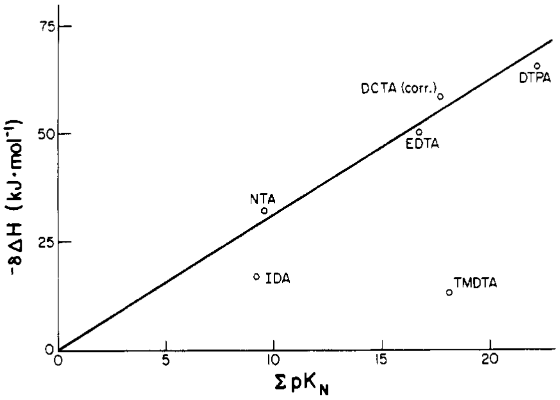

Figure 2. Relation between the residual enthalpy ($\delta(\Delta H)$) and the total basicity of the nitrogen donors ($\sum pK_N$) of the ligands.

where E is the residual error and Δn is the increase in the number of moles formed of the 1:1 complex between successive titration points (x). Δn values were calculated by a nonlinear simplex program (DELTAH). ΔH_{0n1} values are the overall protonation enthalpies. A sample set of these calculations is shown in Table II. The fits of the experimental data and the calculated constants proved to be satisfactory as shown in Figure 1. A summary of the results is given in Table III. The error limits are calculated from the deviations for the individual points averaged over the duplicate runs. The corresponding data for Cm(III) and Eu(III) complexation are included in Table III for comparison.

The values of β_{101} for AmOAc[11] and AmIDA, AmNTA, AmEDTA, and AmDTPA[12] have been measured for the ionic strength used in this study. Those of AmDCTA and AmTMDTA are reported for ionic strength 0.10 M.[10] The latter were corrected for the difference in ionic strength by interpolating the linear relationship of log β_{101} for IDA, NTA, EDTA, and DTPA complexes with Am(III) at both 0.10 M[10] and 0.50 M ionic strength.[12]

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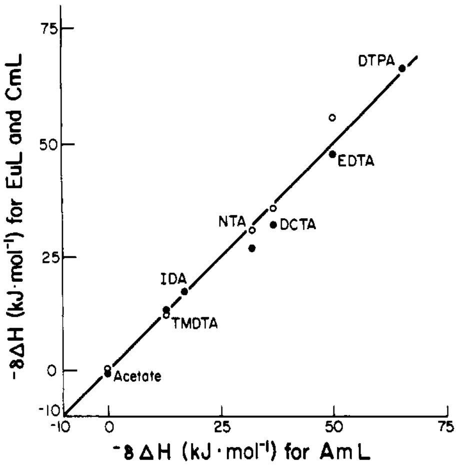

Figure 3. Relation between $\delta(\Delta H)$ for AmL complexes and those obtained for EuL (solid circles) and CmL (open circles) for acetate and a series of amino carboxylate ligands.

Discussion

An analysis of the thermodynamic parameters of complexation of lanthanide cations by a series of amino carboxylate ligands showed that the entropy changes for complexation were proportional to the number of binding carboxylate groups and independent of the number of nitrogen donors.[6] The entropies of 1:1 complexation for Am(III) and Cm(III) with OAc, IDA, NTA, and EDTA (Table III) show the same behavior. The slope of the correlation of ΔS with the number of the carboxylate groups is ca. 60 J K^{-1} mol^{-1} for the Am(III), Cm(III), and Eu(III) systems. This is also the value of ΔS for formation of the monoacetate complex of these cations. Reasons for deviation of the ΔS values for DCTA and DTPA complexation have been discussed elsewhere.[6]

On the basis of this analysis, the residual enthalpy for the metal–nitrogen interaction, $\delta(\Delta H)$, can be calculated from the relationship

$$\delta(\Delta H) = \Delta H_{101} - n\Delta H_{\mathrm{OAc}}$$

where n is the number of binding acetates and ΔH_{OAc} is the enthalpy change for the formation of AmOAc^{2+}. The values of $\delta(\Delta H)$ are plotted against the total basicity of the nitrogen donors, $\sum pK_{\mathrm{N}}$, in Figure 2. The relationship holds for all ligands (including DCTA after correction for excess ligand dehydration) except IDA and TMDTA. The decrease of the Am–N bond strength in AmTMDTA and AmIDA is similar to that observed for Ln–N interaction in TMDTA[4] and MEDTA (*N*-methyl-*N*,*N'*-ethylenedinitrilotriacetate) and EDDA (ethylenedinitrilodiacetate).[13] The latter was attributed either to ring expansion or to lack of formation of chelate rings involving nitrogen, a viable rationale for the results in the actinide systems.

Figure 3 illustrates the relationship between the residual enthalpy for AmL complexes and that for the corresponding EuL and CmL complexes. For this series of ligands, the number of the nitrogen donors varies from 0 to 3; also, the intrinsic basicity of these sites covers a $\sum pK_{\mathrm{N}}$ range of 9–22. The plot in Figure 3 has a slope of unity, indicating no apparent differences in M–N bonding between Am(III), Cm(III), and Eu(III).

In conclusion, the thermodynamic parameters of complexation for both lanthanide and actinide complexes with a series of nitrogen-containing donors are remarkably similar. Slight differences in the $\delta(\Delta H)$ values are within the uncertainties of the experimental measurements. The present results do not support an enhanced covalency in the nitrilo–metal bonds for the actinide complexes over that of the corresponding lanthanides.

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