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Calorimetric Studies of Curium Complexation. 2. Amino Carboxylates

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Calorimetric titrations using the long-lived isotope of curium (curium-248) have been conducted with nitrilotriacetate, *trans*-1,2-cyclohexanedinitrilotetraacetate, and trimethylenedinitrilotetraacetate. The data plus the stability constants measured previously allowed calculations of the thermodynamic parameters of the 1:1 complexation. Similar titrations were conducted with europium to provide comparison of the lanthanide and actinide trivalent ion behaviors. The enthalpy values for the amino polycarboxylate complexing of Cm(III) are greater than those for Eu(III). However, the entropy values for the complexing of both cations are similar. These results are comparable to the previously reported data for EDTA.

A previous paper reported the results of calorimetric studies of curium complexation with acetate and ethylenediaminetetraacetate.[1] The minicalorimeter[2] at Florida State University was used with milligram quantities of a curium sample that was 96.6% ^{248}Cm ($t_{1/2} = 3.4 \times 10^5$ y). The low specific activity (ca. 3×10^7 decays/(m·mg)) eliminated concerns of radiolytic perturbation of the system. This paper reports the extension of these studies to three other amino carboxylate ligands. As in the first study, similar Eu(III) calorimetric studies were conducted to compare with the results of curium.

The high specific activity and general lack of availability of actinide elements have restricted study of their chemical behavior. Samples of high isotopic content of ^{248}Cm offer the opportunity of investigating the behavior of the trivalent cation by macroscopic methods. Comparison of the results of such research with data of trivalent lanthanide cations allows us to investigate the similarities and differences in the behavior of these 4f and 5f elements. The amino carboxylate ligands with both carboxylate (hard base) and nitrogen (softer base) donor sites can be expected to be useful to probe such comparative behavior.

Experimental Section

Reagents. Analytical grade reagents were used for all solutions. The stock solution of $Eu(ClO_4)_3$ was prepared by dissolving the oxide (Aldrich, 99.99%) in perchloric acid and the molarity was determined by complexometric titration with EDTA and xylenol orange. *trans*-1,2-Cyclohexanedinitrilotetraacetic acid (DCTA) was recrystallized from water while nitrilotriacetic acid (NTA) was used as received. Trimethylenedinitrilotetraacetic acid (TMDTA) was synthesized by the method of Tanaka and Ogino[3] and recrystalllized from 25% ethanol. The purity of the reagent was ascertained by a pH titration with standard sodium hydroxide.

The curium solution was purified prior to each run by evaporating the solution to near dryness, fuming the residue with nitric and perchloric acids, and extracting with octylphenyl((*N*,*N*-diisobutylcarbamoyl)-methyl)phosphine oxide (0.5 M in tetrachloroethylene). The curium was reextracted into 1 M HCl solution. Both extraction processes were repeated several times to achieve maximum recovery of the curium. The acidic solution was evaporated to near dryness, and the hydroxide was precipitated by adding sodium hydroxide, digested, centrifuged, washed several times with distilled water, and then dissolved in the minimum amount of perchloric acid. The exact molarity of the curium contents was determined radiometrically by liquid scintillation counting (LSC). All solutions were adjusted to 0.50 M ionic strength by addition of the necessary amounts of $NaClO_4$.

Procedures. Potentiometry. Acid protonation constants of TMDTA at 0.50 M ($NaClO_4$) ionic strength were obtained by titrating a 50.0-mL aliquot of the tetraprotic ligand (1.8 mM) with 0.10 M NaOH. The pH values were recorded by using a Radiometer PHM 84 pH meter fitted with a combined glass–calomel electrode. The electrode was calibrated by using BuffAR (American Scientific Products) pH 7.00 and 0.01 M borax (pH 9.17 at 25 °C). The hydrogen ion concentration was obtained from the relationship[3]

$$-\log [H^+] = pH + 0.20$$

The acid constants were calculated by minimizing the residuals in $\bar{n}_H$ for a series of measurements in the appropriate buffer region.

Table I. Thermodynamics of Stepwise Protonation of NTA, DCTA, and TMDTA (I = 0.50 M ($NaClO_4$); T = 298 K)

ligand	species	log K_a	$-\Delta H$, kJ·mol^{-1}
NTA	HL	9.57 ± 0.01[4]	26.2 ± 0.2[4]
DCTA	HL	11.30 ± 0.07[4]	38.8 ± 0.3[4]
	H_2L	6.51 ± 0.06[4]	10.7 ± 0.3
	H_3L	3.01 ± 0.06[4]	1.4 ± 0.3
	H_4L	2.38 ± 0.06[4]	1.7 ± 0.7
TMDTA	HL	10.16 ± 0.02	29.6 ± 0.8
	H_2L	7.94 ± 0.01	22.7 ± 0.7
	H_3L	2.72 ± 0.02	2.0 ± 0.6
	H_4L	2.55 ± 0.02	3.1 ± 1.1

Table II. Calorimetric Titration Data for Cm^{3+} and Eu^{3+} Ions with DCTA (I = 0.50 μ ($NaClO_4$); T = 298 K)[a]

vol, mL	$-\sum Q^{dil}_{obsd}$,[b] mJ	$\sum Q_{cor}$,[c] mL	$[M^{3+}]$, mM	$[L^{4-}]$, M × 10^{-18}	$[H^+]$, mM	$-\Delta H_{101}$, kJ·mol^{-1}	$\bar{n}$
			(A) Cm^{3+}–DCTA[d]				
0.1	44.8	15.0	2.79	0.20	0.71	10.0	0.20
0.2	92.1	27.4	2.39	0.34	1.04	9.1	0.30
0.3	134.8	44.3	2.01	0.53	1.36	9.8	0.40
0.4	181.4	56.8	1.64	0.79	1.65	9.5	0.50
0.5	224.2	72.3	1.29	1.18	1.92	9.7	0.60
0.6	265.0	88.2	0.96	1.79	2.16	9.9	0.69
0.7	303.4	103.1	0.66	2.88	2.35	10.0	0.78
0.8	337.0	116.2	0.40	5.17	2.45	10.0	0.87
			(B) Eu^{3+}–DCTA[e]				
0.1	54.9	4.9	4.78	0.06	0.38	3.3	0.07
0.2	109.3	10.3	4.31	0.13	0.74	3.4	0.14
0.3	163.7	15.7	3.86	0.22	1.08	3.5	0.21
0.4	216.4	22.7	3.43	0.32	1.40	3.8	0.29
0.5	270.2	28.3	3.02	0.44	1.70	3.8	0.36
0.6	324.5	33.1	2.63	0.59	1.99	3.7	0.43
0.7	377.5	38.5	2.26	0.79	2.26	3.7	0.50
0.8	428.0	45.4	1.91	1.04	2.50	3.8	0.57
0.9	477.6	51.7	1.57	1.38	2.71	3.9	0.63
1.0	529.6	53.4	1.27	1.86	2.89	3.6	0.70
1.1	579.7	53.7	0.98	2.56	3.01	3.3	0.76
1.2	624.0	55.2	0.72	3.66	3.08	3.2	0.82

[a] In both cases, the titrant contents are as follows: [DCTA] = 15.09 mM; C_H = 15.35 mM. Computed constants: $\Delta H_{101}(Cm^{3+}\text{–DCTA}) = -9.7 \pm 1.9$ kJ·mol^{-1}; $\Delta H_{101}(Eu^{3+}\text{–DCTA}) = -3.6 \pm 1.1$ kJ·mol^{-1}. [b] Heats corrected for dilution. [c] Heats corrected for protonation of the ligand. [d] Cup contents: $[Cm^{3+}]$ = 3.58 mM; [DCTA] = 0.36 mM; C_H = 0.37 mM; volume = 4.22 mL. [e] Cup contents: $[Eu^{3+}]$ = 5.28 mM; $C_H = 7.1 \times 10^{-6}$ M; volume = 4.00 mL.

Calorimetry. Enthalpies of complexation of curium ion by the polyamino polycarboxylate ligands were determined by titrating the curium perchlorate solution (ca. 3.5 mM) adjusted to pH ~5 with the ligand buffer (10–15 mM). The curium concentration from LSC was confirmed from the calorimetric end point in the DCTA titration.

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(1) Choppin, G. R.; Liu, Q.; Sullivan, J. C. *Inorg. Chem.* **1985**, *24*, 3968.
(2) Ensor, D. D.; Kulberg, L.; Choppin, G. R. *Anal. Chem.* **1977**, *49*, 1878.
(3) (a) Tanaka, N.; Ogino, H. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 877. (b) Ogino, H.; Takahashi, M.; Tanaka, N. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 424.

0020-1669/87/1326-2318$01.50/0

Table III. Thermodynamic Parameters of Complexation of Cm(III) and Eu(III) with NTA, EDTA, DCTA, and TMDTA ($I = 0.50$ M ($NaClO_4$); $T = 298$ K)

ion	log β_{101}	$-\Delta G_{101}$, kJ·mol^{-1}	ΔH_{101}, kJ·mol^{-1}	ΔS_{101}, J·K^{-1}·mol^{-1}
		(A) NTA		
Cm	11.30 ± 0.01[5]	64.5 ± 0.1	−11.5 ± 2.2	178 ± 8
Eu (small cup)	11.15 ± 0.09[4]	63.6 ± 0.5	−6.4 ± 0.9	192 ± 3
Eu (large cup)	11.15 ± 0.09[4]	63.6 ± 0.5	−6.4 ± 0.5[4]	192 ± 2
		(B) DCTA		
Cm	18.10 ± 0.10	103.3 ± 0.6	−9.7 ± 1.9	314 ± 7
Eu (small cup)	18.10 ± 0.06[4]	103.3 ± 0.3	−3.6 ± 1.1	335 ± 4
Eu (large cup)	18.10 ± 0.06[4]	103.3 ± 0.3	−5.4 ± 1.7	329 ± 6
		(C) TMDTA		
Cm	13.05 ± 0.05	74.5 ± 0.3	+12.6 ± 1.5	292 ± 5
Eu (small cup)	13.1 ± 0.1	74.7 ± 0.6	+13.5 ± 2.0	296 ± 7
Eu (large cup)	13.1 ± 0.1	74.7 ± 0.6	+15.3 ± 2.0	302 ± 7
		(D) EDTA		
Cm	16.87 ± 0.05[5]	96.2 ± 0.3	−29.3 ± 1.3[1]	225 ± 6
Eu	16.23 ± 0.07[4]	92.6 ± 0.4	−22.9 ± 1.3[1]	234 ± 6

Similar titrations for Eu(III) were conducted in both the minicalorimeter and the large calorimeter (60-mL cup size) to check the validity of the minicalorimeter data. The necessary corrections for the heats of dilution of the metal and the ligand were determined in separate runs. Enthalpies of protonation of the free ligands were determined by titrating the sodium salts of the ligands with 0.10 M perchloric acid.

Results

The stepwise protonation constants and enthalpies of the ligands as determined in this work are given in Table I. Table II presents sets of data obtained in the minicalorimeter for the complexation of Cm(III) and Eu(III) ions with DCTA. The complexation enthalpies were computed by fitting the observed heat changes after correction for dilution and protonation of the free ligand to the number of moles of the complex formed. The latter was calculated on an IBM-PC by a nonlinear SIMPLEX program (DELTAH) written in this laboratory by W. Cacheris. The fits of the experimental data and the calculated curves are quite satisfactory as shown in Figure 1. A summary of all the curium thermodynamic values is given in Table III with the values for Eu(III) complexation determined in the minicalorimeter and the large calorimeter. For the sake of comparison, the data reported for complexation by EDTA[1] are also listed. The error limits are 3 times the deviations from the average of each individual point in the titration curve.

The value of log β_{101} ($\beta_{101} = [ML]/[M][L]$) of Cm–NTA is available at 0.50 M ionic strength,[5] whereas those of Cm–DCTA[6] and Cm–TMDTA[7] have been reported only at 0.10 M ionic strength. These latter values were corrected for the difference in ionic strength by interpolation from the linear relationship of log β_{101} available for NTA, EDTA, and DTPA complexes with curium(III)[6,7] at both 0.10 and 0.50 M ionic strength.

Discussion

A major question about the relationship of the lanthanide (4f-electron filling) and the actinide (5f-electron filling) elements is whether the latter have some extra degree of covalency in their chemical bonding. Such an effect has been discussed previously,[8,9] but definitive data have not been available for resolving this question. Any greater tendency to covalency can be expected to be more evident in a comparison of bonding of 4f and 5f elements with soft ligands. Both lanthanide and actinide cations are such hard acids, however, that, in aqueous solution, soft ligands have difficulty in displacing oxygen donors of water molecules or ligands.[10] Amino carboxylic acids are strong chelators and do involve metal interaction with the softer nitrogen donors.

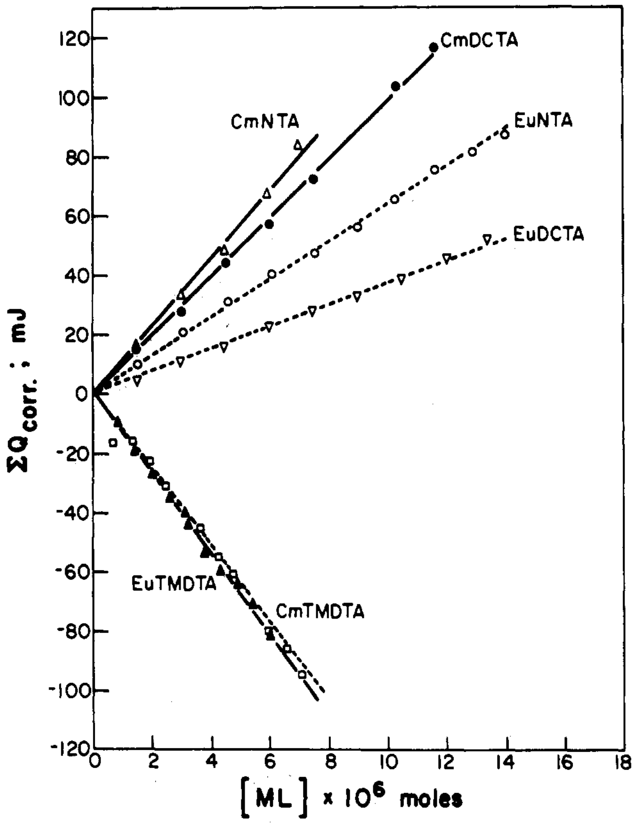

Figure 1. Fit of observed heat (corrected for protonation) to the calculated concentration of [ML] species formed along the titration.

Eu(III) and Cm(III) with $4f^6$ and $5f^7$ electron configurations, respectively, have quite similar radii.[11] This difference in electronic configuration should not be decisive, as it is generally accepted that f orbitals are not involved in any covalent interactions of these elements.[8] For the ligands of this study, we would expect that any enhanced bonding due to increased covalency would be more evident in the DCTA and EDTA complexation (with two M–N bonds) than in the NTA case (only one M–N bond). Comparison of the log β_{101} values of the Eu(III) and Cm(III) complexations in Table III provide no evidence of increased stabilization for the Cm(III) complexes, except possibly in EDTA complexation.

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(4) Choppin, G. R.; Goedken, M. P.; Gritmon, T. F. *J. Inorg. Nucl. Chem.* **1977**, *39*, 2025.

(5) Ensor, D. D. Progress Report DOE/ER/10489-08; Oak Ridge National Laboratory: Oak Ridge, TN.

(6) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum: New York, 1974; Vol. 1.

(7) Choppin, G. R.; Muscatello, A. C. *Inorg. Chim. Acta* **1985**, *109*, 67.

(8) Jørgenson, C. K. *Isr. J. Chem.* **1980**, *19*, 174.

(9) Choppin, G. R. *J. Less-Common Met.* **1983**, *93*, 323.

(10) Musikas, C.; Vitorge, P.; SeMarios, G.; Fitoussi, R.; Cuillerdier, C. In "Abstracts Actinides 81"; Report LBL-12441; Brown, D., Ed.; Lawrence Berkeley Laboratory: Berkeley, CA, 1981; p 265.

(11) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallog.* **1976**, *A32*, 751.

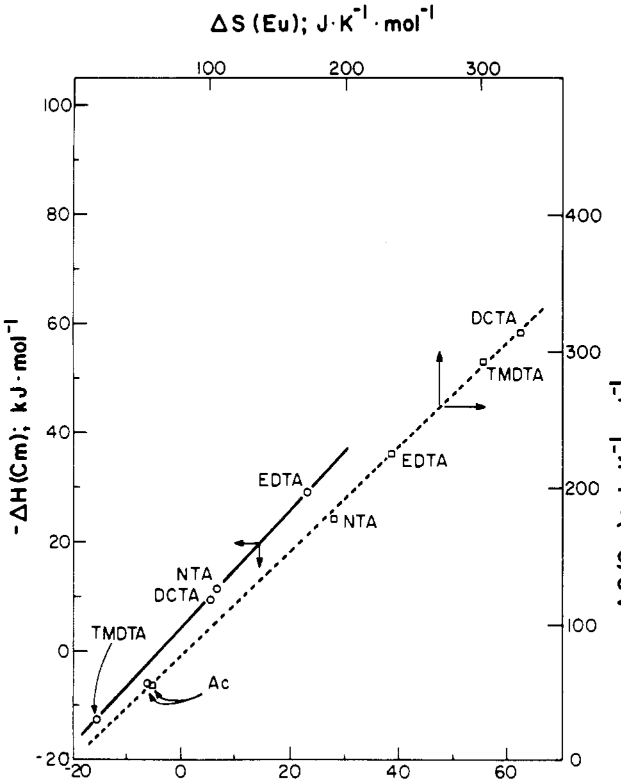

Figure 2. Correlation of ΔH(CmL) with ΔH(EuL) (solid line) and of ΔS(CmL) with ΔS(EuL) (dotted line) for acetate and a series of amino carboxylate ligands.

We would expect an increase in stabilization from enhanced covalency to be manifested in a more exothermic enthalpy. The entropy, however, should be only slightly affected as it is dominated by the dehydration that occurs with complexation.[12] Figure 2 is a plot of the enthalpies and entropies from Table II (values for Eu with the larger calorimeter cup are used in all cases) plus the values for acetate complexation from ref 1. The slope of ΔS(Cm) vs. ΔS(Eu) is 0.96, which can be used as the norm for Cm vs. Eu for the net ionic effects (dehydration + metal–ligand interaction). For the enthalpy curve, the slope is 1.09 if the acetate point is excluded. If our model shows that the entropy changes are related to ionic effects, we would expect the acetate data to correlate with those of the other ligands as it does. Conversely, since there are no nitrogen sites in acetate, the enthalpy values should not correlate with the other enthalpy data if the latter reflect covalency in actinide–nitrogen bonding.

TMDTA forms much weaker complexes with the actinides and lanthanides than expected from the $\sum pK_a$ values (i.e., log β_{101} is >3 units lower than predicted).[7] This is consistent with the results of ^{1}H NMR studies of lanthanide–TMDTA complexation in which it was shown that the Ln–N bonding is weakened.[13] The entropy values for both EuTMDTA and CmTMDTA in Table III reflect more extensive dehydration (presumably of the $TMDTA^{4-}$) upon complexation than for EDTA complexation. The similarly higher entropy values for the DCTA complexes have been correlated with such dehydration.[4] For the DCTA complexation, the enthalpy change is exoergic as the strong metal–nitrogen interaction overcomes the endoergic dehydration. For the TMDTA complexation, the weaker metal–nitrogen interaction is insufficient to overcome the dehydration effect and the enthalpy is endoergic. As would be expected, such weakened metal–nitrogen interaction reduces the difference in the enthalpy values of the actinide and the lanthanide complexes. However, the TMDTA enthalpy values fall on the line with the other amino carboxylates as in Figure 2, supporting the interpretation of enhanced actinide binding to the softer nitrogen donors.

In summary, the thermodynamic data for curium complexation by amino carboxylate ligands can be interpreted as indicating a small degree of enhanced covalency compared to lanthanide complexation. However, such an effect is relatively small and more data are needed before it can be considered as a proven aspect of actinide chemistry.

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Registry No. NTA, 139-13-9; DCTA, 13291-61-7; TMDTA, 1939-36-2; Cm, 7440-51-9; Eu, 7440-53-1.

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[12] Choppin, G. R. *Radiochim. Acta* **1983**, *32*, 43.

[13] Choppin, G. R. *J. Less-Common Met.* **1985**, *112*, 193.