Inorganica Chimica Acta, 109 (1985) 67–70

The Complexation of Trivalent Actinides by TMDTA

GREGORY R. CHOPPIN and ANTHONY C. MUSCATELLO

Department of Chemistry, Florida State University, Tallahassee, Fla. 32306, U.S.A.

Received June 16, 1984

Abstract

The stability constants in 0.10 M (NaCl) ionic strength solution for the formation of $MTMDTA^{-1}$ (M = Am, Cm, Bk and Cf; TMDTA = trimethylenedinitrilotetraacetate) were measured by solvent extraction. The values are 13.45 (Am), 13.79 (Cm), 14.36 (Bk) and 14.66 (Cf) and are much lower than expected from the ΣpK_a of the TMDTA acid. The data do not allow a definite interpretation of this decreased stability which may be due to a generalized weaker bonding or to failure to form the 6-membered N–M–N chelate ring.

Introduction

Aminopolycarboxylate ligands such as N-(2-hydroxyethyl)iminodiacetate (HIDA), nitrilotriacetate (NTA), N-(2-hydroxyethyl)ethylenedinitrilo-N, N′N′triacetate (HEDTA), ethylenedinitrilotetraacetate (EDTA), and diethylenetrinitrilopentaacetate (DTPA) complex strongly with trivalent actinide cations [1]. The stability constants show a linear relation with the sum of the acid constants (ΣpK_a) of the ligands. Such a linear relation reflects that the bonding is similar in nature (ionic) and that, while the number of chelate rings differ in these actinide-ligand complexes, the effect of each chelate ring, whether N–M–O or N–M–N, is the same. All the chelate rings are 5-membered.

To ascertain the relative stability of 5-membered *vs.* 6-membered rings, we have measured the stability constants of Am(III), Cm(III), Bk(III), and Cf(III) with trimethylenedinitrilotetraacetate (TMDTA), in which a 6-membered N–M–N ring is possible.

Experimental

Reagents

TMDTA, trimethylenediaminetetraacetic acid, was synthesized by the method of Tanaka and Ogino [2] as revised by Ogino *et al.* [3]. The precipitate was recrystallized from 25% ethanol and titrated with standardized NaOH which confirmed it to be 100% TMDTA. An amount of the acid was dissolved in two equivalents of 0.1 M NaOH to make a 0.01 M stock solution of TMDTA. Sodium acetate buffer stock (0.200 M) was prepared by adding a sufficient amount of 1.0 M NaOH to 1.00 M acetic acid (Anachemia Chemicals, acculute) to achieve the desired pH when diluted to the correct volume. Reagent grade sodium chloride (Matheson, Coleman, and Bell) was dried at 110 °C and dissolved to make a 1.00 M stock solution. Distilled water, deionized with mixed-bed ion-exchange resin cartridges (Barnstead Ultrapure), was used for all solutions. Di-2-ethylhexylphosphoric acid, HDEHP, (Pfaltz and Bauer, Inc.) was purified by the method of Peppard, *et al.* [4], and dissolved in reagent grade toluene (Mallinckrodt). The solution was diluted to 1.5×10^{-4} M and preequilibrated with a pH 5.5 acetate buffer of 0.02 M concentration and total ionic strength of 0.10 M, adjusted with NaCl.

Radiotracers

The tracers ^{241}Am, ^{244}Cm, ^{249}Bk, ^{252}Cf, and $^{152,154}Eu$ were obtained from Oak Ridge National Laboratory and purified by cation exchange techniques. The purified tracers were evaporated to dryness and redissolved in 0.01 M HCl to a specific activity of about 25,000 cpm/μl. The ^{241}Am, ^{244}Cm, and ^{252}Cf were checked for radiochemical purity by alpha-spectrometry. The $^{152,154}Eu$ was checked by gamma-spectrometry.

Experimental

The stability constants of $Eu(TMDTA)^-$, $Am(TMDTA)^-$, $Cm(TMDTA)^-$, $Bk(TMDTA)^-$, and $Cf(TMDTA)^-$ were determined using liquid–liquid extraction techniques. In each experiment, five aqueous solutions containing varying concentrations of TMDTA were prepared and preequilibrated with toluene. The solutions of 0.10 M (NaCl) ionic strength were buffered with 0.02 M total acetate and the pH adjusted to 5.5. The organic phase was 1.5×10^{-4} M HDEHP in toluene.

Three milliliters of each phase were added with the appropriate radiotracer to a 20 ml vial. A sixth vial contained a blank solution with no TMDTA but

0020-1693/85/$3.30

otherwise identical to the other aqueous phases plus an equal volume of HDEHP solution. The vials were closed with polyseal caps and sealed in plastic bags which were placed on a wheel and equilibrated in a warm bath thermostatted at 25 ± 0.1 °C for at least 24 hours.

After equilibration, the two phases were separated and centrifuged. Samples of 0.500 ml of the separated phases were added to an extractive scintillation cocktail [5] and shaken. After extraction, the samples were counted on a Packard 3320 liquid scintillation counter to 1% or less error. For the blank solutions, samples of 2 ml of each phase were taken to improve the counting statistics of the aqueous phase as the distribution coefficient was so large.

The pH of the aqueous solutions was measured before and after equilibration using a combination electrode with a Beckman Research pH meter. NaCl was used, instead of $NaClO_4$, as the supporting electrolyte to avoid drift in pH readings due to precipitation of $KClO_4$ in the salt bridge. The electrode was standardized with a 0.05 N potassium hydrogen phthalate buffer (pH = 4.008).

From plots of the data as described below, the slope, intercept, 95% confidence limits of the slope, and the standard error of the intercept were determined for straight lines by a linear regression routine. Propagated errors were also calculated.

Results and Discussion

To calculate the stability constants from the extraction data, corrections were necessary for the complexation of the metal ions by acetate (buffer), chloride (background electrolyte), and hydroxide anions. The latter was due to the relatively high pH (*ca.* 5.5) used to partially deprotonate the TMDTA. In the presence of buffer and background electrolyte at pH > 5, but with no TMDTA, the extraction coefficient is given by:

$$D_1 = [M]_0/\{[M^{+3}]_a + \sum_i [MAc_i^{3-i}]_a + \sum_j [M(OH)_j^{3-j}]_a + \sum_k [MCl_k^{3-k}]_a\} \quad (1)$$

Since $\Sigma_n[MX_n^{3-n}] = \Sigma\beta_n[M^{+3}][X^-]^n$, where β_n are the overall stability constants, and defining $\Sigma_i\beta_i[Ac^-]^i \equiv X$, $\Sigma_j\beta_j[OH^-]^j \equiv Y$, and $\Sigma_k\beta_k[Cl^-]^k \equiv Z$, we can rewrite (1) as:

$$D_1 = \frac{[M]_0}{[M^{+3}]_a(1 + X + Y + Z)} \quad (2)$$

Inclusion of TMDTA in the solution requires an additional complexing term in the equation:

$$D_2 = \frac{[M_0]}{[M^{+3}]_a(1 + X + Y + Z + \beta[TMDTA])} \quad (3)$$

where $\beta = [MTMDTA^-]/[M^{+3}][TMDTA^{-4}]$. Setting $C = X + Y + Z$ and dividing (2) by (3) gives:

$$\frac{D_1}{D_2} = \frac{\beta[TMDTA^-] + 1 + C}{1 + C} \quad (4)$$

or

$$(1 + C)\left(\frac{D_1}{D_2} - 1\right) = \beta[TMDTA] \quad (5)$$

The value of [TMDTA] is obtained from the total concentration $[TMDTA]_T$ by:

$$[TMDTA] = \frac{[TMDTA]_T}{\theta} \quad (6a)$$

where

$$\theta = 1 + \sum_{p=1}^{5} [H^+]^p/\beta_p^H \quad (6b)$$

Log $\beta_1^H \simeq 1$, log $\beta_2^H = 2.88$, log $\beta_3^H = 5.45$, log $\beta_4^H = 13.41$, log $\beta_5^H = 23.80$ [1].

The stability constant, β, for formation of $MTMDTA_{(a)}^{-1}$ is obtained from a plot of $\theta(1 + C)((D_1/D_2) - 1)$ *vs.* $[TMDTA]_T$, based on the relation:

$$\theta(1 + C)\left(\frac{D_1}{D_2} - 1\right) = \beta[TMDTA]_T \quad (7)$$

Table I gives the extraction data for Am(III). The distribution coefficient value at zero concentration of TMDTA is D_1. The values of D_2 for the five different TMDTA concentrations are listed under the 'D' column. The stability constants used to calculate the $(1 + C)$ term in eqn. (7) are given in Table II. The

TABLE I. Distribution Data for Am(III). [HDEHP] = 1.5 × 10^{-4} M; [HAc + NaAc] = 0.02 M; I = 0.1 M (NaCl); T = 25.0 °C.

$[TMDTA]_T$ (M) × 10^4	Activity (cpm)		D	pH
	Organic	Aqueous		
0.00	147100	5842	25.17	5.524
	149400	6002	24.89	5.522
0.00	27000	3019	8.941	5.547
	28200	2884	9.785	
0.50	22700	6819	3.329	5.533
	23600	6572	3.584	
1.00	15200	8530	1.784	5.524
	15800	8449	1.875	
2.00	12300	18350	0.671	5.532
	12800	17820	0.716	
3.00	10100	19810	0.511	5.525
	10500	19780	0.530	

TABLE II. Stability Constants Used to Calculate C (Eqn. 7).

Metal	Acetate			Hydroxide	Chloride		C
	Log β_1	Log β_2	Log β_3	Log β_1	Log β_1	Log β_2	
Eu(III)	2.13	3.64	4.24	5.42	−0.1	−0.7	3.88
Am(III)	2.12[e]	3.61[e]	3.95[e]	7.9	−0.1	−0.7	5.05
Cm(III)	2.14[e]	3.67[e]	4.01[e]	7.9	−0.1[e]	−0.7[e]	5.37
Bk(III)	2.16[e]	3.73[e]	4.08[e]	8.2	−0.02	−0.7	6.09
Cf(III)	2.17[e]	3.75[e]	4.17[e]	8.2	−0.02[e]	−0.7[e]	6.20

[a] The values are from Refs. 6 and 7 except where superscripted by e for estimated values. [b] Estimated error of 10%.

TABLE III. Values of θ (Eqn. 7) and the Stability Constants of TMDTA Complexes. T = 25.0 °C, I = 0.1 M (NaCl).

Metal	$[TMDTA]_T$ (M) $\times 10^4$	pcH	$\theta \times 10^{-7}$	Log β
Eu	0.20	5.449	2.86	13.54 ± 0.05
	0.50	5.427	3.16	
	1.00	5.418	3.30	
	2.00	5.423	3.22	
	3.00	5.417	3.31	
Am	0.20	5.438	3.01	13.45 ± 0.04
	0.50	5.424	3.21	
	1.00	5.415	3.34	
	2.00	5.423	3.22	
	3.00	5.416	3.33	
Cm	0.20	5.446	2.90	13.79 ± 0.05
	0.50	5.423	3.22	
	1.00	5.422	3.23	
	2.00	5.425	3.19	
	3.00	5.422	3.23	
Bk	0.20	5.437	3.02	14.36 ± 0.06
	0.50	5.420	3.26	
	1.00	5.421	3.24	
	2.00	5.422	3.23	
	3.00	5.420	3.26	
Cf	0.20	5.445	2.91	14.66 ± 0.04
	0.50	5.426	3.18	
	1.00	5.422	3.12	
	2.00	5.427	3.16	
	3.00	5.422	3.23	

stability constants of trivalent actinide complexes with acetate at 0.1 M ionic strength are not available. However, Choppin and Schneider [8] have shown that a plot of the stability constants of the trivalent actinide complexes with acetate at I = 2 M *vs.* the ionic radii of the metal ions coincides with a similar plot for the lanthanide complexes. Consequently, the values required for this study were obtained from a plot of the known values for the lanthanide complexes at μ = 0.1 M. The values of pcH calculated from the measured pH (using pcH = pH − 0.09) and the corresponding values of θ are given in Table III. Plots used to obtain the β values are shown in Fig. 1. These stability constants and their propagated error limits are given in Table III. The value of β(EuTMDTA) agrees within error limits with the previously reported value of log β = 13.62 ± 0.05 [1].

Figure 2 shows the linear relation between log β for the formation of AmL, where L is acetate, HIDA, NTA, HEDTA, EDTA, and DTPA, and the total ΣpK_a of the ligand acid. The experimental value for AmTMDTA is substantially less than the value of 19.2 predicted from the pK_a value of TMDTA of 24.4. This value of 19.2 for log β would be expected if all four carboxylates and both nitrogen donors are involved in the chelation to a degree comparable to

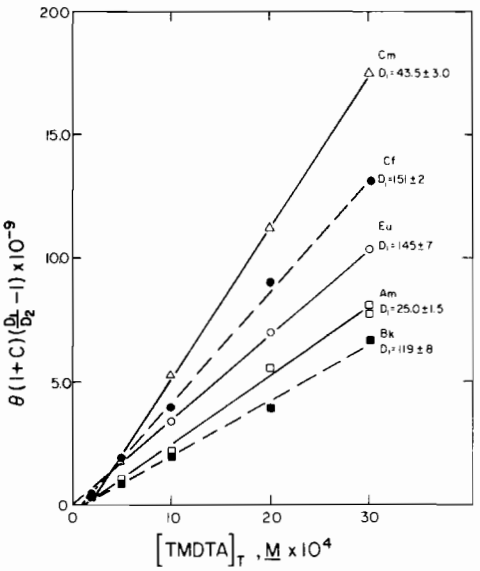

Fig. 1. Extraction of Eu(○), Am(□), Cm(△), Bk(■), and Cf(●), as a function of total TMDTA concentration.

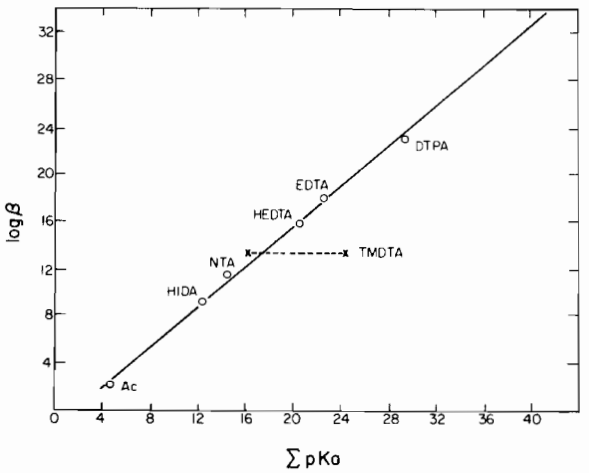

Fig. 2. Plot of log β of 1:1 Am complexation by acetate (Ac) and a series of aminopolycarboxylate ligands as a function of the total protonation constants, ΣpK_a [1]. The points for TMDTA reflect the total ΣpK_a (24.4) and ΣpK_a – 8.0, which assumes binding to only one N site.

that for 5-membered ring formation as in AmEDTA. Also plotted in Fig. 2 is the point for log β of AmTMDTA and (ΣpK_a – 8.0) based on the pK_a for protonation of the second N donor which has a value of 8.0. This value of (ΣpK_a – 8.0) assumes a complex involving binding of all four carboxylates but only one N donor to the metal.

Obviously, the TMDTA complexes are weaker than their EDTA analogs. The correlation in Fig. 2 suggests that the 6-membered N–M–N ring is much weaker than the analogous 5-membered ring. In fact, it is possible that the N–M–N is not formed since log β correlates with (pK_a – 8). However, we cannot make such a conclusion from these data alone; study of the lanthanide–TMDTA complexes by NMR may provide a more definitive understanding of the structure of these complexes [9].

Acknowledgement

This research was supported through a contract with the Office of Basic Energy Sciences, United States Department of Energy.

References

1 A. E. Martell and R. M. Smith, 'Critical Stability Constants, Vol. 1, Amino Acids', Plenum, New York, 1974.
2 N. Tanaka and H. Ogino, *Bull. Chem. Soc. Jpn, 37,* 877 (1964).
3 H. Ogino, M. Takahashi and N. Tanaka, *Bull. Chem. Soc. Jpn, 43,* 424 (1970).
4 D. F. Peppard, G. W. Mason, J. L. Maier and W. J. Driscoll, *J. Inorg. Nucl. Chem., 4,* 334 (1957).
5 G. A. Bruno and J. E. Christian, *Anal. Chem., 33,* 1216 (1961).
6 A. E. Martell and R. M. Smith, 'Critical Stability Constants, Vol. 3, Other Organic Ligands', 1977.
7 A. E. Martell and R. M. Smith, 'Critical Stability Constants, Vol. 4, Inorganic Complexes', 1976.
8 G. R. Choppin and J. K. Schneider, *J. Inorg. Nucl. Chem., 32,* 3283 (1970).
9 P. A. Baisden, G. R. Choppin and B. B. Garrett, *Inorg. Chem., 16,* 1367 (1977).