

involves a nucleophilic attack on chromium by the base as the slow step. General acid catalysis has never been proven for the hydrolysis of dichromate ion, although that reaction is catalyzed by hydrogen ion.

In these investigations on dichromate hydrolysis the reverse reaction was not considered, but in our study both the forward and the reverse reaction are important. The mechanism proposed above offers a reasonable alternative for the base hydrolysis of dichromate, involving an attack by water in the presence of a base which transfers a proton from the water to the other chromium center, before the five-coordinated intermediate is split. The path catalyzed by hydrogen ion

might occur *via* a protonated dichromate ion, with water acting as the base.

One cannot by kinetic means distinguish between the two possibilities of a direct nucleophilic attack and a purely protolytic effect. It is not improbable that in our case not only acid-base catalysis but also nucleophilic catalysis are involved.

Our future plans include further investigation of the kinetics of the condensation of hydrogen chromate with other monoacids.

**Acknowledgment.** We wish to thank Dr. Bassam Z. Shkhashiri for his help with the oxygen-exchange experiment.

## The Interaction of Thorium(IV) with Hydroxyethylethylenediaminetriacetic Acid and Other Ligands in Aqueous Solution<sup>1</sup>

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**Abstract:** Potentiometric equilibrium measurements of hydrogen ion concentration were employed to investigate the interaction of the Th(IV) ion with N-hydroxyethylethylenediaminetriacetic acid (HEDTA) and with the related ligands nitrilotriacetic acid (NTA), N-hydroxyethyliminodiacetic acid (HIMDA), N-methyliminodiacetic acid (MIMDA), oxybis(ethylenetriamino)tetraacetic acid (OETA), and ethylenebis(oxyethylenetriamino)tetraacetic acid (EOTA). Evidence is presented for hydrolysis reactions of the Th(IV) chelates of all these ligands as the pH is increased. Mononuclear monohydroxo species are formed from 1:1 chelates of OETA and EOTA and with the 2:1 chelate of NTA. Fractional neutralization values in the potentiometric titration curves of the 1:1 HEDTA chelate and the 2:1 HIMDA chelate indicate the formation of hydrolyzed polynuclear chelates containing three or some multiple of three Th(IV) ions. The formation constant of the 1:1 Th(IV)-HEDTA chelate was determined to be  $10^{18.9}$  from spectrometric measurement of equilibrium competition between Cu(II) and Th(IV) for the ligand. Equilibrium constants are also reported for the formation of the hydroxo mononuclear Th(IV)-HEDTA chelate, the binuclear  $\mu$ -dihydroxo Th(IV)-HEDTA chelate, the mononuclear hydroxo 1:1 chelates of OETA and EOTA, and the mononuclear hydroxy 1:2 Th(IV)-NTA chelate. Possible arrangements of ligand donor groups and metal ions in the ternuclear and hexanuclear Th(IV)-HEDTA chelate species are inferred, and the possible involvement of the hydroxyethyl group as a bridging ligand is suggested.

In view of the successful analyses of the Th(IV)-ethylenediaminetetraacetic acid (EDTA), Th(IV)-1,2-diaminocyclohexanetetraacetic acid (CDTA), and Th(IV)-diethylenetriaminepentaacetic acid (DTPA) systems described previously,<sup>3</sup> it was decided to investigate the Th(IV)-HEDTA and Th(IV)-HIMDA systems. This study should extend the information on the role of hydroxyethyl groups of organic ligands in hydrolysis andolation of Th(IV) chelates.

The role of ether oxygen as a donor group in the Th(IV) chelates was also investigated by potentiometric titration of solutions of the Th(IV) chelates of a monoether compound, [oxybis(ethylenetriamino)]tetraacetic

acid (OETA), and of a diether compound, [ethylenebis(oxyethylenetriamino)]tetraacetic acid (EOTA).

Potentiometric equilibrium studies have also been carried out on solutions containing 1:2 molar ratios of Th(IV) ion to nitrilotriacetic acid (NTA) and to methyliminodiacetic acid (MIMDA). These chelates are analogous, with respect to the possible number of donor atoms, to the 1:1 Th(IV) chelates of DTPA and EDTA, respectively. These systems afford an interesting comparison, since in each case the 1:2 chelates have one less chelate ring than the analogous 1:1 chelate.

The structures of the ligands used in this investigation are indicated by formulas I-VI.

### Experimental Section

**Spectrophotometric Measurements.** Spectrophotometric measurements were made with a Cary Model 14 PM recording spectrophotometer. Spectra of all solutions were measured in the same silica cell of 1.000-cm path length. All solutions were 0.10 *M* with respect to KNO<sub>3</sub>.

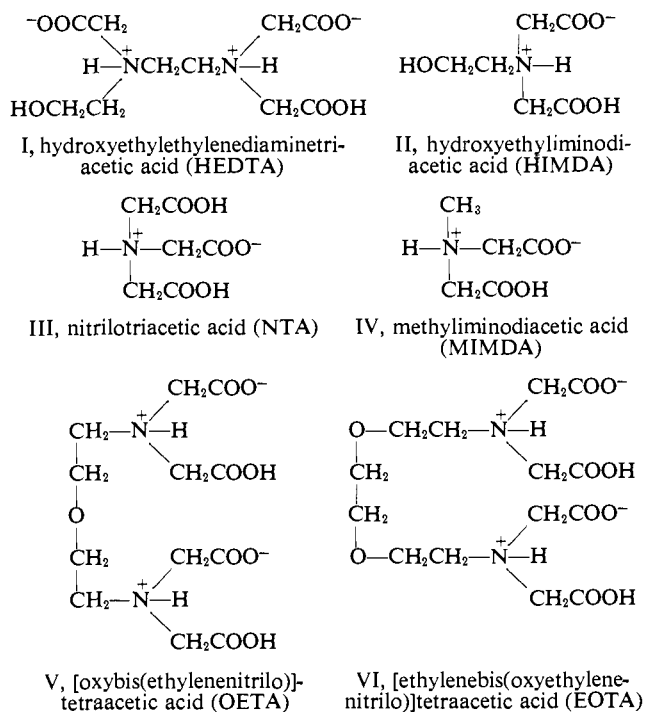
(1) This work was supported by the U. S. Atomic Energy Commission under Contract No. AT (30-1)-1823.

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(3) R. F. Bogucki and A. E. Martell, *J. Am. Chem. Soc.*, **80**, 4170 (1958).

**Potentiometric Measurements.** The potentiometric measurements were made with a Beckman Model G pH meter fitted with glass and calomel extension electrodes. The titrations were performed by adding small increments of standard base solution to a solution containing  $\text{Th}(\text{NO}_3)_4$  and ligand in the specified stoichiometric molar ratios. All titrations were performed in a cell maintained at  $25.00 \pm 0.05^\circ$  and under a nitrogen atmosphere, and all solutions were  $0.1 \text{ M}$  in  $\text{KNO}_3$ .

**Reagents.** The samples of NTA, HIMDA, and MIMDA were obtained through the courtesy of the Dow Chemical Co. The NTA and HIMDA were purified by recrystallization from water. The MIMDA was recrystallized from a water-acetone mixture. The ether compounds, OETA and EOTA, were kindly supplied by the Geigy Chemical Corp. The EOTA sample was recrystallized from water, while the OETA, which analyzed 99+ % pure, by titra-



tion, was used without further purification.

A sample of HEDTA, obtained through the courtesy of the Dow Chemical Co., was recrystallized from a hot acetone-water solution. The sample was suspended in hot acetone, and water was then added dropwise in just sufficient quantity to effect complete solution of the HEDTA. This solution produced a good crop of colorless crystals of HEDTA upon cooling.

When solid samples of HEDTA were dissolved in water and titrated quickly with standard base, the sharp inflection in the titration curve indicated a purity of 99.0%. If the acid solution of HEDTA was allowed to stand for an hour before titrating, the inflection occurred earlier in the curve and indicated a purity of 97%. When the resultant basic solution of HEDTA was allowed to stand for 1 hr and then back-titrated with acid, the inflection again occurred at the position indicating 99% purity. The two inflections in this hysteresis-type effect were quite reproducible in several different forward and back titrations. This behavior may reasonably be explained by the presence of a small amount of a cyclic ester, formed in acid solution by a condensation between the hydroxyethyl group and an acetic acid group. This ester, which contains one titratable proton less than the open form of HEDTA, would be restored to the normal acid-base stoichiometry when the ester is opened by a base-catalyzed hydrolysis at high pH. These observations indicate that an acid stock solution of HEDTA should be standardized by adding a measured excess of base and then, after 1 hr, back-titrating with standard acid. There is no evidence that the cyclic ester persists in the  $\text{Th}(\text{IV})$  complex of HEDTA, even at low pH values.

**Thorium Nitrate.** Analytical reagent grade  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  (Baker and Adamson) was dissolved in distilled water to make a stock solution which was standardized gravimetrically by precipitation of thorium hydroxide with ammonia, followed by ignition of the precipitate to  $\text{ThO}_2$ .

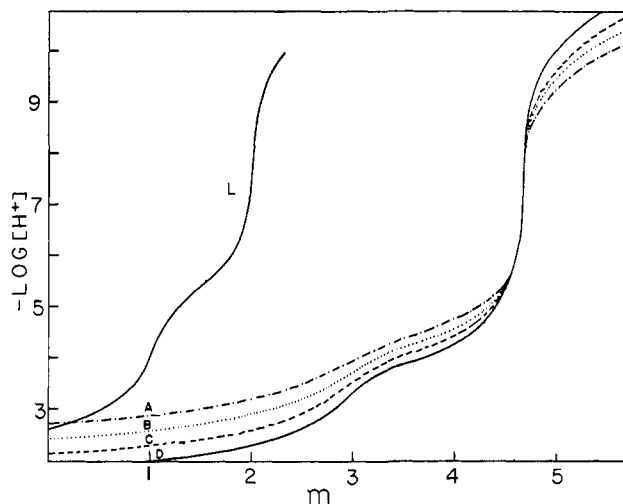


Figure 1. Potentiometric titrations of 1:1  $\text{Th}(\text{IV})$ -HEDTA chelate system at  $25.0 \pm 0.05^\circ$ : (A)  $6.25 \times 10^{-4} \text{ M}$ , (B)  $1.25 \times 10^{-3} \text{ M}$ , (C)  $2.5 \times 10^{-3} \text{ M}$ , (D)  $5.0 \times 10^{-3} \text{ M}$ ;  $m$  = moles of NaOH added per mole of metal chelate;  $\text{KNO}_3 = 0.1 \text{ M}$  at start of titration; L indicates ligand alone.

**Cupric Nitrate.** A  $0.1 \text{ M}$  cupric nitrate stock solution was made by dissolving analytical reagent grade  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in distilled water. The resultant solution was standardized by titration with standard EDTA solution in the presence of murexide indicator, according to the procedure of Schwarzenbach.<sup>4</sup>

## Results and Interpretation

**$\text{Th}(\text{IV})$ -HEDTA Titrations.** Figure 1 shows the titration curves of solutions containing equimolar amounts of  $\text{Th}(\text{IV})$  and HEDTA (represented as  $\text{H}_3\text{L}$ ) with a standard sodium hydroxide solution. At the start of titration [*i.e.*, at  $m = 0$ , where  $m$  is the number of moles of hydroxide ion added per mole of thorium ion present in all forms, and  $T_{\text{Th}}$  is the total concentration of  $\text{Th}(\text{IV})$ ] the ratio  $[\text{H}^+]/T_{\text{Th}}$  is precisely 3.0 at all concentrations studied. This ratio indicates that the formation reaction  $\text{Th}^{4+} + \text{H}_3\text{L} \rightleftharpoons \text{ThL}^+ + 3\text{H}^+$  is essentially complete before any base is added. The small inflection at  $m = 3$  represents the completion of titration of the three hydrogen ions displaced in the association reaction. The concentration-dependent buffer region from  $m = 3$  to 4.67 indicates that hydrolysis with polynucleation occurs in this region. The sharp concentration-independent inflection at precisely  $m = 4\frac{2}{3}$  demonstrates that the hydroxo complexes formed are very stable in solution from pH 5.5 to 8.5 and have the empirical formula  $[(\text{ThL})_3(\text{OH})_3]^{2-x}$ . Since the potentiometric data do not indicate the source of titrated hydrogen ions, up to three of the  $\text{OH}^-$  groups in this formula could represent ethoxo groups from the HEDTA ligands. In addition, two  $\text{OH}^-$  groups are stoichiometrically equivalent to one  $\text{O}^{2-}$  ion (or one oxo bridge). The data are unambiguous, however, in requiring the hydrolyzed species present at the  $4\frac{2}{3}$  inflection to be ternuclear or multiply ternuclear.

**Dimers of  $\text{Th}(\text{IV})$ -HEDTA.** In a previous publication, Bogucki and Martell<sup>3</sup> reported the presence of binuclear, diolated chelate species for the  $\text{Th}(\text{IV})$ -EDTA and  $\text{Th}(\text{IV})$ -CDTA systems. The titration data from the  $\text{Th}(\text{IV})$ -HEDTA system were therefore also tested for binuclear species by the same method.

(4) G. Schwarzenbach, "Complexometric Titration," Interscience Publishers, New York, N. Y., 1957, p 82.

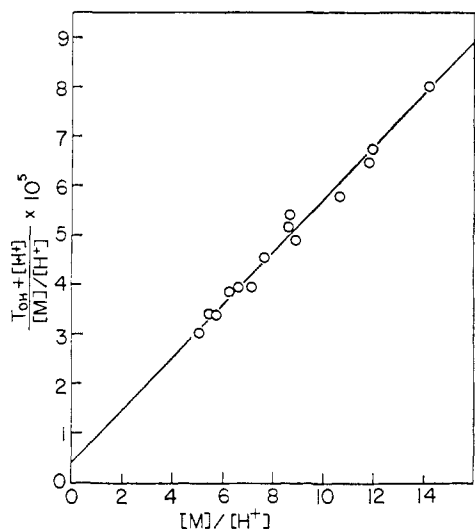
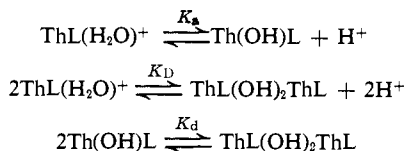


Figure 2. Graphical demonstration of the formation of a binuclear diolate Th(IV)-HEDTA chelate compound;  $T_{OH}$  = total moles of base added per liter of solution beyond  $m = 3$ ;  $[M]$  = concentration of normal, hydrated Th(IV)-HEDTA chelate compound represented in the text as ThL<sup>+</sup>.

The equations for the hydrolysis reactions



may be combined with the material and charge-balance equations to yield the linear expression

$$\frac{[\text{H}^+](T_{OH} + [\text{H}^+])}{[\text{ThL}^+]} = \frac{2K_D[\text{ThL}^+]}{[\text{H}^+]} + K_a \quad (1)$$

from which  $K_D$  and  $K_a$  may be readily derived. The derivation and application of these equations has been previously discussed in detail.<sup>3</sup> A plot of the titration data in Figure 1 according to eq 1 produces a straight line as illustrated in Figure 2. The calculated points of this plot obey a linear relationship from  $m$  values of 3.0 to about 3.4, in which region dimers are thus shown to predominate. Beyond  $m = 3.4$  the deviation from linearity indicates the presence of significant amounts of additional hydrolysis products.

From the linear plot in Figure 2 the values  $pK_a = 5.4$  and  $pK_D = 5.6$  were obtained. These and all of the other constants determined in this study are summarized in Table I.

Table I

Ligand	Reaction	Log $K$
HEDTA ( $\text{H}_3\text{L}$ )	$\text{Th}^{4+} + \text{L}^{3-} \rightleftharpoons \text{ThL}^+$	18.5
	$\text{ThL}(\text{H}_2\text{O})^+ \rightleftharpoons \text{Th}(\text{OH})\text{L} + \text{H}^+$	-5.4
	$2\text{ThL}(\text{H}_2\text{O})^+ \rightleftharpoons [\text{Th}(\text{OH})\text{L}]_2 + 2\text{H}^+$	-5.6
	$2\text{Th}(\text{OH})\text{L} \rightleftharpoons [\text{Th}(\text{OH})\text{L}]_2$	5.2
	$\text{CuHL} \rightleftharpoons \text{CuL}^- + \text{H}^+$	-2.42
EOTA ( $\text{H}_4\text{L}$ )	$\text{ThL}(\text{H}_2\text{O}) \rightleftharpoons \text{Th}(\text{OH})\text{L}^- + \text{H}^+$	-7.3
OETA ( $\text{H}_4\text{L}$ )	$\text{ThL}(\text{H}_2\text{O}) \rightleftharpoons \text{Th}(\text{OH})\text{L}^- + \text{H}^+$	-6.35
NTA ( $\text{H}_3\text{X}$ )	$\text{ThX}_2(\text{H}_2\text{O})^{2-} \rightleftharpoons \text{Th}(\text{OH})\text{X}_2^{3-} + \text{H}^+$	-8.6

**Polynucleation beyond Dimers.** In an attempt to discover the nature of the hydrolysis products beyond

dimers, the data over the entire hydrolysis range ( $m = 3$  to  $4^{2/3}$ ) were subjected to a mathematical analysis based on the linear "core-plus-links" model proposed by Sillén and coworkers.<sup>5-7</sup> This model assumes the addition of hydroxo or oxo-bridged links (e.g.,  $\text{ThL}(\text{OH})_n^{(1-n)}$ ) to a core, in this case  $\text{ThL}^+$ , to form a linear polymer. The failure of the data to fit this model is not unexpected and is discussed below.

**Th(IV)-HEDTA Formation Constant.** A spectrophotometric study of the competition reaction



was used to determine the value of the Th(IV)-HEDTA formation constant. The equilibrium constant for eq 2 is

$$K_{eq} = \frac{[\text{ThL}^+][\text{Cu}^{2+}]}{[\text{CuL}^-][\text{Th}^{4+}]} = \frac{K_{\text{ThL}}}{K_{\text{CuL}}} \quad (3)$$

in which  $K_{\text{ThL}}$  and  $K_{\text{CuL}}$  are the formation constants of the 1:1 chelates of Th(IV) and Cu(II) with HEDTA. The value of  $K_{\text{CuL}}$ , determined under conditions similar to those used in the present study, has been reported by Chaberek and Martell<sup>8</sup> as  $10^{17.4}$ . Thus, if  $K_{eq}$  is evaluated from the competition data, the value of  $K_{\text{ThL}}$  may be derived directly from eq 3.

In order to evaluate  $K_{eq}$ , it is necessary to account for all of the species containing Cu, Th, or L, in the reaction mixture. Under the conditions at which the competition reaction was studied, only a protonated form of the Cu(II) chelate, CuHL, and hydrolyzed forms of the hydrated Th(IV) ion,  $\text{Th}_p(\text{OH})_q^{(+4p-q)}$ , were found to be present at significant concentrations, in addition to the four ions in eq 2.

Separate potentiometric and spectrophotometric studies of the Cu(II)-HEDTA system revealed that the protonated chelate, CuHL, has an acid dissociation constant,  $K_{a(\text{CuHL})}$ , of  $10^{-2.42}$ , and that the three species,  $\text{Cu}^{2+}$ , CuHL, and  $\text{CuL}^-$ , have molar extinction coefficients,  $\epsilon$ , of 7.6, 48, and 100, respectively, at 715 m $\mu$ , the wavelength of maximum absorption for  $\text{CuL}^-$ . Bydalek and Margerum<sup>9</sup> have reported a value for  $K_{a(\text{CuHL})}$  of  $10^{-2.32}$  at 25.0° in 1.25 M NaClO<sub>4</sub>. The agreement is good, in view of the different ionic strengths involved.

Since the Th(IV) ion and its HEDTA chelate do not absorb in the visible region, the total optical density,  $D$ , for the competition reaction mixture will be equal to

$$D = \epsilon_{\text{Cu}}[\text{Cu}] + \epsilon_{\text{CuL}}[\text{CuL}] + \epsilon_{\text{CuHL}}[\text{CuHL}] \quad (4)$$

in which  $\epsilon_i$  represents the molar extinction coefficient of the species  $i$ . The material balance equations are

$$T_{\text{Th}} = [\text{Th}^{4+}] + [\text{ThL}^+] + \sum p[\text{Th}_p(\text{OH})_q^{+4p-q}] \quad (5)$$

$$T_{\text{Cu}} = [\text{Cu}^{2+}] + [\text{CuL}^-] + [\text{CuHL}] \quad (6)$$

$$T_{\text{L}} = [\text{ThL}^+] + [\text{CuL}^-] + [\text{CuHL}] \quad (7)$$

in which  $T_{\text{Th}}$ ,  $T_{\text{Cu}}$ , and  $T_{\text{L}}$  represent the analytical (total) concentrations of Th, Cu, and L, in all forms, respectively. The combination of eq 4-7 with the expression

(5) L. G. Sillén, *Acta Chem. Scand.*, **8**, 299 (1954).

(6) L. G. Sillén, *ibid.*, **8**, 318 (1954).

(7) S. Hietanen and L. G. Sillén, *ibid.*, **8**, 1607 (1954).

(8) S. Chaberek, Jr., and A. E. Martell, *J. Am. Chem. Soc.*, **77**, 1477 (1955).

(9) T. J. Bydalek and D. W. Margerum, *Inorg. Chem.*, **2**, 678 (1963).

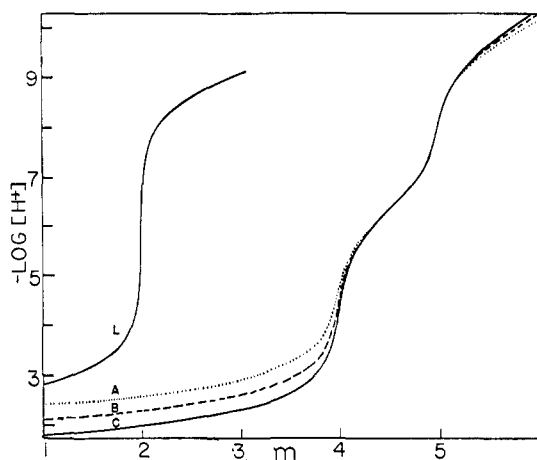


Figure 3. Potentiometric titrations of 1:1 Th(IV)-OETA chelate system at  $25.0 \pm 0.05^\circ$ : (A)  $1.25 \times 10^{-3} M$ , (B)  $2.5 \times 10^{-3} M$ , (C)  $5.0 \times 10^{-3} M$ ; L indicates ligand alone.

for  $K_{a(\text{CuHL})}$  yields

$$[\text{CuL}^-] = \frac{D - \epsilon_{\text{Cu}} T_{\text{Cu}}}{\epsilon_{\text{CuL}} + \epsilon_{\text{CuHL}} \left( \frac{[\text{H}^+]}{K_{a(\text{CuHL})}} \right) - \epsilon_{\text{Cu}} (1 + \frac{[\text{H}^+]}{K_{a(\text{CuHL})}})} \quad (8)$$

The quantities on the right side of eq 8 are all known or measurable. With the evaluation of  $[\text{CuL}^-]$ , the values for  $[\text{Cu}^{2+}]$  and  $[\text{ThL}^+]$  are readily derived from eq 6 and 7 and  $K_{a(\text{CuHL})}$ .

There remains only the separation of  $[\text{Th}^{4+}]$  from  $\Sigma p[\text{Th}_p(\text{OH})_q^{+4p-q}]$  in eq 5.

**Correction for the Hydrolysis of Th(IV).** The evaluation of  $\Sigma p[\text{Th}_p(\text{OH})_q^{+4p-q}]$  from the data requires a knowledge of  $\bar{Z}$ , the average number of  $\text{OH}^-$  ions bound per (unchelated) Th(IV) ion, and a hydrolysis model (i.e., the ratio  $p/q$ ) which is applicable to the experimental conditions.

Kraus and Holmberg<sup>10</sup> and Hietanen<sup>11</sup> have studied the hydrolysis of Th(IV) ion and their reports agree reasonably well on the values for  $\bar{Z}$ , which is defined as

$$\bar{Z} = \frac{\sum q[\text{Th}_p(\text{OH})_q^{+4p-q}]}{\sum p[\text{Th}_p(\text{OH})_q^{+4p-q}]}$$

The hydrolysis models inferred from the data in the two papers differ considerably, however. Whereas Kraus and Holmberg<sup>10</sup> propose the presence mainly of a monohydroxo monomer and a dihydroxo-bridged dimer, both with  $p/q = 1$ , Hietanen<sup>11</sup> postulates trihydroxo-bridged species of varying length,  $\text{Th}[(\text{OH})_3\text{Th}]_n^{n+4}$ , with  $0.67 > (p/q) > 0.33$ .

The  $\bar{Z}$  values used in this study were conveniently calculated from an empirical linear relationship,  $\bar{Z} = ([\text{Th}^{4+}]_t + 0.0025)/0.0304$ , derived from the data of Kraus and Holmberg<sup>10</sup> at pH 3, and in which  $[\text{Th}^{4+}]_t$  is the total concentration of unchelated Th(IV), or  $([\text{Th}^{4+}] + \Sigma p[\text{Th}_p(\text{OH})_q^{+4p-q}])$ . For any assumed hydrolysis model with its corresponding value of  $p/q$ , we have  $[\text{Th}^{4+}] = [\text{Th}^{4+}]_t (1 - \bar{Z}p/q)$ .

In the present study the values calculated for  $\bar{Z}$  are small, and thus the values for  $[\text{Th}^{4+}]$ , and consequently

- (10) K. A. Kraus and R. W. Holmberg, *J. Phys. Chem.*, **58**, 325 (1954).  
 (11) S. Hietanen, *Acta Chem. Scand.*, **8**, 1626 (1954).

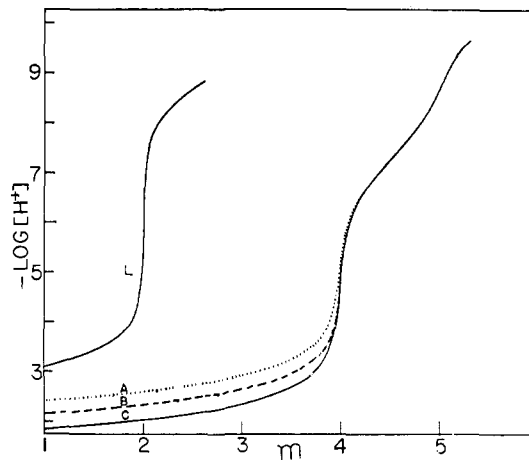


Figure 4. Potentiometric titrations of 1:1 Th(IV)-EOTA chelate system at  $25.0 \pm 0.05^\circ$ : (A)  $1.25 \times 10^{-3} M$ , (B)  $2.5 \times 10^{-3} M$ , (C)  $5.0 \times 10^{-3} M$ ; L indicates ligand alone.

for  $K_{\text{eq}}$ , do not vary much with the hydrolysis model chosen. For example, with various values for  $p/q$ , ranging from 0.5 to 3, the calculated values for  $\log K_{\text{eq}}$  all fell within the range  $1.10 \pm 0.12$ . Inasmuch as the choice of any value for  $p/q$  is somewhat arbitrary, we chose  $p/q = 2$  to determine the constants listed in Table II because this led to better precision than the lower  $p/q$  values previously proposed<sup>10,11</sup> and because it yielded the value  $\log K_{\text{eq}} = 1.10$ , the median value for the several models tested. All of the data for the competition reaction are listed in Table II which shows an average value of  $\log K_{\text{ThL}} = 18.5$ .

Table II. Spectrophotometric Data for 1:1 Th(IV)-HEDTA System<sup>a</sup>

Expt	—Total concn $\times 10^3$ —			$D^b$	$Z^c$	Log $K_{\text{eq}}^d$	Log $K_{\text{ThL}}^e$
	Cu(II)	Th(IV)	HEDTA				
1	10.0	10.0	10.0	0.329	0.182	1.02	18.4
2	6.00	6.00	6.00	0.181	0.135	1.10	18.5
3	3.60	3.60	3.60	0.103	0.112	1.16	18.6
4	20.0	10.0	10.0	0.504	0.221	1.06	18.5
5	12.0	6.00	6.00	0.282	0.157	1.10	18.5
6	7.20	3.60	3.60	0.158	0.123	1.19	18.6

<sup>a</sup>  $\mu = 0.10$  ( $\text{KNO}_3$ ),  $25^\circ$ , pH  $3.00 \pm 0.02$ . <sup>b</sup> Measured at  $7.5 \mu\mu$ . <sup>c</sup>  $\bar{Z}$  is the average number of hydroxyl ions that are bound per unchelated metal ion. <sup>d</sup>  $K_{\text{eq}}$  applies to reaction  $\text{CuL}^- + \text{Th}^{4+} \rightleftharpoons \text{Cu}^{2+} + \text{ThL}^+$ . <sup>e</sup>  $K_{\text{ThL}}$  applies to reaction  $\text{Th}^{4+} + \text{L}^{3-} \rightleftharpoons \text{ThL}^+$ , where  $\text{H}_3\text{L} = \text{HEDTA}$ .

**Th(IV)-OETA and Th(IV)-EOTA Titrations.** The 1:1 chelate systems of Th(IV) with OETA and with EOTA (Figures 3 and 4, respectively) showed remarkably similar titration curves and will be considered together. In both cases, the ratio  $[\text{H}^+]/T_{\text{Th}}$  was equal to 4.0 before the addition of any base, which indicates that the chelates are completely formed with displacement of all four acetic acid protons even at pH values below 2. The four displaced protons produce a steep inflection at  $m = 4$  followed by a buffer region which terminates in a second inflection at  $m = 5$ .

In each system, the curves for various concentrations coalesce into a single line between  $m = 4$  and 5. This lack of dependence on concentration in the buffer region indicates that a mononuclear monohydroxo chelate

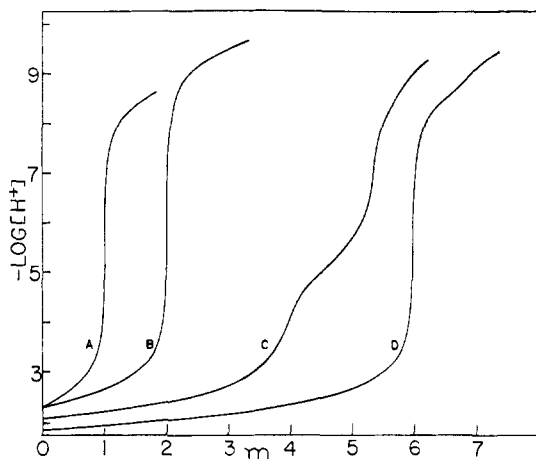
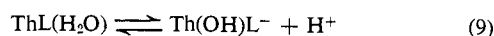


Figure 5. Potentiometric titrations of Th(IV)-NTA and Th(IV)-HIMDA chelate systems at  $25.0 \pm 0.05^\circ$ : A and B indicate the free ligands HIMDA and NTA, respectively; C and D represent the systems Th(IV)-HIMDA and Th(IV)-NTA, respectively, with a ligand-to-metal ratio of 2:1 in each case.

is formed in each system according to the reaction



If  $\text{p}K_a$  is set equal to  $\text{pH}$  at  $m = 4.50$ , in accordance with the simple Henderson relationship, the  $\text{p}K_a$  values for the formation of the monohydroxo chelates are found to be 6.35 for Th(IV)-OETA and 7.30 for Th(IV)-EOTA.

**Th(IV) with NTA, HIMDA, and MIMDA.** The titration curves for the chelate systems formed by Th(IV) with the ligands NTA and HIMDA, each with a metal-to-ligand ratio of 1:2, are shown in Figure 5. The steep inflection at  $m = 6$  in the Th(IV)-NTA curve represents the completion of titration of the six replaceable acetic acid protons from the two NTA ligands and demonstrates that the 1:2 complex is fully formed and stable in the pH range 4–8. The buffer region between  $m = 6$  and 7 indicates the formation of a monohydroxo chelate with a  $\text{p}K_a$  value of 8.6. At  $m = 0$ , the ratio  $[\text{H}^+]/T_{\text{Th}}$  was 5.5 rather than 6.0. This means that at low pH values the 1:2 chelate is not fully formed and/or that protonated chelate species are present. Thus, the behavior of the 1:2 Th(IV)-NTA chelate is qualitatively different from the 1:1 chelate systems of Th(IV) with EDTA, CDTA, HEDTA, OETA, EOTA, DTPA, and 1:2 Th(IV)-HIMDA, all of which, upon mixing at millimolar concentrations, showed a  $[\text{H}^+]/T_{\text{Th}}$  ratio exactly equal to the total number of acetic acid groups in the ligands.

The titration of the 1:2 Th(IV)-HIMDA system yielded curve C in Figure 5. At  $m = 0$ , the 1:2 chelate is already well formed as evidenced by the value  $[\text{H}^+]/T_{\text{Th}} = 4.0$  and the inflection at  $m = 4$ . The buffer region beyond  $m = 4$  terminated in a second inflection at  $m = 5\frac{1}{3}$ . As in the Th(IV)-HEDTA case, the inflection at one-third of an integral  $m$  value signifies the formation of a stable ternuclear or multiply ternuclear hydroxo chelate with an empirical formula, in this case, of  $[(\text{L}_2\text{Th})_3(\text{OH})_4]_x^{2x-}$ .

The 1:2 Th(IV)-MIMDA system behaved quite differently from all of the others. At  $m = 0$ , the ratio  $[\text{H}^+]/T_{\text{Th}}$  was equal to 1.7, whereas the fully formed chelate would require 4.0. Furthermore, at  $m \sim 1.8$  and

$\text{pH} \sim 2.8$ , a white solid began to separate from the solution. This solid persisted to pH values above 9 and thus rendered equilibrium calculations impossible.

## Discussion

**Th(IV)-HEDTA Trimers and Hexamers.** On the basis of the data presented in this study, several conclusions may be drawn regarding the Th(IV)-HEDTA chelate. The formation of the chelate  $\text{ThL}^+$  at low pH is followed by polynucleating hydrolysis reactions in the region pH 3–5. A binuclear hydrolysis species predominates in the region  $m = 3.0$ –3.4. Beyond this region ternuclear or multiply ternuclear species are formed in very slow reactions<sup>12</sup> which finally result in the production of the very stable stoichiometric species  $[\text{Th}_3\text{L}_3(\text{OH})_3]_x^{2x-}$  at  $m = 4\frac{2}{3}$ . The steepness of the inflection at  $m = 4\frac{2}{3}$ , as well as the large pH range of the vertical portion of the curve, argues strongly for a stable, closed geometric configuration such as rings or cage structures, which would prohibit further polynucleation.<sup>13</sup> Finally, the fact that the inflection occurs precisely at  $m = 4\frac{2}{3}$ , quite independent of the total concentration of Th(IV)-HEDTA, suggests that only one polynuclear species is present at the inflection, or at least that the species present can all interconvert without any change in acid-base stoichiometry. A separate detailed computer analysis of the Th(IV)-HEDTA system to determine the minimum number of polynuclear species, and the corresponding equilibrium constants required to fit the potentiometric data, is now in progress and will be reported in a subsequent publication.

In a separate ultracentrifugation study of the Th(IV)-HEDTA system, Gustafson and Martell<sup>14</sup> found an average  $N$  value of 5.2 monomer units ( $\text{ThL}(\text{OH})_{1.67}$ ) per polynuclear species. The  $N$  values increased from 4.6 to 5.5 with a tenfold increase in the total concentration of Th(IV)-HEDTA. Although they proposed that a single hexanuclear species probably existed at the inflection at  $m = 4\frac{2}{3}$ , their results do not seem to exclude the possibility of a trimer-hexamer equilibrium.

The potentiometric and ultracentrifugation data do not provide any direct structural information, but they restrict the alternatives to a point where speculation on the possible structures of the polynuclear species may be warranted. One could conceive of a ternuclear ring with a structure similar to VII with a triply bonded oxo bridge in the center (shaded circle) and hydroxo or ligand-ethoxo bridges (open circles) in the ring. Two of these six-membered rings could associate to form a hexamer, VIII, in which each thorium ion is linked by a dioxygen bridge to each of its four nearest neighbors. Further polynucleation would be unlikely because of the bulky HEDTA groups attached to each thorium ion (shown in schematic fashion for one of the thorium ions). A mixture of VII and VIII would satisfy all of the requirements stated above for the polynuclear species present at  $m = 4\frac{2}{3}$ .

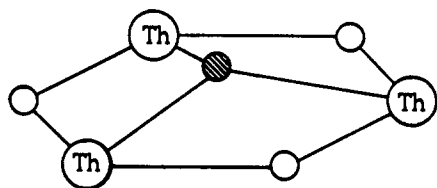
In addition, all of the structural features in VII and VIII have been demonstrated in other compounds. Figgis and Robertson<sup>15</sup> have performed an X-ray analy-

(12) Between  $m = 3.4$  and 4.5, it required several hours, in some cases, to reach equilibrium after addition of an increment of base.

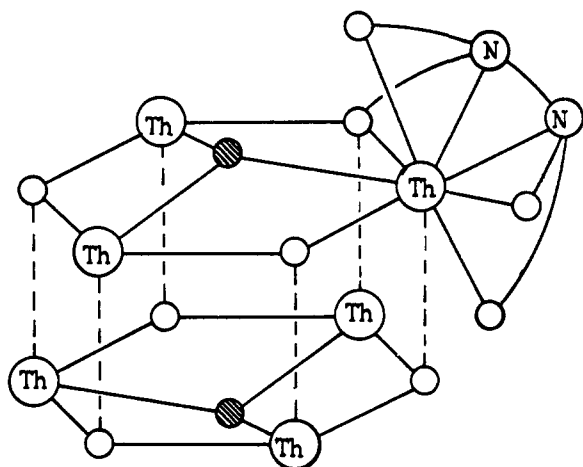
(13) It is highly unlikely that an open-ended linear hydroxo polymer, such as a "core-plus-links" chain, would grow to, say, a hexamer and then remain unchanged over such a large pH range.

(14) R. L. Gustafson and A. E. Martell, *J. Am. Chem. Soc.*, 86, 344 (1964).

sis of basic chromium(III) acetate and found that in  $[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]^+$  the three Cr(III) ions lie at the apices of an equilateral triangle and share a central, trigonally bonded oxo bridge, as proposed for Th(IV) in VII. The octahedral cage of metal ions proposed for



VII



VIII

Th(IV) in VIII has been reported for other metal ions. Levy, Danford, and Agron<sup>16</sup> found that the Bi(III) ions in  $[\text{Bi}_6(\text{OH})_{12}]^{6+}$  occupy octahedral positions, somewhat beyond the face centers of the corresponding cube with a hydroxide ion at the center of each of the 12 edges of the cube. On the basis of Raman spectra evidence, Maroni and Spiro<sup>17</sup> have proposed the existence of the hexanuclear ion  $\text{Pb}_6(\text{OH})_8^{4+}$ , with the six Pb(II) ions forming an octahedral cage and a hydroxide ion at the center of each of the eight octahedral faces. The proposed structure VIII has essentially this structure for the Th(IV) octahedral cage. The nine-coordinate requirement for the Th(IV) ions is not unusual in view of the evidence

(15) B. N. Figgis and G. B. Robertson, *Nature*, **205**, 694 (1965).

(16) H. A. Levy, M. D. Danford, and P. A. Agron, *J. Chem. Phys.*, **31**, 1458 (1959).

(17) V. A. Maroni and T. G. Spiro, *Inorg. Chem.*, **7**, 188 (1968).

(18) T. A. Bohigian and A. E. Martell, *ibid.*, **4**, 1264 (1965).

of Bohigian and Martell<sup>18</sup> that Th(IV) may be up to ten-coordinate in aqueous solution.

Although the exact role of the hydroxyethyl group in the Th(IV) chelates with HEDTA and HIMDA cannot be determined from the data presented here, the striking difference in behavior between the Th(IV)-HIMDA and Th(IV)-MIMDA chelates suggests that the hydroxyethyl group is involved in bonding to the Th(IV) ion in some fashion. It also seems beyond coincidence that, of the fairly large number of Th(IV) chelates of aminopolycarboxylic acids reported in this and other studies,<sup>3,18,19</sup> the only two which show inflections in their titration curves at one-third integral  $m$  values are HEDTA and HIMDA, each of which contains a hydroxyethyl group. Thus, the hydroxyethyl group may be involved in the formation of the ternuclear chelates, possibly through ethoxo bridging.

**Th(IV) with NTA, MIMDA, and EOTA.** The MIMDA molecule may be considered as one-half of an EDTA molecule. Thus, we can formally compare the 1:1 Th(IV)-EDTA chelate with the 1:2 Th(IV)-MIMDA chelate.  $\text{Th}(\text{EDTA})^0$  is fully formed at pH 2 and is soluble over the entire pH range studied, whereas the  $\text{Th}(\text{MIMDA})_2^0$  is formed only to a small per cent at pH 2 and is insoluble above pH 3. It is evident that the loss of the central chelate ring, which includes the two nitrogen atoms, while it may provide some small relief from steric strain, causes a major loss of stability and solubility in  $\text{Th}(\text{MIMDA})_2^0$ .

In a similar comparison, the Th(IV)-DTPA chelate is fully formed at low pH values,<sup>3</sup> whereas 1:2 Th(IV)-NTA is not, although both systems are presumably octacoordinate. In addition, although one might expect  $\text{Th}(\text{NTA})_2^{2-}$  to be less acidic than the singly charged  $\text{Th}(\text{DTPA})^-$ , the  $\text{p}K_a$  values for the formation of the monohydroxo chelates are 8.6 and 8.9, respectively. Thus,  $\text{Th}(\text{NTA})_2^{2-}$  has one less chelate ring than  $\text{Th}(\text{DTPA})^-$  and is also less stable.

The Th(IV)-EOTA chelate is also potentially octadentate, and from the complete displacement of the four acetic acid protons at low pH we may assume that the two nitrogen donors are bound to Th(IV). We can further infer that the two ether oxygen atoms, although certainly weak donors, probably occupy regular coordination sites on Th(IV), inasmuch as this would be required to hold the chelate together. Because of the weak donor properties of the ether oxygen, however,  $\text{Th}(\text{EOTA})^0$  forms a monohydroxo chelate at the low  $\text{p}K_a$  value of 7.3, much lower than the value for  $\text{Th}(\text{DTPA})^-$  and very close to the value of 7.04<sup>3</sup> for hexadentate  $\text{Th}(\text{EDTA})^0$ . The ready addition of a hydroxo ion to these Th(IV) chelates with octadentate ligands is consistent with the proposal of Bohigian and Martell that Th(IV) may well be greater than eight-coordinate in aqueous solution.

(19) G. H. Carey, R. F. Bogucki, and A. E. Martell, *ibid.*, **3**, 1288 (1964).