Formation, Hydrolysis, and Olation of Uranium(IV) Chelates[1,2]

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Abstract: A procedure is outlined for the preparation of pure standard U(IV) chloride solution containing a known amount of excess acid, and potentiometric equilibrium data are reported for the formation of U(IV) chelates of ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), *trans*-1,2-cyclohexanediaminetetraacetic acid (CDTA), N-hydroxyethylethylenediaminetriacetic acid (HEDTA), N-hydroxyethyliminodiacetic acid (HIMDA), diethylenetriaminepentaacetic acid (DTPA), and triethylenetetraminehexaacetic acid (TTHA). The formation constants were calculated, and the tendencies of these metal chelates to form hydroxo derivatives and olated polynuclear species are outlined. The relative stabilities are correlated with the tendencies of the aqueous chelates to undergo hydrolysis and dimerization. Although the U(IV) chelates are more stable and show a greater tendency to hydrolyze than do the corresponding Th(IV) chelates, the U(IV) chelates show less tendency to form polynuclear species than do those of Th(IV).

Very little quantitative work has been published on aqueous equilibria between multidentate ligands and the U(IV) ion. Palei and Hsu[4] noted that U(IV) forms a 1:1 and 1:2 chelate with ethylenediamine-N,N,N′,N′-tetraacetic acid (EDTA). Smith,[5] Klygin, *et al.*,[6] and Krot, *et al.*,[7] determined formation constants for the 1:1 U(IV)–EDTA chelate with Smith[5] noting further hydrolysis of this chelate at low pH to form a monohydroxo chelate. Ermolaev and Krot[8] isolated and studied the 1:1 U(IV)–EDTA chelate and obtained equilibrium constants for the formation of the monohydroxo and the binuclear diolated chelate. With an excess of EDTA, Ermolaev and Krot[8] found that a 2:3 U(IV)–EDTA chelate was formed, while with an excess of U(IV) they postulated the formation of a 2:1 U(IV)–EDTA chelate.

Kuteinikov[9] investigated the 1:1 chelate formed between U(IV) and "Arsenazo" [3-(2-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid], and Nemodruk and Palei[10] studied the chelates formed with Arsenazo III. Adams and Smith[11] determined stability constants for the 1:1 U(IV)–citric acid chelate, while Rydberg, *et al.*,[12–15] obtained values for the overall stability constants of the 1:1, 1:2, 1:3, and 1:4 chelates formed between U(IV) and acetylacetone. Also, Calvin and Zebroski[16] obtained a stability constant for the thenoyltrifluoroacetone chelate of U(IV).

Since the above references cover all of the previous work on the aqueous complex chemistry of U(IV), it is quite evident that relatively little is known about the complexes of this metal ion. Consequently, the purpose of this investigation is to obtain equilibrium data on the coordinating tendencies of the aqueous uranium(IV) ion with a number of chelating ligands. This study will also deal with further reactions of the chelates of U(IV), such as their hydrolysis and olation reactions, of the type that have been found to take place for analogous Zr(IV)[17] and Th(IV)[18] compounds.

Experimental Section

Materials. Preparation of Uranium(IV) Solution. An aqueous uranium(IV) chloride solution was prepared from Fisher certified uranyl nitrate hexahydrate using several ammonia precipitations to remove nitrate. The final precipitate was dissolved in a small excess of hydrochloric acid and diluted to the desired strength.

The electrolysis cell is basically the same as that described by Kern and Orlemann[19] who employed a small anode compartment with a platinum spiral as the anode suspended in a large cathode compartment with a large pool of mercury as the cathode. The capacity of the cell was approximately 100 ml. The reduction was carried out at a potential of 6.0 v for a period of 1 hr resulting in complete reduction to U(IV) plus partial overreduction of some of the U(IV) to U(III). The resulting solution of U(IV) and U(III) in acid media (total U = 0.020 *M*, excess HCl = 0.050 *M*) was then stored under nitrogen in the apparatus designed by McEwan and De Vries.[20] The presence of the U(III) in the stock solution ensured that none of the uranium was in the uranyl form and also served the purpose of removing any remaining traces of oxygen in the system.

The solution was analyzed for total uranium content by precipitation with ammonia, and subsequent ignition to U_3O_8, according to the method of Rodden and Warf.[21] The same solution was also titrated with ceric ammonium sulfate by the method of Sill and Petersen[22] to determine the total U(IV) content. This titration was performed only after exposing the solution to be titrated to the air for a short period of time to oxidize the U(III) present to the U(IV) form. Excellent agreement was obtained between the gravimetric and volumetric determinations.

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[2] Abstracted from a thesis submitted by G. H. Carey to the Faculty of Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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The "free acidity" of the U(IV) stock solution (*i.e.*, the excess acid present if all the U(IV) is considered to be in the form of the pure aquo ion) was determined by potentiometric titration of the solution after the addition of a molar equivalent of recrystallized diethylenetriaminepentaacetic acid (DTPA). Because of the exceptionally high stability of the U(IV)–DTPA chelate in acid solution, direct titration of the solution with standard base gave the "free acidity" plus 5.000 equiv of acid with a high degree of precision.

The stock solution prepared as indicated above remained constant in U(IV) content and free acidity, within the limits of accuracy of available analytical techniques, for over a year.

Ligands. A Fisher certified sample of the disodium salt of N,N,N′,N′-ethylenediaminetetraacetic acid (EDTA) was employed. Nitrilotriacetic acid (NTA), iminodiacetic acid (IMDA), 1,2-cyclohexanediaminetetraacetic acid (CDTA), N-hydroxyethylethylenediaminetriacetic acid (HEDTA), N-hydroxyethyliminodiacetic acid (HIMDA), and triethylenetetraminehexaacetic acid (TTHA) were obtained through the courtesy of the Dow Chemical Co., while diethylenetriaminepentaacetic acid (DTPA) was purchased from K and K Laboratories.

All ligands used were of reagent grade, or of the highest available purity, and were recrystallized whenever necessary; the purity was checked in each case by potentiometric titration and by complete elemental analyses.

Potentiometric Procedure. A Beckman Model G pH meter was used to determine hydrogen ion concentrations. Potentiometric measurements were carried out in a jacketed titration cell of 70-ml capacity which had a magnetic stirrer and was fitted with the aid of a large rubber stopper with nitrogen inlet and outlet tubes, microburet delivery tube, and glass and saturated calomel extension electrodes. Measurements were made at a temperature of 25.3°. The ionic strengths of the media were maintained constant at 0.10 or 1.00 *M* by the addition of potassium chloride to the experimental solution. The electrode system was calibrated with acetic acid, HCl, and NaOH to give $-\log [H^+]$ values directly. With acetic acid, the actual hydrogen ion concentration was determined on the basis of the data tabulated by Harned and Owen.[23] In this work pH is defined as a concentration term, $-\log [H^+]$, rather than the frequently employed activity function, $-\log a_{H^+}$, which is not a measurable quantity.

For the actual titration, a measured quantity of the uranium(IV) chloride stock solution was run from the inert atmosphere buret directly into the titration cell already containing a solution of potassium chloride and the appropriate amount of the acid form of the ligand. In all titrations the amounts of ligand and metal ion employed were such as to achieve as precisely as possible a 1:1 molar ratio in the cases of EDTA, CDTA, HEDTA, DTPA, and TTHA, and a 2:1 molar ratio in the cases of NTA, HIMDA, and IMDA. Oxygen was then run through the solution for 3 min to oxidize the U(III) present, and then nitrogen was bubbled through again to purge the system of oxygen. Nitrogen was kept flowing continuously throughout the rest of the potentiometric determination to prevent oxygen from coming into contact with the uranium(IV) solution. Small increments of base were then added from a microburet, and pH measurements were made until the pH of the solution reached a value of 10 or more. Successive pH readings which showed no variation over a period of 10–30 min were considered as an indication that the system was at equilibrium.

Spectral Measurements. All spectral measurements were made using a Cary 14 recording spectrophotometer. A 10-cm cell was used in all measurements, and all absorbance values reported were extrapolated back to zero time of removal from nitrogen atmosphere, or time of mixing, to avoid possible errors arising from polymerization or oxidation of U(IV).

Calculations. Hydrolysis and Dimerization. If the normal metal chelate is designated as ML, the following reactions may be written for hydrolysis and dimerization

$$\mathrm{ML} \rightleftharpoons \mathrm{MLOH} + \mathrm{H}^+ \qquad K_1 = \frac{[\mathrm{MLOH}][\mathrm{H}^+]}{[\mathrm{ML}]} \tag{1}$$

$$2\mathrm{ML} \rightleftharpoons (\mathrm{MLOH})_2 + 2\mathrm{H}^+ \qquad K_\mathrm{D} = \frac{[(\mathrm{MLOH})_2][\mathrm{H}^+]^2}{[\mathrm{ML}]^2} \tag{2}$$

where MLOH represents the mononuclear monohydroxo chelate compound, and $(MLOH)_2$ represents the binuclear diolated chelate species.

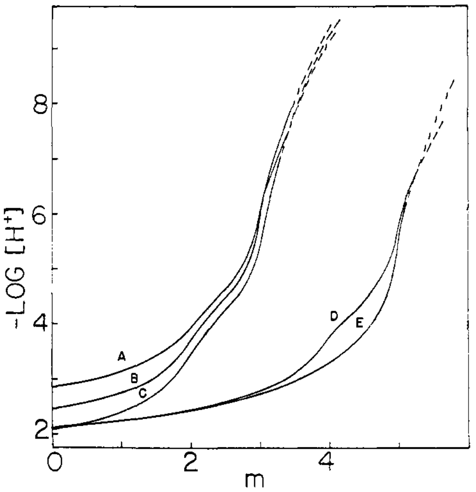

Figure 1. Potentiometric titrations involving uranium(IV) ion at 25.3° and μ = 0.10 (KCl); *m* = moles of base added per mole of metal ion: (A) 1:1 U(IV)–EDTA, 7.50×10^{-4} *M;* (B) 1:1 U(IV)–EDTA, 2.00×10^{-3} *M;* (C) 1:1 U(IV)–EDTA, 5.00×10^{-3} *M;* (D) 1:1 U(IV)–CDTA, 2.00×10^{-3} *M;* (E) 1:2 U(IV)–NTA, 2.00×10^{-3} *M* in U(IV). - - - - indicates drifting of $-\log [H^+]$ readings; protonated forms of ligands at beginning of titration are H_2L^{2-} (EDTA), H_4L (CDTA), and H_3L (HIMDA).

By employing the quantities T_M, the total concentration of metal species, T_L, the total concentration of ligand species (where $T_M = T_L = [ML] + [MLOH] + 2[(MLOH)_2]$), and T_{OH}, the number of moles of base added per liter of solution beyond that required to form the chelate compound ML (where $T_{OH} = [MLOH] + 2[(MLOH)_2] + [OH^-] - [H^+]$), and noting that T_M equals T_L, it follows that

$$(T_{OH} + [H^+] - [OH^-])[H^+]/[ML] = K_1 + 2K_D[ML]/H^+] \tag{3}$$

where $[ML] = T_L - T_{OH} + [OH^-] - [H^+]$. This relationship assumes that dihydroxo forms of the metal chelate and higher polynuclear species are not present. Equation 3 indicates that a plot of $(T_{OH} + [H^+] - [OH^-])[H^+]/[ML]$ against $2[ML]/[H^+]$ should yield a straight line if a dimer is the predominant polynuclear form. The slope of the line would be equal to K_D and the intercept at a $[ML]/[H^+] = 0$ would be equal to K_1. Thus the linearity of a plot of the quantities in eq 3 supports the conclusion that diolated dimer is formed in solution.

U(IV)–TTHA System. If it is assumed that monoprotonated and simple 1:1 chelates are the only species present in the buffer region from *m* = 0 to *m* = 6.00, the dissociation of the monoprotonated species may be given by

$$\mathrm{MHL} \rightleftharpoons \mathrm{ML} + \mathrm{H}^+ \qquad K_\mathrm{MHL} = \frac{[\mathrm{H}^+][\mathrm{ML}]}{[\mathrm{MHL}]} \tag{4}$$

If the total concentration of ligand species T_L is equal to the total concentration of metal species T_M, and T_{OH} is the total moles of base added per liter of solution from the start of the titration, it follows that

$$K_\mathrm{MHL} = \frac{[\mathrm{H}^+](T_\mathrm{OH} - 5T_\mathrm{M} + [\mathrm{H}^+] - [\mathrm{OH}^-])}{(6T_\mathrm{M} - T_\mathrm{OH} - [\mathrm{H}^+] + [\mathrm{OH}^-])} \tag{5}$$

Results

1:1 U(IV)–EDTA System. The 1:1 U(IV)–EDTA was investigated potentiometrically at three different concentrations, 7.5×10^{-4}, 2.0×10^{-3}, and 5.0×10^{-3} *M*, as illustrated by curves A, B, and C of Figure 1. The initial $-\log [H^+]$ value in all three curves is, as precisely as can be measured, two times the initial metal ion concentration, and thus the 1:1 metal chelate compound must be completely formed even before the addition of base. In the low buffer region from *m* = 0 to *m* =

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[23] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed, Reinhold Publishing Corp., New York, N. Y., 1950, pp 485, 523, 578.

Table I. Equilibrium Constants of U(IV) and Th(IV) Chelates

Ligand	Equilibrium quotient	Log equilibrium constant U(IV)[a]	Log equilibrium constant Th(IV)[b]
EDTA (H_4L)	$[ML]/[M^{4+}][L^{4-}]$	25.8 ± 0.2[d] (25.83)[e]	23.2 ± 0.1[f]
	$[ML]/[MLOH^-][H^+]$	4.72 ± 0.01 (4.58 ± 0.01[c])	7.04[h]
	$[ML]^2/[(MLOH)_2{}^{2-}][H^+]^2$	6.53 ± 0.04 (6.68 ± 0.04[c])	9.82[h]
	$[(MLOH)_2{}^{2-}]/[MLOH^-]^2$	2.9 ± 0.05 (2.5 ± 0.05[c])	4.3[h]
CDTA (H_4L)	$[ML]/[M^{4+}][L^{4-}]$	26.9 ± 0.2[d]	24.9 ± 0.2[g]
	$[ML]/[MLOH^-][H^+]$	4.85 ± 0.01	7.58[h]
	$[ML]^2/[(MLOH)_2{}^{2-}][H^+]^2$	6.24 ± 0.04	10.84[h]
	$[(MLOH)_2{}^{2-}]/[MLOH^-]^2$	3.5 ± 0.05	4.3[h]
HIMDA (H_3L)	$[M(HL)_2]/[M(HL)_2(OH)^-][H^+]$	3.67 ± 0.02	...
DTPA (H_5L)	$[ML^-]/[M^{4+}][L^{5-}]$	...	>27[h]
	$[ML^-]/[MLOH^{2-}][H^+]$	7.69 ± 0.02	~8.9[h]
TTHA (H_6L)	$[MHL^-]/[ML^{2-}][H^+]$	2.28 ± 0.03	...

[a] 25°, $\mu = 0.10$ (KCl). [b] 25°, $\mu = 0.10$ (KNO_3). [c] 25°, $\mu = 1.0$ (KCl). [d] 20°, $\mu = 0.10$ (KCl). [e] Reference 7, 25°, $\mu = 0.10$ ($NaClO_4$). [f] Reference 26, 20°, $\mu = 0.10$ (KNO_3). [g] Reference 27, 20°, $\mu = 0.10$ (KNO_3). [h] Reference 18.

2, the only reaction taking place is the titration of the 2 moles of $[H^+]$ ion displaced per mole of ligand (H_2L^{2-}).

After the slight inflection at $m = 2$, there is a second buffer region which is seen to be quite concentration dependent and which culminates in a fairly well-defined inflection at $m = 3.00$. The hydroxo complex formed may be the simple ethylenediaminetetraacetatohydroxouranate(IV) complex (U(IV)-EDTA-OH)$^-$ as suggested by Smith.[5] However, it is possible that this simple monohydroxo chelate will undergo further reaction to form a binuclear diolated chelate species as shown by Ermolaev and Krot.[8]

Analysis of the potentiometric data in the buffer region between $m = 2$ and $m = 3$, shows an increase in the acid dissociation constant of the U(IV) chelate as the concentration increases, if it is assumed that the monohydroxo mononuclear chelate is the only species being formed. The observed change in pK is an indication of the formation of polynuclear hydrolyzed species in solution. In order to test the possibility of the formation of a binuclear species, the data were plotted with the aid of eq 3. A straight-line plot was obtained (Figure 2) confirming the formation of a binuclear diolated chelate, and the corresponding hydrolysis and dimerization constants are listed in Table I.

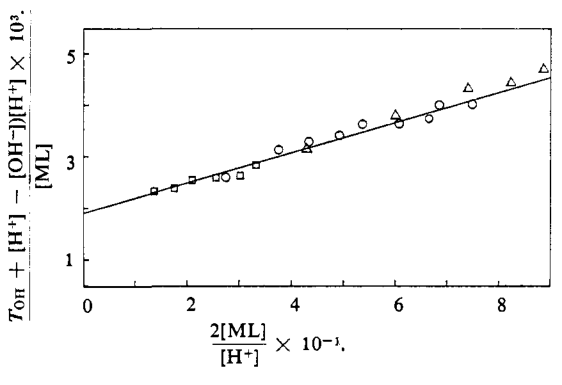

Figure 2. Binuclear diolated chelate formation from 1:1 U(IV)-EDTA chelate in accordance with eq 3 at $\mu = 0.10$ (KCl) and 25.3°: □, $T_M = 7.50 \times 10^{-4}$ M; ○, $T_M = 2.00 \times 10^{-3}$ M; △, $T_M = 5.00 \times 10^{-3}$ M.

Finally drifting of $-\log [H^+]$ values is noted at high pH above $m = 3.2$ for all three concentrations. This phenomenon is an indication of even further hydrolysis and olation of the U(IV) chelate. It should be noted that no precipitation is observed in any of the three different titrations, and that hydrolysis therefore produces only soluble, though perhaps very complex, polynuclear chelates containing hydroxo bridges. Similar results were obtained for this system at ionic strength 1.0 and the equilibrium constants determined are given in Table I.

1:1 U(IV)-CDTA System. The 1:1 U(IV)-CDTA system was studied potentiometrically in a $\mu = 0.10$ M KCl medium at three different concentrations, 7.5×10^{-4} M (not shown), 2.0×10^{-3} M (Figure 1, curve D), and 5.0×10^{-3} M (not shown). The resulting curves are similar to the 1:1 U(IV)-EDTA curves described above. There is a long low buffer region from $m = 0$ to $m = 4$, where the only reaction is the neutralization of the $[H^+]$ ion which was displaced at the start of the titration by complete formation of the 1:1 U(IV) chelate.

At $m = 4.00$ there is a slight inflection followed by a concentration-dependent buffer region and another fairly well defined inflection at $m = 5.00$. Here also, a plot of the data with eq 3 gave a straight line showing the existence of a binuclear diolated chelate. Values of the hydrolysis and dimerization constants were calculated and are given in Table I.

Finally, drifting of $-\log [H^+]$ values indicating further hydrolysis and/or polymerization was noted for m values above 5.3. Once again no precipitate is noted during the titration even at high m and $-\log [H^+]$ values, indicating that the hydroxo species formed at high $-\log [H^+]$ are stable.

1:2 U(IV)-NTA System. Potentiometric curves for 2.0×10^{-3} M (Figure 3, curve E) and 5.0×10^{-3} M (not shown) concentrations were obtained for the 1:2 U(IV)-NTA system. These curves exhibit an initial $-\log [H^+]$ value which is, as precisely as can be determined, six times the initial metal ion concentration, indicating complete formation of the 1:2 U(IV)-NTA chelate at the start of the titration. The sharp inflection at $m = 6.00$ shows that the 1:2 chelate is extremely stable. Beyond a value of $m = 6.0$ ($-\log [H^+] =$

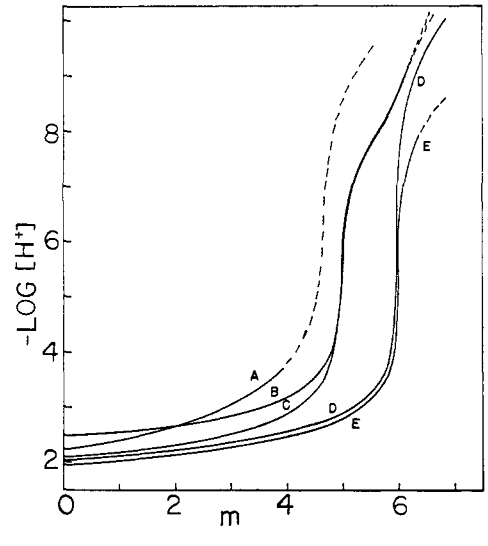

Figure 3. Potentiometric titrations involving uranium(IV) at 25.3° and μ = 0.10 (KCl); m = moles of base added per mole of metal ion; (A) 1:1 U(IV)-HEDTA, 2.00 × 10^{-3} *M;* (B) 1:1 U(IV)-DTPA, 7.50 × 10^{-4} *M;* (C) 1:1 U(IV)-DTPA, 2.00 × 10^{-3} *M;* (D) 1:1 U(IV)-TTHA, 2.00 × 10^{-3} *M;* (E) 1:2 U(IV)-NTA, 2.00 × 10^{-3} *M* in U(IV). ---- indicates drifting of $-\log [H^+]$ readings; all ligands introduced as fully protonated species, H_4L (HEDTA), H_5L (DTPA), H_3L (NTA), and H_6L (TTHA).

~7), the chelate begins to hydrolyze. Since there is no precipitation even at high $-\log [H^+]$ values, soluble polynuclear chelates containing hydroxide ions as bridging groups are probably formed.

1:2 U(IV)-HIMDA System. The 1:2 U(IV)-HIMDA system was studied with U(IV) concentrations of 7.50 × 10^{-4} *M* (not shown), 2.0 × 10^{-3} *M* (Figure 1, curve E), and 5.0 × 10^{-3} *M* (not shown). The initial $-\log [H^+]$ value for all three concentrations corresponds to 4 moles of $[H^+]$ ion per mole of metal ion, thus showing the complete formation of the "normal" 1:2 chelate with no displacement of protons from the hydroxyethyl group at the start of the titration.

The data in the buffer region between m = 4 and m = 5 yielded a constant value of pK_1 for all three concentrations, indicating the formation of a mononuclear hydroxo chelate, or the displacement of a proton from one of the hydroxyethyl groups of the metal chelate. The value of pK_1 is given in Table I.

Finally, there is a fairly good inflection at m = 5.0 followed by drifting of the $-\log [H^+]$ values at m = 5.4 and $-\log [H^+]$ = 7, showing that further extensive hydrolysis and probably polymerization are taking place. Once again no precipitate is noted at any point throughout the titration.

1:2 U(IV)-IMDA System. Since the ligand IMDA is a rough analog of half of an EDTA molecule, it was considered of interest to study the 1:2 U(IV)-IMDA system for comparison with the series EDTA, CDTA, HIMDA. Also, if the hydroxyethyl group of the HIMDA does not combine with the U(IV) in the formation of the 1:2 chelate, the 1:2 curve of U(IV) with IMDA should be approximately the same. However, the resulting 1:2 U(IV)-IMDA titration produced a heavy white precipitate from the start of the titration, and an extremely poor titration curve with a weak inflection somewhere between m = 4.4 and m = 4.7 was obtained.

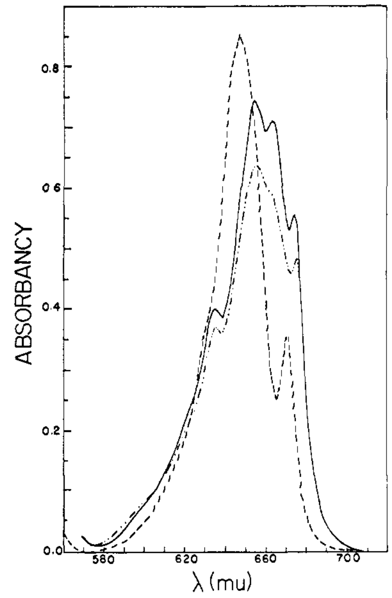

Figure 4. Absorption spectra involving U(IV) ion and U(IV) chelates at μ = 0.10 (KCl) and 20°: ----, U(IV), 1.40 × 10^{-3} *M*, $[HClO_4]$ = 2.50 *M;* ——, 1:1 U(IV)-EDTA, 1.40 × 10^{-3} *M*, $-\log [H^+]$ = 2.12, 1.40; -·-·-·, 1:1 U(IV)-CDTA, 1.40 × 10^{-3} *M*, $-\log [H^+]$ = 2.10.

1:1 U(IV)-HEDTA System. A 2.0 × 10^{-3} *M* solution of U(IV) and HEDTA (Figure 3, curve A) was studied potentiometrically in order to determine the effect of replacing one of the carboxylate groups of EDTA with a hydroxyethyl group in HEDTA. The initial $-\log [H^+]$ value corresponds to a hydrogen ion concentration, as precisely as can be determined, three times that of the analytical metal ion concentration, showing that at the start of the titration the 1:1 U(IV)-HEDTA complex is completely formed and that the hydroxy group of the HEDTA does not react initially with the metal ion with displacement of a hydrogen ion. The lower buffer region up to m = 2 is due to the titration of the free hydrogen ions liberated by the formation of the 1:1 chelate. Beyond this point various hydroxo and/or oleated species are probably formed since drifting of the $-\log [H^+]$ values was noted around m = 3.90 and $-\log [H^+]$ = 3.6. Finally there is a fairly long sloping inflection which occurs between m = 4.65 and m = 4.80. This inflection is probably similar in origin to the inflection noted by Bogucki[24] at $m = 4^2/_3$ for the 1:1 Th(IV)-HEDTA system. Again no precipitate is visible even at high m and $-\log [H^+]$ values.

1:1 U(IV)-DTPA System. Since eightfold coordination in the 1:2 U(IV)-NTA system produced a chelate of extremely high stability, it was of interest to attempt the complete coordination of U(IV) with a single ligand which has eight donors, namely, DTPA. The resulting potentiometric curves for various concentrations of the 1:1 U(IV)-DTPA system (7.5 × 10^{-4} *M* (Figure 3, curve B), 2.0 × 10^{-3} *M* (Figure 3, curve C), and 5.0 × 10^{-3} *M* (not shown)) all display a long buffer region at very low $-\log [H^+]$ values which terminates in an extremely sharp inflection at m = 5.00, showing the formation of a very stable 1:1 chelate. The initial $-\log [H^+]$ values of all three solutions show that all five hydrogens are dissociated

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(24) R. F. Bogucki, and A. E. Martell, *J. Am. Chem. Soc.*, in press.

from the ligand before the addition of base, and thus the 1:1 complex must be completely formed at the start of the titration.

Beyond $m = 5.00$, however, there is a second buffer region around $-\log [H^+] = 8$ which culminates in a slight inflection at $m = 6.0$ for all three concentrations. This second buffer region is seen to be independent of concentration and most likely involves the dissociation of a coordinated water molecule to form a monohydroxo chelate.

Analysis of the data in the buffer region from $m = 5.00$ to $m = 6.00$ yielded a perfectly constant value of pK_1 for all three concentrations, which is given in Table I.

Beyond $m = 6$ (and at high pH) further hydrolysis occurs, as evidenced by the drifting of $-\log [H^+]$ values starting around $m = 6.2-6.4$. No precipitate occurred throughout the entire titration.

1:1 U(IV)–TTHA System. To complete the series EDTA, DTPA, a 1:1 potentiometric curve of U(IV) with decadentate TTHA (Figure 3, curve D) was obtained displaying a long buffer region at low $-\log [H^+]$ culminating in an extremely sharp inflection at $m = 6.00$, indicating the formation of an exceptionally stable 1:1 chelate. The initial $-\log [H^+]$ value of the solution corresponds to 5.24 moles of hydrogen ion dissociated from the hexabasic ligand. As a result of this initial $-\log [H^+]$ reading as well as the raising of the buffer region of the 1:1 U(IV)–TTHA curve over that of a theoretical plot calculated on the assumption of no intermediate hydrogen complex formation (same as Figure 3, curve E), it is probable that a monoprotonated 1:1 U(IV)–TTHA chelate is present in the low buffer region.

Assuming that in the low buffer region the only reaction occurring is the dissociation of the monoprotonated chelate MHL to form the simple 1:1 U(IV)–TTHA chelate, an acid dissociation constant for the MHL species was calculated from 14 experimental points between $m = 0.02$ and $m = 5.44$ using eq 5. A constant value for K_{MHL} was obtained and is shown in Table I, thus verifying the original assumptions.

The extremely high stability of the 1:1 U(IV)–TTHA chelate which is finally formed can be clearly seen in both the extreme sharpness of the inflection at $m = 6.00$ when compared to all the other systems previously mentioned and also in the fact that no hydrolysis or olation of the 1:1 chelate is noted even at the highest $-\log [H^+]$ values attained.

Determination of Stability Constants. 1:1 U(IV)–EDTA. In order to determine the stability constant of U(IV)–EDTA at $\mu = 0.10$ (KCl) and 20.0°, a competition reaction between Th(IV), U(IV), and EDTA was employed. The experiments were carried out at $-\log [H^+] = 1.40$ and $-\log [H^+] = 1.50$ since at these $-\log [H^+]$ values the rate of polymerization of UOH^{+3} is slow,[25] no hydroxo or polynuclear forms of U(IV)–EDTA are present in solution, the U(IV)–EDTA chelate does not dissociate to any detectable extent, and an ionic strength of $\mu \sim 0.10$ can be maintained. The reasonable assumption that no protonated forms of the 1:1 Th(IV)–EDTA chelate are present was also made. This assumption is considered valid in view of the fact that the Fe(III)–EDTA chelate does not form protonated species under the same conditions.

In the normal determination the absorbance of a 1:1:5 U(IV)-EDTA-TH(IV) solution 1.0×10^{-3} *M* in U(IV) was obtained at $\lambda = 6640$ A. Of the various species present in the competition reaction, U(IV), UOH^{+3}, U(IV)–EDTA, Th(IV)–EDTA, and Th(IV), only the U(IV), UOH^{+3}, and U(IV)–EDTA species absorb in the region of interest. The spectra of U(IV) and UOH^{+3} had been investigated previously by Kraus and Nelson,[26] while that of U(IV)–EDTA had been given by Palei and Hsu.[4] There is a shift of the strong U(IV) absorption peak to higher wavelengths upon complexation by EDTA, the maximum difference in absorption between the two curves occurring at $\lambda = 6640$ A. UOH^{+3} absorbs only very slightly at this wavelength.[26] Differences in extinction coefficients at 6640 and 7100 A were used rather than absolute extinction coefficients at one wavelength since small variations in "background" absorption become less important. Using the hydrolysis constant for U(IV) at $\mu = 0.10$ previously determined by Kraus and Nelson,[26] and the molar extinction coefficients for the three U(IV) species in solution, it was possible to measure the concentration of each of these species using the usual relationship

$$A = \epsilon_{\mathrm{U-EDTA}}(10)[\mathrm{U-EDTA}] + \epsilon_{\mathrm{U}}(10)[\mathrm{U(IV)}] + \epsilon_{\mathrm{UOH}}(10)[\mathrm{UOH^{3+}}]$$

where $\epsilon_{\mathrm{U-EDTA}} = 49.34$, $\epsilon_{\mathrm{U}} = 20.60$, and $\epsilon_{\mathrm{UOH}} \cong 3$. Thus by measuring the absorbance of a 1:1:5 U(IV)–EDTA–Th(IV) solution and knowing the stability constant for Th(IV)–EDTA ($\log K_{\mathrm{Th-EDTA}} = 23.2 \pm 0.1$) previously determined by Schwarzenbach, *et al.*,[27] it was a simple matter to determine the equilibrium constant K^*

$$K^* = \frac{[\mathrm{Th(IV)}][\mathrm{U(IV)-EDTA}]}{[\mathrm{Th(IV)-EDTA}][\mathrm{U(IV)}]} = \frac{K_{\mathrm{U-EDTA}}}{K_{\mathrm{Th-EDTA}}} \tag{6}$$

for the displacement reaction

$$\mathrm{Th(IV)\text{-}EDTA} + \mathrm{U(IV)} \overset{K^*}{\rightleftharpoons} \mathrm{U(IV)\text{-}EDTA} + \mathrm{Th(IV)}$$

The value for $K_{\mathrm{U-EDTA}}$ thus obtained is given in Table I.

The order of addition of the various reagents was reversed, and the same results were obtained indicating that equilibrium is reached rapidly in these systems.

1:1 U(IV)–CDTA. The stability for the 1:1 U(IV)–CDTA chelate was determined with a competition reaction with Th(IV) similar to that described above for EDTA. An approximate value of $K_{\mathrm{U-CDTA}}$, given in Table I, was calculated from the value of log $K_{\mathrm{Th-CDTA}} \sim 24.9$ obtained previously by Carey and Martell.[28] The absorption spectrum of the 1:1 U(IV)–CDTA chelate has almost the same shape as that of the U(IV)–EDTA chelate, although its molar

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(25) K. A. Kraus, F. Nelson, and G. L. Johnson, *J. Am. Chem. Soc.*, 71, 2510 (1949).

(26) K. A. Kraus and F. Nelson, *ibid.*, 72, 3901 (1950).

(27) G. Schwarzenbach, R. Gut, and G. Anderegg, *Helv. Chim. Acta*, 37, 937 (1954).

(28) G. H. Carey and A. E. Martell, unpublished results ($\mu = 0.10$ (KNO_3), 20°, spectrophotometrically determined at 2750 A by competition reaction with Fe(III) at pH 1.90). Because of the light sensitivity of the Fe(III)–CDTA chelate, final measurements were made only after true equilibrium was reached in the absence of light.

extinction coefficient is lower. Here again calculations were carried out with spectra obtained at 6640 A.

Discussion

Formation Constants. The chelating tendencies of U(IV) are greater than those of Th(IV), but chelates of the same composition, and probably similar structure, are formed. In all the U(IV) complexes studied except for the 1:1 U(IV)-TTHA chelate, the complex was completely formed at the start of the titration. For the analogous Th(IV) chelates reported by Bogucki,[24] on the other hand, the 1:2 Th(IV)-NTA and 1:2 Th(IV)-HIMDA chelates were incompletely formed at the start of the titration. Thus the chelates formed between U(IV) and these ligands are more stable than the corresponding Th(IV) chelates.

The increase in stability constants for the U(IV)-EDTA and -CDTA chelates over those for the corresponding Th(IV) chelates (Table I) correlates with the fact that the radius of the U(IV) ion is considerably smaller than that of the Th(IV) ion. This decrease in radius is due to the well-known actinide contraction.[29] This factor would lead to more favorable ΔH and ΔS contributions for the formation of the U(IV) relative to the Th(IV) chelates. Ahrland, Chatt, and Davies[30] have shown that highly charged ions of high basicity such as Zr(IV) and Th(IV) tend to form complexes which are principally ionic in nature. Consequently, the uncomplexed U(IV) ion will have a higher charge/radius ratio which will lead to increased bond strength in the U(IV) chelate and a more highly solvated ion (*i.e.*, more negative partial molal entropy) in the case of U(IV) and subsequent greater entropy increase on coordination with a multidentate ligand.

Although stability constants 1:1 U(IV)-DTPA, 1:1 U(IV)-TTHA, and the 1:2 U(IV)-NTA chelates are not reported in this investigation, it is probable that the order of relative stabilities is HIMDA $<$ CDTA $<$ bis-NTA $\sim$ DTPA $<$ TTHA.

Coordination Requirement. In view of the findings of Hoard[31] on crystalline chelate compounds, U(IV), Zr(IV), and Th(IV) have been shown to have a normal coordination requirement of eight and generally to form dodecahedral complexes. However, the potentiometric data obtained in this work provide evidence that for certain chelates in aqueous solution, the coordination number of U(IV) may be expanded to nine or ten. When the number of donor atoms is less than eight (EDTA, CDTA) or so arranged that less than eight donor groups can coordinate simultaneously with the U(IV) ion, chelate formation at low pH is followed by successive hydrolysis steps, often attendant with polymerization to polynuclear chelates having hydroxo bridges between the metal ions. Even with the U(IV) chelates of DTPA and NTA, in which all eight coordination sites on the metal ion are probably filled by the eight available donor groups of the ligands, hydrolysis reactions still occur at high pH. With DTPA a distinct monohydroxo chelate is formed at a pK value of 7.69. These results suggest the dissociation of a proton from a coordinated water molecule to form a nonacoordinated monohydroxouranium(IV) chelate.

Further evidence for the expansion of the coordination number of U(IV) is seen from the fact that U(IV) forms an extremely stable complex with decadentate TTHA which is completely resistant to hydrolysis. This U(IV)-TTHA complex seems to be more stable than either the NTA or DTPA chelate, so that the additional coordinating groups in TTHA seem to be essential for maximum stability. Thus the present work provides evidence for the expansion of the coordination number of U(IV) from the normal value of eight to nine or ten. This conclusion is similar to the results obtained for analogous chelates of Th(IV), described by Carey, Bogucki, and Martell,[32] and by Bohigian and Martell.[33] It is also supported by the work of Muetterties[34] who postulated decadentate structures for the pentakis(tropolono) chelates of thorium(IV) and uranium(IV).

Hydrolysis Constants. The hydrolysis constants for the 1:1 U(IV)-EDTA and the 1:1 U(IV)-CDTA chelates, as well as the analogous Th(IV) chelates, are compared in Table I. The greater hydrolytic tendency of U(IV)-EDTA over that of U(IV)-CDTA is in accord with the lower stability of the former chelate compound. The greater interaction of the U(IV) ion with CDTA would be expected to more strongly saturate the coordinating tendencies of the U(IV), thus resulting in less interaction of the metal ion with coordinated water and a decrease in tendency toward hydrolysis.

The unusually large hydrolysis constant observed for the 1:2 U(IV)-HIMDA chelate suggests a reaction type that is different from simple dissociation of a coordinated water molecule. It is proposed that here hydrolysis involves displacement of the proton from the hydroxyethyl group and results in the formation of a strong alkoxide-U(IV) coordinate bond. At the start of the potentiometric titration, at least one of the two hydroxyethyl groups of the 1:2 U(IV)-HIMDA chelate may take part in weak coordination of the U(IV) ion without dissociation of a proton. The proximity of the hydroxyethyl group to the U(IV) ion would tend to greatly increase the tendency of the group to dissociate a proton, a reaction that does not take place in aqueous solution in the absence of the metal ion.

The 1:1 U(IV)-DTPA chelate forms a mononuclear monohydroxo chelate with a pK value of 7.69 (Table I). As noted previously,[18] formation of the hydroxo chelate might involve either the displacement of a carboxylate donor of the 1:1 U(IV)-DTPA chelate by a hydroxide ion, or the formation of a nonacoordinated monohydroxouranium(IV) chelate.

The greater hydrolytic tendency of the 1:1 chelates of EDTA, CDTA, and DTPA with U(IV) over the corresponding Th(IV) chelates indicated in Table I correlates with the greater charge/radius ratio of the U(IV) ion, giving stronger ionic bonding of U(IV) with the coordinated hydroxide ion, as well as with other coordinated donor groups.

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(30) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12,** 265 (1958).

(31) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2,** 235 (1963).

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

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

(34) E. L. Muetterties, *J. Am. Chem. Soc.*, **88,** 305 (1966).

Dimerization Constants. Comparison of the hydrolysis and dimerization constants of U(IV)–EDTA and U(IV)–CDTA given in Table I shows that the slightly greater hydrolytic tendency of the U(IV)–EDTA chelate is accompanied by a decrease in its tendency to dimerize. For the corresponding Th(IV) chelates, the difference between the hydrolysis constants is greater, the EDTA chelate again showing the greater tendency to hydrolyze, while the dimerization constants of the CDTA and EDTA chelates are about the same. In attempting to rationalize the influence of constitution on the observed hydrolytic and dimerization tendencies, several factors should be considered: (1) a coulombic effect whereby the greater the coulombic attraction between the hydroxide and metal ion as reflected in the acid dissociation constant, the greater should be the tendency of this same hydroxide ion to form a second ionic bond with another metal chelate to yield a dimer; (2) influence of the nature of the ligand as well as the ionic radius and coordination number of the metal ion upon steric and coulombic repulsions between the negative donor groups of the ligands in the dimer; (3) shielding by the hydrocarbon moieties of the ligand, which would increase the tendency of the chelate to dimerize. Comparing the EDTA *vs.* CDTA dimerization tendencies for the same metal ion, the coulombic effect predicts greater dimerization for the EDTA chelate as indicated by its greater tendency to hydrolyze. The coulombic and steric ligand–ligand repulsions should be somewhat greater for the CDTA dimer, because of the directing influence of the cyclohexane ring on the carboxylate donor groups. Also, the greater hydrophobic nature of the cyclohexane group of CDTA will lead to the formation of a more completely shielded dimer and consequently a higher dimerization constant for the CDTA chelates.

For the U(IV) chelates, the shielding effect which predicts CDTA > EDTA seems to outweight the other factors that predict the opposite trend. However, with Th(IV), the coulombic effect assumes greater importance as indicated by the larger variation in hydrolysis constants between the EDTA and CDTA chelates. In this case the opposing effects seem to balance, resulting in approximately equal dimerization constants.

When the dimerization constants of U(IV) and Th(IV) chelates of the same ligand are compared (Table I), it is found that those of the larger Th(IV) ion always have the greater tendency to dimerize. Although the coulombic effect predicts that the smaller size of the U(IV) ion enhances its tendency to form stronger ionic bonds between the chelated metal ion and the hydroxo groups in the dimer, this effect is overshadowed by the greater opportunity for mutual steric and coulombic repulsions between negative donor groups of the two ligands in the smaller U(IV) dimers.

It is evident from the potentiometric data that no dimerization of the monohydroxo U(IV)–DTPA chelate occurs. This lack of dimerization is to be expected since there would be large coulombic and steric repulsions between ligand donor groups in the ligand, and since the mononuclear species is completely, or almost completely, coordinated by the hydroxide ion and the octadentate DTPA anion. These observations are similar to those described by Bogucki and Martell[18] for the analogous DTPA–Th(IV) chelate compound.

The Structure of Hexa(acetylacetonato)aquotricobalt(II)[1]

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Abstract: Partial hydration of the tetramer of bis(acetylacetonato)cobalt(II), $[Co(AcAc)_2]_4$, leads to $[Co(AcAc)_2]_3H_2O$ which can be isolated as pale purple triclinic crystals. The unit cell dimensions are $a = 9.05$, $b = 10.56$, $c = 19.56$ A; $\alpha = 85.80°$, $\beta = 93.71°$, $\gamma = 101.32°$; measured density, 1.44 g/cm³, calculated density (for $Z = 2$), 1.43 g/cm³. The structure was solved, including hydrogen atoms, and refined by least squares to a residual of 7.0%, using 3040 nonzero reflections. The molecule consists of three octahedrally coordinated cobalt atoms. Two acetylacetonato chelate rings are closed about each cobalt atom and certain oxygen atoms are shared by two cobalt atoms. Two of the octahedra are fused together on a face while the other two share an edge, and the water molecule is part of the terminal octahedron which shares an edge with the central one. The structure may be derived from that of the tetramer, $[Co(AcAc)_2]_4$, by removing one terminal $Co(AcAc)_2$ moiety and inserting the water molecule in the hole which remains in $[Co(AcAc)_2]_3$. It is therefore structurally as well as stoichiometrically part of the series $[Co(AcAc)_2]_4$, $[Co(AcAc)_2]_3H_2O$, $[Co(AcAc)_2]_2(H_2O)_2$, $Co(AcAc)_2(H_2O)_2$, all members of which have now been characterized by X-ray crystallographic study.

Beginning with the reports[3,4] of the trimeric structure of bis(acetylacetonato)nickel(II), $[Ni(AcAc)_2]_3$, it has become clear that the stereochemical behavior of the bis(β-ketoenolato)metal(II) compounds of the first-row metals (except copper) is dominated by their tendency to have a coordination number greater than four. Provided they have no access to additional donor mole-

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[2] Union Carbide Predoctoral Fellow, 1964–1965; National Science Foundation Fellow, 1965–1967.

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