of detailed kinetic analysis.[21] Qualitatively, the significant rate increase observed on adding σ-donor ligands to the sample suggests that, in going to the transition state for the metal atom shift, the compound progresses to an appreciable extent along the path toward dissociated cyclopentadienide anion and metal cation, and that the added ligand serves to increase the rate by stabilizing the increased partial positive charge on the metal atom during the shift. However, the persistence of the unsymmetrical mode of collapse of the vinyl signals in the presence of added donor ligands indicates that even under these circumstances dissociation does not become complete.

It is of some interest that the temperature dependence of the nmr spectrum of π-cyclopentadienyliron dicarbonyl σ-cyclopentadienide has been interpreted as indicating that the metal atom in this compound shifts around the cyclopentadienyl ring by a sequence of 1,2 hops.[8] If both this interpretation and that proposed for the organocopper reagent are correct, the difference between these compounds poses an interesting problem. However, the assignment of the vinylic proton chemical shifts in the iron organometallic compound was based on the assumption that the magnitude of the three-bond coupling between the C*H*Fe proton and the vicinal vinyl proton was greater than that of the corresponding four-bond coupling, and the ambiguity in this type of assignment has already been indicated.[16] In consequence, comparison of the two compounds is most profitably deferred until the stereochemistry of the metal atom shift in each has been more clearly defined.

Experimental Section[22]

σ-Cyclopentadienyl(triethylphosphine)copper was prepared using a modification of Wilkinson and Piper's method.[6a] Commercial cuprous oxide (3.6 g), 10 ml of freshly distilled cyclopentadiene, 7 ml of triethylphosphine, and 20 ml of petroleum ether (bp 30–60°) were refluxed under a nitrogen atmosphere with magnetic stirring for 2 hr and then allowed to stir at ambient temperature for 6 hr. The solvent was removed under reduced pressure, and the resulting brown-black syrup was transferred in a nitrogen-filled glove bag directly to a sublimation apparatus. The product was obtained as hard white or pale yellow-green crystals by slow sublimation at 60° and 0.1 mm. The crystals were moderately stable in the absence of oxygen; *solutions* of the organometallic were much less stable.

Nmr samples were prepared by transferring a suitable quantity of the freshly sublimed material to a flame-dried nmr tube under nitrogen. The tube was capped with a serum stopper and cooled to the temperature of a Dry Ice–acetone bath, at which temperature, sulfur dioxide was condensed into the tube. The sample was warmed briefly to approximately −35°, to allow the organocopper reagent to dissolve, and then inserted into the precooled (−40°) probe of the nmr spectrometer. If the sample was permitted to warm to temperatures above −40° for more than approximately 5 min, decomposition of the sample introduced significant absorption due to impurities in the olefin absorption region.

Acknowledgments. We wish to express our thanks to Dr. Robert Siekman for his help in obtaining mass spectra, and to Drs. S. L. Manatt and D. D. Elleman for permission to use their data prior to publication.

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(21) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Am. Chem. Soc.*, **88**, 3185 (1966).

(22) Nmr spectra were taken at 60 MHz using a Varian A-60 spectrometer equipped with a V-6040 variable-temperature probe and controller. Sweep widths were calibrated using a Krohn-Hite Model 450 oscillator and a Hewlett-Packard Model 524 electronic counter. Calibration of the temperature controller was accomplished by measuring peak separations in a methanol sample. Mass spectra were determined with a Hitachi Perkin-Elmer RMU-6D spectrometer. Spectral calculations were carried out using an IBM 7094 computer, and spectra were plotted by a Calcomp plotter.

Mixed Ligand Chelates of Uranium(IV)[1,2]

G. H. Carey and A. E. Martell[3]

Contribution from the Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois. Received December 14, 1966

Abstract: Potentiometric studies are described for mixed ligand U(IV) chelate formation with ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) as primary ligands. Secondary ligands studied are salicylic acid (SA), 5-sulfosalicylic acid (SSA), disodium 1,2-dihydroxybenzene-3,5-disulfonate (Tiron), pyrocatechol (PY), 5-sulfo-8-hydroxyquinoline (HQS), disodium 1,8-dihydroxynaphthalene-3,6-disulfonate (CS), *o*-phthalate (Ph), and iminodiacetic acid (IMDA). For the mixed ligand chelate systems containing EDTA, combination with the primary ligand is complete before combination with the secondary ligand takes place. For the less stable NTA systems, overlapping of reactions of the primary and secondary ligands is much more extensive. The relative magnitudes of the equilibrium constants for combination of secondary ligands with the U(IV)–EDTA chelate are CS > Tiron > PY > SSA > HQS > IMDA ≫ Ph. The mixed ligand chelates of U(IV) are more stable than those of Th(IV) by 1–3 log K units.

Uranium(IV) and thorium(IV) ions are generally considered to have coordination numbers of about eight in solution and probably form dodecahedral complexes similar to the structures of the crystalline Th(IV) complexes determined by Hoard.[4] In the case of the 1:1 complexes of Th(IV) and U(IV) with the N,N,N′,N′-ethylenediaminetetraacetate anion, the ligand can fill no more than six of the eight coordination sites of the metal ion, leaving two coordinating sites free for hydrolysis, polymerization, or olation reactions. A

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(2) Abstracted from a thesis submitted to the Faculty of Illinois Institute of Technology in partial fulfillment of the requirements for the Ph.D. degree, Jan 1966.

(3) Department of Chemistry, Texas A & M University, College Station, Texas.

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

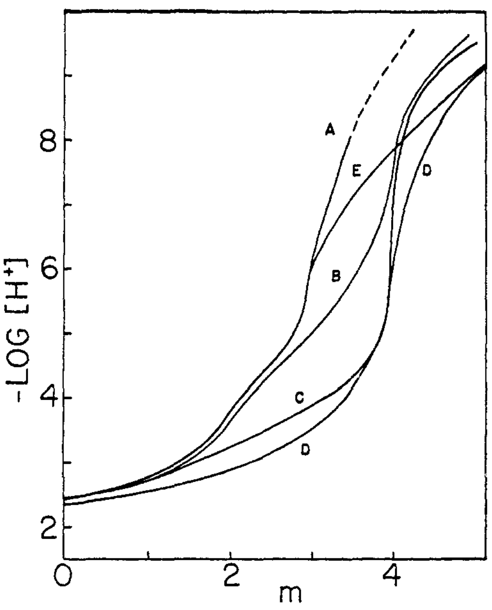

Figure 1. Potentiometric titrations of mixed ligand chelate systems of U(IV) and EDTA; all solutions are 2.0×10^{-3} *M* in U(IV) and adjusted to μ = 0.10 with KCl at the start of the titration; *m* = moles of base added per mole of metal ion: (A) 1:1 U(IV)-EDTA; (B) 1:1:1 U(IV)-EDTA-PY; (C) 1:1:1 U(IV)-EDTA-Tiron; (D) 1:1:1 U(IV)-EDTA-IMDA; (E) composite curve for the 1:1:1 U(IV)-EDTA-Tiron system; ---- indicates drifting of $-\log [H^+]$ readings; EDTA was introduced as the disodium salt.

bidentate ligand could therefore fill these two vacant sites to give a mixed ligand chelate. In the case of a 1:1 complex formed between U(IV) and a quadridentate ligand such as NTA (nitrilotriacetic acid), there are four coordination sites left upon for hydrolysis and olation reactions which, because of their complexity, would be almost impossible to characterize. However, on the addition of two bidentate groups to complete the coordination sphere of the U(IV), a stable mixed ligand complex, resistant to hydrolysis, might conceivably be formed.

In this study, various bidentate ligands are combined with aqueous EDTA and NTA chelates of U(IV), in order to completely fill the coordination sphere of the metal. Although no data have been previously reported on mixed ligand chelates of U(IV), studies of mixed ligand complexes involving thorium(IV),[5] zirconium(IV),[6] the rare earths,[7] and other metals[8] have been published. Comparison of mixed ligand chelate formation of U(IV) with that of Th(IV), and of other metal ions, would yield useful information about the nature of the aqueous complex chemistry of these metal ions.

Experimental Section

Materials. Uranium(IV) Solution. The preparation, storage, and standardization of the unique U(IV)-U(III) stock solution are described in detail in a previous paper.[9] The final solution is approximately 0.026 *M* in UCl_4 and 0.050 *M* in excess HCl.

Ligands. Fisher certified samples of the disodium salt of N,N,N′,N′-ethylenediaminetetraacetic acid (EDTA) and potassium acid phthalate (Ph) were used. The 5-sulfosalicylic acid (SSA), salicylic acid (SA), chromotropic salt (disodium 1,8-dihydroxynaphthalene-3,6-sulfonate (CS)), pyrocatechol (PY), and 8-hydroxy-5-quinolinesulfonic acid (HQS) were purchased from the Eastman Kodak Co., while the nitriiotriacetic acid (NTA) and iminodiacetic acid (IMDA) were obtained through the courtesy of the Dow Chemical Co. Tiron (disodium 1,2-dihydroxybenzene-3,5-disulfonate) was obtained from the La Motte Chemical Products Co.

All ligands used were of reagent grade of the highest available purity and were recrystallized whenever necessary. In the case of the water-soluble ligands, a stock solution 0.020 *M* in the ligand was prepared and standardized potentiometrically with a standard solution of NaOH. With relatively insoluble ligands as well as ligands whose aqueous solutions are susceptible to oxidation or to some other form of decomposition, the purity of the sample was determined and the ligand was introduced into the experimental solution as an accurately weighed solid.

Apparatus and Procedure. A Beckman Model G pH meter was used to determine hydrogen ion concentrations. Potentiometric measurements were carried out in a magnetically stirred, jacketed titration cell of 70-ml capacity fitted 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 strength was maintained at 0.10 *M* by the addition of potassium chloride to the experimental solution. Purified nitrogen was bubbled through the solution in order to exclude carbon dioxide. The electrode system was calibrated with acetic acid, HCl, and NaOH to give $-\log [H^+]$ values directly.

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 ligands. Oxygen was then run through the solution for 3 min to oxidize the U(III) present back to U(IV), and the nitrogen was bubbled through the solution to purge the system of oxygen. Nitrogen was kept flowing continuously throughout the rest of the potentiometric determination to preclude the possibility of any oxygen coming into contact with the uranium(IV) solution. The potentiometric titration was then carried out in the usual manner.

Calculations. Stability constants of mixed ligand chelates were calculated in favorable cases for the combination of the 1:1 EDTA chelates with a second ligand with methods similar to those employed by Thompson and Loraas.[7]

Results

U(IV)-EDTA-Tiron, U(IV)-EDTA-CS, U(IV)-EDTA-PY. The 1:1:1 U(IV)-EDTA-Tiron solution yields a potentiometric curve (Figure 1, curve C) exhibiting a long low buffer region with an extremely sharp inflection at *m* = 4.00. The 1:1 U(IV)-EDTA chelate is completely formed at the start of the titration since the initial hydrogen ion concentration shows that there are two free hydrogen ions present in solution per U(IV) ion. The part of the buffer region from *m* = 0 to *m* ≅ 2.0 consists of the titration of the two free hydrogen ions from the 1:1 U(IV)-EDTA chelates. This can be verified by the perfect match of the 1:1 U(IV)-EDTA curve (Figure 1, curve A) with the mixed ligand curve up to an *m* value of about 1.5.

From *m* ≅ 1.5 to *m* = 4.00 the two hydroxyl groups on the Tiron become bound to the 1:1 chelate to form the 1:1:1 mixed ligand chelate. The buffer region terminates with an extremely sharp inflection at *m* = 4.00 indicating that at this point the mixed ligand chelate is completely formed.

Thus the mixed ligand chelate is formed in two steps. In the first step from *m* = 0 to 2.00 the completely formed 1:1 EDTA-U(IV) species is the only chelate present, while from *m* = 2.00 to 4.00 the Tiron becomes bound to the 1:1 U(IV)-EDTA complex to form the 1:1:1 mixed ligand chelate. This conclusion is strengthened by visual evidence, whereby the solution

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[5] G. H. Carey, R. F. Bogucki, and A. E. Martell, *Inorg. Chem.*, **3**, 1288 (1964).

[6] B. J. Intorre and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 3618 (1961).

[7] L. C. Thompson and L. A. Loraas, *Inorg. Chem.*, **2**, 89 (1963).

[8] W. B. Schaap and D. L. McMasters, *J. Am. Chem. Soc.*, **83**, 4699 (1961).

[9] G. H. Carey and A. E. Martell, *ibid.*, in press.

which is green in color because of the presence of the 1:1 U(IV)–EDTA chelate up to about $m = 2.50$ gradually turns yellow between $m = 2.50$ and 4.00, and becomes completely yellow at $m = 4.00$. This yellow color is probably due to the addition of the Tiron to the 1:1 U(IV)–EDTA chelate to form the mixed ligand chelate.

Another proof for the existence of the mixed ligand chelate is the comparison of the 1:1:1 U(IV)–EDTA–Tiron curve with the composite curve, E. Curve C of Figure 1 shows a difference in slope and a large lowering of the buffer region between $m = 2.00$ and 4.00, relative to the composite, which was calculated on the assumption that no mixed ligand chelate is formed. This evidence of increased interaction in the presence of two different ligands indicates the formation of a relatively stable mixed ligand chelate.

The 1:1:1 U(IV)–EDTA–CS (where CS = disodium 1,8-dihydroxynaphthalene-3,6-sulfonate) curve also exhibits a long low buffer region with an extremely sharp inflection at $m = 4.00$. It is superimposable on the previous 1:1:1 U(IV)–EDTA–Tiron curve up to $m = 4.00$, varying slightly from the latter on further addition of base. Here also a color change is noted between $m = 2.5$ and 4.00 and a comparison of the 1:1:1 U(IV)–EDTA–CS experimental curve with the composite curve from the same system yields a difference in shape and a large lowering of the buffer region between $m = 2.00$ and 4.00. Therefore, it is evident that this system must undergo the same reactions as that of the corresponding Tiron system, with the 1:1 U(IV)–EDTA chelate being present from $m = 0.00$ to 2.00, with formation of the mixed ligand chelate between $m = 2.00$ and 4.00.

The 1:1:1 U(IV)–EDTA–PY system (where PY = pyrocatechol) furnishes a potentiometric curve (Figure 1, curve B) that has a very poor sloping inflection at $m = 2.00$, and a well-defined inflection exactly at $m = 4.00$. The initial [H$^+$] concentration shows that the 1:1 U(IV)–EDTA complex is completely formed at the start of the titration, and the lower buffer region up to $m = 2.00$ merely represents the titration of the 2 equiv of hydrogen ion from the 1:1 U(IV)–EDTA chelate. In the second buffer region between $m = 2.00$ and 4.00 the two hydroxyl groups on the pyrocatechol become bound to the 1:1 chelate to form the 1:1:1 U(IV)–EDTA–PY mixed ligand chelate. The green color present up to about $m = 2.7$ changes completely to yellow by $m = 4.00$. Comparison of the 1:1:1 U(IV)–EDTA–PY experimental curve with the composite curve calculated for no mixed ligand chelate formation shows a difference in shape and lower buffer region for the real system between $m = 2.00$ and 4.00. These observations indicate the formation of the mixed ligand chelate in the second buffer region. It is also noted that the formation of the 1:1:1 U(IV)–EDTA–PY complex occurs at a much higher pH than that of the 1:1:1 U(IV)–EDTA–Tiron mixed ligand complex.

It is of interest to compare the above three mixed ligand systems with the behavior of the simple 1:1 U(IV)–EDTA (Figure 2, curve A) chelate compound. With the latter, hydrolysis occurs in the 4.0–5.5 pH range to give a binuclear chelate. With the 1:1:1 U(IV)–EDTA–Tiron system there is no drifting of $-\log [H^+]$ values, or precipitation, which would denote a tendency toward hydrolysis and possibly olation, while with CS and PY drifting is noted starting around $-\log [H^+] = 9.4$ and 10.6, respectively. Thus it is seen that there is a remarkable difference between the hydrolysis tendencies of the chelate and the mixed ligand chelate and that the addition of a second binuclear ligand effectively hinders hydrolysis and polymerization.

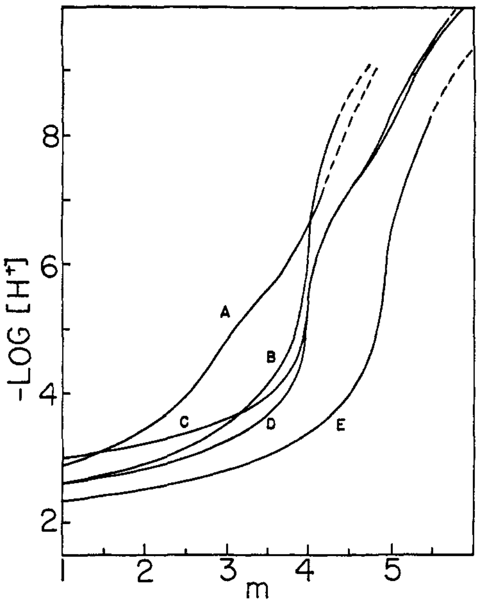

Figure 2. Potentiometric titrations of mixed ligand chelate systems of U(IV) and EDTA; all solutions were adjusted to $\mu = 0.10$ with KCl at the start of the titration; m = moles of base added per mole of metal ion: (A) 1:1:1 U(IV)–EDTA–Ph, 2.0×10^{-3} *M;* (B) 1:1:1 U(IV)–EDTA–SA, 2.0×10^{-3} *M;* (C) 1:1:1 U(IV)–EDTA–HQS, 7.5×10^{-4} *M;* (D) 1:1:1 U(IV)–EDTA–HQS, 2.0×10^{-3} *M;* (E) 1:1:1 U(IV)–EDTA–SSA, 2.0×10^{-3} *M;* - - - - indicates drifting of $-\log [H^+]$ readings; ETDA was introduced as the disodium salt.

U(IV)–EDTA–SA, U(IV)–EDTA–SSA, U(IV)–EDTA–IMDA, U(IV)–EDTA–Ph. The addition of an equivalent of SA (salicylic acid), SSA (5-sulfosalicylic acid), or IMDA (iminodiacetic acid) to the U(IV)–EDTA chelate produced three mixed ligand systems, each of which yielded analogous potentiometric curves indicating reaction of a similar nature. In the 1:1:1 U(IV)–EDTA–SA system (Figure 2, curve B) and the 1:1:1 U(IV)–EDTA–IMDA system (Figure 1, curve D), the titration curves exhibit a single long buffer region at low $-\log [H^+]$ values which terminates in a fairly sharp inflection at $m = 4.00$, while the 1:1:1 U(IV)–EDTA–SSA curve (Figure 2, curve E) yielded a similar curve with an inflection at $m = 5.00$. The lower part of the buffer region from $m = 0.00$ to 3.00 for the 1:1:1 U(IV)–EDTA–SA and 1:1:1 U(IV)–EDTA–IMDA curves, and from $m = 0.00$ to 4.00 for the 1:1:1 U(IV)–EDTA–SSA curve, corresponds to the titration of the hydrogen ion displaced from the 1:1 U(IV)–EDTA complex, and the acidic hydrogen ions from the secondary ligand (1 equiv in the case of the SA and IMDA and 2 in the case of the SSA). Subsequently, between $m = 3$ and 4 with SA and IMDA and $m = 4$ and 5 for SSA, an additional hydrogen ion is displaced from the ligand, showing the formation of the 1:1:1 mixed ligand chelates U(IV)–EDTA–SA, U(IV)–EDTA–IMDA, and U(IV)–EDTA–SSA, respectively.

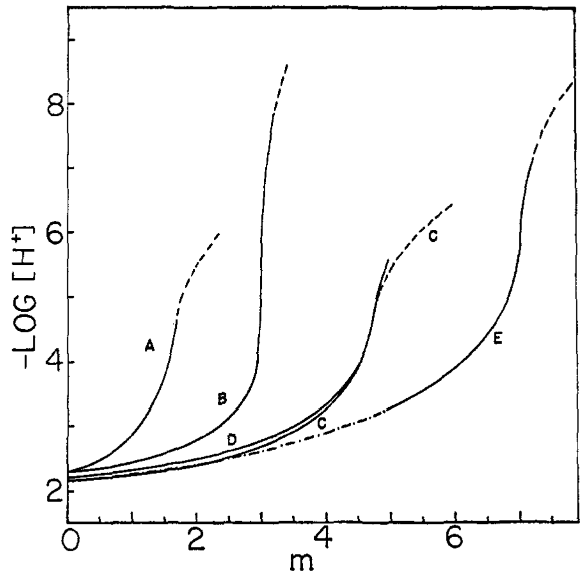

Figure 3. Potentiometric titration of mixed ligand chelate systems of U(IV) and NTA. All solutions were adjusted to μ = 0.10 with KCl at the start of the titration; m = moles of base added per mole of metal ion: (A) 1:4 U(IV)-Tiron, 1.0 × 10^{-3} M in U(IV), also 1:1.5 U(IV)-Tiron, 1.0 × 10^{-3} M in U(IV); (B) 1:2 U(IV)-NTA, 1.0 × 10^{-3} M in U(IV); (C) 1:1:2 U(IV)-NTA-Tiron, 2.0 × 10^{-3} M in U(IV); (D) composite curve derived from A and B; (E) 1:1:2 U(IV)-NTA-HQS, 2.0 × 10^{-3} M in U(IV); - - - - indicates drifting of $-\log [H^+]$ readings; - · - · indicates the presence of precipitate in the solution; for curves A and B the actual m values are twice the m values shown.

Hydrolysis is noted above $-\log [H^+] = 8.5$ for SA and SSA, while with IMDA no drifting is noticed even at a $-\log [H^+]$ value of 9.0.

The 1:1:1 U(IV)-EDTA-Ph curve (Figure 2, curve A) (where Ph = potassium acid phthalate) exhibits a buffer region which culminates in a sloping and almost imperceptible inflection around m = 3.00. Since the composite curve for this system assuming no mixed ligand chelate formation predicts a slightly higher $-\log [H^+]$ value than the experimental curve between m = 2.00 and 3.00, it is concluded that a mixed ligand chelate is being formed in this region. This mixed ligand chelate once formed undergoes hydrolysis around $-\log [H^+] = 6.50$, above which drifting of the $-\log [H^+]$ value is noted.

U(IV)-EDTA-HQS. The 1:1:1 U(IV)-EDTA-HQS system (HQS = 8-hydroxy-5-quinolinesulfonic acid), 2.0 × 10^{-3} M in U(IV), yields a potentiometric curve (Figure 2, curve D) which has a long buffer region at low $-\log [H^+]$ culminating in a well-defined inflection at m = 4.00. Beyond this inflection there is another buffer region which is concentration independent (Figure 2, curves C and D) and which culminates in a sloping inflection around m = 5.00. Thus in the lower buffer region a 1:1:1 mixed ligand chelate is formed, while in the second buffer region a distinct monohydroxo mixed ligand chelate is formed, with a calculated $pK_1 = 7.14 \pm 0.01$ for the two different concentrations. Thus the mixed ligand chelate formed in the lower buffer region is not very stable and undergoes hydrolysis to mononuclear monohydroxo mixed ligand chelate around $-\log [H^+] = 7.1$. However, this monohydroxo mixed chelate, once formed, is quite stable since drifting of the pH meter readings indicating further hydrolysis was noted only at very high $-\log [H^+]$ values above 10.0.

U(IV)-NTA, U(IV)-NTA-HQS. The 1:1 U(IV)-NTA system (not shown) is characterized by a colloidal precipitate and drifting of pH values from the start of the titration. There is a single inflection at m = 4.75. Consequently the 1:1 U(IV)-NTA chelate undergoes hydrolysis and olation reactions, forming an insoluble hydroxo chelate, even at very low $-\log [H^+]$ values.

The potentiometric titration curve of the 1:1:2 U(IV)-NTA-HQS system (Figure 3, curve E) has a long, low pH buffer region from m = 0 to 7.0, which terminates in a sloping but fairly well-defined inflection at m = 7.00. This system is at first heterogeneous since HQS is only slightly soluble in aqueous solution and remains as a precipitate in strong acid solution. It dissolves slowly as base is added and finally disappears completely at m = 4.9 ($-\log [H^+] = 3.3$). Continuation of the potentiometric titration yields a good inflection at 7.00 equiv of base per U(IV) ion. Also, no white colloidal precipitate similar to that of the 1:1 U(IV)-NTA system is noted at any time during the titration. Thus, in the lower buffer region the 1:1:1 mixed ligand chelate which is initially formed is replaced by the 1:1:2 U(IV)-NTA-HQS mixed ligand chelate. Color changes noted in the lower buffer region during the titration are consistent with the formation of these mixed ligand chelate species. The final mixed ligand chelate is stable up to $-\log [H^+] = 7.1$ where a hydroxo complex begins to form, as indicated by a drifting of $-\log [H^+]$ values above 7.1.

U(IV)-NTA-CS, U(IV)-NTA-IMDA, U(IV)-NTA-SSA. The potentiometric curves of systems containing a 1:1:2 molar ratio of U(IV), NTA, and secondary ligand do not provide sufficient information to establish the existence of mixed ligand chelates. In these cases the composite curves formed by the horizontal addition of the 1:1 U(IV)-NTA curve with the free ligand curves closely approximate the experimental curves. Therefore, mixed ligand chelate formation cannot be established from the potentiometric data. Nonformation of mixed ligand chelates in the cases of the 1:1:2 U(IV)-NTA-CS and U(IV)-NTA-IMDA systems is indicated by the fact that a colloidal precipitate of a hydroxo species is present from the start of the titration. This is similar to the precipitate noted in the case of the 1:1 U(IV)-NTA chelate. However, it should be pointed out that weak mixed ligand chelates may be formed during the initial stages of the titration. However, these species are not detectable with the experimental methods employed in the present study.

U(IV)-NTA-Tiron. The mixed ligand potentiometric curve (Figure 3, curve C) for a 1:1:2 molar ratio of U(IV), NTA, and Tiron has a buffer region at low $-\log [H^+]$ values with a poorly defined inflection at m = 4.50. Beyond this inflection drifting is noted at and beyond m = 4.70 ($-\log [H^+] = 4.3$), showing that hydrolysis and olation reactions may take place in this region. A similar inflection at m = 4.50 was noted previously by Carey, *et al.*,[5] for the 1:1:2 Th(IV)-NTA-Tiron system and was found to have been caused not by the formation of a mixed ligand chelate, but by the simultaneous formation of two distinct simple chelates $Th(NTA)_2^{2-}$ and $Th_2(Tiron)_3^{4-}$. The

Table I. Comparison of Formation Constants of Mixed Ligand Chelates from the 1:1 Chelates of U(IV) and Th(IV) with EDTA (H_2L^{2-}) and 1 Mole of an Additional Ligand (H_nA) [25°, $\mu = 0.10$ (KCl)]

Added ligand	Equilibrium quotient[a]	Formation constant[b] log *K* 1:1 Th-EDTA[e]	Formation constant[b] log *K* 1:1 U-EDTA
None	$[ML]/[M^{4+}][L^{4-}]$	23.2 ± 0.1[c]	25.8 ± 0.2[d]
1,2-Dihydroxybenzene-3,5-disulfonate anion (A^{4-})	$[MLA^{4-}]/[ML][A^{4-}]$	13.4 ± 0.1[e]	15.61 ± 0.05
1,8-Dihydroxynaphthalene-3,6-disulfonate anion (A^{4-})	$[MLA^{4-}]/[ML][A^{4-}]$	13.66 ± 0.02[e]	16.22 ± 0.01
Pyrocatechol anion (A^{2-})	$[MLA^{2-}]/[ML][A^{2-}]$	12.90 ± 0.05[e]	14.16 ± 0.5
5-Sulfosalicylate anion (A^{3-})	$[MLA^{3-}]/[ML][A^{3-}]$	9.29 ± 0.02[e]	11.08 ± 0.05
Iminodiacetic anion (A^{2-})	$[MLA^{2-}]/[ML][A^{2-}]$	6.70 ± 0.02[e]	8.2 ± 0.1
o-Phthalate anion (A^{2-})	$[MLA^{2-}]/[ML][A^{2-}]$	3.09 ± 0.02[e]	4.2 ± 0.1
8-Hydroxyquinoline-5-sulfonate (A^{2-})	$[MLA^{2-}]/[ML][A^{2-}]$	6.98 ± 0.02[e]	9.72 ± 0.04
	$[MLA^{2-}]/[MLA(OH)^{3-}][H^+]$	8.02 ± 0.02[f]	7.14 ± 0.01

[a] M indicates both U(IV) and Th(IV). [b] Numberical values were calculated from many experimental points taken over a wide range of neutralization value. [c] Reference 12. [d] Reference 9. [e] Reference 5. [f] Reference 13.

latter complex has been described by Murakami and Martell.[10,11]

In order to determine if a similar explanation applies to the 1:1:2 U(IV)–NTA–Tiron system, a potentiometric curve was run employing the correct stoichiometric amounts of U(IV) and Tiron. The resulting curve yielded a potentiometric titration (Figure 3, curve C) with a low buffer region and a poor sloping inflection at $m = 3.00$. Color changes are also noted and, coupled with the inflection at $m = 3.00$, indicate that a 1:1.5 U(IV)–Tiron complex, similar to the $Th_2(Tiron)_3$ complex, is probably formed initially. It has been shown previously[9] that 1 mole of U(IV) combines with 2 moles of NTA to give an extremely stable 1:2 U(IV)–NTA complex which yields a curve with an inflection at $m = 6.00$. Thus in the 1:1:2 mixed ligand system half of the U(IV) combines with all of the NTA present in the solution giving the 1:2 U(IV)–NTA complex, while the other half of the U(IV) combines with the Tiron giving the $U^{IV}{}_2(Tiron)_3{}^{4-}$ complex. Thus at $m = 4.5$, the solution is 1×10^{-3} *M* in the 1:2 U(IV)-NTA complex, 0.5×10^{-3} *M* in the 2:3 U(IV)–Tiron complex, and 2.50×10^{-3} *M* in excess free Tiron.

In order to verify this interpretation two additional solutions were measured potentiometrically: a solution 1.0×10^{-3} *M* in the 1:2 U(IV)–NTA chelate (Figure 3, curve B) that gave an inflection at $m = 6.0$, and a 1:4 U(IV)–Tiron solution 1.0×10^{-3} *M* in U(IV) (Figure 3, curve A) that gave an inflection at $m = 3.00$. The addition of the ordinates of these two curves yields curve D which is superimposable on the actual experimental curve beyond the inflection at $m = 4.5$. This furnishes convincing evidence that in the lower buffer region what is occurring is the formation of the two distinct species $U^{IV}(NTA)_2{}^{2-}$ and $U^{IV}{}_2(Tiron)_3{}^{4-}$ rather than the mixed ligand chelate. This conclusion is also supported by color changes in the solution during the titration. The general sequence of reactions in this mixed ligand system may be summarized as

$$U^{IV} + H_3L + 2H_2A^{2-} \rightleftharpoons U^{IV}L^+ + 2H_2A^{2-} \rightleftharpoons$$
$$0.5U^{IV}(L)_2{}^{2-} + 0.25U^{IV}{}_2(A)_3{}^{4-} + 1.25H_2A^{2-} \rightleftharpoons$$
$$\text{hydrolysis} \rightleftharpoons \text{olation}$$

where NTA = H_3L and Tiron = H_2A^{2-}. Finally, drifting indicating hydrolysis is noted at and beyond $-\log [H^+] = 4.3$ ($m = 4.6$) for the 1:1:2 system, as expected, since these conditions are the same as those under which hydrolysis occurs for the 1:4 and 1:1.5 U(IV)–Tiron systems.

Equilibrium Constants. The formation constants for the combination of 1 mole of a secondary ligand with the U(IV)–EDTA chelate compound are given in Table I.

Discussion

The present work on mixed ligand U(IV) chelates, as well as the previous study of mixed ligand chelates of Th(IV),[5] leads to a logical classification of reaction systems containing two different ligands into the following basic types (L represents a "primary" ligand and A represents a "secondary" ligand, and ionic charges are omitted for clarity).

1. Combination of the metal ion with both ligands simultaneously to form a mixed ligand chelate in a single step.

$$A + L + M \rightleftharpoons MLA$$

2. Formation of a mixed ligand chelate in two overlapping steps reflecting slight differences in the affinities of the ligands for the metal ion.

$$A + L + M \rightleftharpoons ML + A \rightleftharpoons MLA$$

3. Formation of a mixed ligand chelate in two distinctly separated steps, reflecting a large difference in the affinity of the ligands for the metal ion.

$$A + L + M \rightleftharpoons ML + A \rightleftharpoons MLA$$

4. Formation of a mixture of two simple chelate compounds rather than a mixed ligand chelate.

$$xL + yA + 2M \rightleftharpoons ML_x + MA_y$$

5. A simple complex is formed between one ligand and the metal ion while the other ligand remains unbound in the solution.

$$A + L + M \rightleftharpoons ML + A$$

All the above five types may be further subdivided according to whether the mixed complex or simple

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(10) Y. Murakami and A. E. Martell, *J. Am. Chem. Soc.*, **82**, 5605 (1960).

(11) Y. Murakami and A. E. Martell, *Bull. Chem. Soc. Japan*, **39**, 1077 (1966).

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

(13) G. H. Carey and A. E. Martell, unpublished results.

complex once formed is resistant (class A) or susceptible (class B) toward hydrolysis. It should be understood that the above is not intended to be an exhaustive classification system, but merely one which covers the reaction types of various mixed ligand chelate systems that have been observed thus far.

Mixed Ligand Chelates of EDTA. Table II summarizes the evidence for mixed ligand chelate systems of EDTA. It should be noted that the reactions listed may be classified as 2A or 2B, the one exception being the 1:1:1 U(IV)–EDTA–PY system, which is classified as 3B. Mixed ligand complexes are formed by all of the secondary ligands investigated, and the mixed complexes once formed are quite stable. In cases where the secondary ligand contains an aromatic hydroxyl group, the high stabilities of the mixed ligand chelates is evidenced by the lack of hydroxo complex formation in the case of the 1:1:1 U(IV)–EDTA–Tiron chelate, and the high pH at which hydroxo complex formation is observed in the other systems.

Table II. Mixed Ligand Complexes Formed from U(IV)–EDTA (UL) [25°, μ = 0.10 (KCl)]

Ligand added	Inflection[a]	Species formed	Hydroxo complex formation	Reaction type
None	2, 3	UL, $ULOH^-$ $(ULOH)_2{}^{2-}$	pH >4.0	..
Tiron (H_2A^{2-})	4	ULA^{4-}	None	2A
CS (H_2A^{2-})	4	ULA^{4-}	pH >9.4	2B
PY (H_2A)	2, 4	ULA^{2-}	pH >10.6	3B
HQS (H_2A)	4, 5	ULA^{2-}, $ULAOH^{3-}$	pH > 7.1	2B
SSA (H_3A)	5	ULA^{3-}	pH >8.5	2B
SA (H_2A)	4	ULA^{2-}	pH > 8.5	2B
IMDA (H_2A)	4	ULA^{2-}	pH >9.0	2B
Ph (HA^-)	3	ULA^{2-}	pH >6.5	2B

[a] Numbers represent moles of base added per mole of UL.

It is of interest to consider the equilibrium constants for the formation of the mixed ligand chelates, listed in Table I, from the point of view of the constitution of the added ligand. It is seen that CS forms the most stable mixed ligand chelate of all the compounds listed and that the corresponding Tiron complex has nearly the same stability, while the affinity of the catecholate anion for the U(IV)–EDTA chelate is slightly lower. The fact that these stabilities are much higher than any of the other values listed in Table I may be rationalized on the basis that, of the donor groups investigated, the phenoxide groups have the highest affinity for the U(IV) ion. The Tiron and chromotropic salt data are also interesting as an indication that under certain conditions a six-membered chelate ring may be more stable than an analogous five-membered ring.

Two other ligands, HQS and SSA, which provide one phenoxide ion each, form mixed ligand chelates which are somewhat less stable, but nevertheless still appear quite high in the sequence of relative stabilities. In accordance with these observations the least stable mixed ligand chelates are those which are formed from secondary ligands (IMDA and Ph) having primarily carboxylate groups as electron donors.

Table III summarizes the results for mixed ligand chelates of NTA. The first three examples listed are seen not to involve mixed ligand chelate formation, and hence these systems belong to class 5B. It is noted that hydroxo complex formation is first observed in all five cases around the same low pH where hydroxo complex formation of the U(IV)–NTA chelate itself occurs. This observation supports the argument that no mixed ligand complex is formed. In the case of HQS, however, the fact that hydroxo complex formation takes place at a higher pH than that at which the 1:1 U(IV)–NTA chelate hydrolyzes is evidence for mixed ligand chelate formation.

Table III. Mixed Ligand Complexes Formed from U(IV)–NTA (UL^+) [25°, μ = 0.10 (KCl)]

Ligand added	Inflection[a]	Species formed	Hydroxo complex formation	Reaction type
None	~4.75	Hydrolysis product of UL^+	pH >2.5	...
CS (H_2A^{2-})	~4.8, ~6.75	None	pH >2.5	5B[b]
SSA (H_3A)	~8.75	None	pH >3.0	5B[b]
IMDA (H_2A)	~6.70	None	pH >2.2	5B[b]
HQS (H_2A)	7.00	ULA^-, $ULA_2{}^{3-}$	pH >7.1	2B
Tiron (H_2A^{2-})	4.50	$UL_2{}^{2-}$, $U_2A_3{}^{4-}$	pH >4.3	4B

[a] Numbers indicate moles of base added per mole of UL^+.
[b] Weak mixed ligand complexes may be formed initially.

Finally, as discussed in detail above, the 1:1:2 U(IV)–NTA–Tiron system (reaction type 4B) is unique when compared to all the other systems studied. The stabilities of the individual single-ligand chelates are so high that the mixed ligand chelate is not formed to any detectable extent.

Coordination Number of U(IV). It has been noted in the present investigation that in the great majority of the mixed ligand chelates studied, the U(IV) ion seems to have an effective coordination number of eight. Hence, the resulting U(IV) mixed ligand complexes will probably have dodecahedral arrangements of donor groups similar to that shown by A in Figure 4 for the 1:1:1 U(IV)–EDTA–Tiron complex.

However, the 1:1:1 U(IV)–EDTA–IMDA system indicates the possibility of the expansion of the coordination number of U(IV) from a value of eight to that of nine. Formation of an EDTA–IMDA mixed ligand chelate may be interpreted as involving the displacement of one of the carboxylate groups of EDTA to make way for the three donor groups of IMDA, thus keeping the total coordination of U(IV) at eight. On the other hand, the relatively high stability constant for the addition of IMDA argues in favor of expansion of the coordination number of U(IV) to nine. Thus the 1:1:1 U(IV)–EDTA–IMDA mixed ligand chelate would probably involve nonacoordination of U(IV) in aqueous solution, as is indicated by Figure 4B. Although no structural data are available for nonacoordination in solution, the trigonal prismatic +3 structure suggested[14] seems to offer the most favorable reduction in mutual repulsions between the negative carboxylate donor groups of the ligand and a reasonable arrangement of the metal chelate rings. The rather stable 1:1:1 monohydroxo U(IV)–EDTA–HQS species

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(14) A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, New York, N. Y., 1962, pp 98–100.

may also involve similar nonacoordination of U(IV).

The postulated expansion of the coordination number of U(IV) to nine for the 1:1:1 U(IV)–EDTA–IMDA and the 1:1:1 monohydroxo U(IV)–EDTA–HQS mixed ligand chelate is similar to expansion of the coordination number of Th(IV) from eight to nine for the 1:1:1 Th(IV)–EDTA–IMDA and 1:1:1 Th(IV)–HEDTA–NTA mixed ligand chelates postulated by Carey, *et al.*[5] Also, possible expansion of the U(IV) coordination number from eight to a higher value was previously noted by the present authors[9] for the monohydroxo 1:1 U(IV)–DTPA chelate and the 1:1 U(IV)–TTHA chelate (where DTPA is diethylenetriaminepentaacetic acid and TTHA is triethylenetetraminehexaacetic acid).

Equilibrium constants for the formation of mixed ligand chelates of U(IV) from the U(IV)–EDTA chelate are compared in Table I with those of the analogous Th(IV) chelates previously reported by Carey, *et al.*[5] In all the mixed ligand systems studied there is the expected increase in formation constants when Th(IV) is replaced by U(IV) in the mixed ligand chelate. This increased stability is due to the smaller radius of the U(IV) ion, which results in more favorable ΔH and ΔS effects. The favorable enthalpy effect is due to the greater ionic bond strength of U(IV) complexes.

In addition, there will also be a favorable entropy effect since the smaller U(IV) chelate of the primary ligand will be more strongly hydrated in solution than the corresponding Th(IV) chelate. Consequently, reaction with the secondary ligand to form the 1:1:1 U(IV) mixed ligand chelate results in a greater entropy increase through displacement of coordinated water molecules than occurs with the analogous Th(IV) chelate.

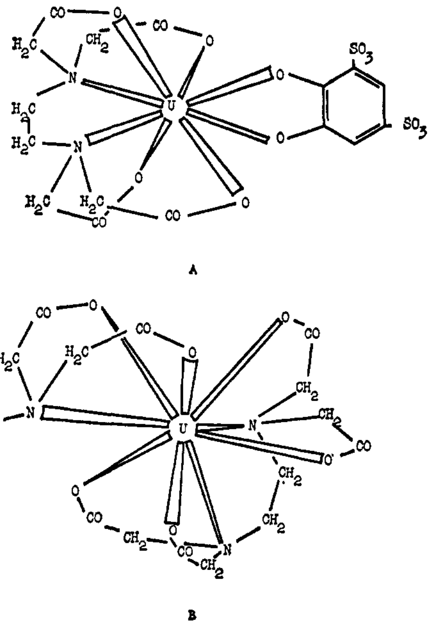

Figure 4. (A) Eight-coordinated 1:1:1 U(IV)–EDTA–Tiron mixed ligand chelate; (B) nine-coordinated 1:1:1 U(IV)–EDTA–IMDA mixed ligand chelate.

Table I also shows that the formation of the monohydroxo mononuclear mixed ligand chelate from the 1:1:1 Th(IV)–EDTA–HQS mixed ligand chelate occurs more readily when the Th(IV) ion is replaced by the U(IV) ion. This may also be considered to be principally a consequence of the smaller radius of the U(IV) ion.