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

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Mixed ligand chelates of thorium(IV) have been prepared in solution and studied potentiometrically. These new compounds were formed by the reaction of various bidentate ligands with Th(IV) chelates of multidentate ligands such as N,N,N′,N′-ethylenediaminetetraacetic acid, cyclohexane-*trans*-1,2-diaminotetraacetic acid, N-2-hydroxyethyl-N,N′,N′-ethylenediaminetriacetic acid, and nitrilotriacetic acid. When the stoichiometry ratios of the two ligands are such that the coordination vacancies of the metal ion are completely filled, the mixed ligand chelates thus formed are usually more stable toward hydrolysis than the analogous Th(IV) chelates containing only one type of ligand. The results obtained with a wide variety of mixed chelates of Th(IV) indicate that they may be divided into several classifications, depending on the order in which the ligands coordinate with the metal, on whether or not hydrolysis steps take place, and on whether the system disproportionates into a mixture of complexes each containing one type of ligand.

Introduction

Mixed ligand complex formation was considered of special interest since it offers an alternative reaction to hydrolysis and olation of metal ions. Thorium(IV), which has a coordination number of about eight in solution, is generally considered to form dodecahedral complexes, in view of the findings by Hoard[3] on crystalline Th(IV) chelates. In the case of the 1:1 complex of Th(IV) and EDTA (ethylenediaminetetraacetic acid), hexadentate EDTA can fill no more than six of the eight coordination sites of the metal ion. This leaves two coordinating sites free for hydrolysis, polymerization, or olation reactions. A 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 Th(IV) and a quadridentate ligand such as NTA, there are four coordination sites left open for hydrolysis or 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 Th(IV), a stable mixed ligand complex might conceivably be formed which would be resistant to hydrolysis.

Thus in this study, sufficient amounts of various bidentate ligands are added to the 1:1 aqueous solutions of Th(IV) with EDTA, CDTA (*trans*-1,2-diaminocyclohexanetetraacetic acid), NTA (nitrilotriacetic acid), and HEDTA (N-2-hydroxyethyl-N,N′,N′-ethylenediaminetriacetic acid) in order to fill completely the coordination sphere of the metal. In order to accomplish this with EDTA, CDTA, and HEDTA, a 1:1:1 molar ratio of Th(IV) to sexadentate and bidentate ligands was employed, while with NTA, a 1:1:2 molar ratio of Th:NTA:bidentate ligand was used.

Previous studies of mixed ligand complexes involving zirconium(IV),[4] the rare earths,[5] and other metals[6] have been reported.

Experimental

Methods.—A Beckman Model G pH meter was used to determine hydrogen ion concentrations. Potentiometric measurements were carried out in a jacketed titration cell of 75-ml. capacity, which was fitted with a magnetic stirrer, nitrogen inlet and outlet tubes, a microburet delivery tube, and glass and calomel extension electrodes. Measurements were made at a temperature of 25.3°. The ionic strength was maintained relatively constant by the use of a medium of 0.1 *M* potassium nitrate and relatively low concentrations of ligand and metal ion. Purified nitrogen was bubbled through the solution in order to exclude carbon dioxide. The concentration of metal ion was adjusted to approximately 2×10^{-3} *M* in all cases. The electrode system was calibrated with acetic acid, HCl, and NaOH to give $-\log [H^+]$ values directly.

Materials.—The thorium content of a stock solution of about 0.02 *M* thorium(IV) nitrate, prepared by dissolving pure $Th(NO_3)_4 \cdot 4H_2O$ in water, was determined gravimetrically by ignition to ThO_2.

Tiron (disodium 1,2-dihydroxybenzene-3,5-disulfonate) was obtained from the La Motte Chemical Products Co., Baltimore, Md., and was used without further purification after the establishment of its purity and standardization of an aqueous solution by potentiometric titration.

Fisher certified samples of the disodium salt of N,N,N′,N′-ethylenediaminetetraacetic acid (EDTA), oxalic acid, and potassium acid phthalate (KHP) were used. The 5-sulfosalicylic acid (SSA), salicylic acid (SA), chromotropic salt (1,8-dihydroxynaphthalene-3,6-disodium sulfonate (CS), pyrocatechol (PY), and 8-hydroxy-5-quinolinesulfonic acid (HQS) were purchased from the Eastman Kodak Co., while the nitrilotriacetic acid (NTA), iminodiacetic acid (IMDA), 1,2 cyclohexanediaminetetraacetic acid (CDTA), and N-hydroxyethylethylenediaminetriacetic acid (HEDTA) were obtained through the courtesy of the Dow Chemical Company.

All ligands employed were of reagent grade or of the highest purity and were recrystallized whenever necessary. In the case of water-soluble ligands a stock solution 0.02 *M* in the ligand was prepared and standardized potentiometrically. With relatively insoluble ligands (*e.g.*, HQS, CDTA), as well as ligands whose aqueous solutions are susceptible to oxidation or some other form of decomposition (*e.g.*, CS, PY, HEDTA), the purity of the sample was determined, and a weighed amount of the ligand was used in every determination involving it.

Calculations.—Stability constants of mixed ligand chelates were calculated in favorable cases for the combination of the 1:1 EDTA, as well as the 1:1 CDTA, chelates with a second ligand with methods similar to those employed by Thompson and

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[1] This work was supported by the U. S. Atomic Energy Commission under Contract AT(11-1)-1020.

[2] A portion of this work was reported as paper no. 72, Inorganic Chemistry Division, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 12, 1963.

[3] J. T. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).

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

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

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

Loraas.[5] In the case of the mixed EDTA–Tiron chelate, this approach did not yield a satisfactory equilibrium constant. On the other hand, a model involving stepwise dissociation of two protons from the phenolic groups of Tiron did prove to be in accord with the experimental data. Thus the equilibria for the formation of the mixed EDTA–Tiron chelate are expressed in terms of K_{MLHA}, or $[\text{MLHA}^{3-}][\text{H}^+]/[\text{ML}][\text{H}_2\text{A}^{2-}]$, and K_{MLA}, or $[\text{MLA}^{4-}][\text{H}^+]/[\text{MLHA}^{3-}]$, calculated by the method described by Bogucki.[7]

Results

In all the cases discussed it may be assumed that due to the great stability of the 1:1 complexes of EDTA, NTA, and CDTA with Th^{4+}, the Th^{4+} and these multidentate ligands are completely in the form of the 1:1 chelates at the start of all the titrations performed. The addition of the second bidentate ligand to form the mixed ligand chelate therefore turns out to be the only matter under consideration.

The results of our study, described below, have led to the classification of the reactions of systems containing a mixture of ligands into five basic types. Consideration of these types is desirable at this point as a means of facilitating the description of the results of this investigation. They are as follows.

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

$$\text{A} + \text{L} + \text{M} \rightleftharpoons \text{MLA}$$

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

$$\text{A} + \text{L} + \text{M} \rightleftharpoons \text{ML} + \text{A} \rightleftharpoons \text{MLA}$$

(3) Formation of a mixed ligand chelate in two distinctly separated steps, reflecting a wide difference in the affinities of the ligands for the metal ion

$$\text{A} + \text{L} + \text{M} \rightleftharpoons \text{ML} + \text{A} \rightleftharpoons \text{MLA}$$

(4) Formation of a mixture of two simple chelate compounds, rather than mixed ligand chelates containing two different ligands bound to the same metal ion

$$x\text{L} + y\text{A} + 2\text{M} \rightleftharpoons \text{ML}_x + \text{MA}_y$$

(5) No mixed chelate is formed. A simple complex is formed between one ligand and the metal ion while the other ligand remains unbound in the solution

$$\text{A} + \text{L} + \text{M} \rightleftharpoons \text{ML} + \text{A}$$

All the above five types may be further subdivided according to whether the mixed complex or simple 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 classifies the reactions of various mixed ligand chelate systems presented in this study. Further types of reactions will most likely be added to the above five in the future.

It is of interest at this point to consider some of the factors which control the formation of the mixed ligand chelate, MLA, in solution relative to the competing formation of a hydroxo metal chelate, MLOH. In the absence of other interfering equilibria, the ratio of the mixed ligand chelate to the hydroxo form is expressed by

$$\frac{[\text{MLA}]}{[\text{MLOH}]} = \frac{K_{\text{MLA}}}{K_{\text{MLOH}}}[\text{A}][\text{H}^+]$$

where K_{MLA} is the formation constant for the mixed ligand chelate from ML and A, and K_{MLOH} is the acid dissociation constant of the metal chelate ML. Thus, to achieve $[\text{MLA}]/[\text{MLOH}] > 1$, with a concentration of secondary ligand anion of 10^{-3} *M*, in a neutral solution of pH 7, it is necessary that the ratio of values of the equilibrium constants $K_{\text{MLA}}/K_{\text{MLOH}}$ be greater than 10^{10}. Such a simple comparison frequently cannot be made, however, since many systems are considerably more complex, because of the presence of other hydrolyzed species, such as polynuclear complexes, in solution.

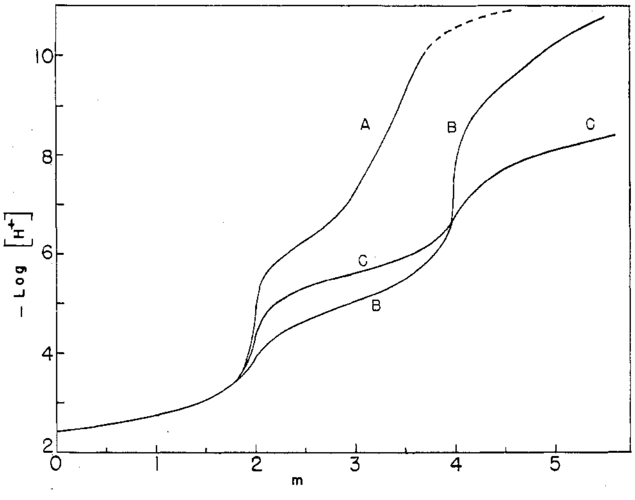

Fig. 1.—Potentiometric titrations of mixed ligand chelate systems of EDTA; all solutions are 2.0×10^{-3} *M* in thorium nitrate and 0.10 *M* in KNO_3 at the start of the titration; *m* = moles of base added per mole of metal ion; A, 1:1 Th–EDTA; B, 1:1:1 Th–EDTA–Tiron; C, 1:1:1 Th–EDTA–pyrocatechol; ---- represents drifting pH values.

Mixed Ligand Chelates of EDTA

Th–EDTA–Tiron; Th–EDTA–CS; Th–EDTA–PY.—The 1:1:1 Th–EDTA–Tiron solution yields a potentiometric curve (Fig. 1, curve B) exhibiting inflections at *m* = 2 and *m* = 4. The 1:1 Th–EDTA complex is completely formed at the start of the titration since the initial $[\text{H}^+]$ concentration shows that there are two free hydrogens present in solution per gram-ion of Th(IV). Up to *m* = 2, therefore, the buffer region is nothing more than the titration of two hydrogen ions from the disodium salt of the EDTA. This can be verified by the perfect match of the 1:1 Th–EDTA curve with the mixed ligand curve up to *m* = 2. In the second buffer region from *m* = 2 to *m* = 4, the two hydroxyl groups on the Tiron become bound to the 1:1 chelate to form the 1:1:1 mixed ligand chelate. This is a stepwise reaction, however, in which a protonated chelate is formed first and then dissociates to

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(7) R. F. Bogucki, Ph.D. Thesis, Clark University, 1959, p. 57.

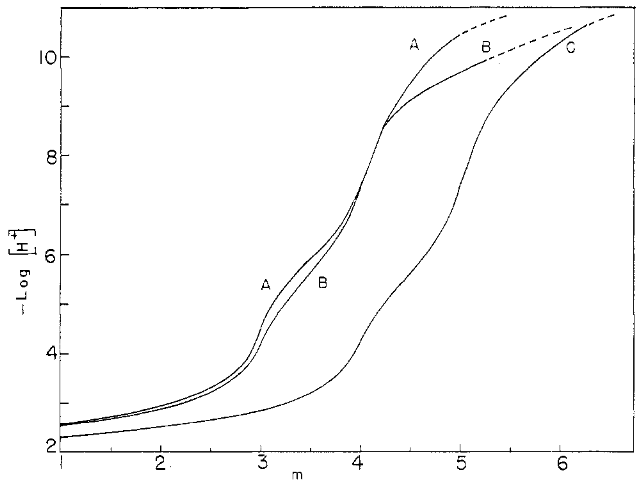

Fig. 2.—Potentiometric titrations of mixed ligand chelate systems of EDTA; all solutions are 2.0×10^{-3} *M* in thorium nitrate and 0.10 *M* in KNO_3 at the start of the titration; m = moles of base added per mole of metal ion; A, 1:1:1 Th–EDTA–SA; B, 1:1:1 Th–EDTA–IMDA; C, 1:1:1 Th–EDTA–SSA; ---- represents drifting pH values.

form the "normal" mixed ligand chelate. The stepwise nature of this reaction has been proved by a mathematical analysis of the system.[7] It also should be noted that once it is formed, no hydrolysis of the mixed ligand chelate is noted even at a pH as high as 11.00 (m = 6.0). It is of interest to compare the EDTA–Tiron mixed ligand system with the behavior of the simple Th(IV)–EDTA chelate compound. With the latter hydrolysis occurs in the 5.5–6.4 pH range to give a binuclear chelate which hydrolyzes further beyond pH 6.4.[8] Thus it is seen that there is a remarkable difference noted between the hydrolysis tendencies of the chelate and the mixed ligand chelate and that the addition of a second binuclear ligand effectively prevents hydrolysis and polymerization.

The 1:1:1 Th–CS–EDTA curve also exhibits inflections at m = 2 and 4, is superimposable with the 1:1:1 Th–EDTA–Tiron curve up to m = 4, and varies slightly from the latter system on further addition of base. Therefore this system undergoes reaction type 3A, as is true of the corresponding Tiron system, with the 1:1 EDTA chelate present in the low buffer region and the formation of a mixed ligand chelate in the second buffer region. Once again no hydrolysis of the mixed ligand chelate is noted even at high pH (11.0).

Finally, the 1:1:1 Th–pyrocatechol–EDTA system (Fig. 1, curve C) exhibits inflections at m = 2 and 4, and the same type of species are believed present in the two buffer regions as was true of the two mixed ligand chelates described above. The similarity of these three reactions indicates that binding to the metal ion occurs through the hydroxo groups rather than the sulfonate groups. The mixed ligand chelate of EDTA and pyrocatechol is formed at higher pH values than are the corresponding compounds of the sulfonated catechols. This shows that the sulfonate groups in Tiron and CS have the effect of increasing the reactivity of the aromatic hydroxyl groups in the coordination of metal ions. In this case also no hydrolysis of the mixed ligand complex was observed, even at the highest pH attained experimentally.

The three systems described above can be classified under reaction type 3A, since they involve the formation of hydrolysis-resistant mixed ligand chelates in two distinctly separated steps.

Th–EDTA–SA; Th–EDTA–SSA; Th–EDTA–IMDA.—The addition of an equivalent of SA, SSA, and IMDA to the Th(IV)–EDTA chelate produced three mixed ligand systems each of which yielded analogous potentiometric curves indicating reactions of a similar nature. In the 1:1:1 Th–EDTA–SA system (Fig. 2, curve A) and the 1:1:1 Th–EDTA–IMDA system (Fig. 2, curve B), the titration curves have two inflections occurring at m = 3 and m = 4 in both cases, while the 1:1:1 Th–EDTA–SSA curve (Fig. 2, curve C) yielded inflections similar in appearance at m = 4 and m = 5. The lower buffer regions in the three curves are indicative of nothing more than the titration of the two free hydrogen ions displaced from the 1:1 Th–EDTA complex and the titration of the easily replaceable hydrogens from the free second ligand (one equivalent in the case of the SA and IMDA and two in the case of the SSA), thus accounting for the first inflections occurring at 3, 3, and 4 equivalents, respectively. The horizontal addition of the 1:1 Th–EDTA curve with the respective free ligand curve in all three cases yields a curve which closely approximates the experimental curve shown up to the first inflection, thus verifying the interpretation that no protonated mixed ligand chelate species are formed in the lower buffer region.

In the second buffer region between m = 3 and 4 with SA and IMDA, and m = 4 and 5 with SSA, the final hydrogen ion is displaced from the ligand, showing the formation of the 1:1:1 mixed ligand chelates Th–EDTA–SA, Th–EDTA–IMDA, and Th–EDTA–SSA, respectively.

Finally, the formation of a hydroxo complex is noted beginning at a pH of 10.5 for SSA and SA and at a pH of 9.8 for IMDA. Thus the mixed ligand complex once formed is stable toward hydrolysis up until these rather high pH values. Although these steps leading up to mixed ligand chelate formation are the same (class 3) as the three mixed ligand chelates described above, their susceptibility toward hydrolysis indicates that they are somewhat less stable and therefore belong to class 3B.

Finally, it should be noted that for the IMDA mixed ligand complex there are nine possible coordinating groups present. The mixed ligand chelate is formed and hence it appears either that one of the carboxyl groups of IMDA or EDTA remains uncombined with the metal ion or that the coordination number of the Th^{4+}, usually considered to be eight, has been enlarged to nine.

Th–EDTA–KHP; Th–EDTA–HQS.—With the 1:1:1 Th–EDTA–KHP system (Fig. 3, curve A) a

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

rather poorly-defined sloping inflection is noted at $m = 3$ indicating that in the low buffer region a weak mixed ligand complex is formed. This mixed ligand complex once formed undergoes hydrolysis almost immediately at pH 7.0, as can be seen from the second buffer region, which implies hydroxo complex formation.

The 1:1:1 Th–EDTA–HQS titration curve (Fig. 3, curve B) shows inflections at $m = 4$ and 5 and the hint of an inflection at $m = 2$. The lower buffer region up to $m = 2$ is fairly superimposable on that of the 1:1 Th–EDTA chelate, and hence this is most likely the only complex of Th present under the conditions corresponding to this portion of the curve. However, beyond the slight inflection at $m = 2$ there is another buffer region which culminates in a well-defined inflection at $m = 4$ and which indicates the formation of the mixed ligand chelate. Finally there is another buffer region between $m = 4$ and $m = 5$ indicating most likely the formation of a hydroxo mixed ligand complex species, which has not yet been characterized.

On the basis of these observations, these two systems fall into class 2B, the formation of a mixed chelate in two overlapping steps. In the case of the HQS mixed ligand chelate, the reaction may possibly be type 3B, the formation of a mixed ligand chelate in two distinctly separated steps.

Th–EDTA–Oxalic Acid.—A precipitate developed when oxalic acid was added to the solution of the EDTA–Th^{4+} chelate. This precipitate was most likely due to the formation of insoluble thorium oxalate. The precipitate remained throughout the titration until a value of $m = 3.85$ was reached, whereupon on being left overnight the solution became clear and a constant pH value was obtained. Continuation of the titration (Fig. 3, curve C) yielded a sharp inflection at $m = 4.0$. Thus the dissolving of the insoluble oxalate complex, as well as the inflection at $m = 4.0$, give ample evidence of the formation of the 1:1:1 mixed ligand complex. This complex is stable until the pH is increased beyond 8.0 ($m = 5.5$), whereupon a second buffer region indicates the formation of a hydroxo complex species. Thus the reaction may be classified as type 2B (or less likely, reaction type 1B).

Mixed Ligand Chelates of NTA

Th–NTA–PY, 1:1:2.—A comparison of the 1:1 Th–NTA curve (Fig. 4, curve A) with that of the mixed ligand system (Fig. 4, curve B) indicates that the two curves are almost superimposable. Hence it is most probable that no mixed ligand complex is formed, and that only the 1:1 Th–NTA complex and the free pyrocatechol ligand are present throughout the titration. Furthermore, the fact that hydroxo complex formation is noted at the same pH (4.0) as for the 1:1 Th–NTA chelate itself offers additional proof of the absence of any mixed ligand complex species. Thus this system may be classified as 5B.

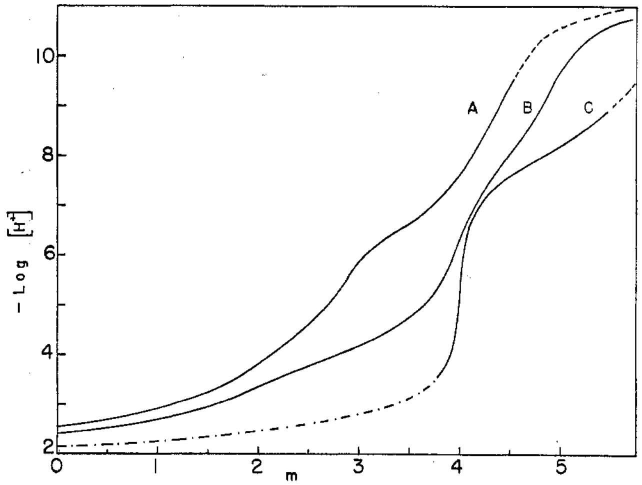

Fig. 3.—Potentiometric titrations of mixed ligand chelates of Th(IV) and EDTA; all solutions are 2.0×10^{-3} *M* in thorium nitrate and 0.10 *M* in KNO at the start of the titration; m = moles of base added per mole of metal ion; A, 1:1:1 Th–EDTA–KHP; B, 1:1:1 Th–EDTA–HQS; C, 1:1:1 Th–EDTA–oxalic acid; – – – – represents drifting pH values; – · – · indicates regions where small amount of precipitate was noted.

Th–NT-ACS, 1:1:2; Th–NTA–SSA, 1:1:2; Th–NTA–IMDA, 1:1:1; Th–NTA–KHP, 1:1:2.—In all these systems the potentiometric curves are inconclusive in attempting to establish the existence of any mixed ligand chelates. In all cases the horizontal addition of the 1–1 Th–NTA curve with the free ligand curves yields a curve which closely approximates the experimental curves and hence no mixed ligand chelate formation can be established from the potentiometric data. Further proof of the lack of formation of any mixed ligand chelates is afforded by the fact that hydroxo complex formation is noted around pH 4.0–4.5 in all cases, the same pH at which hydrolysis occurs for the 1:1 Th–NTA chelate alone. All of these systems therefore can be classified under reaction type 5B. However, it should be noted that it is possible that some weak mixed ligand chelates are formed during the initial stages of the titration, and these species are undetectable by the method employed in the present study.

Th–NTA–HQS, 1:1:2.—This system, consisting of a 1:1:2 molar ratio of Th(IV), nitrilotriacetic acid, and 8-hydroxyquinoline-5-sulfonic acid, is at first heterogenous since HQS is only slightly soluble in aqueous solution and remains as a precipitate in acid solution. It dissolves slowly as base is added and finally disappears completely at $m = 4.5$ and pH 3.5. Continuation of the potentiometric titration (Fig. 4, curve C) yields a good inflection at 7.0 equivalents of base per gram-ion of metal. Thus in the lower buffer region the 1:1:1 mixed ligand chelate, and finally the 1:1:2 Th–NTA–HQS chelate, is formed. The final mixed ligand chelate is stable up to pH 8.2 where a hydroxo complex begins to be formed as indicated by a high pH buffer region beyond $m = 7$. This raising of the hydrolysis threshold in the system, as compared to that of the 1–1 NTA–Th chelate, helps to demonstrate further the formation of the mixed ligand complex. As a

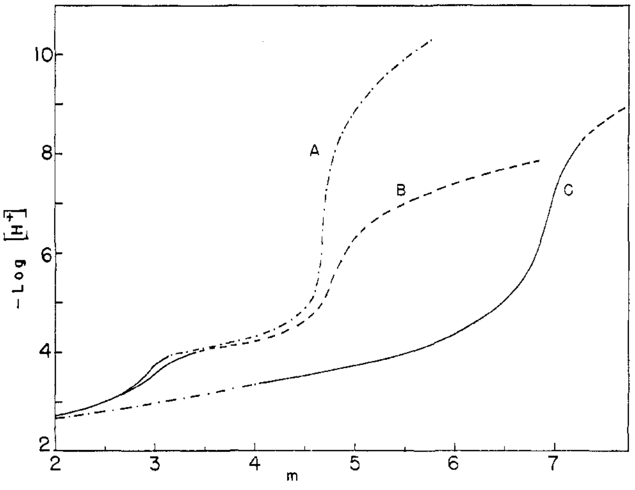

Fig. 4.—Potentiometric titrations of mixed ligand chelates of Th(IV) and NTA; all solutions are 2.0×10^{-3} *M* in thorium nitrate and 0.10 *M* in KNO_3 at the start of the titration; *m* = moles of base added per mole of metal ion; A, 1:1 Th–NTA; B, 1:1:2 Th–NTA–pyrocatechol; C, 1:1:2 Th–NTA–HQS; - - - - represents drifting pH values; – · · · indicates regions where small amount of precipitate was noted.

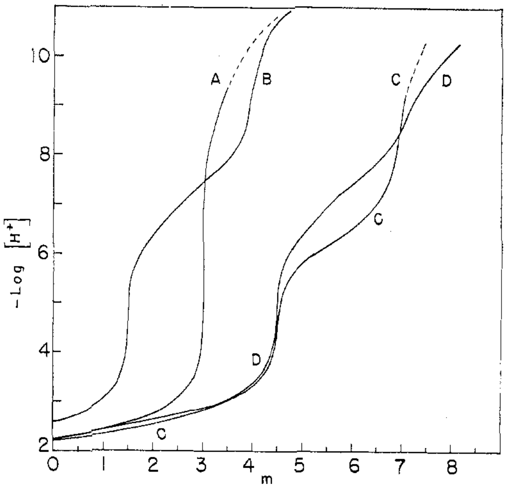

Fig. 5.—Potentiometric titrations of mixed ligand chelate systems of NTA; all solutions are 0.10 *M* in KNO_3 at the start of the titration; *m* = moles of base added per mole of metal ion; A, 1:2 Th–NTA (1.0×10^{-3} *M* in Th(IV)); B, 1:4 Th–Tiron (1.0×10^{-3} *M* in Th(IV)); C, 1:1:2 Th–NTA–Tiron (2.0×10^{-3} *M* in Th(IV)); D, composite curve derived from A and B; - - - - represents drifting pH values. For curves A and B the actual *m* values are twice the *m* values shown.

result of this analysis this mixed ligand system is classified as type 2B.

Th–NTA–Tiron, 1:1:2.—The mixed ligand potentiometric curve (Fig. 5, curve C) for a 1:1:2 molar ratio of Th, NTA, and Tiron has a buffer region at low $-\log [H^+]$ values with a sharp, well-defined inflection at *m* = 4.50. Beyond this inflection there is a second higher buffer region which terminates in another inflection at *m* = 7.0. There was no perceptible drifting up to $-\log [H^+] = 9.30$, the inflection at *m* = 4.5 was found to be completely reproducible, and the following is offered as an explanation of this unique potentiometric equilibrium curve.

It has been definitely established[9] that thorium–Tiron systems form an extremely stable complex, $Th_2(Tiron)_3{}^{4-}$, which results in a sharp inflection in the potentiometric curve at 3 equivalents of base per gram-ion of metal. This inflection is observed regardless of the ratio of [Tiron] to $[Th^{4+}]$, as long as this ratio is greater than 1.5:1.[10] Also, one mole of thorium combines with two moles of NTA to give an extremely stable 1:2 Th–NTA complex which will yield a curve with an inflection at *m* = 6.[11] These two observations, taken together, provide an explanation of the inflection at *m* = 4.5 for the mixed ligand system containing both NTA and Tiron. At the start of the potentiometric titration, a 1:1 complex of Th and NTA is completely formed, as evidenced by the initial $-\log [H^+]$ reading which shows three free $[H^+]$ ions present per mole of metal ion. As the titration continues, disproportionation of the 1:1 Th–NTA chelate takes place, and two distinct complexes are subsequently formed in the lower buffer region. Half of the Th^{4+} combines with all of the NTA present in the solution giving the 1:2 $Th\text{–}NTA^{2-}$ complex, while the other half of the Th^{4+} combines with the Tiron giving the $Th_2(Tiron)_3{}^{4-}$ complex. Thus there is present at *m* = 4.5 a 1×10^{-3} *M* solution of 1:2 Th–NTA complex and a 0.5×10^{-3} *M* solution of the 2:3 Th–Tiron complex, plus a 2.50×10^{-3} *M* solution of excess free Tiron.

In order to verify this interpretation two additional solutions were measured potentiometrically. A solution 1.0×10^{-3} *M* in the 2:1 NTA–Th chelate (Fig. 5, curve A) gave an inflection at *m* = 6, and a 4:1 Tiron–Th(IV) solution 1.0×10^{-3} *M* in Th(IV) (Fig. 5, curve B) gave inflections at *m* = 3 and at *m* = 8.0. The addition of the ordinates of these two curves yields curve D, which is superimposable on the actual experimental curve up past 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 $Th(NTA)_2{}^{2-}$ and $Th_2(Tiron)_3{}^{4-}$ rather than a mixed ligand chelate. Furthermore, the lowering of the second buffer region in the experimental curve, as compared with the composite curve, shows that further complexing involving the excess Tiron present in the solution must be occurring in this region. This further complexing probably involves the formation of a mixed ligand chelate or a chelate of thorium and Tiron containing more than a 3:2 molar ratio of Tiron to thorium. The general sequence of reactions in this mixed ligand system may be summarized as follows

$$\begin{gathered}
Th^{4+} + H_3L + 2H_2A^{2-} \\
\downarrow\uparrow \\
Th(L)^{+} + 2H_2A^{2-} \\
\downarrow\uparrow \\
{}^{1}/_{2}Th(L)_2{}^{2-} + {}^{1}/_{4}Th_2(A)_3{}^{4-} + {}^{5}/_{4}H_2A^{2-} \\
\downarrow\uparrow \\
{}^{1}/_{2}Th(L)_2{}^{2-} + {}^{1}/_{2}Th(A)_x{}^{4-4x} + Th(L)(A)_2{}^{7-}
\end{gathered}$$

where $x > {}^{3}/_{2}$; NTA = H_3L; Tiron = H_2A^{2-}.

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[9] R. L. Gustafson and A. E. Martell, *J. Am. Chem. Soc.*, **82**, 5610 (1960).

[10] Y. Murakami and A. E. Martell, *ibid.*, **82**, 5605 (1960).

[11] R. F. Bogucki, ref. 7, p. 41.

Finally, in order to characterize definitely the reaction occurring in the lower buffer region as the formation of $Th(NTA)_2^{2-}$ and $Th_2(Tiron)_3^{4-}$ a potentiometric titration was performed employing the exact stoichiometric amounts of metal ion and ligands capable of forming just the two postulated chelate species with no excess ligand. The resulting curve, for a 1:1:0.75 molar ratio of Th(IV), NTA, and Tiron, respectively, was found to be exactly superimposable on the 1:1:2 experimental curve (Fig. 5, curve C) to just beyond $m = 4.5$, in agreement with the assignment of two separate chelate species and no mixed ligand chelates to the lower buffer region. Thus the Tiron–NTA mixed ligand system is classified as involving reactions of type 4B. It should also be noted that in the curve involving the 1:1:0.75 stoichiometric ratio, hydroxo complex formation occurs at pH 6.5 and $m = 4.8$, thus indicating that in the second buffer region of the 1:1:2 curve a further reaction is taking place with the Tiron, providing additional hydrolysis resistance to the system. Thus, the second buffer region of Fig. 5, curve C, does not involve mere titration of the free excess Tiron and/or hydrolysis of the 3:2 Tiron–thorium chelate originally formed, but indicates combination of the excess Tiron with one of the metal chelates present.

Mixed Ligand Chelates of CDTA

In all the 1:1:1 Th–CDTA–bidentate ligand curves attempted (*e.g.*, Tiron CS, PY, KHP, HQS, SSA, IMDA) the resulting potentiometric curves have the same shape as those of the analogous EDTA curves. In general, the EDTA and CDTA curves were found to be superimposable in all pH regions except those in which the mixed ligand chelates are being formed. In all the curves studied the buffer region in which the mixed chelate is being formed occurs at a slightly higher pH with CDTA than in the case of the EDTA curves.

Mixed Ligand Chelates of HEDTA

A study of the possible formation of mixed ligand chelates involving HEDTA as the multidentate ligand was also undertaken. Most of the mixed ligand systems investigated gave results which have not yet yielded to interpretation. However, the following systems have been interpreted in the present study and are therefore discussed.

Th–HEDTA–NTA, 1:1:1.—A solution consisting of equimolar ratios of Th(IV) ion, HEDTA, and NTA was characterized by a potentiometric titration curve having a low buffer region with a single sharp inflection at $m = 6.0$, thus indicating the formation of a strong mixed ligand complex containing Th, HEDTA, and NTA in equimolar ratios. In this metal chelate the hydroxyl group of HEDTA is not dissociated and is therefore presumed not to be coordinated to thorium. This complex seems to be extremely stable since no hydroxo complex formation is noted even at pH 11.00. The reaction type indicated here is either 1A or 2A.

Th–HEDTA–Tiron, 1:1:1.—A system consisting of equimolar ratios of Th(IV), HEDTA, and Tiron is characterized by a potentiometric titration curve having inflections at $m = 4.75$ and 6.00. The inflection at 4.75 equivalents of base indicates the existence of an olated polynuclear species being formed between the Th and the HEDTA. The inflection at $m = 6.00$, however, shows the rearrangement of the initially formed olated species and subsequent addition of the Tiron to form a 1:1:1 mixed ligand complex which is probably mononuclear. In this mixed complex either the hydroxyl group of the HEDTA or a hydroxide ion from dissociated water is coordinated to the Th^{4+} ion in order to account for the inflection of $m = 6.00$. This mixed ligand complex is extremely stable even at a pH of 11.00. The reaction type here is definitely 3A.

Equilibrium Constants.—The formation constants calculated for the combination of one mole of a second ligand to the Th(IV)–EDTA as well as the Th(IV)–CDTA chelate compounds are given in Table I.

TABLE I

FORMATION CONSTANTS OF MIXED LIGAND CHELATES FROM THE 1:1 CHELATE (ThL) AND ONE MOLE OF AN ADDITIONAL LIGAND (H_nA)

Added ligand	Equilibrium quotient	Formation constant[a] 1:1 Th–EDTA log *K*	1:1 Th–CDTA log *K*
1,2-Dihydroxybenzene-3,5-disulfonate anion (A^{4-})	$\frac{[ThLHA^{3-}]}{[ThLA^{4-}][H^+]}$	4.46 ± 0.05	
	$\frac{[ThLHA^{3-}]}{[ThL][HA^{3-}]}$	5.35 ± 0.05	
	$\frac{[ThLA^{4-}]}{[ThL][A^{4-}]}$	13.4 ± 0.1	12.67 ± 0.07
1,8-Dihydroxynaphthalene-3,6-disulfonate anion (A^{4-})	$\frac{[ThLA^{4-}]}{[ThL][A^{4-}]}$	13.66 ± 0.02	13.13 ± 0.02
Pyrocatechol anion (A^{2-})	$\frac{[ThLA^{2-}]}{[ThL][A^{2-}]}$	12.90 ± 0.05	12.26 ± 0.05
8-Hydroxyquinoline-5-sulfonate (A^{2-})	$\frac{[ThLA^{2-}]}{[ThL][A^{2-}]}$	6.98 ± 0.02	6.69 ± 0.02
5-Sulfosalicylate anion (A^{3-})	$\frac{[ThLA^{3-}]}{[ThL][A^{3-}]}$	9.29 ± 0.02	8.87 ± 0.08
Iminodiacetate anion (A^{2-})	$\frac{[ThLA^{3-}]}{[ThL][A^{2-}]}$	6.70 ± 0.02	6.11 ± 0.08
o-Phthalate anion (A^{2-})	$\frac{[ThLA^{2-}]}{[ThL][A^{2-}]}$	3.09 ± 0.02	2.63 ± 0.03

[a] Numerical values given were calculated from many experimental points taken over a wide range of neutralization values.

Direct calculation of the formation constant of $ThLA^{4-}$ from ThL and A^{4-} for Tiron did not correlate with experimental data, because of the presence of the monoprotonated intermediate $ThLHA^{3-}$ in significant concentrations in the buffer region of interest. Allowance for this fact (*i.e.*, calculation of the stepwise constants shown in the table) produced the desired agreement. In all other cases listed the calculation of the mixed ligand constant as a single step gave the desired agreement.

Discussion

Table II summarizes the evidence for mixed ligand chelate systems of EDTA. It should be noted that all the reactions listed may be classified as 2B, 3B, or 3A. Mixed ligand complexes are formed for all of the EDTA and CDTA chelates of the secondary ligands investigated, and the mixed complexes once formed are quite stable. Exceptional stability is apparent from the data of Table I in cases where the secondary ligand contains an aromatic hydroxyl group, which coordinates with the metal ion. The resistance of these mixed ligand chelates to hydrolysis, a direct result of their high stability, is evidenced by the lack of hydroxo complex formation in the first three cases given in Table II and the extremely high pH at which hydroxo complex formation is noted in the other systems.

TABLE II

MIXED COMPLEXES FORMED FROM Th–EDTA (ThL)

Ligand added	Inflection[a]	Species formed	Hydroxo complex formation	Reaction type
Tiron (H_2A^{2-})	2,4	$ThLA^{4-}$	None	3A
CS (H_2A^{2-})	2,4	$ThLA^{4-}$	None	3A
PY (H_2A)	2,4	$ThLA^{2-}$	None	3A
Oxalic acid (H_2A)	4	$ThLA^{2-}$[b]	pH >8.0	1B or 2B
HQS (H_2A)	4,5	$ThLA^{2-}$, $ThLAOH^{3-}$	pH >8.0	2B
SSA (H_3A)	4,5	$ThLA^{3-}$	pH >10.5	3B
SA (H_2A)	3,4	$ThLA^{2-}$	pH >10.5	3B
IMDA (H_2A)	3,4	$ThLA^{2-}$	pH >9.8	3B
KHP (HA^-)	3	$ThLA^{2-}$	pH >7.0	2B

[a] Numbers represent moles of base added per mole of ThL. [b] Other species formed as intermediates.

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 properties of the added ligand. It is seen that CS forms the most stable mixed ligand chelate of all the compounds listed. This fact becomes understandable if one accepts the interpretation that the basic phenolate ion is the most effective coordinating group for the incompletely-coordinated Th(IV) ion. Thus, CS, which provides two phenoxide groups arranged so as to form a six-membered chelate ring, forms slightly more stable mixed ligand chelates than does Tiron, which provides two phenoxide ions so as to form a five-membered ring. Pyrocatechol, which does not have the stabilizing influence of the sulfonate groups of Tiron, forms a slightly less stable mixed ligand complex than Tiron. These are the only three ligands that provide two phenoxide groups. Two other ligands, 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 having primarily carboxylate groups as electron donors.

The mixed ligand chelates of CDTA offer some very interesting correlations with the corresponding EDTA compounds. As noted above, the mixed ligand CDTA chelates are quite similar stoichiometrically to the corresponding EDTA chelates, but have characteristic differences, as indicated by the higher pH of the buffer regions of the titration curve associated with the formation of these mixed ligand chelates.

This raising of the pH buffer region in which formation of the mixed ligand chelate occurs has twofold significance. First of all it shows that the corresponding mixed ligand chelates are slightly less stable in the CDTA series as compared with the EDTA series. This is readily verified by a comparison of the two sets of formation constants listed in Table I. Thus, the Th–EDTA complex has a greater tendency to form mixed ligand chelates than the corresponding Th–CDTA complex. Secondly, the perfect stoichiometric agreement between the CDTA series as compared to the EDTA, except in those portions of the curves where mixed ligand chelate formation has been postulated, helps to strengthen further the conclusions inferred above that mixed ligand chelates are actually formed in these regions.

The relative stabilities of the EDTA and CDTA mixed ligand chelates are precisely what one would predict from the higher stabilities of the CDTA chelates over analogous EDTA compounds. Thus the greater interaction of CDTA with metal ion saturates the coordination tendencies of the Th(IV) ion to a greater extent and leaves less residual affinity for the secondary ligand involved in the formation of the mixed ligand chelate.

Table III summarizes the findings for mixed ligand chelates of NTA. The first five examples listed are seen not to involve mixed ligand chelate formation, and hence these systems belong to class 5B. The fact that hydroxo complex formation is first noted in all five cases around the same low pH where hydroxo complex formation is noted with the 1:1 Th–NTA chelate alone supports the argument that no mixed ligand complex is formed. In the case of the HQS, however, the fact that hydroxo complex formation takes place at a high pH as compared to that of the 1:1 Th–NTA chelate is evidence for mixed ligand chelate formation.

TABLE III

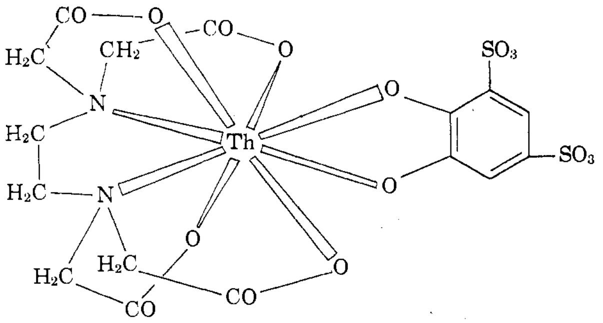
MIXED COMPLEXES FORMED FROM Th–NTA (ThL^+)

Ligand added	Inflection[a]	Species formed	Hydroxo complex formation	Reaction type
PY (H_2A)	3.0	None[b]	pH >4.0	5B
CS (H_2A^{2-})	~7	None[b]	pH >5.8	5B
SSA (H_3A)	~9	None[b]	pH >4.1	5B
IMDA (H_2A)[c]	~5.6	None[b]	pH >4.5	5B
KHP (HA^-)	~6.4	None[b]	pH >4.1	5B
HQS (H_2A)	7.00	$ThLA^-$ $ThLA_2^{3-}$	pH >8.2	2B
Tiron (H_2A^{2-})	4.50, 7.00[d]	ThL_2^{2-} $Th_2A_3^{4-}$	pH >9.2	4B

[a] Numbers indicate moles of base added per mole of ThL^+. [b] Weak mixed complexes may be formed initially. [c] Ratio was 1:1:1 Th–NTA–IMDA. [d] Second step involves combination with excess Tiron present.

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

It has been noted in the present investigation that in the great majority of the mixed ligand chelates studied, the Th(IV) ion exhibits a coordination number of eight. Hence, the resulting Th(IV) mixed ligand complex will display a dodecahedron structure similar to that shown by I for the 1:1:1 Th(IV)–EDTA–Tiron complex.



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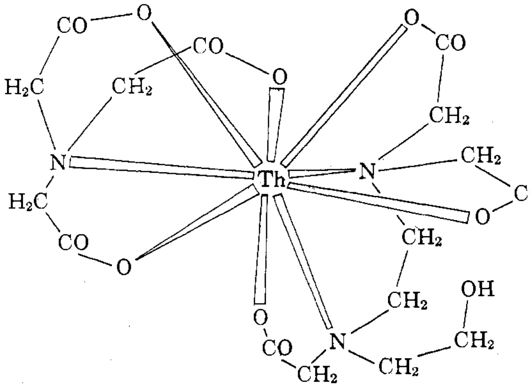

II

However, both the 1:1:1 Th–EDTA–IMDA and the 1:1:1 Th–HEDTA–NTA systems indicate the possibility of the expansion of the coordination number of Th(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 Th(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 Th(IV) to nine. For the NTA–HEDTA mixed ligand chelate, it seems unlikely that one of the carboxylate groups of the pentadentate HEDTA anion is displaced from the coordination sphere of the metal ion, since that would leave one of the amino groups without an adjacent coordinated carboxylate group. Thus, since the nitrilotriacetate anion is probably quadridentate, the NTA–HEDTA mixed ligand chelate would involve nonacoordination of Th(IV) in aqueous solution, as is indicated by II. Although no structural data are available for nonacoordination in solution, the trigonal prism +3 structure chosen[12] seems to offer the greatest reduction in mutual repulsions between the negative carboxylate donor groups of the ligand and a reasonable arrangement of the metal chelate rings.

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[12] A. F. Wells, "Structural Inorganic Chemistry," 3rd Ed., Oxford University Press, New York, N. Y., 1962, pp. 98–100.

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Distortions about Six-Coordinate Ferrous Ion[1a]

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The ionic model is used to account for possible tetragonal distortions of ferrous compounds. The near-infrared spectrum of FeF_2 is reported and analyzed. It is shown that distortions are not possible when the force constant for distortion is large as for example in the case of FeO. However, it is very likely that distortions of about 0.1 Å. do occur if the force constant is small as in the case of $Fe(OH_2)_6^{2+}$.

The consequences of the Jahn–Teller theorem for transition metal chemistry were first investigated by Van Vleck.[2] The Jahn–Teller effect is commonly considered to be difficult to establish. Of it Low[3] says "indeed it seems nearly a property of the Jahn–Teller effect that whenever one tries to find it, it eludes the possibility of being measured." However, the stereochemistry of Cu^{2+} ($3d^9$) and Mn^{3+} ($3d^4$) compounds offers the best evidence that Jahn–Teller distortions do occur; references to this work may be found in the very thorough review and topological treatment of the subject by Liehr.[4] These two ions in an octahedral field have orbital degeneracy in the e_g, σ antibonding component of the d subshell. It would be very interesting to discover if degeneracy in the t_{2g}, π antibonding component would lead to significant distortions. It is commonly assumed that such distortions if detectable at all would be difficult to estab-

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[1] (a) Supported by the National Science Foundation; (b) Alfred P. Sloan Foundation Fellow.

[2] J. H. Van Vleck, *J. Chem. Phys.*, **7**, 72 (1939).

[3] W. Low, *Phys. Rev.*, **109**, 256 (1958).

[4] A. D. Liehr, *J. Phys. Chem.*, **67**, 389 (1963).