[Contribution of the Department of Chemistry of Clark University]

Hydrolysis and Olation of Th(IV) Chelates of Polyaminopolycarboxylic Acids[1]

By Raymond F. Bogucki and Arthur E. Martell

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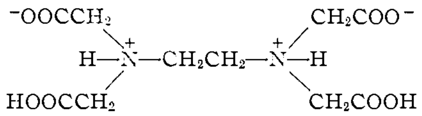
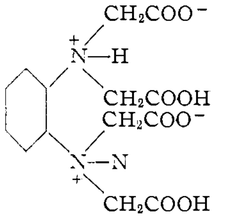
The ethylenediaminetetraacetate and the 1,2-diaminocyclohexanetetraacetate chelates of Th(IV) have been found to form binuclear diolate chelates in aqueous solution. Through measurement of the influence of concentration on the potentiometric titration curves, the acid dissociation constants of the normal chelate compounds and the dimerization constants of the hydrolysis products have been determined. The Th(IV) chelate of heptadentate or octadentate diethylenetriaminepentaacetic acid forms a completely coördinated, monohydroxo chelate which shows no tendency to form polynuclear substances.

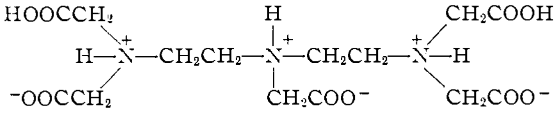
It is well known that Th(IV) salts hydrolyze in aqueous solution to form polynuclear olated complexes.[2,3] A potentiometric study[4] of the interaction of Th(IV) ion with ethylenediaminetetraacetic acid (EDTA) showed that further hydrolysis of the normal 1:1 chelate occurred at high *p*H. It was therefore decided to study the hydrolysis of this chelate compound and of analogous substances to determine the nature of the reactions of thorium (IV) chelates in aqueous solution. The ligands selected for initial study are EDTA, *trans*-1,2-diaminocyclohexanetetraacetic acid (CDTA) and diethylenetriaminepentaacetic acid (DTPA). This paper is the first of a number of studies undertaken in these laboratories of the hydrolytic tendencies of metal chelates of metals of oxidation state III or higher.



I, EDTA



II, CDTA



III, DTPA

Experimental

Materials.—The commercial disodium salt of EDTA was recrystallized twice from water and a measured amount of the resulting dihydrate was dissolved in distilled water to make a stock solution. The calculated molarity of this solution was checked by titration with standard base. Commercial samples of CDTA and DTPA were recrystallized from water and dried under vacuum. Individual samples of the pure acid form of CDTA and DTPA were weighed out for each titration. Although the DTPA was found to be anhydrous, the CDTA was found to be a monohydrate in which the water was so strongly bound that it could not be dried below 170°. No mention of this unusual property has been made in the literature. Analytical reagent grade $Th(NO_3)_4 \cdot 4H_2O$ (Baker and Adamson) was dissolved in distilled water to make a stock solution which was standardized gravimetrically by precipitation of thorium hydroxide with ammonia, followed by ignition to ThO_2. Carbonate-free potassium hydroxide was made by the method described by Schwarzenbach and Biedermann.[5]

Apparatus and Procedure.—Equimolar amounts of thorium nitrate and chelating agent were placed in a glass cell, the temperature of which was maintained at 25.00 ± 0.05°. A Beckman Model G *p*H meter fitted with extension glass and saturated calomel electrodes was calibrated with acetic acid as well as with standard HCl and NaOH to give hydrogen ion concentrations directly. The calibration titrations on successive days were reproduced to ±0.01 *p*H unit. The ionic strength of the solution was maintained at approximately 0.1 with KNO_3. Titration of this solution was performed with carbonate-free potassium hydroxide in a nitrogen atmosphere. The EDTA and CDTA chelates were titrated at four different concentrations and the DTPA chelate at two concentrations. Each titration was followed potentiometrically during the addition of small increments of base until the *p*H had reached a value of 10 or more. In the *p*H range above 9 equilibrium was attained slowly with the EDTA and CDTA chelates and more time was required for the determination of each experimental point.

Discussion

The potentiometric titration curves of the system Th(IV)–EDTA (Fig. 1) show a steep inflection at $m = 2$, indicating formation of a stable 1:1 chelate. Since the disodium salt of EDTA was used, the inflection at $m = 2$ corresponds to the titration of the third and fourth protons from the EDTA molecule to give the normal hydrated 1:1 metal chelate compound indicated by IV, in which EDTA is represented as hexadentate and Th(IV) is represented as having a coördination number of 8.[6] For all concentrations of metal chelate employed, hydrogen ion concentrations along the initial buffer region of this curve are within experimental error of what would be expected if the metal chelate IV were completely formed. It is therefore not possible to calculate the formation constant of IV from potentiometric titration data. The same conclusion applies to the formation of the Th(IV) chelates of CDTA and DTPA.

At higher *p*H there is a second buffer region which seems to require slightly more than one additional mole of base per mole of metal ion. The main portion of the buffer region itself is seen to be quite concentration-dependent, in accordance

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

(2) S. Hietanen, *Acta Chem. Scand.*, **8**, 1626 (1954).

(3) K. A. Kraus and R. W. Holmberg, *J. Phys. Chem.*, **58**, 325 (1954).

(4) M. J. Cabell, A.E.R.E. Report C/R 813, Ministry of Supply, Harwell, Berks., England, 1951.

(5) G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 311 (1948).

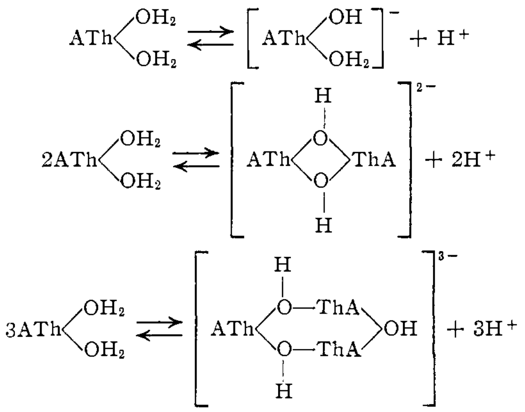
(6) The schematic structure shown (a square Archimedean antiprism) represents the most reasonable configuration consistent with the available experimental data.

with a reaction of the type

$$n\text{ThA} + n\text{H}_2\text{O} \rightleftarrows [\text{AThOH}]_n^{-n} + n\text{H}^+$$

where A^{-4} represents the tetranegative ethylenediaminetetraacetate ligand. If *n* is 2 or more, an increase in concentration would shift the equilibrium to the right and decrease the *p*H of the buffer region, in accordance with observations.

For the purpose of carrying out a mathematical analysis of this reaction it was initially assumed that the olated form is either binuclear or trinuclear, to give the possible equilibria



It is of course possible that, in addition to the binuclear and trinuclear species shown above, linear polymers or cyclic structures of higher order also are formed.

Equilibrium Constant for Olation of Th(IV)–EDTA.—On the basis of the formation of the simple binuclear or trinuclear species, the following relationships may be employed

$$K_A = [B][H^+]/[A] \qquad (1)$$

$$K_D = [D][H^+]^2/[A]^2 \qquad (2)$$

$$K_T = [T][H^+]^3/[A]^3 \qquad (3)$$

where A is the normal EDTA–Th(IV) chelate compound, supposedly in the diaquo form; B is the monohydroxo chelate; D is the binuclear diolate chelate species and T is the trinuclear triolate chelate compound. If C_{OH} represents the calculated concentration of base added at any point in the titration beyond $m = 2$, then it follows that

$$C_{OH} = [B] + 2[D] + 3[T] + [OH^-] - [H^+] \qquad (4)$$

This relationship assumes that no dihydroxo forms of the metal chelate are present. Also in the following treatment the *p*H of the experimental points is such that both $[H^+]$ and $[OH^-]$ may be neglected. The total concentration of ligand species present, T_A, is given by the expression

$$T_A = [A] + [B] + 2[D] + 3[T] \qquad (5)$$

If it is assumed that only one polynuclear form is present, the above equations may be combined to give the expressions

For a Binuclear Chelate

$$\frac{C_{OH}}{[A]/[H^+]} = \frac{[B]}{[A]/[H^+]} + \frac{2K_D[A]}{[H^+]} \qquad (6)$$

For a Trinuclear Chelate

$$\frac{C_{OH}}{[A]/[H^+]} = \frac{[B]}{[A]/[H^+]} + \frac{3K_T[A]^2}{[H^+]^2} \qquad (7)$$

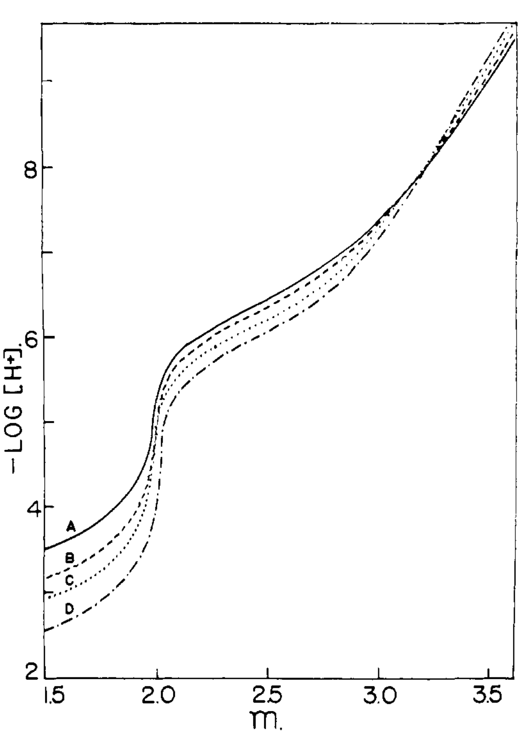


Fig. 1.—Potentiometric titrations of 1:1 Th(IV)–disodium dihydrogen ethylenediaminetetraacetate chelate system at 25 ± 0.05°: A, 6.25×10^{-4} *M*; B, 1.25×10^{-3} *M*; C, 2.50×10^{-3} *M*; D, 5.00×10^{-3} *M*; *m* = moles of KOH added per mole of metal chelate; $\mu = 0.1$ (KNO_3).

Equation 6 indicates that a plot of $C_{OH}/([A]/[H^+])$ against $[A]/[H^+]$ should give a straight line if a dimer is present. The slope of the line would be equal to $2K_D$ and the intercept at $[A]/[H^+] = 0$ would be equal to K_A. If a trimer is present, a straight line will be formed when $C_{OH}/([A]/[H^+])$ is plotted against $[A]^2/[H^+]^2$. The slope of this line would be equal to $3K_T$ and the intercept at $[A]^2/[H^+]^2 = 0$ would be equal to K_A. The linear plot of $C_{OH}/([A]/[H^+])$ in Fig. 2 is striking evidence for the presence of a binuclear chelate V in equilibrium with the mononuclear forms in solution. The points on this plot were taken from the first portion of the buffer regions up to $m = 2.6$ for all four concentrations. Beyond this neutralization value, the results deviated from the linear plot, probably because of the presence of dihydroxo species, and possibly oxolated forms which were assumed to be absent in the calculations. A similar plot of the data with equation 7 failed to give a linear relationship, in agreement with the conclusion that the principal olated form is binuclear. Mathematical treatment of the second buffer region above $m = 3$ was prevented by lack of good equilibrium data in this region, where the *p*H meter readings were found to drift considerably.

The equilibrium constants obtained by this graphical solution are given in Table I. It should be noted that the true dimerization constant K_d, which represents the reaction

$$2\text{ThA(OH)} \rightleftarrows \text{Th}_2\text{A}_2\text{(OH)}_2$$

is obtained by dividing K_D by the square of K_A.

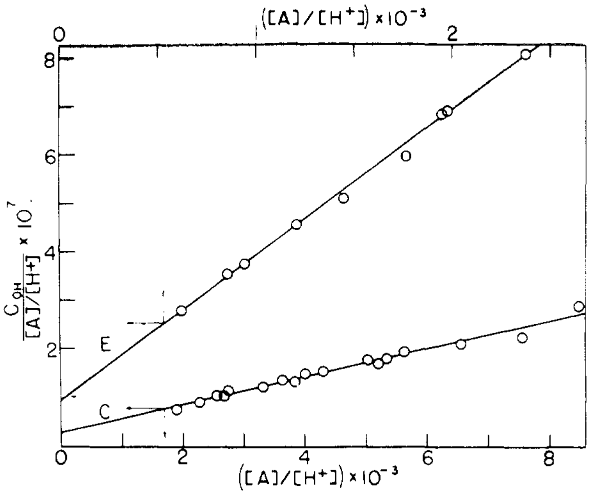


Fig. 2.—Graphical demonstration of formation of binuclear diolate Th(IV) chelate compounds: E, Th(IV)–EDTA; C, Th(IV)–CDTA; C_{OH} = total moles of base added per liter of solution beyond first inflection; [A] = concentration of normal hydrated 1:1 chelate compound.

Equilibrium Constant for Olation of Th(IV)–CDTA.—The ligand *trans*-1,2-diaminocyclohexanetetraacetic acid is similar to EDTA, and offers a unique opportunity for testing and extending the treatment given above for the determination of hydrolysis and olation equilibria of the Th(IV)–EDTA chelate system. The titration curves of the 1:1 Th(IV)–CDTA chelate at various concentrations, given in Fig. 3, indicate that the stability of this chelate is at least as great as, or greater than, that of EDTA. The Th(IV)–CDTA chelate is a weaker acid than the corresponding Th(IV)–EDTA chelate since the buffer region between $m = 4$ and $m = 5$ in Fig. 3 lies at higher $-\log [H^+]$ values than do the corresponding buffer regions of Fig. 1. The Th(IV)–CDTA titration data were given the same mathematical treatment as outlined above for the Th(IV)–EDTA system, and the graphical solution for equation 6 is shown in Fig. 2. The values of $C_{OH}/([A]/[H^+])$ and $[A]/[H^+]$ were taken from the portions of the buffer regions between $m = 4.1$ and $m = 4.5$. In this case, as in the EDTA system, the linearity of the graph demonstrates the presence of the binuclear species in solution having a structure similar to that indicated by V. Here also a similar plot of the data in accordance with equation 7 failed to give a straight line. Above $m = 4.5$, the experimental points again deviated considerably from linearity, probably indicating the presence of appreciable amount of higher hydrolytic forms. The equilibrium constants obtained from this graphical solution are listed in Table I.

TABLE I

EQUILIBRIUM RELATIONSHIPS FOR Th(IV) CHELATES AT 25°, $\mu = 0.1$ (KNO_3)

Ligand	Type formula	Equilibrium constant Quotient	Log K
Ethylenediaminetetraacetic acid	H_4A	$[ThA]/[Th][A]$	23.2 ± 0.1[a]
		$[ThA]/[ThA(OH)][H^+]$	7.04 ± 0.05
		$[ThA]^2/[Th_2A_2(OH)_2][H^+]^2$	9.82 ± 0.05
		$[Th_2A_2(OH)_2]/[ThA(OH)]^2$	4.3 ± 0.1
1,2-Diaminocyclohexanetetraacetic acid	H_4A	$[ThA]/[Th][A]$	>23 (estimated)
		$[ThA]/[ThA(OH)][H^+]$	7.85 ± 0.05
		$[ThA]^2/[Th_2A_2(OH)_2][H^+]^2$	10.84 ± 0.05
		$[Th_2A_2(OH)_2]/[ThA(OH)]^2$	4.3 ± 0.1
Diethylenetriaminepentaacetic acid	H_5A	$[ThA]/[Th][A]$	>27 (estimated)
		$[ThA]/[ThA(OH)][H^+]$	≈8.9

[a] 20°, $\mu = 0.1$, G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).

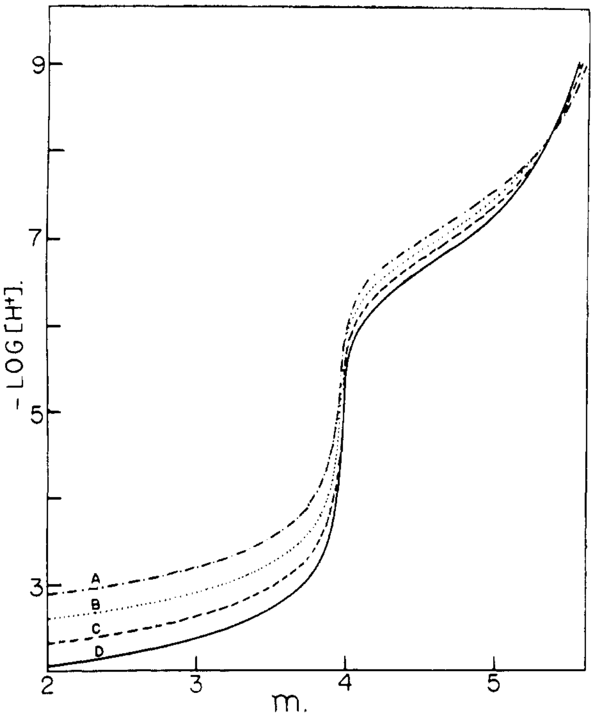
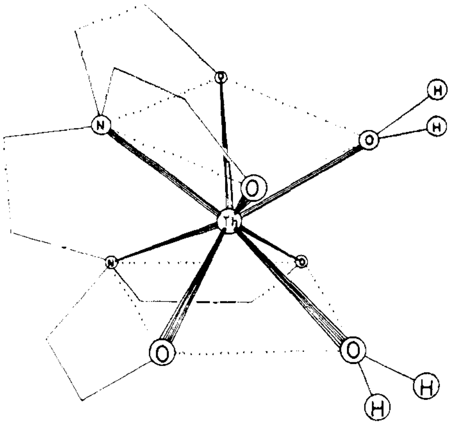


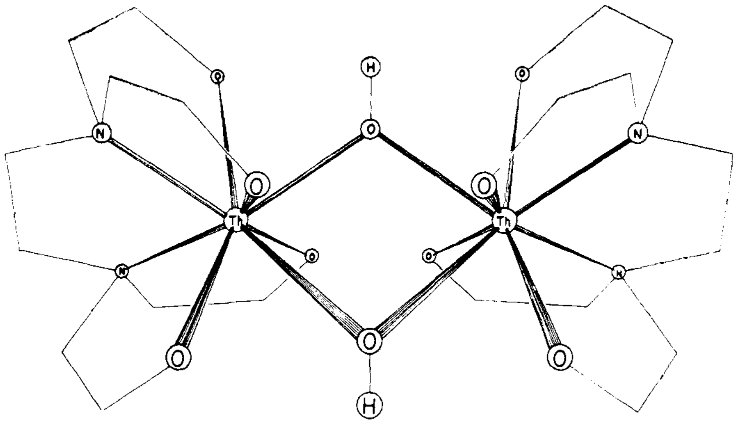
Fig. 3.—Potentiometric titration of 1:1 Th(IV)–CDTA chelate system at 25 ± 0.05°: A, 6.25×10^{-4} *M*; B, 1.25×10^{-3} *M*; C, 2.5×10^{-3} *M*; D, 5.00×10^{-3} *M*; m = moles of KOH added per mole of metal chelate; $\mu = 0.1$ (KNO_3).

Hydrolysis of the Th(IV)–DTPA Chelate.—The reaction of diethylenetriaminepentaacetic acid, III, with Th(IV) ion offers a very interesting comparison with the interactions of EDTA and CDTA with Th(IV). The potentially octadentate character of DTPA might conceivably result in complete coördination of the Th(IV) ion, which is generally ascribed a coördination number of 8, whereas EDTA and CDTA could at best occupy only six coördination positions around the metal ion. The low buffer region in Fig. 4, which terminates in a very steep inflection at $m = 5$ corresponds to the formation of the normal 1:1 Th(IV) chelate, which probably has the structure indicated by VI. Calculations of the hydrogen ion concentrations at $m = 0$ indicate that it is just five times the metal chelate concentration, and that the metal chelate compound is completely formed even at the beginning of the titration where the value of $-\log [H^+]$ is as low as 1.5. This fact, and the very considerable rise in pH at the inflection, indicates the great stability of the Th(IV)–DTPA chelate compound.

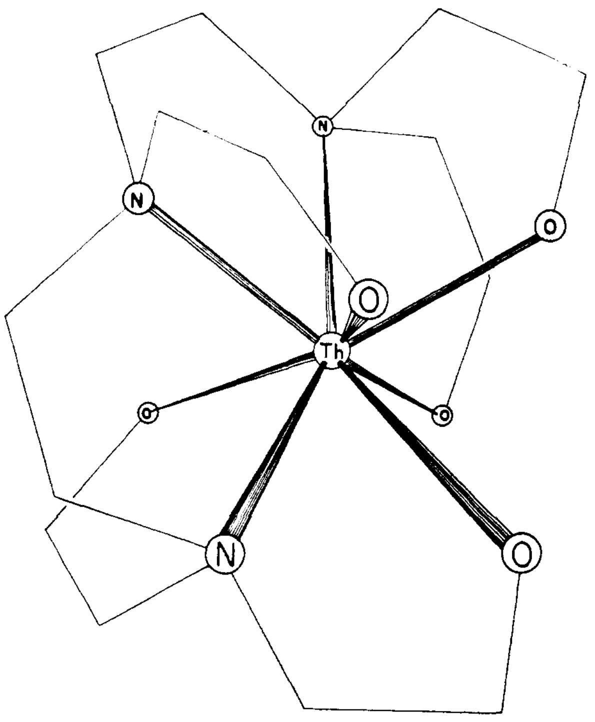
Above $-\log [H^+] = 8$, there is a second buffer region which requires an additional mole of base per mole of chelate compound. Since it is apparent from Fig. 4 that a change in concentration of the metal chelate does not shift the acid–base equilib-



IV



V



VI

rium, the second buffer region may be interpreted in terms of the simple reaction

$$\mathrm{ThZ^- + H_2O \rightleftarrows ThZ(OH)^{2-} + H^+}$$

where H_5Z represents the acid form of DTPA. In this reaction a hydroxyl ion becomes directly coordinated with the metal to give a mononuclear hydroxothorium chelate. The formation of this compound raises the question of the octadentate nature of the diethylenetriaminepentaacetate ligand with respect to Th(IV). It is possible that the ligand is in this case heptadentate and that the hydrolysis merely involves the dissociation of a coordinated water molecule. This interpretation, however, does not seem very likely in view of the fact that the very low initial buffer region in Fig. 4 would require the presence of a dissociated acetate group at *p*H 1.5. The remaining alternative, that a monohydroxo heptadentate chelate with an undissociated free carboxyl group is formed at *p*H 1.5, is also ruled out because of the fact that more positive forms of Th(IV), including the aquo ion, do not form hydroxo complexes at so low a *p*H, and the fact that a buffer region corresponding to the titration of the supposedly free carboxyl group is absent from the titration curves. Thus it seems clear that the initial chelate formed is octadentate, as indicated by VI, and that formation of the hydroxo chelate involves the displacement of a carboxylate donor by a hydroxide ion.

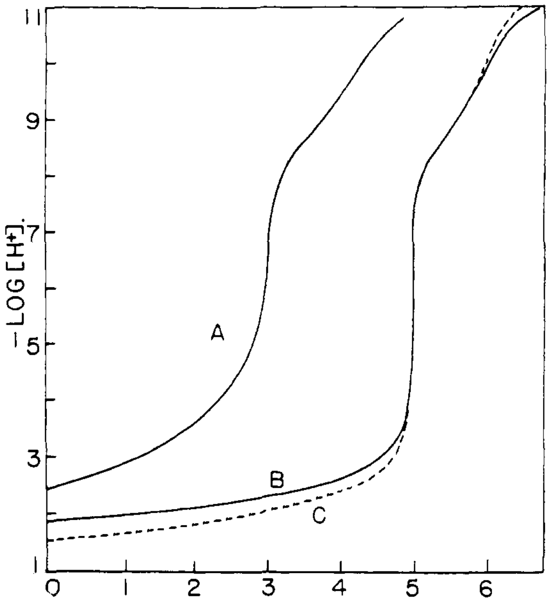


Fig. 4.—Potentiometric titration of 1:1 Th(IV)–DTPA chelate system: A = free DTPA; B = metal chelate at 2.5×10^{-3} *M;* C = metal chelate at 5.0×10^{-3} *M;* t = 25°; μ = 0.1 (KNO_3).

The concentration constants listed in Table I apply only under the reaction conditions, 25° and 0.1 ionic strength. The values given for the formation constants of CDTA and DTPA were calculated on the basis of the maximum possible degree of dissociation of the Th(IV) chelates based on the maximum experimental error in the determination of hydrogen ion concentration. The CDTA and DTPA chelates are probably considerably more stable than is indicated by the values listed, and there can be little doubt that the order of relative chelate stabilities is EDTA < CDTA << DTPA. To the best knowledge of the authors, the DTPA chelate is the most stable aqueous coördination compound of Th(IV) thus far investigated.

The greater hydrolytic tendency of Th(IV)–EDTA over that of Th(IV)–CDTA is in accord with the lower stability of the former chelate compound. The greater interaction of the Th(IV) ion with CDTA thus results in less interaction of the metal with the remaining coördinated water molecules.

It is interesting to note that the equilibrium constants for the formation of the binuclear species from the monohydroxothorium chelates are identical within experimental error for EDTA and CDTA, even though the interaction of Th(IV) with the hydroxyl ion is greater in the EDTA chelate. The equivalence of the two dimerization constants is perhaps the result of the cancelling of two opposing tendencies: 1, the greater tendency for dimerization of the Th(IV)–CDTA chelate as the result of more effective bridging by the OH group, and 2, the somewhat greater steric effects for the CDTA chelate, which would tend to work against formation of the dimer.

It is remarkable that the dimerization constants of these chelate compounds are within the range of dimerization constants noted by Pokras[7] for a series of hydroxo metal ions, as well as the dimerization constant for the Th(IV) ion calculated from the results of Kraus and Holmberg,[3] all of which contain no ligands other than water and hydroxide. This agreement is probably to a large extent fortuitous, since the lower ionic charge in the metal chelates would tend to increase the dimerization tendency over that observed for the more highly charged ions reviewed by Pokras. This effect would be largely balanced by greater steric effects in the chelates, and a reduction in the number of aquo sites through which olate bridging can take place.

[7] L. Pokras, *J. Chem. Educ.*, **33**, 223 (1956).

WORCESTER, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CONNECTICUT]

The Interaction of 2-Methyl-2-amino-3-butanone Oxime with Nickel(II) and Copper(II) Ions[1]

BY R. KENT MURMANN

RECEIVED FEBRUARY 28, 1958

The interactions of 2-methyl-2-amino-3-butanone oxime (AO) and some of its derivatives with Cu(II) and Ni(II) ions have been investigated quantitatively. The thermodynamic stability of $[Ni(AO)(H_2O)_4]^{+2}$ is small compared to that of $[Ni(AO)_2(H_2O)_2]^{+2}$ while the Cu(II) complexes follow the normal order. Alkyl substitution on the amine-nitrogen reduces the stability of the nickel complexes but does not prevent hydrogen-bond formation while Cu(II) forms a bi-nuclear structure involving hydroxo bridges. Differences in the thermodynamic stability of the hydrogen bond in the complexes of these ions are great with Ni(II) being the most stable. Addition of acid to complexes of the type $[M(AO)_2–H]^+$ results in the instantaneous formation of $[M(AO)_2(H_2O)_2]^{+2}$ which decomposes at a measurable rate. This rate of dissociation follows the law $d[Ni(AO)_2]^{+2}/dt = k[Ni(AO)_2]^{+2}[H^+]$. Substitution of an N-alkyl group has an accelerating effect while increasing the number of chelate rings decreases the rate. These results are discussed with reference to the solubility differences of Cu(II) and Ni(II) dimethylglyoximates.

Introduction

The interaction of transition metal ions with aliphatic *syn*-α-dioximes has long been of importance in analytical chemistry. Recently there has been an increased interest in this type of coordination compound directed primarily toward explaining the solubility differences between Cu(II) and Ni(II) compounds.[2–4] Although these efforts met with considerable success there are some species which do not appear to behave according to the existing theories (*i.e.*, the dioxime of glyoxal). It was felt that stability constant studies would be of value in showing the inherent differences in the chelating ability of closely related metal ions.

The low solubility which characterizes many of the α-dioxime chelates prevents accurate determination in aqueous solution of the thermodynamic quantities involved in their formation. However, (AO)[5a] has been shown to form similar compounds containing only one hydrogen bond, which possess more satisfactory characteristics.[1]

This paper presents the results of studies directed toward elucidation of the properties of intramolecular hydrogen bonds in coördination compounds and toward evaluation of their influence on the configuration of the metal complex and on the stability of intermediate species. The behavior of this ligand provides a further insight into the remarkable difference in solubility of the Cu(II) and Ni(II) dimethylglyoximates.

Previously it was established[1] that with Ni(II) the main species formed in neutral solution with excess (AO) has the structure B. Under basic conditions a second proton can be removed leading to a species of probable structure C. Compound B can be converted under acidic conditions to A which is thermodynamically unstable but somewhat less so kinetically. Copper ions form essentially identical species, the major differences being in the

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[1] For previous paper in this series, see R. Kent Murmann, THIS JOURNAL, **79**, 521 (1957).

[2] L. E. Godychi and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953).

[3] R. G. Charles and H. Freiser, *Anal. Chim. Acta*, **11**, 101 (1954).

[4] A. G. Sharpe and D. B. Wakefield, *J. Chem. Soc.*, 281 (1957).

[5] (a) The ligands discussed here are designated as follows: (AO) = 2-amino-2-methyl-3-butanone oxime; (*n*-PrAO) = 2-*n*-propylamino-2-methyl-3-butanone oxime; (*n*-AmAO) = 2-*n*-pentylamino-2-methyl-3-butanone oxime; (PhAO) = 2-phenylamino-2-methyl-3-butanone oxime; (EnAO) = 2,2′-ethylenediamino-bis-(2-methyl-3-butanone) dioxime; (En) = ethylenediamine, DMG = dimethylglyoxime, (Gly) = glyoxaldioxime; (b) the designation –H is meant to express the essentially complete ionization of an oxime hydrogen.