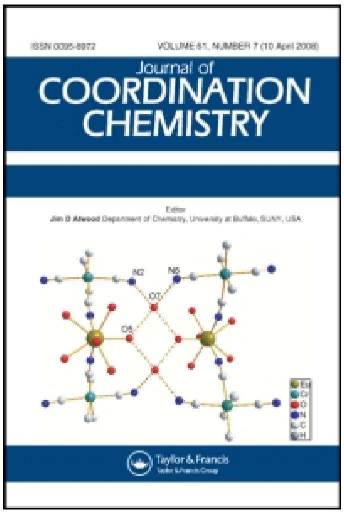

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STRUCTURE AND CONFORMATION OF Th(IV)-COMPLEXES OF TRIETHYLENETETRAMINEHEXAACETIC ACID IN AQUEOUS SOLUTION

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STRUCTURE AND CONFORMATION OF Th(IV)-COMPLEXES OF TRIETHYLENETETRAMINEHEXAACETIC ACID IN AQUEOUS SOLUTION[1]

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The aqueous (D_2O) infrared and proton nmr spectra of triethylenetetraminehexaacetic (TTHA) and the 1 : 1 Th(IV)—TTHA chelate have been studied as a function of "*a*" value (*a* = moles of base/mole of ligand). With the aid of infrared and nmr data the specific successive protonation sites of the anion are described as a function of increasing hydrogen ion concentration. The nmr spectra of Th(IV)—TTHA indicate that with increasing alkalinity protonated species persist until *a* = 4 (pD 1.47), where an extremely stable $[\mathrm{Th(IV)—TTHA}]^{2-}$ chelate predominates. The nmr spectra of the Th(IV)—TTHA complex at *a* = 6 exhibit characteristic multiplet splitting patterns for the ligand geminal acetate protons, indicating environmental non-equivalence of the ligand atoms. A ten-coordinate Th(IV) complex is proposed for Th(IV)—TTHA. Certain acetate protons in the Th(IV)—TTHA chelate undergo stereospecific deuteration in alkaline D_2O at 95°.

INTRODUCTION

In view of the aqueous (D_2O) infrared and proton nmr analysis of the Th(IV)–diethylenetriaminepentaacetic acid (DTPA) system described previously,[4] it was decided to investigate the structure of the Th(IV) complex of the next higher EDTA analog, triethylenetetraminehexaacetic acid (TTHA) in aqueous solution. This study extends the information about the specific metal-donor bonds formed, relative coordinate bond strengths and their steric configuration with respect to both the coordination sphere of Th(IV) ion and the multidentate structure of the ligand.

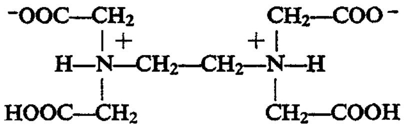
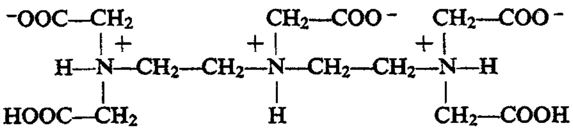
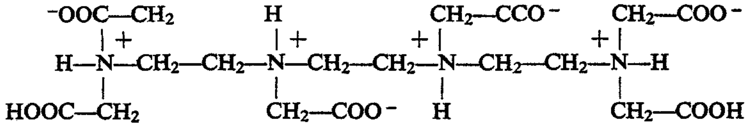
An earlier potentiometric study of the 1 : 1 Th(IV)—TTHA system[5] shows a steep inflection at six equivalents of base per mole of ligand, and no subsequent hydrolysis step, indicating that the complex formed is extremely stable. The Th(IV)—TTHA complex was reported to be considerably more stable than that of Th(IV)—DTPA, which has been shown to hydrolyze at higher pH to give a monohydroxo species. This higher stability indicates higher coordination and hence must involve coordination of an additional nitrogen atom plus one or more of the carboxylate groups attached to the nitrogen atom. A comparison of the stabilities of the mononuclear Th(IV) chelates of EDTA, DTPA, and TTHA (Table 1) reveals that there is a steady increase in the value of log $K^{\mathrm{Th}}_{\mathrm{ThL}}$ with increase in size of the ligand (log $K^{\mathrm{Th}}_{\mathrm{Th\text{-}EDTA}} = 23.2$,[6] log $K^{\mathrm{Th}}_{\mathrm{Th\text{-}DTPA}} = 28.78$,[7] log $K^{\mathrm{Th}}_{\mathrm{Th\text{-}TTHA}} = 31.9$,[8]). To achieve higher stability than that of the Th(IV)—DTPA chelate, the TTHA must indeed be nona- or decacoordinate.

Because of the importance of TTHA as a chelating agent, an investigation of the various protonated forms of TTHA is valuable for assignment of nmr peaks and infrared bands to its metal chelates. A protonation scheme has previously been suggested for TTHA[5] on the basis of its potentiometric titration curve and calculated pKa values. The present work introduces new experimental evidence for the protonation scheme by utilizing the aqueous infrared and nmr spectra of TTHA. Sudmeier and Reilley[9,10] have demonstrated the usefulness of proton nuclear magnetic resonance studies of protonation of polyamine and aminocarboxylate compounds in aqueous solution. The nmr determination of protonation schemes is based upon the chemical shifts of nonlabile protons (protons attached to carbon atoms) as a function of pH. The nonlabile methylenic protons adjacent to carboxylate and amine groups are sensitive to changes in the electronic environment caused by protonation.

Nakamoto and coworkers[11–13] have shown that the combination of infrared spectra with potentiometric titrations can be especially useful in the determination of the structures of EDTA-type compounds in aqueous solution. Structures of the

TABLE I

Thorium(IV) chelates of aminopolycarboxylic acids

Ligand	Log K_{ThL}
EDTA  $H-\underset{HOOC-CH_2}{\overset{^-OOC-CH_2}{\overset{+}{N}}}-CH_2-CH_2-\underset{CH_2-COOH}{\overset{CH_2-COO^-}{\overset{+}{N}}}-H$	23.2[a]
DTPA  $H-\underset{HOOC-CH_2}{\overset{^-OOC-CH_2}{\overset{+}{N}}}-CH_2-CH_2-\underset{H}{\overset{CH_2-COO^-}{\overset{+}{N}}}-CH_2-CH_2-\underset{CH_2-COOH}{\overset{CH_2-COO^-}{\overset{+}{N}}}-H$	28.78[b]
TTHA  $H-\underset{HOOC-CH_2}{\overset{^-OOC-CH_2}{\overset{+}{N}}}-CH_2-CH_2-\underset{CH_2-COO^-}{\overset{H}{\overset{+}{N}}}-CH_2-CH_2-\underset{H}{\overset{CH_2-CCO^-}{\overset{+}{N}}}-CH_2-CH_2-\underset{CH_2-COOH}{\overset{CH_2-COO^-}{\overset{+}{N}}}-H$	31.9[c]

[a] $t = 20°$ C, $u = 0.1$ M KNO_3, G. Schwarzenbach, R. Gut, and G. Anderegg, *Helv. Chim. Acta* **37**, 937 (1954).

[b] $t = 20°$ C, $u = 0.1$ M $NaClO_4$, E. Bottari and G. Anderegg, *Helv. Chim. Acta* **50**, 2349 (1967).

[c] $t = 25°$ C, $u = 0.1$ M KNO_3, L. Harju, *Anal. Chim. Acta* **50**, 475 (1970).

predominant aqueous species of aminocarboxylates at various *p*H values are deduced from the following three types of antisymmetric carboxyl stretching bands: (A) un-ionized carboxyl (COOH) band, (B) α-ammonium carboxylates ($R_2N^+HCH_2COO^-$) band and (C) α-aminocarboxylate ($R_2NCH_2COO^-$) band. Type A absorbs at 1730~1700 cm^{-1} whereas type B and C absorb at 1630~1620 and 1585~1575 cm^{-1}, respectively. The molar extinction coefficients of type B and C carboxylate bands per group are approximately equivalent, and about three times that of type A carboxyl groups.

EXPERIMENTAL

Triethylenetetraminehexaacetic acid was obtained from the Dojindo Pharmaceutical Laboratories, Kumamoto, Japan. The compound was recrystallized from a minimum volume of hot water. In order to minimize the amount of protium oxide generated by dissolution of TTHA in D_2O, the acidic protons of TTHA were replaced by deuterium atoms by the following method: TTHA was dissolved in a minimum volume of D_2O by adding NaOH and the D_2O was stripped twice by evaporation, with subsequent additions of 99.8% D_2O to enrich the isotopic yield. The ligand was precipitated as the hexaacid d_6–TTHA by adding the appropriate amount of DCl. Potentiometric titration of the d_6–TTHA yielded the correct equivalent weight.

Thorium(IV) chloride solutions were prepared by dissolving anhydrous thorium(IV) chloride (Alfa Inorganics) in D_2O. An equivalent amount of DCl was added to the $Th(Cl)_4$ solution to prevent hydrolysis and the resulting solution was filtered before standardization. Thorium was standardized gravimetrically by precipitation of thorium hydroxide with ammonia, followed by ignition of the precipitate to ThO_2.

Deuterium oxide (99.8% minimum isotopic purity) was obtained from Diaprep Incorporated. Deuterium chloride (38% DCl in D_2O with 99% deuterium enrichment) and sodium deuteroxide (40% NaOD in D_2O with 99% deuterium enrichment) were obtained from Bio-Rad Laboratories.

Potentiometric Measurements

A Radiometer Model PHM4c *p*H meter was used to determine deuterium ion concentrations directly. Measurements of deuterium ion concentrations were carried out in a 6-ml jacketed, miniature titration cell equipped with magnetic stirrer and a ground glass top through which were inserted nitrogen inlet and outlet tubes, and a Sargent miniature combination electrode. Gilmont 2-ml micrometer syringes were used for the potentiometric titrations. The pH meter-combination electrode assembly was calibrated for D+ concentrations with standard solutions of DCl and NaOD according to the procedure described by Kim and Martell.[14] In this paper pD refers to $-\log [D^+]$. All titrations were maintained at approximately 1.0 M ionic strength with KCl. TTHA and Th(IV)—TTHA chelate concentrations were approximately 0.10 M. In order to measure the nmr and infrared spectra of the same solutions as used for potentiometric titrations, samples were studied at pD's which corresponded to the number of equivalents of base added per equivalent of ligand.

Infrared Spectra

Infrared spectra were measured with a Beckman IR-12 double beam recording spectrophotometer. KRS–5 (thallium bromide-iodide) absorption cells with 0.025 mm spacers were employed. The infrared frequencies reported are accurate to $\pm 3\ \text{cm}^{-1}$.

NMR Spectra

The proton magnetic resonance spectra were recorded with a Varian HA-100 High Resolution NMR instrument equipped with a V-6040 variable temperature probe. All 60-Mc proton magnetic resonance spectra were recorded with either a Varian A-60 High Resolution Spectrometer or the Varian T-60 NMR instrument. Chemical shifts are reported in ppm (δ scale) downfield from an internal capillary of tetramethylsilane (TMS). Except where noted, all spectra were recorded at the ambient temperature of the probe, 31° ± 1°. Hexamethyldisiloxane (HMDS) was used as an external reference for the high temperature nmr spectra. Bulk susceptibility corrections were not made.

RESULTS

Triethylenetetraminehexaacetic Acid

The potentiometric titration curves of TTHA and 1 : 1 (Th(IV)—TTHA are illustrated in Figure 1. The aqueous infrared and nmr spectra of TTHA are summarized in Table II and Figure 2, respectively. Although the data are summarized in terms

TABLE II

Aqueous ir frequencies of TTHA and its (1 : 1) Th(IV) Chelates[a]

			Observed Frequencies, cm^{-1}			
Ligand	Metal	a[b]	$-COOH$	$>\overset{+}{N}H-CH_2-COO^-$	$-COO-M$	$-COO^-$
TTHA		1	1722m	1630s		—
TTHA		2	1722w	1630s		—
TTHA		3	—	1630s		1587m
TTHA		4	—	1630s		1585s
TTHA		5	—	1628m		1585s
TTHA		6	—	—		1585s
TTHA	Th(IV)	0	1730m	—	1620s	—
TTHA	Th(IV)	1	1730m	—	1620s	—
TTHA	Th(IV)	2	1730w	—	1619s	—
TTHA	Th(IV)	3	1730w	—	1619s	—
TTHA	Th(IV)	4	1730w	—	1618s	—
TTHA	Th(IV)	5	—	—	1617s	—
TTHA	Th(IV)	6	—	—	1617s	—

[a] Abbreviations used in this table: s, strong, m, medium; w, weak; sh, shoulder.

[b] a = moles of base/moles of ligand.

of "a" value (a = moles base/mole ligand) the predominant species in solution will be discussed in terms of protonation starting with the fully deprotonated TTHA species at $a = 6.00$.

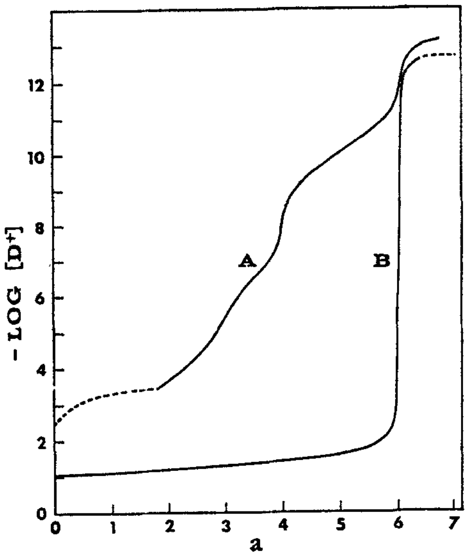


FIGURE 1 Potentiometric titration of the 1 : 1 Th(IV)—TTHA chelate at 25.00±0.05° in 1.0 M KCl; concentration of TTHA and of Th(IV)—TTHA complex = 0.10 M; a = moles of base added per mole of TTHA; (A) TTHA; (B) Th(IV)—TTHA; ----- indicates presence of solid phase.

At $a = 6.00$ (pD 11.99) only one infrared band is observed from 1500 to 1800 cm^{-1} and this absorption (1585 cm^{-1}) corresponds to six type C bands. The nmr of TTHA at $a = 6.00$ (Figure 2) exhibits four singlets corresponding to two types of acetate methylenic protons ($>N-CH_2-CO_2^-$) and two types of ethylenic groups

$$(>N-CH_2-CH_2-N<).$$

At $a = 5.00$ (pD 10.00) a new type B band appears at 1628 cm^{-1}. Taking into account the molar extinction coefficients of type B and C bands, the ratio of type B to type C bands is approximately 1 to 4. The nmr spectra of TTHA at $a = 5.00$ shows that the two types of acetate resonances (labeled a and d in Figure 2) are superimposed, thus producing a singlet at 3.83 ppm. The ethylenic protons b and b' again appear as a singlet and all resonances appear to be deshielded equally.

The infrared spectra of TTHA at $a = 4.00$ (pD 8.08) exhibit one type B band at 1630 cm^{-1} and one type C band at 1585 cm^{-1}. The infrared data show that the ratio of the optical density of type B to type C band is slightly greater than 1.0. From the nmr of this sample, it is apparent that a protons are deshielded more than d protons, implying a higher population of protons on the end nitrogen atoms than on the middle nitrogen atoms. It is also of interest to note that protons b and b' are not only deshielded more than c protons but also characterized by a very closely spaced A_2B_2 pattern indicating that δb and $\delta b'$ are now slightly different.

At $a = 3.00$ (pD 5.42) two bands are observed in the carboxyl region, a very strong band at 1630 cm^{-1} and a weaker band at 1587 cm^{-1}. The ratio of the optical density of type B band (1630 cm^{-1}) to type C band (1587 cm^{-1}) is approximately 4.5 to 1.0. In going from $a = 4.00$ to $a = 3.00$ the nmr shows that a protons are again deshielded more than d protons implying a further increase of proton population on the end nitrogens relative to the middle nitrogen atoms. Greater separation of the two halves of the A_2B_2 pattern also indicates that $\Delta\delta bb'$ is larger, as occurs when protons become unequally distributed among end and middle nitrogen atoms.

Infrared spectra of TTHA at $a = 2.00$ (pD 3.71) has one large band at 1630 cm^{-1} and a weak band

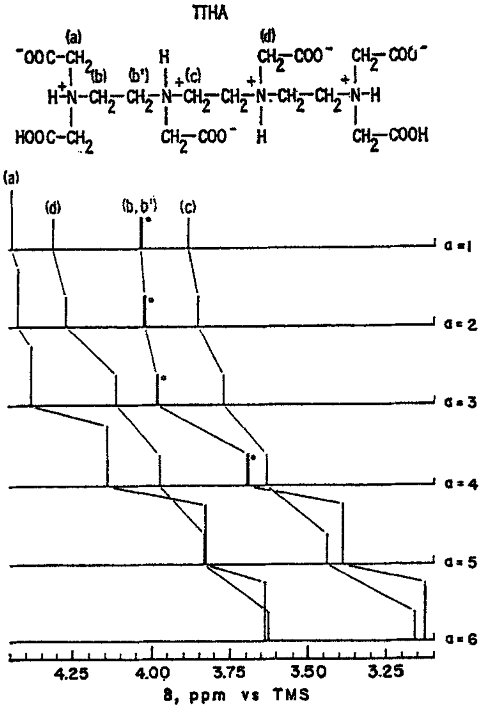


FIGURE 2 Diagrammatic presentation of the chemical shifts of TTHA as a function "a" value: asterisk denotes A_2B_2 pattern.

around 1722 cm^{-1}. It is difficult to calculate the intensity of this type A band 1722 cm^{-1}; however, by utilizing the extinction coefficients of type A and B bands,[12] the ratio of the optical density of type A to type B is estimated to be about 1.0 to 5.0. The nmr spectra shows that the *d* protons have been deshielded more than *a* and *c* protons from $a = 3.00$ to $a = 2.00$. This implies that the middle acetate groups are becoming protonated in this pD region. The two halves of the A_2B_2 pattern of the *b* and *b′* protons are closer together than they were at $a = 3.00$ signifying that $\Delta\delta bb'$ is somewhat smaller.

Although the solubility of $[d_5\text{–TTHA}]^-$, corresponding to $a = 1.00$ (pD 3.32), is limited, enough of the sample is in solution to obtain a satisfactory infrared and nmr spectra. One strong infrared band is observed at 1630 cm^{-1} and a band of medium intensity is observed at 1722 cm^{-1}. Considering the differences in extinction coefficients for type A and B bands, the ratio of the optical density of type A band (1722 cm^{-1}) to type B band (1630 cm^{-1}) is approximately 1.0 to 2.0. Very little change is noted in the nmr spectra from $a = 2$ to $a = 1$, except that *d* protons are again deshielded more than any other protons. This indicates further protonation of the middle acetate groups. It should also be noted that the A_2B_2 pattern of *b* and *b′* protons is virtually identical to that A_2B_2 pattern at $a = 2$.

Unfortunately, the spectrum of the fully protonated TTHA (d_6–TTHA) was not obtained because of its low solubility.

Th(IV)—TTHA System

The potentiometric titration curve of Th(IV)—TTHA (Figure 1) exhibits a very flat buffer region with a steep inflection at $a = 6$, thus indicating the formation of a very stable complex. The inflection extends from pD $\sim$ 3 to pD $\sim$ 12 with no visible Th(IV) hydrolysis until pD $\sim$ 12.6. Because of the low solubility of some protonated Th(IV)—TTHA species, the lower portion of the titration ($a = 0$ to $a = 3$) was obtained by starting with Na_3–TTHA (pD 5.42), slowly adding an equivalent amount of $THCl_4$ and titrating with DCl. Samples obtained in this manner for $a = 3$ to $a = 0$ remained supersaturated for several days; thus allowing infrared and nmr analysis. Conversely, the second portion of the titration curve from $a = 3$ to $a = 6$ was produced by starting with Na_3–TTHA, slowly adding an equimolar amount of $ThCl_4$ and titrating with NaOD.

As in the Th(IV)—DTPA (diethylenetriaminepentaacetic acid) case, protonated species also exist for Th(IV)—TTHA in the lower portion of the buffer region. Infrared spectra of Th(IV)—TTHA at $a = 0$ (pD 1.07) shows that the band at 1730 cm^{-1} (protonated carboxyl) is only about one sixth as intense as the band at 1620 cm^{-1} (coordinated carboxyl); however, considering the small extinction coefficient reported for the protonated carboxyl group, this could account for protonation of a little less than half of the acetate groups of the ligand. The nmr spectra of this protonated complex at $a = 0$ (Figure 3A) shows two broad peaks at 4.60 and 4.35 ppm and several overlapping peaks from 4.20 to 3.75 ppm. By integration of the spectra, the ratio of the two broad peaks to the overlapping peaks is approximately 3.0 to 4.0. Since TTHA has twenty-four nonlabile protons, the integration ratio corresponds to approximately ten protons for two broad peaks and fourteen protons for the overlapping peaks (4.20 to 3.75 ppm). At 50° the nmr spectra is unchanged; however at 70° all resonances are broadened to the extent that the overlapping peaks appear as featureless plateau while the other two peaks (4.60 and 4.35 ppm) are still observable but greatly broadened.

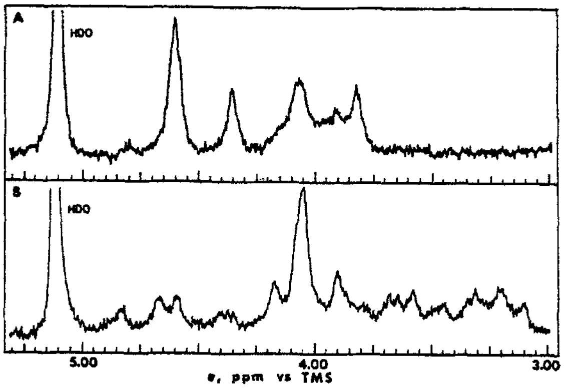


FIGURE 3 The 100Mc proton nmr spectra of the 1 : 1 Th(IV)—TTHA complex: (A) $a = 0.00$, pD 1.07; (*B*) $a = 4.00$, pD 1.47.

Proceeding from $a = 0.00$ (pd 1.07) to $a = 4.00$ (pD 1.47) the infrared band at 1730 cm^{-1} (unionized carboxyl) gradually diminishes while the band around 1620 cm^{-1} (coordinated carboxyl) intensifies. The corresponding nmr spectra shows a decrease in the peaks at 4.60, 4.35, and 3.82 ppm an intensification of the peaks of 4.07 and 3.90 ppm, and the appearance of new peaks from 3.05 to

4.17 ppm. At $a = 4.00$ (Figure 3B) two additional resonances are observed at 4.67 and 4.83 ppm. The temperature dependence of the Th—TTHA complex at $a = 4.00$ is demonstrated by the broadending at 80°. A slight downfield shift of the resonances at 4.07 and 4.17 is also observed when raising the temperature from 30° to 80°.

Infrared spectra for Th(IV)—TTHA at $a = 5.00$ (pD 1.62) and $a = 6.00$ (pD 6.95) are identical and produce only one strong carboxyl band. From $a = 4$ to $a = 5$ the nmr spectra becomes much sharper and continues to sharpen from $a = 5$ to $a = 6$. The nmr spectra at $a = 5$ and $a = 6$ are superimposable with the only difference being the added sharpness of the spectra at $a = 6$. To facilitate interpretation of the 100-Mc spectra of Th(IV)—TTHA at $a = 6$ (pD $\sim$ 9), 60-Mc spectra of the thorium complex have been recorded. Figure 4B illustrates the 100-Mc spectra with assignments of AB patterns. The spectrum contains three acetate AB patterns and complex ethylenic resonances for the three ethylenic groups. The intensities of the AB patterns indicates that each AB pattern represents two CH_2 groups. Because the chemical shifts for the complex and the chemical shift differences for the methylenic protons, δA–δB, do not change from pD $\sim$ 4 to pD $\sim$ 12.5, assignments for the resonances have been made easier. The higher field ethylenic resonances appear to be overlapping A_2B_2 or $AA'BB'$ patterns owing to the different chemical shifts of axial and equatorial protons of the chelate rings. The lower field parts of the ethylenic resonances overlap part of the higher field acetate resonances, thus preventing accurate integration of the acetate resonances. The chemical shift differences (δA–δB) for the three AB patterns designated one, two and three (Figure 4B) are 0.80, 0.21 and 0.10 ppm, respectively. The AB proton coupling constants (16.0, 17.7 and 17.9 cps) are similar to those obtained for Th(IV)—DTPA,[4] Co(III)—DTPA,[15] and various metal-EDTA complexes.[16–19] The acetate AB patterns are not affected by increasing the temperature at 95°; however, a portion of the broad ethylenic resonances are resolved into many sharper resonances.

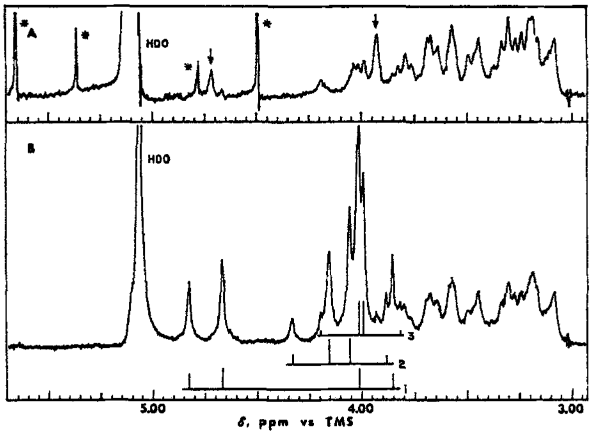


FIGURE 4 The 100-MC proton nmr spectra of the 1 : 1 Th(IV)—TTHA complex at $a = 6.00$; (A) after 2 hours at 95° in alkaline D_2O (pD 12.42); (B) acetate AB quartets before deuterium exchange.

When $[Th(IV)—TTHA]^{2-}$ is heated at 95° C in basic D_2O solutions, the acetate resonances diminish in intensity due to isotopic exchange of its CH_2 protons with solvent deuterium. Figure 4A shows the nmr spectrum of Th(IV)—TTHA (pD 12.42) after two hours at 95°. Heating for several additional hours produced no additional changes, except a gradual decrease of the two new resonances (3.93 and 4.72 ppm) denoted by arrows. The spinning side bands of the enlarged HDO peak in Figure 4A are denoted by asterisks. To study the effect of basicity on the rate of hydrogen-deuterium exchange, the same experiment was conducted at several different pD values, and followed by nmr measurements at 95°. Higher base strengths accelerated the decrease of the acetate AB resonances with an upper limit of basicity around pD 12.50. Above pD 12.50, thorium(IV) begins to hydrolyze and free TTHA is observed in the nmr spectra. Hydrolysis of thorium(IV) is readily detected because the regenerated TTHA resonances remain separated from the resonances of the coordinated TTHA over the entire pD and temperature range studied.

DISCUSSION

TTHA Protonation Scheme

Although the infrared and nmr methods for determing protonation schemes are only qualitative methods, the methods should compliment each other for determining predominant species in solution. Proton distribution percentages were calculated using substituent shielding constants as reported by Sudmeier and Reilley;[10] however, in all cases the summation of the calculated proton distribution percentages exceeded the theoretical maximum values. Similar discrepancies for EDTA were attributed to inadequate additivity of substituent shielding constants.[10]

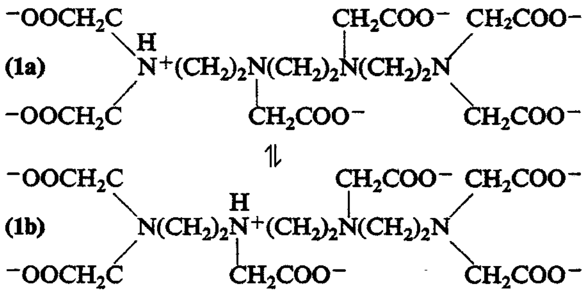
The protonation constants reported for TTHA from potentiometric studies[5] are summarized

$$X^{6-} \xrightarrow[10.19]{k_1} HX^{5-} \xrightarrow[9.40]{k_2} H_2X^{4-} \xrightarrow[6.16]{k_3} H_3X^{3-} \xrightarrow[4.16]{k_4}$$
$$H_4X^{2-} \xrightarrow[2.95]{k_5} H_5X^{-} \xrightarrow[2.42]{k_6} H_6X$$

where H_6X represents TTHA, and numbers represent logarithms of the successive protonation constants.

Both the infrared and nmr data indicate that upon addition of one equivalent of acid to the hexanegative anion of TTHA, X^{6-}, the middle and end nitrogen atoms are almost equally protonated with slightly more protonation of the middle nitrogen. Structures **1a** and **1b** are compatible with the observed spectra.

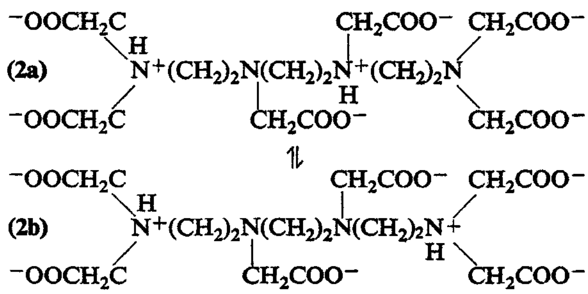
(two identical forms HL^{5-})


(1a)
(1b)

(two identical forms)

Although the infrared and nmr data support structure **2a** as the predominant species in solution at $a = 4$, the A_2B_2 pattern and the relative chemical shifts indicate slightly greater protonation of the end nitrogen atoms. Some of structure **2b** is no doubt present in solution.

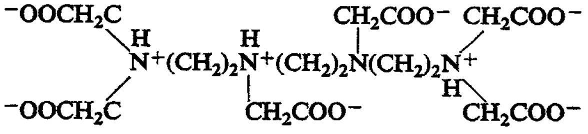
(two identical forms H_2L^{4-})


(2a)
(2b)

Bohigian[5] mentioned the possibility of both species existing in this region; however, he favored **2b** on the basis of the weak coulombic repulsion between alternate positive nitrogen atoms.

Both the infrared and nmr spectra at $a = 3$, support structure **3** as the predominant species in solution.

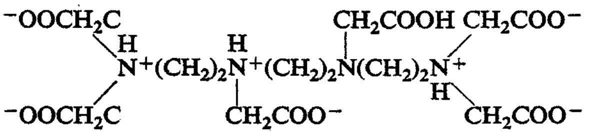
(two identical forms, H_3L^{3-})


(3)

This conclusion is in agreement with Bohigian[5] who pointed out that this reaction is similar to the second protonation step of EDTA. The resulting pK_3 of TTHA (6.16) happens to be exactly the same as pK_2 of EDTA.

At $a = 2$, the appearance of an infrared band at 1722 cm^{-1} (un-ionized carboxyl) and the greater deshielding of *d* protons suggest **4** as the predominant species

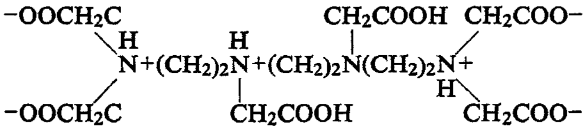
(two identical forms, H_4L^{2-})


(4)

This unique structure is ascribed to the coulombic repulsion and inductive effects from two adjacent positive ammonium groups in decreasing the proton affinity of the central basic nitrogen atoms. Bohigian and Martell[5] suggested that the carboxylate group competes with the weakly basic central nitrogens for the proton, resulting in an equilibrium between three tautomeric species, two of which are represented by **4** and a third form with all nitrogens protonated; however, the relative optical density of the IR absorption of the protonated carboxyl (1722 cm^{-1}) suggest **4** as the predominant species in solution. Comparison of the fourth protonation constant of TTHA ($pK_4 = 4.16$) with pK_4 of triethylenetetramine (3.32)[20] suggest that the fourth protonation step of TTHA could be attributed to protonation of a carboxyl of a neutral α-amino group ($>NCH_2COOH$). Protonation of a carboxyl of a neutral amine group has also been observed for the binegative anion of DTPA (H_3X^{2-}).[10, 13] The un-ionized carboxyl band for the binegative anion of DTPA occurs at 1720 cm^{-1} and is very similar to the un-ionized carobxyl band for the binegative anion of TTHA (1722 cm^{-1}). When DTPA and TTHA are dissolved in an excess of acid, both exhibit un-ionized carboxyl bands at 1730 cm^{-1} which is indicative of an α-ammonium protonated carboxyl ($>N^+HCH_2COOH$). Although no model compounds exist for calculation of the pK for protonation of a carboxyl group one carbon removed from a neutral amine; one can extrapolate such a pK from similar compounds if only inductive effects are involved. The pK for such a carboxyl group should be half way between the pK's of n-valeric acid, $CH_3CH_2CH_2CH_2COOH$ (4.84),[21] and ethoxy acetic acid, $CH_3—CH_2—O—CH_2COOH$ (3.65).[21] The estimated pK for the protonation of a carboxyl group one carbon away from a neutral amine would be 4.25 which compares favorably with the fourth protonation constant of TTHA (4.16).

At $a = 1$, the intensification of the infrared band at 1722 cm^{-1} and the larger downfield shift of the *d* protons indicates that structure **5** represents the predominant species in solution. The assignment of the last two protons

(two identical forms, H_5L^-)



(5)

($a = 2$ and $a = 1$) to the middle acetate groups is based strictly on the nmr data. Because of the magnitude of the errors in the calculated protonation percentages at $a = 1$ as much as 5 to 10% of the end acetate groups could be protonated. Sudmeier and Reilley[10] suggested that poor agreement between calculated and experimental data may be attributed to lack of knowledge of the effect of average rotamer populations. It can be reasoned that individual rotamer states are probably prevalent for the protonated species of TTHA in order to minimize coulombic repulsions between groups with like charges.

Th(IV)—TTHA System

The infrared and nmr data for Th(IV)—TTHA indicates that protonated species persist until $a = 4$ where the stable $[Th(IV)—TTHA]^{2-}$ chelate predominates. The intensity of the protonated carboxyl band at 1730 cm^{-1} suggest that approximately two carboxyl groups are protonated at $a = 0.00$ (pK 1.07). This observation is valid if the molar extinction coefficient for the coordinated carboxyl is close to that for α-aminocarboxylate. From a comparison of the infrared bands of 0.10 M TTHA at $a = 6$ and 0·10 M Th(IV)—TTHA at $a = 6$, it is apparent that the molar extinction coefficients are very similar for these two types of carboxyl bands.

In view of the lability of the Th(IV)—TTHA complex at $a = 0$ and the possibility of several protonated species in equilibrium it is difficult to assign a definite structure to the complex. However, the predominate species in solution can be deduced from the nmr spectra. The nmr peaks at 4.60 and 4.35 ppm (Figure 3A) are assigned to the protonated (uncoordinated) portion of TTHA because of the similarity to the nmr spectra of superprotonated TTHA at $a = -3$ (pD 1.02). Although neutral TTHA (H_6X) is only slightly soluble in aqueous solutions, it readily dissolves upon addition of three equivalents of DCl ($a = -3$). The peak of 4.60 ppm is assigned to the methylenic protons of two terminal and one middle acetate group while the 4.35 ppm resonance is attributed to the ethylenic group between the uncoordinated carboxyl groups. The protonated ligand resonances could be interpreted alternatively as being due to free ligand. The broad peak at 4.00 ppm is assigned to the methylenic protons of the three coordinated carboxyl groups, the ethylenic group of the coordinated end of TTHA is assigned to the resonance at 3.82 ppm and the middle ethylenic group appears to be spread out from 3.85 ppm to 4.20 ppm. The lability of this protonated complex is indicated by the "lifetime broadening"[22] of the resonances at 70°, which occurs when the rate of intermolcular exchange increases. This broadening is caused by a decrease in the lifetimes of the segments of TTHA in the coordinated and uncoordinated states, thus producing an averaging of the two states.

As base is slowly added to the complex, thereby reducing the proton competition for the coordination sites of TTHA, the uncoordinated segment of TTHA is observed to gradually wrap around the thorium(IV) ion until coordination is complete around $a = 4$ (pD 1.47). Thus at this stage the ligand donor groups are fully coordinated and two equivalents of hydrogen ion are present in solution.

The nmr spectra at $a = 4$ (Figure 3B) shows that a small amount of the complex remains only partially coordinated. The fact that only a slight upfield shift (less than 10 cps) is noted for the nmr resonances from $a = 4$ to $a = 6$ (pD 7.0) confirms earlier predictions that the four nitrogens and six carboxylate groups of TTHA are coordinated to the Th(IV)—ion to give a deca—coordinate complex. The presence of only one carboxyl infrared band (coordinated carboxyl) from $a = 4$ to $a = 6$ offers additional evidence supporting a ten-coordinate Th(IV)—TTHA chelate.

The 100-Mc nmr spectrum of a solution of the Th(IV)—TTHA complex at $a = 6$ (Figure 4B) contains three different acetate AB quartets and overlapping complex patterns for the ethylenic resonances. The temperature dependence of the complex ethylenic resonances implies faster intramolecular exchange of the ethylenic protons (ring twisting) at higher temperatures; thereby minimizing the exchange broadening of spectral lines. Similar examples of restricted internal rotation and interconversion of molecular conformers have been studied by Dahlqvist and Forsen.[23] They have computed the nmr spectra of ABCD and AA′BB′ systems undergoing different intramolecular exchange rates. Due to the overlap of the ethylenic resonances and their different intramolecular exchange rates, we are unable to assign chemical shifts to these protons.

In this extremely stable complex, the conformation of the glycinate type chelate rings are fixed, resulting in symmetrical AB quartets due to geminal coupling of acetate protons in different chemical environments. Since the four terminal acetato functions and the two middle acetato functions form equivalent sets in the free ligand, it is seen that the thorium(IV) ion coordinates to TTHA in such a manner as to bring about a sharp chemical distinction between pairs of these groups. We propose that this environmental non-equivalence of pairs of acetate groups is characteristic of a particular geometrical isomer of the deca-coordinate Th(IV)—TTHA chelate. As pointed out previously,[4] several ten-coordinate complexes of Th(IV) have been proposed and recently an X-ray study revealed a ten-coordinate Th(IV) complex with a bicapped square antiprismatic structure.[24] Although Muetterties[25, 26] suggests that polyhedral isomerizations or intramolecular rearrangements will be very easy in such large polyhedra, the stereochemical requirements of a decadentate ligand as TTHA may favor one particular geometrical isomer. The large chemical shift difference for one AB quarter ($\delta_A - \delta_B = 0.80$ ppm) is probably indicative of a particular isomer; however, any speculation as to the geometrical structure of the complex at this point would be premature. Similar chemical shift differences in acetate AB patterns have been used by others[16, 27] for assignment of in-plane and out-of-plane acetate groups of cobalt(III)-EDTA type complexes.

The inert nature of the Th(IV)—TTHA complex at $a = 6$ is exemplified by the small amount of hydrolysis of thorium(IV) at higher *p*H (pD 12.42) and high temperature (95°). Deuterium exchange of the acetate protons was observed under those conditions and was followed by nmr by observing decreases in spectral intensities of the AB patterns. Hydrogen deuterium exchange of this type have previously been reported for Co(III)-EDTA[15, 28, 29] type compounds and some bivalent metal-EDTA chelates.[30] The AB quartets labelled 2 and 3 (Figure 4B) undergo faster exchange than quartet 1; however no preferential decrease of either upfield or downfield portion of quartets #2 or 3 was observed. After two hours of heating the TH(IV)—TTHA solution (pD 12.42) at 95°, the nmr spectra (Figure 4A) shows that the acetate AB patterns have disappeared and two new peaks are apparent. The two new resonances at 3.93 and 4.72 ppm ($\delta_A - \delta_B = 0.79$ ppm) are assigned to the remaining hydrogen atoms of quartet #1 which are decoupled by deuteration of their geminal hydrogen atoms. The peak is broadened by unresolved coupling to the geminal deuterium atom. Intensities of the remaining hydrogen atoms of quartet #1 indicate that the downfield portion has decreased in intensity faster than the upfield portion. Similar base-catalyzed exchange of this type has been reported for the out-of-plane acetate groups in several Co(III)-EDTA type complexes, while the in-plane acetate groups exchange much more slowly.[28, 29] Williams and Busch[28] reported that the out-of-plane glycinate rings are vitually strain free and undergo faster deuterium exchange while the in-plane rings are strained and bent resulting in an elongation of the metal-carboxylate bond and consequently slower exchange rate.

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