correlation of the bending frequencies among similar linear molecules and has proposed a set of frequencies for C_4, C_5, and C_6.

It should be mentioned here that some electronic transitions of these carbon molecules were observed in the region of 5500–2500 Å, but the identification of the molecules producing the bands is difficult. This is an area worthy of more experimental and theoretical research, since the spectra of these molecules might be observable in stars or comets.

Acknowledgments. The authors are very grateful to Mr. G. Sanchez and Professor W. B. Person for their generosity in allowing us access to Professor J. Overend's program for the computation of vibrational frequencies and force constants and for their instruction in its use.

Structure and Conformation of Thorium(IV) Complexes of Diethylenetriaminepentaacetic Acid in Aqueous Solution[1]

A. R. Fried, Jr., and A. E. Martell*[2]

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843. *Received June 22, 1970*

Abstract: The aqueous (D_2O) infrared and proton nmr spectra of the 1:1 complexes of thorium(IV)–diethylenetriaminepentaacetic acid (DTPA) have been studied as a function of "*a*" value (*a* = moles of base added/mole of metal ion). On the basis of ir and nmr data, plausible solution structures are proposed and compared with proposed structures from previous potentiometric studies. Unlike the 10^{-3} *M* potentiometric study of Th(IV)–DTPA at *a* = 0, the 0.10 *M* ir and nmr spectra at *a* = 0 confirm the presence of a 1:1 complex in which the ligand is pentadentate. A structure is proposed for the 1:1 DTPA complex at *a* = 5 (pD 5.3) on the basis of the nmr spectra. Infrared and nmr data for the complex at *a* = 6 (pD 10.24 indicate that the monohydroxo chelate is nine-coordinate.

The detection of the formation of mononuclear and polynuclear chelates of multidentate ligands of Th(IV) ion in aqueous solution and determination of equilibrium constants for their formation, hydrolysis, and polymerization reactions have led to the need for further information about the structure and conformation of the molecular species in solution. The development of fundamental understanding of the nature of these chelate compounds requires microscopic information about the specific metal–donor bonds formed, relative coordinate bond strengths, and their steric configuration with respect to both the coordination sphere of the metal ion and the multidentate structure of the ligand. The combination of potentiometric data of these chelates with the corresponding infrared and proton magnetic resonance spectra under varying solution conditions provides the method for obtaining microscopic information about substances in solution. The nmr spectra are of particular importance because they can provide information about stoichiometry, structures, and certain bonding features of the complexes.

The basic principles of the application of proton nmr to the elucidation of bonding in labile metal chelates of aminopolycarboxylic acids have been described by Reilley[3] and Sawyer.[4] The proton nmr spectra of the ethylenediaminetetraacetic acid complexes of zirconium(IV), hafnium(IV), and palladium(II) in aqueous solution have been described by Aochi and Sawyer.[5] Recently Smith and Betts[6] have isolated a cobalt(III)–DTPA complex and proposed a solution structure using proton nmr spectroscopy. A particularly successful example of structure determination of complexes in solution by nmr has recently been reported for Al(III) chelates of vitamin B_6 Schiff bases by Abbott and Martell.[7]

Nakamoto[8] and coworkers have explained the structures of the predominant species in solution of various aminopolycarboxylic acid chelates at various pH values by combining the results of infrared studies with those of potentiometric titrations. The following antisymmetric carboxylate stretching frequencies were found:[9] type A, un-ionized carboxyl (R_2N-CH_2COOH), 1730–1700 cm^{-1}; type B, α-ammonium carboxylate (R_2N^+H-CH_2COO^-), 1630–1620 cm^{-1}; type C, α-amino carboxylate (R_2N-CH_2COO^-), 1595–1575 cm^{-1}. In these investigations they also establish that coordinated carboxyl groups absorb between 1650 and 1590 cm^{-1}, the exact frequency depending on the nature of the metal. This technique was later extended to various complexes containing amide carbonyl groups by Kim and Martell. This work was recently summarized.[10]

Previous potentiometric studies of the interaction of Th(IV) ion with ethylenediaminetetraacetic acid

---

(1) This work was supported by the U. S. Atomic Energy Commission under Contract No. AT(40-1)3621 with the Texas A&M Research Foundation.

(2) To whom inquiries may be addressed.

(3) R. J. Day and C. N. Reilley, *Anal. Chem.*, **36**, 1073 (1964).

(4) R. J. Kula, D. T. Sawyer, S. I. Chan, and C. M. Finley, *J. Amer. Chem. Soc.*, **85**, 2930 (1963).

(5) Y. O. Aochi and D. T. Sawyer, *Inorg. Chem.*, **5**, 2085 (1966).

(6) B. B. Smith and R. H. Betts, *J. Amer. Chem. Soc.*, **91**, 7749 (1969).

(7) E. H. Abbott and A. E. Martell, *ibid.*, **91**, 6866 (1969).

(8) (a) K. Nakamoto, Y. Morimoto, and A. E. Martell, *ibid.*, **83**, 4528 (1961); (b) *ibid.*, **84**, 2081 (1962); (c) *ibid.*, **85**, 309 (1963).

(9) K. Nakamoto and P. J. McCarthy, "Spectroscopy and Structure of Metal Chelate Compounds," Wiley, New York, N. Y., 1968, pp 276–277.

(10) A. E. Martell in "Recent Topics in Coordination Chemistry," S. Misumi and K. Ueno, Ed., Special Publication No. 84, Nankodo, Tokyo, Japan, 1968, pp 47–67.

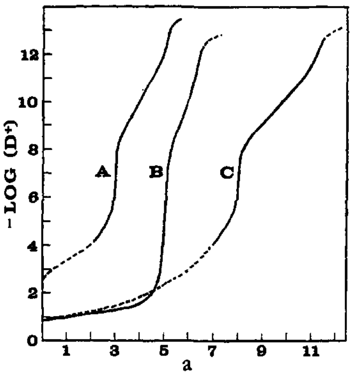

Figure 1. Potentiometric titration of Th(IV)–DTPA chelate systems at 25 ± 0.05°; all solutions are 0.10 *M* in Th(IV) ion and 1.0 *M* in KCl; *a* = moles of base added per mole of metal ion: (A) DTPA, (B) Th(IV)–DTPA (1:1), (C) Th(IV)–DTPA (1:2).

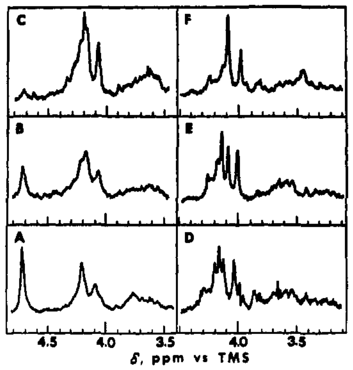

Figure 2. Proton nmr spectra (100 Mc) of thorium(IV)–DTPA: (A) *a* = 0, (B) *a* = 2, (C) *a* = 3, (D) *a* = 4, (E) *a* = 5, (F) *a* = 6; concentration of 1:1 complex, 0.10 *M*.

(EDTA, H_4L) and diethylenetriaminepentaacetic acid (DTPA, H_5L) by Bogucki and Martell[11] showed that hydrolysis of the normal 1:1 chelates ThL and ThL^-, respectively, occurred above pH 6. The second buffer region for the 1:1 Th(IV)–EDTA complex has been attributed to the formation of a dimer species $Th_2(OH)_2L_2^{2-}$ while the second buffer region in the 1:1 Th(IV)–DTPA system was indicative of formation of a mononuclear hydroxo-thorium chelate, $ThOHL^{2-}$ [11]. The 1:1 hydroxo-thorium chelate of Th(IV)–DTPA has raised a question concerning the octadentate nature of the DTPA ligand with respect to Th(IV). It has been proposed that the formation of the hydroxo chelate involves the displacement of a carboxylate donor by a hydroxide ion.[11,12] One of the motivations for the present investigation was to determine whether an alternative mechanism, the loss of a proton in a nonacoordinated complex, could be responsible for the hydrolysis.

Experimental Section

Reagents. Diethylenetriaminepentaacetic acid (98%) was obtained from J. T. Baker Chemical Co. and recrystallized from water. After recrystallization, a satisfactory equivalent weight for the anhydrous diethylenetriaminepentaacetic acid (DTPA) was confirmed by potentiometric titration with standard base.

Reagent grade disodium salt of EDTA (Fisher Scientific Co.) was recrystallized from water and methanol. After drying to the dihydrate, the equivalent weight of the dihydrate disodium salt of EDTA was also confirmed by potentiometric titration.

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

Thorium chloride solutions were prepared by dissolving anhydrous thorium chloride, $ThCl_4$ (Alfa Inorganics), in D_2O. An equivalent amount of DCl was added to the $ThCl_4$ 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. Thorium was also standardized by titration with standard EDTA solution in the presence of Alizarin Red S and Methylene Blue, according to the procedure of Ford and Fritz.[13]

Potentiometric Measurements. A Radiometer pH meter (Type PHM4) was used to determine deuterium ion concentrations. 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 system was calibrated for D^+ concentration 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 25.00 ± 0.05° under a nitrogen atmosphere and the ionic strengths of the solutions were maintained at approximately 1.0 *M* with KCl. Thorium ion concentrations were ∼0.100 *M* and the ratios of concentrations of metal ion to ligand were 1:1 and 1:2. In order to measure the nmr and ir 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 thorium ion.

Infrared Spectra. Infrared spectra were measured with a Beckman IR-12 double-beam recording spectrophotometer. KRS-5 (thallium bromide–iodide) absorption cells of 0.045 mm thickness were employed. The wave numbers reported are accurate to ±3 cm^{-1}.

Nmr Spectra. The proton magnetic resonance spectra were recorded with either a Varian HA-100 or a Varian A-60 high-resolution nmr instrument equipped with a V-6040 variable-temperature probe. Chemical shifts were measured in parts per million (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 ± 2°. Hexamethyldisiloxane (HMDS) was used as an external reference for the high-temperature nmr spectra. Bulk susceptibility corrections were not made. The 220-Mc spectrum of Th(IV)–DTPA was recorded on a Varian HR-220 spectrometer at Varian Associates, Palo Alto, Calif.

Results and Discussion

Thorium(IV)–DTPA Complexes. The 1:1 Th(IV)–DTPA system offers a very interesting comparison with the 1:1 Th(IV)–EDTA chelate, because DTPA has eight potential coordination sites as compared to six for EDTA. Potentiometric titrations of the 0.10 *M* Th(IV)–DTPA systems in D_2O are illustrated in Figure 1. The dotted lines of the potentiometric titrations indicate that a precipitate was present. The "*a*" value of the abscissa scale of the potentiometric diagram corresponds to the number of moles of base per mole of metal ion. Typical proton nmr spectra of the 1:1 Th(IV)–DTPA system for *a* = 0, 2, 3, 4, 5, and 6 are illustrated in Figure 2, and the infrared spectra obtained are summarized in Table I.

---

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

[12] R. S. Sievers and J. D. Bailar, Jr., *Inorg. Chem.*, 1, 174 (1962).

[13] J. J. Ford and J. S. Fritz, U. S. Atomic Energy Commission Report No. ISC-520, June 1954.

[14] M. K. Kim and A. E. Martell, *Biochemistry*, 3, 1169 (1964).

Table I. Aqueous Ir Frequencies of DTPA and Its (1:1) Th(IV) Chelates[a]

Ligand	Metal	a^b	Obsd frequencies, cm^{-1}			
			-COOH	$>\overset{+}{N}H\text{-}CH_2COO^-$	-COO···M	-COO$^-$
DTPA		−3	1730 (s)	1630 (m)		
DTPA		1	1720 (m)	1630 (s)		
DTPA		2	1720 (m)	1630 (s)		
DTPA		3		1630 (s)		1590 (sh)
DTPA		4		1628 (sh)		1585 (s)
DTPA		5				1585 (s)
DTPA	Th(IV)	0	1730 (m)		1617 (s)	
DTPA	Th(IV)	1	1730 (m)		1616 (s)	
DTPA	Th(IV)	2	1730 (w)		1615 (s)	
DTPA	Th(IV)	3	1730 (w)		1615 (s)	
DTPA	Th(IV)	4			1615 (s)	
DTPA	Th(IV)	5			1615 (s)	
DTPA	Th(IV)	6			1610 (s)	
DTPA	Cu(II), Th(IV)	0	1730 (m)		1618 (s)	

[a] Abbreviations used in this table: s, strong; m, medium; w, weak; sh, shoulder. [b] a = moles of base/mole of Th(IV).

1:1 Th(IV)-DTPA, a = 0 (pD 0.90). Infrared data for the 1:1 Th(IV)-DTPA complex at a = 0 indicates an absorption at 1730 cm^{-1} signifying a protonated carboxyl group (-COOH). The nmr spectra (Figure 3A) shows one sharp peak at 4.72 ppm, two broader peaks at 4.1 and 4.2 ppm, and a very broad resonance from 3.5 to 3.9 ppm. The integration of these three regions gives ratios of 4:8:6, thus accounting for the 18 nonlabile protons of DTPA. The sharp resonance at 4.72 ppm has now been identified as the methylene groups of a protonated iminodiacetate moiety. The ethylenic group adjacent to the free (uncoordinated iminodiacetic acid segment produces an A_2B_2 pattern with a large chemical shift difference between A and B protons; thus, the A_2 portion for this ethylenic group overlaps part of the acetate methylene resonances at 4.1 ppm. The broad, featureless resonances of the other ethylenic groups will be explained later. Assignments for the uncoordinated part of the ligand were identified through the ir and nmr spectra of DTPA at a = −3. DTPA has low solubility in water but readily dissolves upon addition of more acid; consequently, 3 equiv of DCl (a = −3) was added to dissolve DTPA in deuterium oxide and the nmr and ir spectra were obtained.

It has been suggested that the 4.72-ppm resonance could be interpreted alternatively as being due to free ligand. Differentiation of free-ligand resonances from coordinated-ligand resonances is difficult because of overlap; however, in solutions containing two DTPA ligands per thorium(IV) at pD 0.90, the middle acetate resonance of the free ligand appears slightly downfield from resonances of the coordinated DTPA. Failure to observe this free-ligand resonance in the 1:1 system at a = 0 (pD 0.90) suggests that little or no free DTPA ligand is present under these conditions. In the 1:2 system most of the uncomplexed-DTPA resonances remain separated from the resonances for the coordinated DTPA over the pD range studied. Further clarification of the 1:1 Th(IV)-DTPA complex at a = 0 was made by observing the effect of Cu(II) ion on the nmr resonances of the uncoordinated iminodiacetic acid group. Li and coworkers[15,16] have described how to determine bonding sites in a variety of ligands by adding a paramagnetic ion and observing the broadening of certain nmr resonances of the free ligand. When the Th(IV)-DTPA solution is made 10^{-4} M in Cu(II), the peak at 4.72 ppm (methylene groups of the iminodiacetate segment) is preferentially broadened and the ethylenic group adjacent to this protonated iminodiacetate group is also affected. An illustration of the effect of Cu(II) ion on the 1:1 Th(IV)-DTPA complex at a = 0 is given in Figure 3B along with a plausible structure of the complex. The structure of the 1:1 Th(IV)-DTPA complex at a = 0 (pD 0.90) is shown with iminodiacetic group completely protonated (nitrogen and both carboxyl groups are protonated) because the ir of the DTPA at a = −3 (pD 1.05) indicates that approximately 80% of the acetate groups are protonated at this pD. No N-H resonance or H-N-CH coupling is observed because of rapid N-H proton exchange. Addition of an equimolar amount of Cu(II) ion to the Th(IV)-DTPA at a = 0 only produced a slight lowering of the pD; thus, it appears that there is only a slight interaction of Cu(II) with this protonated iminodiacetic group at this pD (pD 0.90). Infrared spectra of the 1:1 Cu(II)-Th(IV)-DTPA solution indicates that the absorption at 1730 cm^{-1} (-COOH) is approximately the same as in the 1:1 Th(IV)-DTPA complex (*cf.* Table I), thus confirming that the contribution of Cu(II) coordination must be small. The logarithms of the formation con-

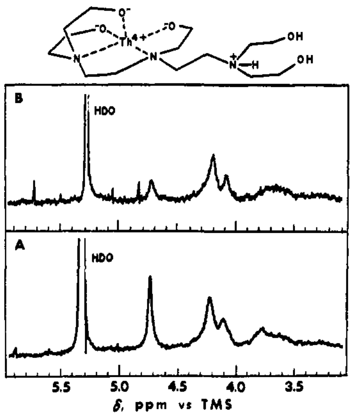

Figure 3. Model and 100-Mc proton nmr spectra of 1:1 Th(IV)-DTPA at a = 0: (A) Th(IV)-DTPA, 0.10 M; (B) Th(IV)-DTPA, 0.1 M plus ~10^{-4} M $CuCl_2$.

---

(15) N. C. Li, R. L. Scruggs, and E. D. Becker, *J. Amer. Chem. Soc.*, **84**, 4640 (1962).

(16) R. Mathur and N. C. Li, *ibid.*, **86**, 1289 (1964).

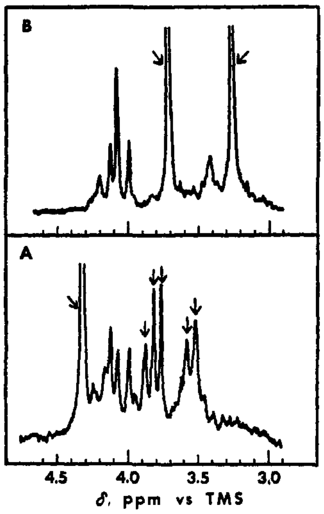

Figure 4. Proton nmr spectra (100 Mc) of 1:2 Th(IV)–DTPA system; arrows denote free DTPA: (A) $a = 8$ (pD 6.87); (B) $a = 11$ (pD 11.43).

stants of Cu(II) and Th(IV) with DTPA are 21.1 and >27,[17] respectively, thus ruling out the possibility of Cu(II) displacing Th(IV) from the complex.

Unlike the 10^{-3} M potentiometric study of Th(IV)–DTPA at $a = 0$, the 0.10 M ir and nmr spectra at $a = 0$ confirm the presence of a 1:1 Th(IV)–DTPA species in which DTPA has a free (uncoordinated) iminodiacetic acid group. DTPA functions as a pentadentate ligand in this case. Bogucki and Martell[11] calculated the hydrogen ion concentration at the beginning of the potentiometric titration ($a = 0$) and concluded that the metal chelate compound was completely coordinated even when the value of $-\log[H^+]$ was as low as 1.5. Previous results agree with the 0.10 M samples because the 1:1 Th(IV)–DTPA is completely formed at $a = 4$ (pD 1.56) in the potentiometric titrations at 0.10 M.

As base (NaOD) is very slowly added to the complex in going from $a = 0$ (pD 0.90) to $a = 4$ (pD 1.56), the nmr peak at 4.72 ppm gradually disappears and the acetate resonances ($N{-}CH_2COO\cdots M$) from 4.0 to 4.3 appear much sharper (Figure 2). The ir spectra and integration of the nmr spectra at $a = 4$ indicate that no free (uncoordinated) acetic acid groups remain in this region. In going from $a = 4$ (pD 1.46) to $a = 5$ (pD 5.3), only a slight change is noted in the nmr spectra and virtually no change occurs in the ir spectra. Thus it seems that all five carboxylate groups and all three nitrogens of the DTPA must be coordinated to the Th(IV) ion.

1:1 Th(IV)–DTPA, $a = 5$ (pD 5.3). The nmr spectra of the fully deprotonated 1:1 Th(IV)–EDTA complex is relatively simple, with two sharp peaks corresponding to the ethylenic and acetate protons; however, the nmr spectra of 1:1 Th(IV)–DTPA at $a = 5$ exhibit multiplet splitting patterns in the acetate region and one very broad resonance for the ethylenic groups. The multiplet acetate resonances suggest that the conformation of the acetate chelate rings is rigid, resulting in spin–spin coupling of geminal protons in different chemical environments. Day and Reilley[3] first proposed that this type of splitting pattern results from the interaction of two nonequivalent methylenic protons of each acetate group.

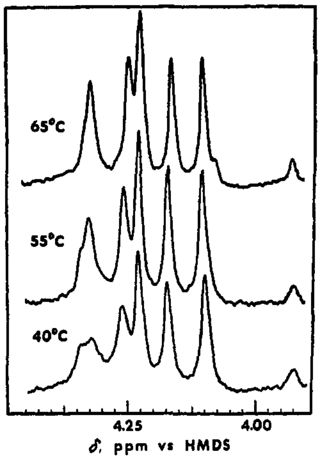

Figure 5. Temperature dependence of the 100-Mc proton nmr spectra of the acetate resonances for the 1:1 DTPA complex at $a = 5$ (pD 5.3).

It is interesting to note that rapid ligand exchange of β-diketone ligands occurs upon mixing solutions of Zr(IV), Hf(IV), Ce(IV), and Th(IV) with acetylacetonates and trifluoroacetylacetonates, and the thorium(IV) system exhibits the highest exchange rate.[18] No evidence of environmental nonequivalence of ligand atoms was obtained by nmr studies of tetrakis(trifluoroacetylacetonato) derivatives of Zr(IV), Hf(IV), Ce(IV), and Th(IV) even at temperatures as low as $-105°$. However, the appearance of separate resonance lines for the Th(IV)–DTPA chelate and the free DTPA in the 1:2 Th(IV)–DTPA system (Figure 4) indicate that the intermolecular exchange kinetics are slow with respect to the nmr time scale. Some steric restriction to nitrogen inversion must prevail; otherwise, if nitrogen inversion were fast enough, two acetate groups could interchange and give an averaged single resonance.

Because of the temperature dependence of the acetate resonances (Figure 5), peak assignments are difficult at room temperature. However, at higher temperatures characteristic splitting patterns are observed. Interpretation of the 100-Mc spectra of the Th(IV)–DTPA complex at pD 5.3 was achieved by careful analysis and comparison of the 60-, 100-, and 220-Mc spectra. The 100-Mc spectrum of the complex at 70° (Figure 6) contains two acetate AB patterns, one acetate singlet (4.18 ppm), and a complex ethylenic resonance pattern from 3.05 to 3.85 pm. The relative areas of the AB patterns indicate each AB pattern corresponds to two methylenic groups while the acetate singlet represents one methylenic group. In Figure 6 the chemical shift difference ($\delta_A - \delta_B$) and the coupling constant for the higher field AB pattern are 0.15 ppm and 17.3 cps, respectively, while the chemical shift difference and coupling constant for the lower field AB pattern are 0.19 ppm and 16.2 cps. Because of the broadness of the resonances and the lack of resolution for the splitting at 60 Mc, 220-Mc spectra of the complex have been recorded. In Figure 7, the 220-Mc spectrum at 50° not only illustrates the asymmetry of the lower field AB pattern at lower temperature but also shows two distinct ethylenic

---

[17] L. G. Sillen and A. E. Martell, "Stability Constants of Metal Ion Complexes," Special Publication No. 15, The Chemical Society, London, 1964.

[18] T. J. Pinnavaia and R. C. Fay, *Inorg. Chem.*, 5, 233 (1966).

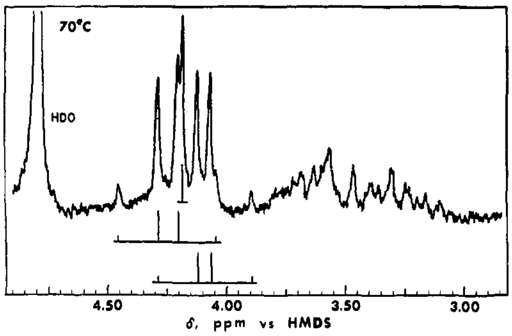

Figure 6. Proton nmr spectrum (100 Mc) of the 1:1 Th(IV)–DTPA chelate at a = 5 and 70°.

resonances. When the temperature is raised from 31 to 80°, the coupling constant for the higher field AB pattern decreases from 17.7 to 17.2 cps while the chemical shift difference decreases from 0.179 to 0.145 ppm. The coupling constant of the lower field AB pattern does not change with temperature; however, the value of $\delta_A - \delta_B$ increases from 0.161 ppm at 31° to 0.194 ppm at 80°. Below 25° the downfield AB quartet collapses to a very broad resonance. Figure 5 illustrates the 100-Mc nmr spectra of the acetate region as a function of temperature. The decrease in the chemical shift difference for the high-field AB pattern is consistent with an increase in the AB interchange rate at higher temperatures.[19] AB interchange occurs when two protons of a particular carbon atom interchange their magnetic environments by breaking the metal–nitrogen bond, allowing nitrogen inversion, and re-forming the metal–nitrogen bond with the acetate groups interchanged. However, the increase in the value of $\delta_A - \delta_B$ for the other AB quartet at higher temperatures must involve a different process. Since geometrical isomerism is expected to occur quite easily for these large polyhedra,[20] there exists the possibility of a rapid interconversion between geometrical isomers of the chelate in solution. The nmr results are compatible with a slowing down of the interconversion between two isomers, resulting in a broadening of the simple time-averaged spectrum.

Hydrolysis of the Th(IV)–DTPA Chelate. A monohydroxo thorium chelate is formed when the potentiometric titration proceeds from a = 5 to a = 6.[11] Infrared data for the DTPA complex at a = 6 (pD 10.24) show only one strong band at 1610 cm^{-1}, suggesting that all carboxyl groups are coordinated. If a carboxyl group were displaced by a hydroxide ion, the uncoordinated carboxyl should appear as a shoulder or separate band around 1600 cm^{-1} as in the case of some cobalt(III) complexes.[21] If an acetate were uncoordinated in the hydroxo chelate, that particular acetate resonance would be expected to shift upfield in the nmr spectra in going from a = 5 (pD 5.3) to a = 6 (pD 10.24). Inspection of the nmr spectra of Figure 2 shows that no acetate peaks move upfield relative to the others from a = 5 to a = 6; thus, it can be concluded that a nine-coordinate monohydroxo chelate is formed at a = 6. Several other reports have proposed nine- and ten-coordinate complexes of Th(IV).[22-25] Muetterties[25] suggested that ten-coordination may be relatively common in thorium(IV) chelates and suggested one possible idealized geometry as a symmetrically bicapped square antiprism. Recent X-ray studies have revealed a ten-coordination Th(IV) complex with a bicapped square antiprismatic structure[26] and a nine-coordinate complex with a monocapped square antiprismatic structure.[27]

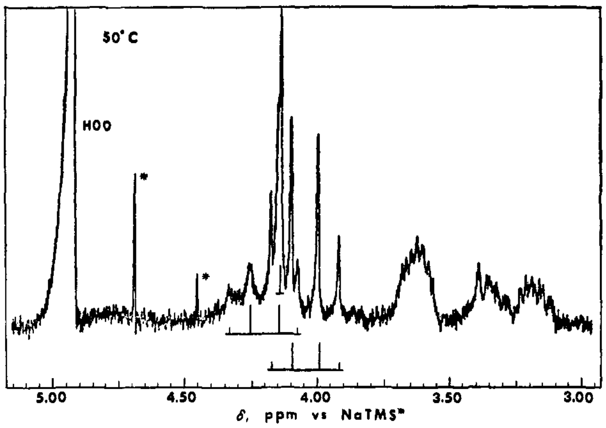

Figure 7. Proton nmr spectrum (220 Mc) of the 1:1 Th(IV)–DTPA chelate at a = 5 and 50°; NaTMS* = sodium 2,2-dimethyl-2-silapentane-5-sulfonate.

Although no specific acetate assignments are attempted, consideration of the observed spectra permits reasonable speculation concerning the structures of these complexes. We propose that the apparent environmental nonequivalence of the acetate groups is characteristic of a particular geometry of the DTPA chelate. One possible structure would be the monocapped square antiprism with a coordinated solvent mole (D_2O) occupying one site at a = 5. The hydrolysis step would therefore involve the ionization of a D^+ from the coordinated deuterium oxide molecule. The acetate resonances at a = 6 exhibit the same temperature dependence as the acetate resonances at a = 5. At 55 and 65° two peaks could be resolved from the large peak at 4.09 ppm (Figure 2F), indicating that one of the inner members of the high-field quartet coincides with the acetate singlet at lower temperatures. The hydroxide ion seems to have a greater effect on one of the two ethylenic groups of the complex. A very broad singlet for one of the ethylenic groups implies faster partial rotation or ring twisting for one of the ethylenic groups than for the other.

Recent investigations of the intra- and intermolecular acetate scrambling in Ni(II)–nitrilotriacetic acid complexes[28] helps to explain why geometrical isomers might be observed for Th(IV)–DTPA. The intramolecular displacement of a water molecule by an acetate group in $Ni(NTA)(H_2O)_2^-$ is reported to be faster than the rate of displacement of one acetate group by another in Ni-

---

[19] J. L. Sudmeier and C. N. Reilley, *Inorg. Chem.*, **5**, 1047 (1966).

[20] E. L. Muetterties and C. W. Alegranti, *J. Amer. Chem. Soc.*, **91**, 4420 (1969).

[21] F. L. Garvan, "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, p 317.

[22] G. Goldstein, O. Menis, and D. L. Manning, *Anal. Chem.*, **32**, 400 (1960).

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

[24] T. A. Bohigian, Jr., and A. E. Martell, *ibid.*, **4**, 1264 (1965).

[25] E. L. Muetterties, *J. Amer. Chem. Soc.*, **88**, 305 (1966).

[26] M. N. Anhtar and A. J. Smith, *Chem. Commun.*, 705 (1969).

[27] N. Singer and B. F. Studd, *ibid.*, 342 (1970).

[28] L. E. Erickson, F. F. L. Ho, and C. N. Reilley, *Inorg. Chem.*, **9**, 1148 (1970).

$(NTA)_2^{4-}$. If these results are applicable to the Th(IV)–DTPA case, then intramolecular rearrangement of Th(IV)–TTHA (triethylenetetraminehexaacetic acid) should be even slower. The Th(IV)–TTHA chelate is reported to be decadentate and to have a higher stability than the DTPA complex.[24] The Th(IV)–TTHA system is currently under investigation.

1:2 Th(IV)–DTPA System. As mentioned earlier, uncomplexed DTPA resonances remain separated from the resonances for the coordinated DTPA over the entire pD range studied. The proton nmr spectra of the 1:2 Th(IV)–DTPA system at $a = 8$ (pD 6.87) and the 1:2 Th(IV)–DTPA solution at $a = 11$ (pD 11.43) are illustrated in Figure 4. Resonances for uncomplexed DTPA are indicated by arrows. The 1:2 system at $a = 8$ is just a composite of the 1:1 chelate at $a = 5$ and the free DTPA at $a = 3$, while the 1:2 system at $a = 11$ is simply a composite of the 1:1 chelate at $a = 6$ and the free DTPA at $a = 5$. The chemical shift assignments of DTPA at various pH values have been described by Sudmeier and Reilley.[29] Even at 80° intra- and intermolecular exchange must be slow on the nmr time scale for the 1:2 Th(IV)–DTPA system at $a = 11$ because sharp, separate resonances are still observed for both coordinated and free DTPA.

Ethylenic Resonances. Some explanation of the broad ethylenic resonances will be discussed now. The ethylenic resonances were not mentioned earlier because the broad, almost featureless absorbance ascribed to the ethylenic protons is persistent throughout the entire pD range studied. Similar broad ethylenic resonances were observed in the Pb(II) and La(III) complexes with DTPA.[30]

The broad resonances for the ethylenic protons suggest that hindered and slow rotation of the ethylenic groups must be occurring. A model of the DTPA ligand coordinated to a Th(IV) ion indicates that several rotational conformers of the ethylenic protons would accompany partial (hindered) rotation of the ethylenic backbone of the chelate. The possibility of unequal population of rotational conformers along with the experimentally supported possibility of different rates for partial rotation of the two ethylenic groups of DTPA would further complicate the spectra. Four different sets of $A_2'B_2'$ patterns slowly interconverting would probably give the observed broad, featureless resonance.

Spectra of the ethylenic region of the DTPA complex at $a = 5$ and 65° indicate that faster partial rotation of the ethylenic groups has sharpened the ethylenic resonances, but the patterns are still too complicated for any definite assignments. The ethylenic portion of the spectra of the DTPA complex at $a = 6$ and higher temperatures indicates that one portion of the ligand backbone is undergoing faster partial rotation than the other, thus producing one ethylenic resonance that is relatively narrow at 65°. This obvious nonequivalence of the two ethylenic groups might be due to an increase in the lability of part of the chelate, which in turn is due to the decrease in the effective charge of the central ion through coordination with the deuterioxide ion, OD^-.

Th(IV)–EDTA System. The 1:1 Th(IV)–EDTA complex exhibits one sharp acetate peak and one sharp ethylenic peak, thus indicating labile bonding (fast intramolecular rearrangement). In the complex a thorium(IV) dimer[11] is required to explain the second buffer region in the potentiometric titration. However, on the basis of the nmr and ir data, no conclusions can be made regarding the structure of the dimeric unit.

The nmr data gave no evidence of the formation of 2:3 or 1:2 Th(IV)–EDTA complexes when the appropriate ratios of metal to ligand were used. Separate resonances in the 1:2 system were observable for the coordinated EDTA and monoprotonated EDTA at 31°, but intermolecular exchange was rapid enough at 65° to produce one relatively broad acetate peak and a very much broadened ethylenic resonance. Intermolecular exchange of coordinated EDTA and fully deprotonated EDTA was rapid enough at room temperature (31°) to exhibit two slightly broadened peaks, one for the acetates and the other for the ethylenic groups.

---

(29) J. L. Sudmeier and C. N. Reilley, *Anal. Chem.*, 36, 1698 (1964).

(30) A. Yingst and A. E. Martell, manuscript in preparation.