New Multidentate Ligands. IX. Metal Chelates of Triethylenetetraminehexaacetic Acid with Trivalent Metal Ions[1]

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Abstract: Potentiometric equilibrium studies are reported for the interaction of triethylenetetraminehexaacetic acid (TTHA) with La(III), Nd(III), Sm(III), Ho(III), Ga(III), and Bi(III) ions. Evidence is presented for the formation in solution of mononuclear chelates, protonated mononuclear chelates, and binuclear chelate compounds (except Bi(III)) with a 2:1 molar ratio of metal ion to ligand. Equilibrium constants are reported for the formation of these metal chelate species, and suggestions are made concerning the nature and arrangement of the metal–ligand coordinate bonds of the chelate compounds formed. Studies are reported of mixed-ligand complexes involving La(III), TTHA, and several auxiliary ligands.

The utility and versatility of ethylenediaminetetraacetic acid (EDTA) as a titrant for metal ions has prompted the search for ligands with an even greater affinity and selectivity for metal ions. One fruitful approach has been the study of higher homologs of EDTA, such as diethylenetriaminepentaacetic acid (DPTA) and, more recently, triethylenetetraminehexaacetic acid (TTHA). For instance, Frost[3] reported the acid dissociation constants of the various protonated forms of TTHA while Grimes and coworkers[4] reported the formation constants for mononuclear and binuclear complexes of TTHA with alkaline earth metal ions. Pribil and coworkers[5] have reported analytical applications of TTHA. More recently Bohigian and Martell[6,7] reported the formation constants of TTHA with mononuclear, polynuclear, and protonated metal chelate species in solution. We report here similar studies involving TTHA and a number of trivalent metal ions, including La(III), Nd(III), Sm(III), Ho(III), Ga(III), and Bi(III). We present evidence for mononuclear, protonated mononuclear, and binuclear species in solution together with the formation constants of the various species.

Experimental Section

Potentiometric Measurements. The experimental method consisted of potentiometric titration of the hexabasic acid TTHA in the absence and presence of the metal ion being studied. The ionic strengths of the media were maintained constant at 0.10 *M* by the addition of potassium nitrate to the experimental solution. Potentiometric measurements were carried out in a double-walled titration cell of 100-ml capacity. The temperature was maintained at 25.0 ± 0.02° by circulation of water thermostated at this temperature through the outer jacket of the potentiometric cell. A Beckman Model 1019 pH meter fitted with extension glass and calomel electrodes was calibrated so as to determine the hydrogen ion concentration directly. This was done by direct titration of dilute HCl with NaOH, and by titration of acetic acid with NaOH so that the observed pH meter reading was compared with the actual hydrogen ion concentration determined on the basis of the data tabulated by Harned and Owen.[8]

Reagents. Triethylenetetraminehexaacetic acid (TTHA) was prepared by Professor I. Murase of Kyushu University, Fukuoka, Japan. The purity of TTHA was established by nitrogen, carbon, and hydrogen analysis and by potentiometric titration. The equivalent weight was determined by titration of the ligand in the presence of somewhat more than two times the molar ratio of copper(II) ion and nickel(II) ion as described by Bohigian and Martell.[7] Metal nitrate salts of 99.9% purity were obtained from the K&K Chemical Co.

Results and Calculations

Potentiometric Data. Equilibrium potentiometric titration curves for 1:1 and 2:1 molar ratios of La(III) and Sm(III) to TTHA are presented in Figures 1 and 2. The curves for Nd(III) and Ho(III) and Bi(III) at 1:1 and 2:1 metal–ligand ratios are illustrated in Figure 2. The 1:1 curves for the lanthanides are quite similar, consisting of a long buffer region in the acid region terminated by a sharp inflection at $a = 6$ moles of base per mole of ligand. In the cases of Sm(III) and Ho(III) there is a clearly visible inflection at $a = 5$ indicating the formation of reasonably stable monoprotonated metal chelate species. Detailed numerical analysis, described below, indicated that several protonated species were formed with each metal–TTHA system.

When 2 moles of metal per mole of ligand is present in solution, the titration curve parallels that of the corresponding 1:1 curve, indicating that the two metal ions may form the binuclear species consecutively rather than in a single step. Titration, with base, of a solution of 2:1 metal–ligand ratio, beyond $a = 6$ moles of base per mole of ligand, results in drifting of pH values and the formation of a fine white precipitate. Examination of the precipitate showed that there was no organic matter; the 2:1 complex thus apparently disproportionates to the very stable 1:1 complex and the very insoluble metal hydroxide.

Several attempts were made, using auxiliary ligands, to stabilize the 2:1 lanthanum–TTHA chelate. Titrations were made with 2:1:2 ratios of lanthanum(III), TTHA, and a secondary bidentate ligand such as Tiron, 8-hydroxyquinoline-5-sulfonic acid, or 5-sulfosalicylic acid. The potentiometric data are shown in Figure 3. In the case of 8-hydroxyquinoline-5-sulfonic acid a

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

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[3] A. E. Frost, *Nature*, **178**, 322 (1956).

[4] J. H. Grimes, A. J. Huggard, and S. P. Wilford, *J. Inorg. Nucl. Chem.*, **25**, 1225 (1963).

[5] R. Pribil and V. Vesely, *Talanta*, **9**, 939 (1962); **10**, 899 (1963); **11**, 319, 1545 (1964); **12**, 475 (1965).

[6] T. A. Bohigian and A. E. Martell, *Inorg. Chem.*, **4**, 1264 (1965).

[7] T. A. Bohigian and A. E. Martell, *J. Am. Chem. Soc.*, **89**, 832 (1967).

[8] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed, Reinhold Publishing Corp., New York, N. Y., 1950, p 523.

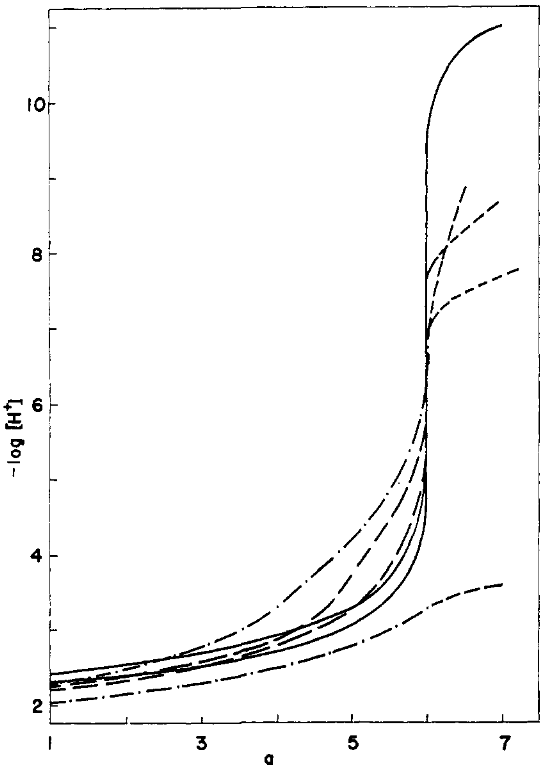

Figure 1. Potentiometric titration of La(III) (——), Sm(III) (— — —), and Ga(III) (—·—·—) chelates of TTHA at 25° in 0.10 M KNO$_3$. Upper curve of each pair is 1:1 metal–ligand ratio; lower curve, 2:1 ratio of metal to ligand.

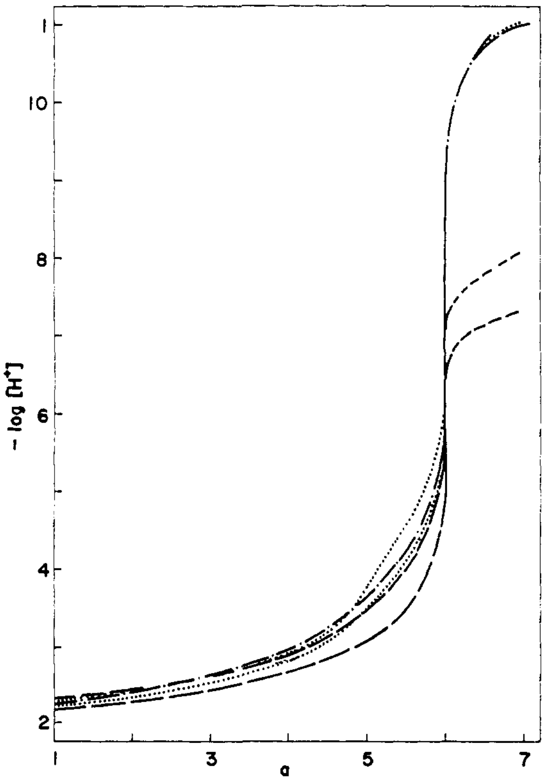

Figure 2. Potentiometric titration of Nd(III) (— — —), Ho(III) (······), and Bi(III) (—·—·—) chelates of TTHA at 25° in 0.10 M KNO$_3$. Upper curve of each pair is 1:1 metal–ligand ratio; lower curve (when present), 2:1 ratio of metal to ligand.

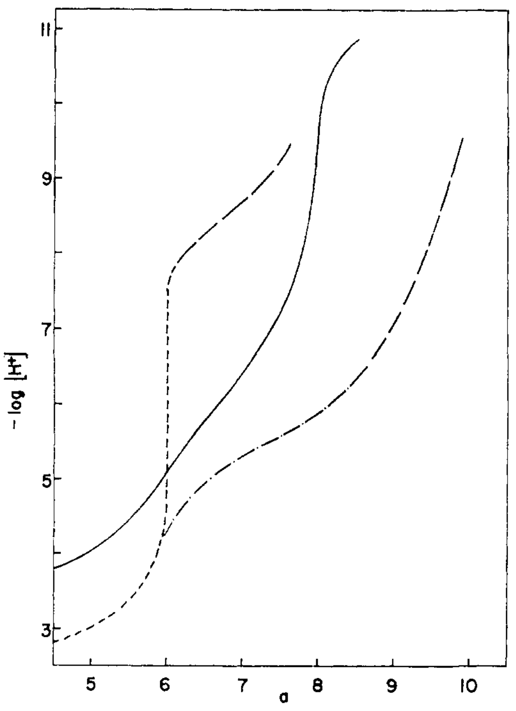

Figure 3. Mixed-ligand titration data for La–TTHA–Aux. The ligand is in the molar ratio 2:1:2; the La–TTHA curve is shown for comparison. Auxiliary ligands: ———, 8-hydroxyquinoline-5-sulfonic acid; —·—·—, Tiron; - - - - -, La–TTHA in the absence of auxiliary ligand.

stable complex was formed, resistant to further hydrolysis to pH 11. The other two ligands appeared to form complexes with the binuclear La–TTHA complex, but hydrolyzed with drifting of pH values above pH 8. Attempts to calculate log β for the mixed-ligand reaction involving Tiron gave a rather constant value of about 12 until approximately one-fourth of the Tiron had been neutralized. At this point the log β values began to drift downward even though there was no drifting in pH readings until about 60% of the Tiron had been neutralized. There were insufficient data to attempt a calculation for the equilibrium of the mixed-ligand system for 5-sulfosalicylic acid.

The curve for Ga(III), 1:1, is similar to those of the lanthanides except that drifting beyond $a = 6$ occurs in the 1:1 system. There was no evidence of an inflection in the 2:1 case. There was no evidence of a precipitate forming in either case, even to the region where $a = 9$ moles of base per mole of ligand. No attempt was made to establish the nature of the equilibria beyond the point where $a = 6$ moles of base per mole of ligand had been added.

Bismuth produced a 1:1 titration curve very similar to the other trivalent ion studies reported here. Attempts to obtain the corresponding 2:1 titration curve gave rise to a precipitate in all pH ranges.

Calculations. The calculations of the various equilibrium constants for the 1:1 complexes were carried out in two parts. Recognizing that there was a distinct buffer region in the range $a = 5$–6 (and perhaps lower stoichiometries), a least-squares variation of the method of Carlson, *et al.*,[9] was employed to determine the number and values of the acid dissociation constants. These constants were then used to calculate the formation constants for the fully deprotonated complexes.

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[9] G. A. Carlson, J. P. McReynolds, and F. H. Verhoek, *J. Am. Chem. Soc.*, 67, 1335 (1945).

Table I. Logarithms of Formation Constants

Reaction	Metal					
	La(III)	Nd(III)	Sm(III)	Ho(III)	Ga(III)	Bi(III)
$ML^{3-} + H^+ = MHL^{2-}$	3.51	3.94	4.49	4.67	4.52	4.16
$MHL^{2-} + H^+ = MH_2L^-$	3.11	2.93	2.60	2.33	3.54	2.84
$MH_2L^- + H^+ = MH_3L$					2.29	2.11
$M^{3+} + L^{6-} = ML^{3-}$	16.7	16.6	15.7	15.4	15.1	17.7
$2M^{3+} + L^{6-} = M_2L$	19.3	20.3	20.8	18.3	25.1	
$La_2L^{3-} + 2HQS^{2-} = La_2L(HQS)_2^{7-}$	7.3					

The details are outlined below; the symbols used are the following: $T_{\rm L}$ = total analytical concentration of ligand in all forms; $T_{\rm M}$ = total analytical concentration of metal ion in all forms; $T_{\rm OH}$ = total molar concentration of base added to the experimental solution; a = number of moles of standard base added per mole of ligand; H_nL = acid form of the ligand where n represents the number of equivalents of titratable hydrogens per mole of ligand; K_n = proton association constants of the ligand. Log association constants previously determined[6] are: $K_1 = 10.19$, $K_2 = 9.40$, $K_3 = 6.16$, $K_4 = 4.16$, $K_5 = 2.95$, $K_6 = 2.42$.

The average number of protons bound to the metal chelate complex is described by

$$\bar{n}_{\rm H} = \frac{[\mathrm{MHL}] + [\mathrm{MH_2L}] + \ldots + n[\mathrm{MH}_n\mathrm{L}]}{[\mathrm{ML}] + [\mathrm{MHL}] + [\mathrm{MH_2L}] + \ldots + [\mathrm{MH}_n\mathrm{L}]}$$

Substitution of the various $\beta_i^{\rm H}$ constants followed by algebraic arrangement produces the general relationship

$$\bar{n}_{\rm H} + [\mathrm{H}^+](\bar{n}_{\rm H} - 1)\beta_i^{\rm H} + [\mathrm{H}^+]^2(\bar{n}_{\rm H} - 2)\beta_2^{\rm H} + \ldots + [\mathrm{H}^+]^N(\bar{n}_{\rm H} - N)\beta_N^{\rm H} = 0 \quad (1)$$

Equation 1 is linear in $\beta_i^{\rm H}$ terms and subject to numerical analysis by a variety of methods. The method of least-squares analysis permits numerical analysis of all the data simultaneously and was employed here to determine the protonation constants of the complexes. The appropriate titration data were evaluated assuming different degrees of maximum protonation of the metal chelate complex. The residual data represented the formation of the various protonated metal chelate species and was evaluated as described below.

The protonated constants obtained above may be combined with the following mass balance equations (neglecting charges):

$$T_{\rm M} = [\mathrm{M}] + [\mathrm{ML}] + [\mathrm{MHL}] + \ldots + [\mathrm{MH}_N\mathrm{L}] = [\mathrm{M}] + [\mathrm{ML}][1 + \sum_{i=1}^{N}\beta_i^{\rm H}[\mathrm{H}]^i] \quad (2)$$

$$T_{\rm L} = [\mathrm{L}] + [\mathrm{HL}] + [\mathrm{H_2L}] + \ldots + [\mathrm{H_6L}] + [\mathrm{ML}] + [\mathrm{MHL}] + \ldots + [\mathrm{MH}_N\mathrm{L}] = [\mathrm{L}][1 + \sum_{i=1}^{6}\beta_i^{\rm H}[\mathrm{H}^+]^i] + [\mathrm{ML}][1 + \sum_{i=1}^{N}\beta_i^{\rm H}[\mathrm{H}^+]^i] \quad (3)$$

$$T_{\rm OH} = 6[\mathrm{L}] + 5[\mathrm{HL}] + 4[\mathrm{H_2L}] + \ldots + [\mathrm{H_5L}] + 6[\mathrm{ML}] + 5[\mathrm{MHL}] + \ldots + (6 - N)[\mathrm{MH}_N\mathrm{L}] = [\mathrm{L}][6 + \sum_{i=1}^{i=5}(6 - i)\beta_i^{\rm H}[\mathrm{H}^+]^i] + [\mathrm{ML}][6 + \sum_{i=1}^{N}(6 - i)\beta_i^{\rm H}[\mathrm{H}^+]^i] \quad (4)$$

Simultaneous eq 2, 3, and 4 may be solved in the usual way for the quantities [M], [ML], and [L]; these may be combined to calculate $\beta_{\rm ML}$, the formation constant for the fully deprotonated metal chelate complex. Bohigian's protonation constants[6] for the free ligand were employed in these calculations. The numerical values obtained are shown in Table I. The same equations were applied to the data of the various lanthanides in a 2:1 stoichiometry over the range a = 0–3.5. A satisfactory value of $\beta_{\rm ML}$, showing little variation, was obtained using the assumption that a diprotonated species was being formed as in the 1:1 case. Calculation of the formation constant of the binuclear complex from free metal ion and the 1:1 complex was accomplished by the method of L'Heureux and Martell.[10] The formation constant for the binuclear gallium(III) complex was calculated according to the method of Bohigian.[7]

Discussion

Mononuclear Chelates. For the lanthanides the potentiometric data suggest, and the formation constants confirm, that there are several interesting trends to be found among the results of the 1:1 titrations. For instance, the dissociation of the proton from the species MHL^{2-} becomes progressively more difficult with increasing atomic number or decreasing ionic radius. On the basis of an electrostatic model, Ho(III), which has the smallest ionic radius, would be expected to form the complex MHL^{2-} with the most acidic proton rather than the least acidic. An alternative model, involving steric forces, provides a satisfactory qualitative explanation: as the metal ion becomes smaller, coordination of the fourth nitrogen atom to the metal ion produces greater crowding of the donor groups about the metal ion. This crowding results in weaker binding of the metal, thereby providing less competition by the metal for the site (*i.e.*, a terminal amino group) to a proton. This explanation is consistent with the values of log $\beta^{\rm H}_{\rm MHL}$ reported for Bi(II) and Ga(III).

The trend in the dissociation of a proton from the species MH_2L^- may be understood in terms of the previously mentioned electrostatic model. The smaller Ho(III) is the source of stronger electrostatic forces than La(III), and thereby has a greater attraction for the amine lone pair. Steric forces important in the dissociation of a proton in MHL^{2-} are, of course, relatively less important here because fewer donor nitrogen atoms are competing for sites on the metal ion.

The formation of the fully deprotonated species, ML, seems to be governed by the same steric factors that pertain to the loss of a proton from MHL^{2-}. Interestingly enough, combination of the appropriate constants from Table I reveals that, for the reaction

$$M^{3+} + H^+ + L^{6-} = MHL^{2-}$$

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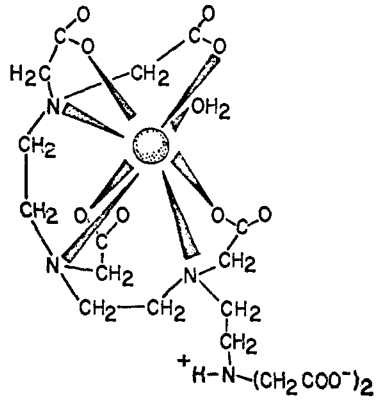
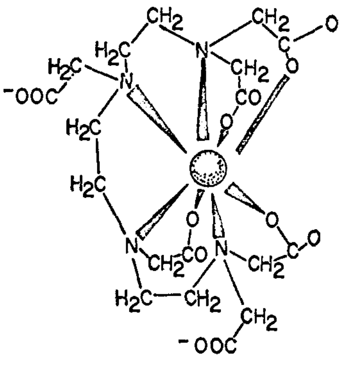
[10] G. A. L'Heureux and A. E. Martell, *J. Inorg. Nucl. Chem.*, **28**, 481 (1966).



I MHL^{2-}



II ML^{3-}

the steric and electrostatic forces are rather evenly balanced for the lanthanides with no apparent trend.

The various trends in the formation constants and the arguments to understand them suggest that the species MHL^{2-} and ML^{3-} have structures I and II, respectively. The number of bound acetate groups is somewhat arbitary, but guided by the findings in a recent review by Muetterties.[11] Undoubtedly the complexes of Ga(III and Bi(III) are similar.

The tendency of both gallium and bismuth to form triprotonated complexes appears curious at first, although it may be readily understood if one does not attempt to ascribe a common cause for both sets of equilibria. The small gallium ion (radius = 0.62 Å[12]) is unable to coordinate a large number of donors simultaneously. Bismuth, although larger (radius = 0.96 Å[12]), does not have sufficient polarizing power to force coordination to the same extent as the lanthanides which are of about the same radius. As a consequence, bismuth competes less effectively with protons for coordination sites.

The unusually high stability of the binuclear gallium complex relative to those of the lanthanides is also understood in terms of ionic radius. The first-coordinated gallium, because it binds fewer groups, provides less competition to the entering second metal ion for coordination sites, thereby permitting a rather firm binding of the second metal ion. The absence of a sharp inflection at $a = 6$ moles of base per mole of ligand indicates that the metal ion is probably not coordinatively saturated, since it appears to take up additional hydroxide. The competition between the first and second metal ions in the binuclear lanthanide complexes probably accounts for the tendency of this group to disproportionate in alkaline solutions, although the insolubility of the hydroxide contributes considerably.

(11) E. L. Muetterties and C. M. Wright, *Quart. Rev.* (London), **21**, 109 (1967).

(12) L. H. Ahrens, *Geochim. Cosmochim. Acta*, **2**, 155 (1952).