

Complexes of the Rare Earths. III. Mixed Complexes with N-Hydroxyethylethylenediaminetriacetic Acid¹

BY LARRY C. THOMPSON AND JUDITH A. LORAAS²

Received May 9, 1962

The tendency of the 1:1 rare earth-N-hydroxyethylethylenediaminetriacetic acid (Ln(HEDTA)) chelates to form mixed 1:1:1 chelates with glycine, ethylenediaminediacetic acid (EDDA), iminodiacetic acid (IMDA), and N-hydroxyethyliminodiacetic acid (HIMDA) has been investigated. Mixed complex formation was found in all cases but formation constants could only be obtained for the IMDA, HIMDA, and some of the EDDA complexes. The mixed complexes are quite stable and the formation constants exhibit trends which can reasonably be explained by the properties of the ligands and steric factors. Evidence for a coordination number larger than six in the rare earths is summarized and additional evidence is presented which indicates that in these mixed chelates the rare earths have an expanded coordination number.

In recent years the formation of complexes containing two different ligands has become of interest to coordination chemists and the formation constants of some of these complexes have been determined.³ Since all of these studies have involved transition metals, we thought that it would be of interest to study the same phenomena with the rare earth ions. Moreover, in view of the recent suggestion⁴ that the rare earth ions might exhibit a maximum coordination number larger than the six which is commonly assumed, we thought that it might be possible to obtain additional evidence in support of this idea by investigating some selected mixed complexes.

For this study a ligand which forms very stable 1:1 rare earth chelates was chosen, and the tendency of these chelates to bind a second ligand was measured. Essentially the system then corresponds to measuring the formation of MAB from MA and B. This is the same procedure used by Intorre and Martell⁵ for some Zr(IV) chelates, except they did not measure any formation constants. The ligand N-hydroxyethylethylenediaminetriacetic acid (HEDTA), which has been considered to occupy five coordination positions around the rare earth ion,⁶ was chosen as A since it has these advantageous characteristics for the formation of mixed complexes: (1) The rare earth-HEDTA (Ln(HEDTA)) chelates are neutral, thus minimizing the electrostatic repulsion toward the incoming ligand B. (2) There is little tendency for the Ln(HEDTA) species to add a second HEDTA molecule to form the 2:1 chelate Ln(HEDTA)₂⁷ (charges on ions will be omitted except where needed for clarity), thus lessening the

tendency toward disproportionation; *i.e.*, the equilibrium $2\text{Ln}(\text{HEDTA})\text{B} \rightleftharpoons \text{Ln}(\text{HEDTA})_2 + \text{LnB}_2$ should lie far to the left for the ligands used in this study. (3) The Ln(HEDTA) species have large stability constants (log *K* values from 13–16)⁸ and ligand exchange is eliminated, *i.e.*, $\text{Ln}(\text{HEDTA}) + \text{B} \rightleftharpoons \text{LnB} + \text{HEDTA}$ cannot occur if B forms much less stable complexes with the rare earths, a condition which is met in this study. (4) Since the Ln(HEDTA) complexes are probably only pentadentate, this leaves the possibility of three coordination positions available for the second ligand if a coordination number of eight is assumed.

The ligands which were chosen to be studied were glycine (gly), iminodiacetic acid (IMDA), N-hydroxyethyliminodiacetic acid (HIMDA), and N,N'-ethylenediaminediacetic acid (EDDA). The structural formulas of these compounds and HEDTA are given on the next page together with those of the other ligands which are mentioned in the Discussion.

Experimental

Solutions.—The HEDTA was generously supplied by Geigy Chemical Corporation and was purified as described in the literature.⁸ The HIMDA was obtained through the courtesy of the Dow Chemical Company and was recrystallized from water before use. The glycine was purchased from Calbiochem and was their A grade. It was used without further purification. Approximately 0.005 *M* solutions were prepared by dissolving the required amount of acid in de-ionized water. These solutions were standardized (except in the case of glycine) by adding an excess of standard copper nitrate solution and titrating the liberated hydrogen ions potentiometrically. The preparation and standardization of the 0.005 *M* rare earth nitrate,⁹ 0.005 *M* IMDA, 0.005 EDDA, and 1.000 *M* potassium nitrate solutions have been described previously.¹⁰ Solutions 0.005 *M* in cadmium nitrate, copper nitrate, cobalt(II) nitrate, and nickel nitrate were prepared from the analytical reagents and standardized complexometrically with EDTA.

Experimental Procedure.—Solutions containing the rare earth ion, HEDTA, and the second ligand were prepared and made up

(1) Presented before the Division of Inorganic Chemistry at the 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962.

(2) National Science Foundation Undergraduate Research Participant, 1961–1962.

(3) W. B. Schaap and D. L. McMasters, *J. Am. Chem. Soc.*, **83**, 4699 (1961), and references therein.

(4) G. Anderegg, P. Nägeli, F. Müller, and G. Schwarzenbach, *Helv. Chim. Acta*, **42**, 827 (1959).

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

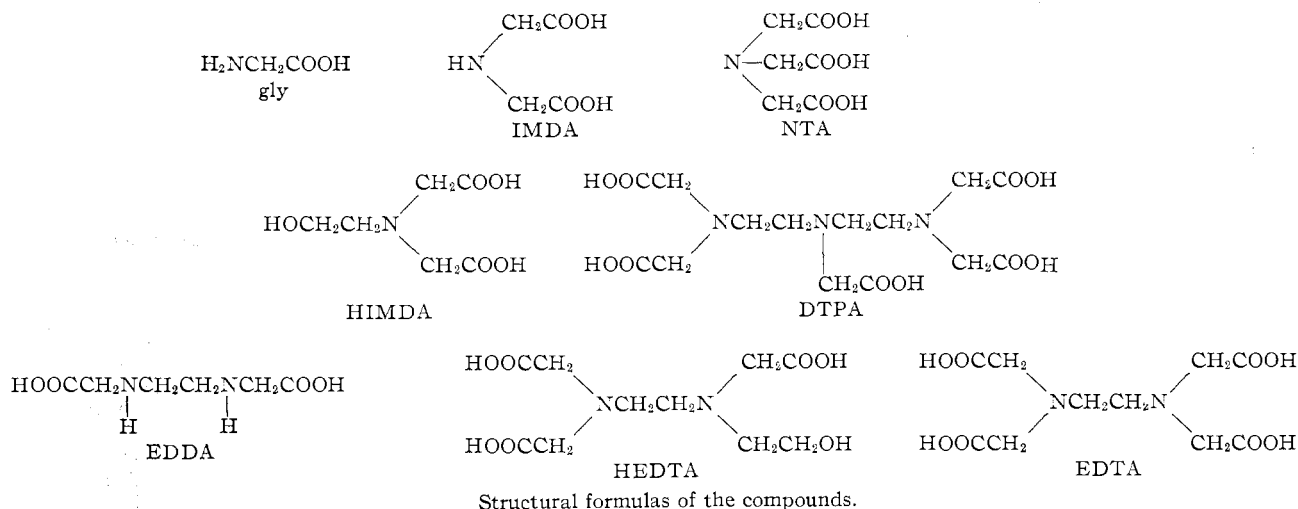
(6) T. Moeller and E. P. Horwitz, *J. Inorg. Nucl. Chem.*, **12**, 49 (1959).

(7) The tendency toward formation of 2:1 HEDTA-rare earth chelates has apparently never been investigated. We have tentative data which give a value of log *K*₂ = 3.7 for samarium and ~4 for lutetium. Both values indicate that the disproportionation equilibrium lies to the left.

(8) F. H. Spedding, J. E. Powell, and E. J. Wheelwright, *J. Am. Chem. Soc.*, **78**, 34 (1956).

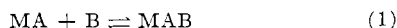
(9) The rare earth materials were generously supplied by Lindsay Chemical Division, American Potash and Chemical Corporation, West Chicago, Illinois.

(10) L. C. Thompson, *Inorg. Chem.*, **1**, 490 (1962).



to ionic strength 0.1 with the 1.000 *M* potassium nitrate solution. The rare earth ion and HEDTA were always in the ratio 1:1, but the amount of ligand B was varied. After equilibration at 25° the solutions were titrated potentiometrically as previously described.¹⁰

Calculations.—The calculations of the acid dissociation constants were carried out by the method given by Chaberek and Martell.¹¹ The formation constants were calculated using the expressions



$$C_M = [\text{MA}]_t = [\text{MA}] + [\text{MAB}] \quad (2)$$

$$C_B = [\text{B}]_t = [\text{H}_2\text{B}] + [\text{HB}] + [\text{B}] + [\text{MAB}] \quad (3)$$

$$a^*C_B + [\text{H}] - [\text{OH}] = [\text{HB}] + 2[\text{B}] + 2[\text{MAB}] \quad (4)$$

where a^* is the moles of base added per mole of B in excess of the three moles needed to neutralize H_3A completely. Combining eq. 3 and 4 gives the expression for [B]

$$[\text{B}] = \frac{(2 - a^*)C_B - [\text{H}] + [\text{OH}]}{2 \frac{[\text{H}]^2}{k_1 k_2} + \frac{[\text{H}]}{k_2}} \quad (5)$$

where k_1 and k_2 are the acid dissociation constants of B. Using this value of [B], eq. 2 and 3 can be solved for [MA] and [MAB], respectively. The equilibrium constant for reaction 1 then is obtained easily

$$K = \frac{C_B - [\text{B}] \left\{ \frac{[\text{H}]^2}{k_1 k_2} + \frac{[\text{H}]}{k_2} + 1 \right\}}{[\text{B}] \left\{ C_M - C_B + [\text{B}] \left(\frac{[\text{H}]^2}{k_1 k_2} + \frac{[\text{H}]}{k_2} + 1 \right) \right\}} \quad (6)$$

In the case of glycine the terms involving k_1 are zero and in eq. 5 the term $(2 - a^*)$ becomes $(1 - a^*)$.

The above equations are valid providing that the chelate MA can be treated as an undissociated specie in the pH range in which MAB is formed. A simple calculation shows that at pH 6 and selecting $\log K = 13$ (a much lower limit than actually is present) the chelate MA is dissociated only to the extent of 0.1%.

Results

A consideration of the titration curves presented in Fig. 1 and 2 shows that in each case there is a decided lowering of the high buffer region of both the $\text{Ln}(\text{HEDTA})$ chelate and the free acid when a mixture of the two is titrated. A lowering of this kind is indicative of the formation of a new kind of complex species in the solution. The experimental data were analyzed on the basis of the assumption of a mixed

chelate of the type MAB and the results which were obtained for the logarithms of the formation constants of these chelates corresponding to reaction 1 are listed in Table I.

For both the $\text{Ln}(\text{HEDTA})(\text{IMDA})$ and $\text{Ln}(\text{HEDTA})(\text{HIMDA})$ species the values which were obtained using various ratios of $\text{Ln}(\text{HEDTA})$ and either IMDA or HIMDA agreed well within the experimental error. For the other two ligands, glycine and EDDA, the formation constants were not so reliable. In the solutions containing $\text{Ln}(\text{HEDTA})$ and either of these ligands in a 1:1 ratio, the formation constants which were found generally had a tendency to drift toward higher values as a increased. Examination of Fig. 1 and 2 shows that the $\text{Ln}(\text{HEDTA})(\text{gly})$ and $\text{Ln}(\text{HEDTA})(\text{EDDA})$ curves are close to the titration curve for $\text{Ln}(\text{HEDTA})$. Furthermore, the titration

TABLE I
LOGARITHMS OF THE FORMATION CONSTANTS FOR THE SPECIES
 $\text{Ln}(\text{HEDTA})\text{X}$

$$K = \frac{[\text{Ln}(\text{HEDTA})\text{X}]}{[\text{Ln}(\text{HEDTA})][\text{X}]} \quad \mu = 0.1 (\text{KNO}_3) \quad T = 25^\circ$$

| Metal ion | IMDA | HIMDA | EDDA |
|---------------------|-----------------------|-----------------|-----------------|
| $\text{H}^+ (pk_1)$ | 2.58 ± 0.01^a | 2.16 ± 0.01 | 6.48 ± 0.01 |
| $\text{H}^+ (pk_2)$ | 9.33 ± 0.01 | 8.75 ± 0.01 | 9.57 ± 0.01 |
| La^{3+} | $3.22 \pm 0.03^{a,b}$ | 4.04 ± 0.02 | 3.90 ± 0.05 |
| Ce^{3+} | 3.50 ± 0.01 | 4.07 ± 0.02 | 3.60 ± 0.04 |
| Pr^{3+} | 3.84 ± 0.01 | 4.20 ± 0.02 | 3.43 ± 0.05 |
| Nd^{3+} | 4.07 ± 0.01 | 4.23 ± 0.03 | 3.14 ± 0.06 |
| Sm^{3+} | 4.57 ± 0.02 | 4.49 ± 0.03 | 3.02 ± 0.06 |
| Eu^{3+} | 4.77 ± 0.01 | 4.61 ± 0.02 | ... |
| Gd^{3+} | 4.96 ± 0.01 | 4.57 ± 0.03 | ... |
| Tb^{3+} | 5.18 ± 0.01 | 4.73 ± 0.03 | ... |
| Dy^{3+} | 5.33 ± 0.01 | 4.81 ± 0.03 | ... |
| Ho^{3+} | 5.37 ± 0.01 | 4.76 ± 0.03 | ... |
| Er^{3+} | 5.30 ± 0.01 | 4.62 ± 0.03 | ... |
| Tm^{3+} | 4.95 ± 0.02 | 4.26 ± 0.01 | ... |
| Yb^{3+} | 4.74 ± 0.04 | 4.05 ± 0.03 | ... |
| Lu^{3+} | 4.51 ± 0.02 | 3.88 ± 0.03 | ... |
| Y^{3+} | 5.10 ± 0.01 | 4.39 ± 0.01 | ... |

^a 95% confidence interval (see H. A. Laitinen, "Chemical Analysis," McGraw-Hill Book Company, Inc., New York, N. Y., 1960, Chap. 26). ^b These are the average values of at least eight calculations in the range $a^* = 1.25$ –1.70.

(11) S. Chaberek and A. E. Martell, *J. Am. Chem. Soc.*, **74**, 5052 (1952).

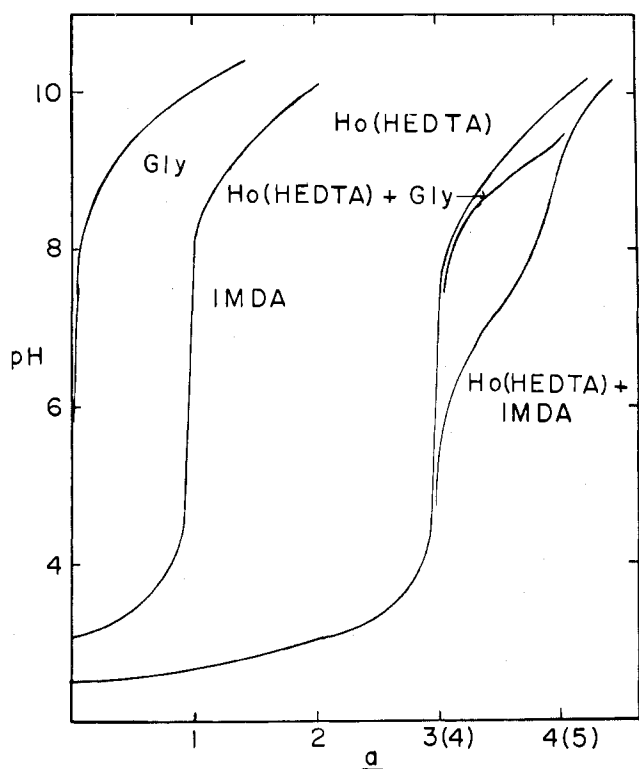
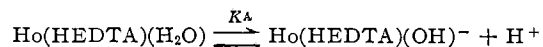


Fig. 1.—Titration curves for glycine, IMDA, and Ho(HEDTA) showing the presence of mixed chelates. The values of a in parentheses refer to Ho(HEDTA) + IMDA (a = moles of base per mole of B).

curve for Ho(HEDTA) is lower than would have been expected since a similar curve for La(HEDTA) lies in the pH region greater than 10 at a values slightly larger than three. This examination reveals the hitherto unreported observation that the HEDTA chelates of the heavier rare earths undergo a hydrolytic reaction resulting in the species Ln(HEDTA)(OH)⁻.¹² Since it previously has been reported that the lanthanum chelate is not hydrolyzed,¹³ this is a further example of the danger of extending the results for the light rare earths to the heavy rare earths. The acid dissociation constant for the reaction



is $-\log K_A = 9.06 \pm 0.04$ and this phenomenon will be reported more fully in a future publication. The effect of this hydrolysis upon our calculations is discussed below.

The formation constants for the Ln(HEDTA)-(EDDA) chelates reported here were obtained from measurements on solutions containing EDDA and HEDTA in a 2:1 ratio.

Discussion

Ln(HEDTA)-gly System.—In the glycine system it has not been possible to calculate reliable values for

(12) The formation of hydroxo complexes of this type with the Ln(HEDTA) species has been noted also by Dr. J. E. Powell (private communication).

(13) R. C. Courtney, R. L. Gustafson, S. Chaberek, and A. E. Martell, *J. Am. Chem. Soc.*, **80**, 2121 (1958).

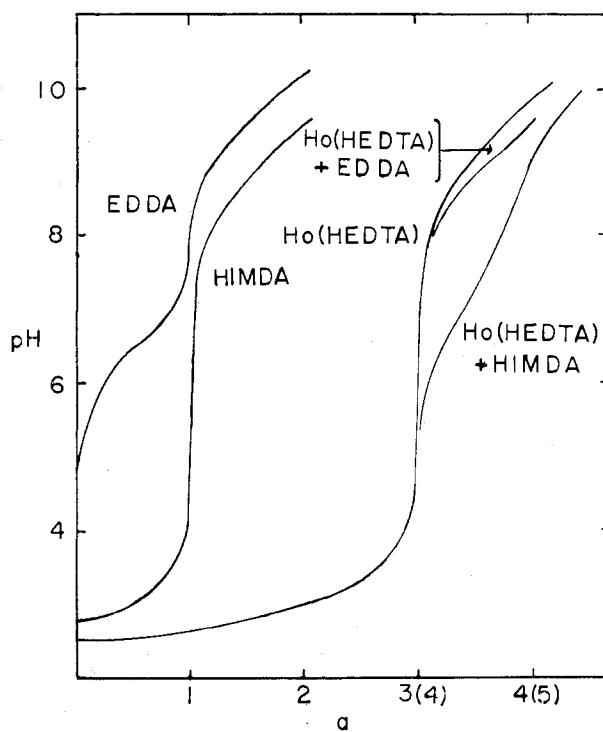


Fig. 2.—Titration curves for EDDA, HIMDA, and Ho(HEDTA) showing the presence of mixed chelates. The values of a in parentheses refer to Ho(HEDTA) + HIMDA and Ho(HEDTA) + EDDA.

the formation constants because the buffer region for the mixed complexes overlaps with the buffer region of the hydrolysis mentioned above. However, since the hydrolytic buffer region is lowered in the presence of glycine, it can be assumed that there is interaction between the Ln(HEDTA) species and glycine.

Ln(HEDTA)-IMDA System.—The mixed complexes with IMDA as the second ligand are considerably more stable than the glycine complexes as shown by the fact that the buffer region is much lower than the hydrolytic buffer region of Ln(HEDTA). This is to be expected since IMDA forms much more stable simple complexes with the rare earths than does glycine. Moreover, if it is assumed that the coordination number of the rare earth ions is eight in these mixed complexes, then there are three coordination positions available for the second ligand which could be completely occupied by IMDA, but could not be completely occupied by glycine.

The trends observed in the values of $\log K$ for the IMDA species can be reasonably explained as follows: The larger size of the lighter rare earths should allow sufficient room for the IMDA molecule to become attached to the Ln(HEDTA) species and the formation constants should be influenced predominantly by the increasing affinity of the rare earth ion for complex formation as the atomic number increases. A point should be reached, however, at which the increasing steric factor due to shrinkage of the available space in which to add the second ligand should counterbalance the increasing complex-forming tendency. Beyond this the steric hindrance should be the predominant

factor in determining the stability of the complex.

The increasing stability up to dysprosium can be explained by the tendency toward formation of more stable complexes as the atomic number increases. The dysprosium, holmium, and erbium chelates represent the counterbalancing of the two factors and the increasing steric hindrance can explain the decrease to lutetium.

In the case of the IMDA mixed chelates, yttrium falls between either gadolinium and terbium or erbium and thulium. It is of interest to note that in the simple 2:1 IMDA-rare earth chelates yttrium is between samarium and europium.¹⁰ The other rare earth ions also can be compared with the 2:1 IMDA species. It is found that in all cases the 2:1 IMDA chelate is more stable than the mixed chelate (in terms of $\log K$). This is to be expected since the formation of the 2:1 chelate is aided by the fact that it is formed by the combination of a unipositive and a dinegative specie, whereas the mixed complex is formed from a neutral and a dinegative specie. This neutralization of charge and the absence of any steric hindrance in the 2:1 IMDA chelates thus explains the larger formation constants. In this connection it should further be noted that the difference in stabilities increases from lanthanum ($\Delta = 0.87 \log K$ unit) to cerium ($\Delta = 1.03 \log K$ units), *decreases* to dysprosium, for which this difference is only $0.10 \log K$ unit, and finally increases to lutetium ($\Delta = 1.22 \log K$ units).

Ln(HEDTA)-HIMDA System.—The trends noted above for the formation constants of the mixed chelates with IMDA are, in general, also found in the mixed chelates with HIMDA and probably are due to the same causes. The position of yttrium is not definite and it can be placed either between neodymium and samarium or between erbium and thulium. In the 2:1 HIMDA chelates it is between samarium and europium.

The difference in the formation constants between the corresponding 2:1 HIMDA chelates and the mixed HIMDA chelates is quite different from that which occurs with IMDA. This difference increases from lanthanum ($\Delta = 1.93 \log K$ units)¹⁴ to gadolinium ($\Delta = 3.41 \log K$ units) and then remains constant at about $3.3 \log K$ units through holmium. There is finally a regular increase to lutetium, for which the difference is $4.16 \log K$ units.

As long as the hydroxyl group of HIMDA is not coordinated in the mixed chelate, the HIMDA specie should be less stable than the IMDA specie due to the decreased basicity of the nitrogen atom caused by the inductive effect of the hydroxyl group.¹⁵ In addition, in the very bulky mixed chelate there may be an additional steric factor caused by the hydroxyethyl group which would serve to reduce the stability constants. These observations reasonably account for the chelates of the rare earths heavier than samarium, but for the

first five rare earths the HIMDA mixed chelates are the more stable. One possible explanation for this is that there is some participation of the hydroxyl group in the complexes of the larger rare earths and that this correspondingly leads to a more stable complex. The very small spread in the values of $\log K$ for the mixed HIMDA chelates lends support to this explanation, but it is in no way conclusive.

Ln(HEDTA)-EDDA System.—Formation constants for the mixed chelates with EDDA are given only for the first five rare earths. Beyond these the hydrolysis of the Ln(HEDTA) species makes the calculations unreliable. As with HIMDA, the formation constant for the lanthanum EDDA chelate is larger than for the lanthanum IMDA chelate. This might be an indication that all four coordinating groups of EDDA are participating in the complex formation. The succeeding rare earths are much less stable and the stability decreases regularly. This is most likely due to increasing steric hindrance as the size of the "hole" on the Ln(HEDTA) chelate decreases. Molecular models indicate that the mixed EDDA chelates should be subject to more strain than the mixed HIMDA chelates.

Coördination Number in the Mixed Chelates.—In the previous discussion nothing specific has been said as to why such mixed chelates exist. Two possible explanations are readily apparent: (1) the coördination number of the rare earth ion is six and the incoming ligand displaces one or more chelated acetato groups of the HEDTA molecule (as well as a molecule of water), or (2) the coördination number of the rare earth ion is expanded to eight. In the absence of definitive structure studies, it is, of course, impossible to make an absolute choice between the two alternatives. At the present we prefer the second explanation and will present some observations which tend to support it.

Evidence recently has been presented in which the assumption of a coördination number of seven or eight seems to explain the experimental observations more satisfactorily than a coördination number of six. For the simple crystalline EDTA complexes, Hoard¹⁶ has shown that if the metal ion is large, a seven-coördinate structure can be attained in which there is no strain in any of the five-membered rings with a water molecule occupying the seventh position. Such a structure has been proposed for the rare earth-EDTA chelates.¹⁷

The magnitudes of the formation constants of the 2:1 chelates of several ligands also indicate a coördination number larger than six. The formation constants of the 2:1 IMDA chelates of cobalt, nickel, and zinc, which can form six-coördinate species, are approximately $2 \log K$ units smaller than for the 1:1 chelates.¹¹ The same difference also is found between the 1:1 and 2:1 rare earth-IMDA chelates,¹⁰ indicating a

(14) Formation constants for the HIMDA-rare earth 2:1 chelates are taken from unpublished observations in this Laboratory.

(15) S. Chaberek, R. C. Courtney, and A. E. Martell, *J. Am. Chem. Soc.*, **74**, 5057 (1952).

(16) J. L. Hoard, M. Lind, and J. V. Silverton, *ibid.*, **83**, 2770 (1961).

(17) J. L. Hoard, G. S. Smith, and M. Lind, in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Company, New York, N. Y., 1961, p. 296.

similar type of coordination. The corresponding difference for the HIMDA chelates of those divalent metals, in which there may be participation of the hydroxyl group, is from 3.7 to 4.6 log K units.¹⁵ In the rare earths, however, this difference is only 1.2–2.0 log K units,¹⁴ indicating a somewhat different type of coordination. A similar, but more pronounced, situation is found in both the NTA¹⁸ and EDDA¹⁹ chelates. Anderegg⁴ also has pointed out the possibility that the rare earth–DTPA chelates may be eight-coordinate. Additional support for octacoordination in the rare earths comes from a recent paper by Irving and Edgington²⁰ on the solvent extraction of europium(III).

Data of this kind definitely point toward the possibility of a rare earth coordination number larger than six and the mixed complexes must be examined in this light. Consequently, the tendency of IMDA to interact with the HEDTA chelates of cadmium, nickel, and cobalt, which do not exhibit coordination numbers larger than six, was investigated. The results of this study are given in Fig. 3. The interesting point is that all three titration curves are identical between a values of four and five and that this region is identical within experimental error with the high buffer region of IMDA itself. Consequently there is no indication for the existence of mixed chelates of the type $M(\text{HEDTA})(\text{IMDA})$ where M is Co^{2+} , Ni^{2+} , or Cd^{2+} . If the formation of mixed chelates with the rare earths were due to the displacement of some of the coordinated groups of HEDTA, it would be reasonable to expect that mixed chelates with these divalent metals also would be found. That they are not would indicate a different explanation for their formation with the rare earth–HEDTA chelates.

Since the $M(\text{HEDTA})^-$ species and the $\text{Ln}(\text{HEDTA})^0$ species differ with respect to charge, the non-existence of mixed chelates with the former might be due to the electrostatic repulsion with the dinegative IMDA species. In order to check this possibility, the interaction of IMDA with several $\text{Ln}(\text{EDTA})^-$ chelates has been investigated. The results of one of these titrations is given in Fig. 3. It is evident that mixed complexes are formed with the $\text{Ln}(\text{EDTA})^-$ chelates. These mixed chelates are 1–2 log K units less stable than the corresponding HEDTA mixed chelates but the electrostatic repulsion does not prohibit their formation.

If the mixed $\text{Ln}(\text{HEDTA})$ chelates actually contain the rare earth ion with a coordination number larger than six and the release of coordinated groups is not re-

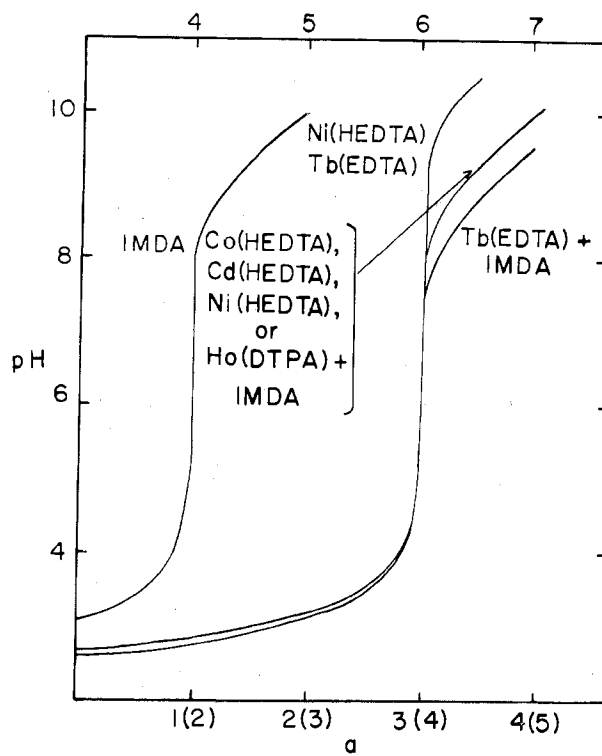


Fig. 3.—Titration curves showing the presence and absence of mixed complexes in various systems. The values of a in parentheses refer to $\text{Co}(\text{HEDTA})$, $\text{Cd}(\text{HEDTA})$, or $\text{Ni}(\text{HEDTA}) + \text{IMDA}$. The values of a at the top of the figure refer to $\text{Ho}(\text{DTPA}) + \text{IMDA}$. The break in the $\text{Tb}(\text{EDTA})$ titration curve comes at $a = 2$ but is superimposed on the $\text{Ni}(\text{HEDTA})$ curve for purposes of comparison.

sponsible for the mixed complexes, then the $\text{Ln}(\text{DTPA})$ species, which presumably already have the rare earth ion in an expanded coordination number, should show no tendency to interact with a second ligand. The results obtained from a titration of a 1:1 mixture of $\text{Ho}(\text{DTPA})$ and IMDA are presented in Fig. 3. The titration curve, which is identical with that for a mixture of $M(\text{HEDTA})$ ($M = \text{Ni}, \text{Co}, \text{Cd}$) and IMDA in the high buffer region, does not show the presence of any mixed chelate.

In view of these observations, we feel that the rare earth ion in these mixed chelates exhibits a coordination number larger than six.

Acknowledgment.—This investigation was supported in part by PHS Research Grant RG-8394 from the Division of General Medical Studies, Public Health Service, in part by a grant from the Graduate School of the University of Minnesota, and in part by the National Science Foundation through its Undergraduate Research Participation Program.

(18) G. Schwarzenbach and R. Gut, *Helv. Chim. Acta*, **39**, 1589 (1956); G. Anderegg, *ibid.*, **43**, 825 (1960).

(19) L. C. Thompson, *J. Inorg. Nucl. Chem.*, in press.

(20) H. Irving and D. N. Edgington, *ibid.*, **21**, 169 (1961).