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Chelating Polymers. IV. Monomeric N-Hydroxyalkylaminoacetic Acids as Chelating Compounds*

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ABSTRACT

The compounds N-(2-hydroxy-2-phenylethyl)aminoacetic acid and N-(2-hydroxy-2-phenylethyl)iminodiacetic acid were prepared and then characterized by elemental analysis, thermogravimetric analysis, ir spectroscopy, solubility studies, and potentiometric titration studies. They were reacted with $PrCl_3$, $HoCl_3$, $YbCl_3$, and $Cu(NO_3)_2$. The resulting rare earth complexes were analyzed by elemental analysis, ir spectroscopy, thermogravimetric analysis, and stability constant determinations. The stability constants of the aminoacetic acid and the iminodiacetic acid complexes of these same rare earths were also determined. All of the stability constants were measured using a potentiometric titration technique in 50% v/v dioxane-water at 25°C and at an ionic strength of 0.1 (KCl). The copper complexes were analyzed by ir spectroscopy and thermogravimetric

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*Taken in part from the Ph.D. dissertation of W. F. Strazik.

analysis, and their properties were compared to those of the rare earth complexes. The results suggest chelation in all of the metal complexes. They further suggest that the alcoholic oxygen atom in both of the prototype ligands acts as a donor in the rare earth chelates but not in the copper complex.

INTRODUCTION

Many different methods have been used to separate the rare earth elements. Generally, these involve one or some combination of the following procedures which have been discussed extensively in the literature [1-6]:

1) Fractional crystallization of isomorphous salts
2) Fractional precipitation from solution
3) Fractional thermal decomposition of salts
4) Ion exchange processing
5) Solvent extraction
6) Selective oxidation or reduction
7) Physical differences methods

A method of separating the rare earths, which has not been explored to any appreciable extent, is separation on a chelating polymer. Most of the research using chelating polymers in metal separations has involved the group IA, IIA, and transition metals. Only five reports of attempts to separate the rare earths using chelating polymers have been found in the literature [7-11]. This research was undertaken for the purpose of synthesizing and characterizing various chelating polymers and evaluating their capacities of rare earth separators. Also, as part of this investigation, prototype monomeric compounds and prototype polymeric compounds were prepared, characterized, and their complexing characteristics with various metal ions determined. Specifically, the cross-linked chelating polymers prepared were co-poly[1-(N-aminoacetic acid)-2-hydroxy-propyl methacrylate]-[allyl methacrylate] and co-poly [1-(N-iminodiacetic acid)-2-hydroxy-propyl methacrylate]-[allyl methacrylate]; the prototype monomeric compounds were N-(2-hydroxy-2-phenylethyl)aminoacetic acid and N-(2-hydroxy-2-phenylethyl)iminodiacetic acid; the linear prototype polymeric compounds were poly-1-(N-aminoacetic acid)-2-hydroxy-propyl methacrylate and poly-1-(N-iminodiacetic acid)-2-hydroxy-propyl methacrylate.

The investigations reported in this paper differ from those reported in the first three papers of this series [12-14] in three general ways:

1) The polymer system is of the addition type rather than of the condensation type.
2) The prototype polymeric compounds are low molecular weight linear polymers.
3) The metals of interest are the trivalent rare earths rather than the divalent transition metals.

Experimentally, this investigation is divided into three parts: (a) The synthesis and characterization of prototype monomeric compounds; (b) the synthesis and characterization of prototype polymeric compounds; and (c) the synthesis and characterization of cross-linked chelating polymers. The prototype monomeric compounds were prepared by reacting the various aminocarboxylic acid ligands with styrene oxide. The prototype polymeric compounds were prepared by postreacting these same ligands with a low molecular weight, linear poly(glycidyl methacrylate) polymer. Based on the information obtained from the preparations of the two types of prototype compounds, the cross-linked chelating polymers were prepared. The preparations of these latter polymers involved postreacting cross-linked co-poly[glycidyl methacrylate]-[allyl methacrylate] copolymers with the various aminocarboxylic acid ligands.

The characterization of each of the prototype monomeric compounds included structural verification of the compound and the determination of several of its properties. It also included studies of the complexation behavior of the compound with several different trivalent rare earths and with divalent copper ions.

In this paper, only the results of the research with the prototype monomeric compounds are reported. The research with the prototype polymeric compounds and the cross-linked chelating copolymers is reported in the following paper [15].

EXPERIMENTAL

A thermogravimetric analyzer and the general method used by Kolat and Powell [16] were combined to determine the metal content of certain solid rare earth compounds. The procedure consisted of thermally decomposing the compounds by heating them to 950-1000°C in air, cooling the resulting metal oxide residues to room temperature, and then weighing them.

The rare earth chloride solutions were standardized by either an ion exchange technique [17] or by the complexometric titration method of Fritz et al. [18]. Other solutions were analyzed for their rare earth content by complexometric titrations or, in the case of very low concentrations of metal, by using Arsenazo as an indicator in colorimetric determinations [19].

Physical Measurements

Ir spectra were obtained on a Perkin-Elmer 421 Grating Spectrophotometer in the range 3900-600 cm^{-1}, and on a Perkin-Elmer 521 Grating Spectrophotometer in the range of 700-300 cm^{-1}. Spectra of solid samples were obtained using the potassium bromide disk technique [20]. Approximately 1-2 mg of the sample were ground with 300 mg of potassium bromide in a Wig-L-Bug for 15 sec before being pressed into a disk. Spectra of liquid samples were obtained using liquid cells equipped with sodium chloride windows. Wave number calibration was made by comparison with polystyrene and carbon dioxide standard peaks.

Absorption measurements in the visible region were made on a Beckman Model D4 Spectrophotometer using 1 cm corex cells.

Most potentiometric titrations were done using a Beckman Model 76 Expanded Scale pH Meter with glass and saturated calomel electrodes. The titrations for the stability constant determinations were done on a Beckman Model 1019 Research pH Meter in conjunction with a Sargent Model TE Thermoelectric Temperature Regulating Magnetic Stirrer and a Sargent Model C Automatic Constant Rate Burette. A Sargent combination glass-saturated calomel electrode was used with the latter pH meter. Both meters were calibrated with standard Beckman Buffer Solutions. The sodium hydroxide, hydrochloric acid, and perchloric acid used in these titrations were prepared and standardized by conventional methods.

Thermogravimetric data were obtained on a du Pont 950 Thermogravimetric Analyzer employing the recording system of the du Pont 900 Differential Analyzer. Lamp nitrogen and dried air atmospheres were used in these measurements.

Thin-layer chromatography on Eastman Chromogram Sheets [21] was used to check the purity of several samples in this research.

Syntheses

Prototype Monomeric Compound I: N-(2-Hydroxy-2-phenyl ethyl)aminoacetic Acid, Sodium Salt, $C_6H_5CH(OH)CH_2NHCH_2COONa$.

This compound was prepared following the general procedure of D'Alelio for reacting amino acids with epoxy compounds [22].

Sodium aminoacetate (3.60 g, 0.0372 mole) was dissolved in a mixture of 36 ml of water and 240 ml of anhydrous methanol which was contained in a 500-ml three-necked flask. The flask was equipped with a water condenser, heating mantle, magnetic stirrer, thermometer, and dropping funnel. The sodium aminoacetate solution was heated to 65°C and then a solution of styrene oxide (4.465 g, 0.0372 mole) in 36 ml of anhydrous methanol was added, dropwise and with stirring, over a period of 7 hr. After all of the styrene oxide had been added, the clear yellow reaction mixture was stirred at 65°C for 6 hr. It was then cooled to room temperature and concentrated to approximately 30 ml in a flash evaporator. The resulting viscous yellow liquid was extracted five times with diethyl ether and then evaporated to dryness in vacuo over phosphorus pentoxide. The dry yellow solid (7.28 g) was then ground to a fine powder and placed in 125 ml of anhydrous ethanol. The resulting mixture was stirred at 45°C for 10 min, centrifuged, and decanted. The yellow decantate was evaporated to dryness in a vacuum oven at 50°C. The solid was then reprecipitated from ethanol two more times. After further drying for 10 hr at 80°C in an Abderhalden drying apparatus, there was obtained 6.1 g (75% yield) of a very hydroscopic bright yellow solid (I).

This product (I) was found to be soluble in water, in anhydrous methanol, and in anhydrous ethanol; slightly soluble in dioxane and in dimethylsulfoxide; and insoluble in acetone and in ether.

Thin-layer chromatography, with absolute ethanol as the eluting solvent, showed Compound I to be a pure compound. It was analyzed by potentiometric titrations, thermogravimetric analysis, and ir spectral analysis.

Analysis: Calculated for $C_{10}H_{12}NO_3Na$ + 2% H_2O: C, 54.40%; H, 5.65%; N, 6.32%; H_2O, 2.0%. Found: C, 54.70%; H, 5.76%; N, 6.34%; H_2O, 2.1%.

Prototype Monomeric Compound (II): N-(2-Hydroxy-2-phenylethyl)iminodiacetic Acid, Disodium Salt Monohydrate, $C_6H_5CH(OH)CH_2N(CH_2COONa)_2 \cdot H_2O$. This compound was prepared following the general procedure used to make the sodium salt of N-(2-hydroxy-2-phenylethyl)aminoacetic acid.

Disodium iminodiacetic (2.41 g, 0.0136 mole) was dissolved in a mixture of 76 ml of water and 90 ml of redistilled dioxane in a 500-ml three-necked flask. The flask was equipped with a water condenser, heating mantle, magnetic stirrer, thermometer, and dropping funnel. After the solution had been heated to 80°C, a solution of styrene oxide (1.63 g, 0.0136 mole) in 24 ml of redistilled dioxane and 6 ml of water was added, dropwise and with stirring, over a period of 6 hr. The yellow reaction mixture was stirred and heated at 80°C for an additional 6 hr after all of the styrene oxide had been added. It was then cooled to room temperature, filtered, and evaporated to 10 ml in a flash evaporator. The resulting viscous orange liquid was placed in a separatory funnel and extracted six times with 30 ml portions of diethyl ether. During the extractions, a solid appeared to form in the water-ether dispersions. However, as the liquid phases separated, this solid redissolved. The extracted aqueous phase was evaporated to dryness in vacuo over phosphorus pentoxide. The dry-gold-colored solid (3.5 g) was then stirred in 80 ml of anhydrous methanol and the resulting mixture was centrifuged and decanted. Two hundred and forty milliliters of ether were added to the decantate, and the precipitate that formed was stirred in the mother liquor for several minutes at room temperature. This mixture was then centrifuged and decanted. The tan residue was placed in 60 ml of anhydrous methanol, centrifuged, and reprecipitated with ether two more times. After the final residue was dried for 12 hr in vacuo over phosphorus pentoxide at room temperature and for 12 hr in vacuo at 80°C, there was obtained 2.75 g (68% yield) of a very hydroscopic gold-colored solid (II).

Solubility studies showed that II was soluble in water and in anhydrous methanol; slightly soluble in anhydrous ethanol; and insoluble in acetone, in ether, and in dioxane. Thin-layer chromatography, using absolute methanol as the eluting solvent, showed II to be a pure compound.

The product II was analyzed by potentiometric titrations, thermogravimetric analysis, and ir spectral analysis.

Analysis: Calculated for $C_{12}H_{13}NO_5Na_2 \cdot H_2O$: C, 45.71%; H, 4.76%;

N, 4.45%; H_2O, 5.7%. Found: C, 45.74%; H, 4.40%; N, 4.48%; H_2O, 5.5%.

Deuterated Prototype Monomeric Compounds. Both sodium N-(2-hydroxy-2-phenylethyl)aminoacetate and disodium N-(2-hydroxy-2-phenylethyl)iminodiacetate were deuterated according to the general procedure used by Hooper to deuterate DL-threonine and its metal complexes [23]. For example, sodium N-(2-hydroxy-2-phenylethyl)aminoacetate (0.04 g), was dissolved in 3 ml of 99.8% D_2O and then sealed in a glass container and heated to 75°C for 20 hr. The solvent was then evaporated under reduced pressure and the entire procedure repeated two more times. The final residue was dried in vacuo at 80°C over phosphorus pentoxide for 12 hr. The ir spectra of the deuterated compounds were recorded.

Metal Complexes of the Prototype Monomeric Compounds. The Pr(III), Ho(III), Yb(III), and Cu(II) complexes of N-(2-hydroxy-2-phenylethyl)aminoacetic acid were prepared following the two general procedures reported in the first paper in this series [12]. In the first procedure, sodium hydroxide was slowly added to an aqueous mixture of the metal salt and the acid form of the ligand. In the second procedure, a concentrated solution of the sodium salt form of the ligand was slowly added to an aqueous solution of the metal salt.

The preparation of bis-[N-(2-hydroxy-2-phenylethyl)aminoacetate]-praseodymium(III) monohydrate is given as an example of the preparation procedure. Sodium N-(2-hydroxy-2-phenylethyl)aminoacetate (0.090 g, 0.414 mmole) was dissolved in 4.00 ml of 0.1048 M hydrochloric acid, and the solution was diluted to 9.0 ml with deionized water. To this was added 5.00 ml of 0.0414 M praseodymium(III) chloride solution. The resulting solution was warmed and stirred, by magnetic stirrer, as 4.19 ml of 0.0998 M sodium hydroxide was slowly added over a 50-min period. Precipitation began after approximately 2.00 ml of the base had been added. After all of the base had been added, the mixture was stirred for an additional 30 min at room temperature before it was centrifuged. After centrifugation the mother liquor, which was light green at a pH of approximately 7, was decanted. The yellow-green residue was washed three times with 8 ml portions of deionized water. Each washing consisted of stirring the solid for 5-10 min in the water, centrifuging, and decanting. The final residue was dried in a vacuum oven over phosphorus pentoxide at 60°C for 12 hr and then at room temperature for another 12 hr. The dry yellow-green product weighed 0.080 g (70% yield).

The Pr(III), Ho(III), and Yb(III) complexes of N-(2-hydroxy-2-phenylethyl)iminodiacetic acid were prepared by a modification of this procedure. This modified procedure consisted essentially of slow addition of solid disodium N-(2-hydroxy-2-phenylethyl)iminodiacetate monohydrate to a concentrated aqueous solution of a rare earth chloride. The preparation of N-(2-hydroxy-2-phenylethyl)-iminodiacetatopraseodymium(III) monohydrate is given as an example of the preparation procedure. Solid disodium N-(2-hydroxy-2-phenylethyl)iminodiacetate monohydrate (0.171 g, 0.538 mmole) was added slowly and with vigorous stirring to 4.0 ml of a 0.134 M aqueous solution of praseodymium(III) chloride. A light-green precipitate formed almost immediately. The reaction mixture was stirred and heated on a steam bath for 15 min. After cooling to room temperature, it was centrifuged and the light-green mother liquor was decanted. The solid residue was washed three times with 1 ml portions of deionized water. Each washing consisted of stirring the solid for 5-10 min in the water, centrifuging, and decanting. Some of the product appeared to dissolve in the water washings. The final residue was dried in vacuo over anhydrous calcium sulfate at 40°C for 20 hr and then at room temperature for another 20 hr. The dry light-green product weighed 0.070 g (32% yield).

All of the metal complexes of both prototypes were analyzed by thermogravimetric analysis, by ir spectroscopy, and by elemental analysis. The latter results are given in Table 1.

Potentiometry

The acid dissociation constants of the prototype monomeric compounds N-(2-hydroxy-2-phenylethyl)aminoacetic acid and N-(2-hydroxy-2-phenylethyl)iminodiacetic acid were determined in 50% v/v dioxane-water at 25°C. The ionic strength was kept constant by using 0.1 M potassium chloride solutions. The acid dissociation constants of aminoacetic acid and of iminodiacetic acid were also determined under the same conditions. The stability constants of all of the above compounds with various trivalent rare earth ions were also measured in 50% v/v dioxane-water at 25°C and 0.1 (KCl) ionic strength. In these measurements, the potentiometric titration method used by Chaberek and Martell [24] was followed with the exception that the solvent was a dioxane-water mixture rather than pure water. This was a necessary alteration because of the insolubility of the metal complexes in water.

TABLE 1. Metal Complexes of Prototype Compounds

Formula	Analysis (%)						
	C	H	N	Metal	H_2O	Cl	
$Pr(C_{20}H_{23}N_2O_6)\cdot H_2O$	44.00	4.58	5.13	25.82	3.29	0	Calc
	44.06	4.44	3.79	26.6	3.2	0	Found
$Ho(C_{20}H_{23}N_2O_6)\cdot H_2O$	42.11	4.39	4.91	28.95	3.16	0	Calc
	42.03	4.60	3.44	29.1	3.3	0	Found
$Yb(C_{20}H_{23}N_2C_6)\cdot H_2O$	41.52	4.33	4.84	29.93	3.12	0	Calc
	41.38	4.44	3.22	30.00	3.1	0	Found
$Pr(C_{12}H_{12}NO_5)\cdot H_2O$	35.21	3.43	3.43	-	4.41	0	Calc
	35.22	3.87	3.40	-	4.5	0	Found
$Ho(C_{12}H_{12}NO_5)\cdot H_2O$	33.25	3.23	3.23	-	4.16	0	Calc
	33.09	3.47	3.38	-	4.3	0	Found
$Yb(C_{12}H_{12}NO_5)\cdot H_2O$	32.65	3.18	3.18	-	4.08	0	Calc
	32.92	3.83	3.20	-	4.50	0	Found

The automatic buret, the temperature regulating magnetic stirrer, and the pH meter used for the above determinations were specified in the Physical Measurements portion of the Experimental section. The titration cell used in these experiments was a 250-ml beaker with a ground-glass bottom. The cell was covered with a Lucite plate, through which holes were bored to accommodate an electrode, a nitrogen inlet tube, the buret tip, the thermistor probe for the temperature regulator, a thermometer, and a glass rod bent at one end for removing droplets from the buret tip. The titration solution was stirred and kept at 25 ± 0.05°C by the temperature regulating magnetic stirrer. The pH meter and the automatic buret could be read to 0.001 pH unit and 0.002 ml, respectively.

The general procedure consisted of potentiometric titration of each compound both in the absence of and in the presence of a trivalent rare earth ion. The ionic strength was maintained constant by using 0.1 M potassium chloride as a supporting electrolyte and by employing relatively low concentrations of metal and ligand compound. The titrations of the prototype monomeric compounds were carried out using 1:1 and 2:1 molar ratios of prototype-to-metal ion, whereas those of the ligands, aminoacetic acid and iminodiacetic acid, were carried out using only the 1:1 molar ratio of ligand-to-metal ion. The acid dissociation constant for each prototype monomeric compound was taken to be the average value of at least four measurements, whereas those of aminoacetic acid and iminodiacetic acid were taken to be the average value of two measurements. At least three measurements were performed for each stability constant with the prototype monomeric compounds. Single measurements were performed for each stability constant with aminoacetic acid and iminodiacetic acid.

A typical procedure used for determining the stability constants of a rare earth with the prototype monomeric compounds and with aminoacetic acid and iminodiacetic acid is as follows: to 0.200 mmole of the ligand in its sodium salt form were added 25.00 ml of 0.020 M perchloric acid, 25.00 ml of 0.44 M potassium chloride solution, 55.00 ml of redistilled dioxane, and 5.00 ml of a 0.040 M rare earth chloride solution. The solution was mixed by the magnetic stirrer while nitrogen, presaturated with 50% v/v dioxane-water, bubbled through the solution. After 10 min the nitrogen bubbler was raised from the solution and held above the liquid for the remainder of the experiment. The first pH reading was then taken. Sodium hydroxide (0.0998 M) was next added in 0.25 ml increments. After each addition the solution was mixed until equilibrium was reached, and then the pH was taken.

The same procedures were used to determine the acid dissociation constants of all of the compounds except that deionized water was added in place of the rare earth solutions.

The calculations were basically the same as those used by Chaberek and Martell [24]. However, because of the presence of the dioxane in the system, appropriate corrections had to be made [25]. Since the total volume of a one-to-one mixture of dioxane and water is not the sum of the volumes of the components added, a volume correction had to be applied. The actual volumes of solutions used in this work were obtained by multiplying the calculated total volumes by 0.981. Because of the lag in response of the glass electrode to hydrogen ions in dioxane-water solutions, a pH correction factor had to be applied. In this work the corrected pH values were obtained by adding 0.07 pH units to each pH reading.

The acid dissociation constants determined in this investigation are tabulated in Table 2.

TABLE 2. Acid Dissociation Constants in 50% v/v Dioxane-Water at 25°C and 0.1 (KCl) Ionic Strength

Compound	pk_1	pk_2
N-(2-Hydroxy-2-phenylethyl)aminoacetic acid	3.27	8.52
N-(2-Hydroxy-2-phenylethyl)iminodiacetic acid	3.62	8.83
Aminoacetic acid	3.45	9.95
Iminodiacetic acid	3.83	10.05

The stability constants in this investigation were determined according to the graphical method proposed by Bjerrum [26]. In this method, $\bar{n}$, the average number of moles of ligand bound per metal ion, is plotted against pA, the negative logarithm of the ligand anion. When $\bar{n} = 0.5$, $(MA) = (M)$, provided (MA_2) approaches zero. At this point, $K_1 = 1/(A)$ or $\log K_1 = pA$. Similarly, when $\bar{n} = 1.5$, $(MA_2) = (MA)$, provided (M) approaches zero. At this point $K_2 = 1/(A)$ or $\log K_2 = pA$. In these equations, $(\bar{n})$ represent molar concentrations, M and A represent metal and ligand ions, respectively, and K_1 and K_2 are the first and second step stability constants, respectively.

The values of $\bar{n}$ and (A) were calculated by means of the following equations:

$$\bar{n} = \frac{1}{C_M} \left(C_A - \left[\frac{(H^+)^2}{k_1k_2} + \frac{(H^+)}{k_2} + 1\right](A)\right.$$

and

$$(A) = \frac{(2)C_A - (H^+) + (OH^-)}{\dfrac{2(H^+)^2}{k_1k_2} \quad \dfrac{(H^+)}{k_2}}$$

where C_M represents the total concentration of metal ion species, (OH^-) represents the molar concentration of hydroxyl ion, C_A represents the total concentration of ligand anion, (H^+) is the hydrogen ion concentration, and k_1 and k_2 are the first and second acid dissociation constants, respectively. The derivation of these equations may be found in the paper by Chaberek and Martell [24].

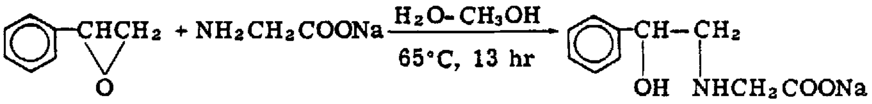
The stability constants were calculated on a Univac 1107 computer using a program originally written by Durham [27] and modified to be used in this investigation.

The chelate stability constants that were determined in this investigation are tabulated in Table 3.

DISCUSSION

Prototype Monomeric Compound N-(2-Hydroxy-2-phenylethyl)aminoacetic Acid and Its Metal Complexes

This ligand was obtained in its sodium salt form according to Eq. (1).



(1

TABLE 3. Stability Constants in 50% v/v Dioxane-Water at 25°C and 0.1 (KCl) Ionic Strength

	Metal					
	Praseodymium(III)		Holmium(III)		Ytterbium(III)	
Compound	log K_1	log K_2	log K_1	log K_2	log K_1	log K_2
N-(2-Hydroxy-2-phenylethyl)-aminoacetic acid	5.40	4.35	5.57	5.06	5.64	5.38
N-(2-Hydroxy-2-phenylethyl)-iminodiacetic acid	9.11	5.15	9.56	5.74	9.62	5.32
Aminoacetic acid	5.4	-	5.8	-	6.0	-
Iminodiacetic acid	7.3	-	8.0	-	8.2	-

An ir spectral analysis indicated that the major by-products of this reaction were phenyl 1,2-ethanediol and unreacted sodium aminoacetate.

That the isolated product was the desired product was established by its physical and chemical properties. Thin-layer chromatography established that the isolated product was free of any sizable amounts of impurities. The elemental analysis of the product was in good agreement with that calculated for sodium N-(2-hydroxy-2-phenylethyl)aminoacetate containing 2% (by weight) of water. That 2% (by weight) water was present was shown by a thermogravimetric analysis of a sample of the product that had been dried (10 hr at 80°C) in the same manner as the sample that was subjected to the elemental analysis. The molecular weight of the isolated product was obtained by potentiometrically titrating the sodium salt to its isoelectric point with standard acid as well as by back-titrating the acid form of the product to its sodium salt form with standard base. The molecular weight, taken as the average of the measured values of several such titrations, was 212. This is in good agreement with the theoretical value of 217 for sodium (N-(2-hydroxy-2-phenylethyl)-acetate.

The first and second acid dissociation constants of the product were obtained from potentiometric titrations in 50% v/v dioxane-water at 25°C and 0.1 (KCl) ionic strength. Because of the Zwitterion form of aminocarboxylic acid ligands, the first acid dissociation constant is actually a measure of the acidity of the carboxyl oxygen atom while the second acid dissociation constant may be taken as an indication of the basicity of the nitrogen atom (Eq. 2)

$$C_6H_5CH(OH)CH_2\overset{+}{N}H_2CH_2COOH \underset{pk_1}{\rightleftharpoons}$$

$$C_6H_5CH(OH)CH_2\overset{+}{N}H_2CH_2COO \underset{pk_2}{\rightleftharpoons} C_6H_5CH(OH)CH_2NHCH_2COO^- \qquad (2)$$

The measured values, along with those of some analogous compounds, are shown in Table 4.

An examination of Table 4 discloses several pertinent points. First it is noted that the apparent acid dissociation constants of aminoacetic acid determined in 50% v/v dioxane-water are higher than those values determined in an aqueous system. This is to be expected in view of the fact that the 50% v/v dioxane-water binary

TABLE 4. Acid Dissociation Constants of Aminoacetic Acid and N-Substituted Aminoacetic Acids

Compound	Medium	Temp. (°C)	Ionic strength	pk_1	pk_2	Ref.
Aminoacetic acid	Water	25	0.1 ($NaClO_4$)	2.43	9.62	29
N-Ethylaminoacetic acid	Water	25	0.1 ($NaClO_4$)	2.30	10.10	29
N-Diethylaminoacetic acid	Water	25	0.1 ($NaClO_4$)	2.04	10.47	29
N-Hydroxyethylaminoacetic acid	Water	20	0.05 (KCl)	-	0.1	31
N,N-Bis(2-hydroxyethyl)aminoacetic acid	Water	30	0.1 (KCl)	2.00[a]	8.08	32, 33
Aminoacetic acid	50% v/v dioxane-water	25	0.1 (KCl)	3.45	9.95	b
N-(2-Hydroxy-2-phenylethyl)-aminoacetic acid	50% v/v dioxane-water	25	0.1 (KCl)	3.27	8.52	b

[a] This value was obtained at 20°C in Ref. 32.

[b] This work.

solvent at 25°C has a lower dielectric constant, approximately 34 [28], than that of pure water, approximately 78. The lower dielectric constant promotes greater electrostatic interactions and consequently greater ionic association. Second, the effect of N-substituents on the acid dissociation constants of aminoacetic acid is worthy of note. When an amine hydrogen atom is displaced by an aliphatic alkyl group, the acid strength of the carboxylic acid group increases slightly and the basicity of the amine group increases. However, if the substituted alkyl group contains an hydroxyl group, the acid strength of the carboxylic acid group again increases slightly, but the basicity of the amine group decreases markedly. The effect of the aliphatic substituents that do not contain hydroxyl groups is readily explained by an inductive effect [29]. The effect of the hydroxyalkyl substituents could be explained by an inductive effect [30] or by hydrogen bonding; that is, besides its inductive effect, the hydroxyl group can form a hydrogen bond to the amine nitrogen through a five-membered ring structure. This would decrease the availability of the nitrogen electrons for reactions with other protons and hence would explain the noted decrease in basicity. Finally, one can see that the measured acid dissociation constants of N-(2-hydroxy-2-phenylethyl)aminoacetic acid are consistent with those of other N-hydroxyalkyl-substituted aminoacetic acid derivatives.

From a comparison of the ir spectra of sodium N-(2-hydroxy-2-phenylethyl)aminoacetate and its deuterated product with each other and with the spectra of related compounds, several important band assignments were made. These assignments are summarized in Table 5. While it is realized that some of the bands may be due to the absorption of more than one group within the molecule, only the more important groups have been listed.

The correlations, for the most part, are consistent with those that have been assigned to other compounds containing an aromatic ring, an OH group, and/or an aminocarboxylate group [23, 34-38]. The band assignments of the deuterated product are in good agreement with those assigned by Hooper [23] for deuterated threonine.

It should be pointed out that the 1200 to 1000 cm^{-1} region of these spectra is somewhat difficult to interpret. The peak at 1060 cm^{-1} has been assigned to the C—O stretching vibration of the alcoholic COH group. This assignment is in agreement with that of Morris and Busch [39] who assigned the alcoholic C—O stretch of hydroxyethylethylenediaminetriacetic acid to the region 1030 to 1085 cm^{-1}. The peak at 1125 cm^{-1} has been assigned to the C—N—C stretching vibration. This peak occurs within the region (1150-1080 cm^{-1})

assigned to Colthup [40] to the C—N—C stretching vibration of compounds of the type RCH_2NHCH_2R. Several investigators [41-43], working with EDTA and its derivatives, have assigned bands within the region 1135 to 1100 cm^{-1} to the C—N—C stretching vibration of these molecules. The difficulty is that upon deuteration, the 1125 cm^{-1} peak appears to decrease in intensity. This would not be expected if this peak was due solely to a C—N—C vibration. Also, the 1060 cm^{-1} peak appears to remain constant in intensity but to broaden on the lower frequency side in the deuterated product. This could be explained by a slight shift of the C—O stretch to lower frequency brought about by the replacement of the H atom by a D atom in the COH alcoholic group.

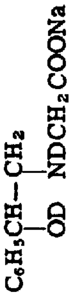
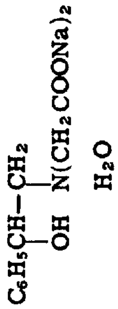
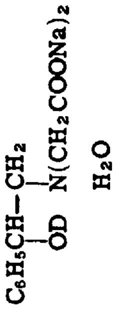
It appears that the best explanation of this spectral region is that there are very few, if any, pure vibrational or bending modes. Whereas the peak at 1125 cm^{-1} is probably associated with the C—N—C stretching vibration, it is probably also associated with other vibrational or bending modes of this complex molecule. The same explanation also applies to the assignment of a band to the C—O stretching vibration of the alcoholic COH group.

The praseodymium(III), holmium(III), ytterbium(III), and copper(II) complexes of N-(2-hydroxy-2-phenylethyl)aminoacetic acid, prepared as described in the Experimental section, were each analyzed for chloride ion. The analyses were carried out with silver nitrate in dilute nitric or acetic acid solutions. The use of these acid solutions served a threefold purpose: (a) The dissociation of the complex was effected; (b) the low pH prevented the formation of the insoluble silver salt of the ligand as well as of the insoluble metal hydroxides; and (c) the metal acetates and nitrates formed were soluble in the solution. The analyses showed that there was no chloride ion in any of the metal complexes.

The thermogravimetric analysis was performed on each of the metal complexes. The resulting thermograms are shown in Fig. 1. Table 6 summarizes the results obtained from these thermogravimetric analyses.

From the thermograms it was noted that all of the complexes, under the conditions described, began to decompose at between 180 and 200°C. These decomposition temperatures were taken to be the temperatures at which the weight loss curves began to drop below the slopes due to the water loss. It was further noted that each of the rare earth complexes lost between 3.1 and 3.3% of its weight by the time it reached its procedural decomposition temperature. These weight losses correspond well to the theoretical water

TABLE 5. Some Characteristic Infrared Absorption Frequencies (cm^{-1}) and Their Tentative Assignments for the Prototype Monomeric Compounds and Their Deuterated Products[a]

Compound				Assignments
 $C_6H_5\underset{\text{OH}}{\underset{\mid}{C}H}-\underset{\text{NHCH}_2\text{COONa}}{\underset{\mid}{C}H_2}$	 $C_6H_5\underset{\text{OD}}{\underset{\mid}{C}H}-\underset{\text{NDCH}_2\text{COONa}}{\underset{\mid}{C}H_2}$	 $C_6H_5\underset{\text{OH}}{\underset{\mid}{C}H}-\underset{\text{N(CH}_2\text{COONa)}_2}{\underset{\mid}{C}H_2}$ H_2O	 $C_6H_5\underset{\text{OD}}{\underset{\mid}{C}H}-\underset{\text{N(CH}_2\text{COONa)}_2}{\underset{\mid}{C}H_2}$ H_2O	
3300 (S,VB)		3250 (S,VB)		OH stretching; H_2O; NH stretching
3060 (M)	3080 (Sh)	3060 (M)	3080 (Sh)	
	3060 (M)		3060 (M)	CH (aromatic) stretching
3025 (M)	3025 (M)	3030 (M)	3030 (M)	
2925 (M)	2925 (M)	2920 (M)		
2880 (M)	2880 (M)	2860 (M)	2940-2820 (M,B)	CH (Aliphatic) stretching
2825 (M)	2825 (M)	2830 (M)		
	2380 (S,VB)		2330 (S,VB)	OD stretching; D_2O; ND stretching
1585 (VS,B)	1585 (VS,B)	1587 (S,B)	1590 (S,B)	COO antisymmetric stretching

1490 (M)	1490 (M)	1495 (M)	1495 (M)	CC (aromatic) skeletal stretching
1403 (S)	1403 (S)	1405 (S)	1405 (S)	COO symmetric stretching
1330 (Sh)		1330 (M)	1330 (W)	OH in-plane deformation
1125 (M)	1125 (W)	1225 (M)	1125 (M-W)	CNC out-of-phase stretching
1060 (M)	1060 (M,B)	1062 (M)	1060 (M,B)	CO stretching
	975 (Sh,B)		950 (Sh,B)	OD in-plane deformation
750 (M)	750 (M)	755 (M)	755 (M)	CH (aromatic) out-of-plane stretching
695 (S)	695 (S)	695 (S)	695 (S)	
631 (W)	635 (Sh)	630 (W)	630 (W)	COO wagging
534 (W)				COO rocking

[a] Abbreviations used in this table: S, strong; M, medium; W, weak; B, broad; Sh, shoulder; V, very.

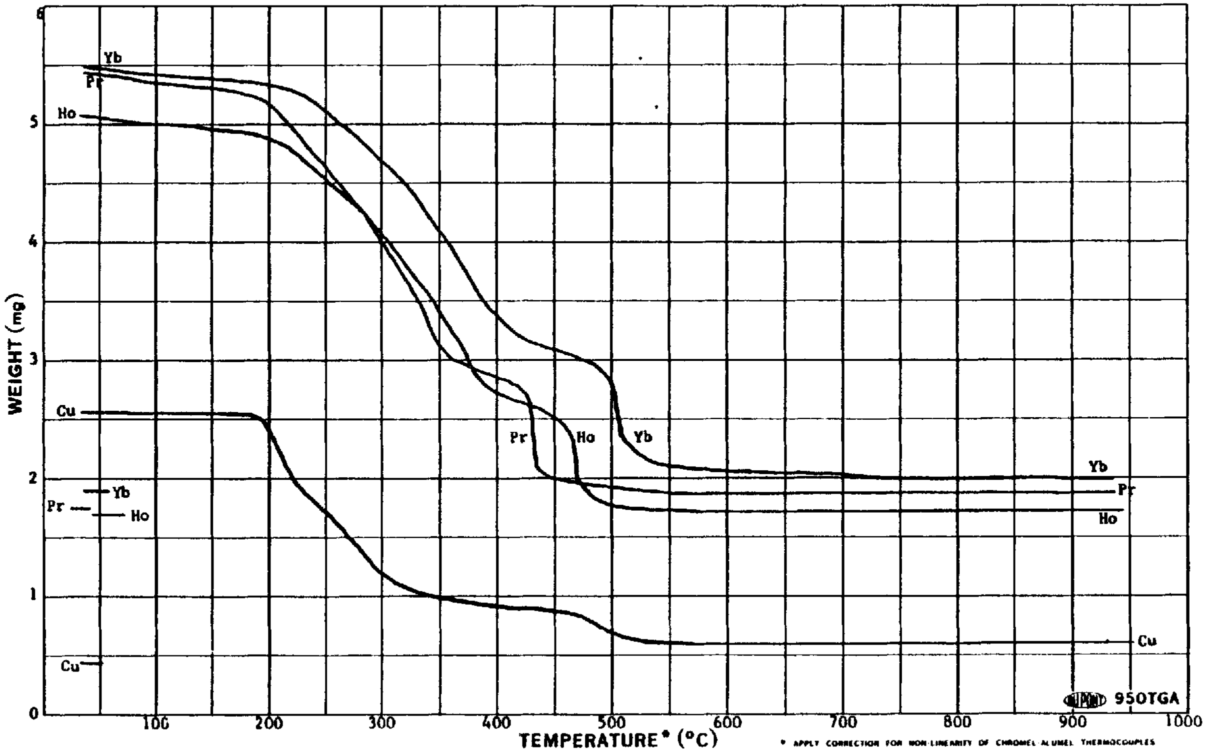


FIG. 1. TGA in air of metal complexes of N-(2-hydroxy-2-phenylethyl)aminoacetic acid.

TABLE 6. Some Results Obtained from the Thermogravimetric Analyses of Various Metal-N-(2-hydroxy-2-phenylethyl)aminoacetic Acid Complexes

	% Water[b]		% Metal[b]		Mol wt	
Complex[a]	Calc	Found	Calc	Found	Calc	Found
Pr(III)$L_2 \cdot H_2O$	3.29	3.2	25.82	26.6	546	532
Ho(III)$L_2 \cdot H_2O$	3.16	3.3	28.95	29.1	570	567
Yb(III)$L_2 \cdot H_2O$	3.12	3.1	29.93	30.0	578	575
Cu(II)L_2	0.00	0.0	14.00	13.7	452	462

[a] L = ligand.
[b] Per cent by weight.

percentages for monohydrates of complexes containing a ligand-to-metal molar ratio of 2:1. The copper complex, however, appeared to be anhydrous.

The thermogravimetric analyses enabled determination of the per cent metal in a complex. This was possible because all of the complexes decomposed to well-defined oxides [44, 45] at relatively low temperatures of less than 600°. A similar type of analysis was used by Kolat and Powell [16] when analyzing for the metal content of other aminocarboxylic acid complexes of the rare earths. By establishing the per cent content of metal in a given weight of sample, and by assuming a mononuclear complex, the molecular weights of these compounds were determined. The results, together with those calculated for a 2:1 ligand-to-metal molar ratio are tabulated in Table 6. The error limits of the metal percentages are ±0.2% for the rare earth complexes and ±0.3% for the copper complex. The measured molecular weights have error limits of ±4% for the rare earth complexes and ±8% for the copper complex. These error limits are based on the accuracy of the thermogravimetric analyzer (±0.2% of the full weight scale used) as stated by the manufacturer. One can readily see that the measured values are consistent with those of the proposed 2:1 ligand-to-metal molar ratio complexes.

The rare earth complexes were analyzed for carbon, hydrogen, nitrogen, and chlorine. The results confirmed the previous conclusion that there was no chlorine present in any of the samples. The carbon and hydrogen analyses were in agreement with the proposed 2:1 structures that were indicated by the thermogravimetric analyses. However, in each case the nitrogen analysis was much lower than the expected value. This is most puzzling, especially because of the excellent agreement of the carbon, hydrogen, metal, and water analyses. It should be pointed out that the source of these low values may be in their measurements rather than in the composition of the complexes. This is indicated by a comparison of the elemental analyses that were reported for two different samples of the ytterbium complex. These values were reported as 1) C, 42.18%; H, 4.50%; N, 4.71%; and 2) C, 42.10%; H, 4.31%; N, 3.41%. The agreement between the carbon and hydrogen analyses and the disagreement between the nitrogen analyses is readily apparent. Furthermore, if it is accepted that the carbon atoms in the complexes must have come from the ligand, then there should be at least 2 nitrogen atoms per 20 carbon atoms. This is based on the analysis of the ligand itself. However, using the holmium complex as an illustration, the empirical formula obtained from the reported elemental analyses indicates that there are only 1.4 atoms of nitrogen per 20 atoms of carbon. This indicates that either another carbon atom source is present in the complex or that the ligand has decomposed. Both of these possibilities seem highly unlikely, especially because of the agreement of all the other data.

To further substantiate the proposed structures of these compounds, the ir spectra of the Pr(III), Ho(III), Yb(III), and Cu(II) complexes were measured from 3900 to 250 cm^{-1}.

The important spectral assignments are given in Table 7. Because of the broadness of many of these peaks, the peak positions represent estimated centers of the absorption maxima. Also, as in the peak assignments of the ligand, only the most important absorbing group for a given peak is listed.

A comparison of these spectra with that of sodium N-(2-hydroxy-2-phenylethyl)aminoacetate indicates that complexation definitely has occurred. Interaction between the carboxylate group and the metal ions is shown by the positions of bands associated with this group. For example, whereas the antisymmetric carboxylate stretching peak is strong and rather broad in the spectrum of both the ligand and a metal complex, there is a definite shifting to higher

TABLE 7. Some Characteristic Infrared Absorption Frequencies (cm^{-1}) and Their Tentative Assignments for Various Metal Chelates of N-(2-Hydroxy-2-phenylethyl)aminoacetic Acid[a]

Metal				
Pr(III)	Ho(III)	Yb(III)	Cu(II)	Assignments
3280 (S,VB)	3300 (S,VB)	3300 (S,VB)	3260 (S,VB)	OH stretching; NH stretching; H_2O
3080 (Sh)	3080 (Sh)	3080 (Sh)	3060 (M)	
3060 (M)	3060 (M)	3060 (M)		
3025 (M)	3025 (M)	3025 (M)	3030 (M)	CH (atomatic) stretching
2930 (Sh)	2940 (Sh)	2940 (Sh)	2950 (Sh)	
2890 (M)	2900 (M)	2900 (M)	2920 (M)	
2840 (M)	2840 (M)	2850 (M)	2870 (Sh)	CH (aliphatic) stretching
1580 (VS,B)	1591 (VS,B)	1596 (VS,B)	1617 (VS,B)	COO antisymmetric stretching
1398 (S)	1399 (S)	1396 (S)	1374 (S)	COO symmetric stretching
1330 (Sh)	1320 (Sh)	1320 (Sh)	1320 (Sh)	OH in-plane deformation
1105 (Sh)	1105 (Sh)	1105 (Sh)	1100 (Sh)	CNC out-of-phase stretching
1058 (M)	1056 (M)	1058 (M)	1057 (M)	CO stretching
631 (W)	635 (W)	642 (W)	650 (W) 633 (W)	COO wagging
540 (W)	542 (W)	544 (W)	578 (W) 537 (W)	COO rocking

[a] Abbreviations used in this table: S, strong; M, medium; W, weak; Sh, shoulder; B, broad; V, very.

frequencies in the latter. That these absorption frequencies are not much different from those of the sodium salt indicates that the metal-to-oxygen bond is highly ionic in character.

Further insight into the complexation characteristics of these compounds is possible by comparing the frequency separations between the antisymmetric and symmetric carboxylate stretching vibrations. Separations of 182, 183, 191, 200, and 243 cm^{-1} were noted for the sodium salt and the Pr(III), Ho(III), Yb(III), and Cu(II) complexes, respectively. Since the separation of these stretching frequencies has been taken as an indication of the relative covalent nature of the carboxylate-metal interaction [23, 34-37, 46, 47], one must conclude that while all of the interactions are mostly electrostatic in nature, the degree of covalent bonding decreases in the order $Cu > Yb > Ho > Pr > Na$. Based on the electronic configuration and the radii of the respective metal ions, this is the expected order.

Interaction between the amine nitrogen atom of the ligand and the metal ions is somewhat more difficult to substantiate by ir spectroscopy. The N—H stretching vibration is of no use because of the broadness of the cm^{-1} band in both the ligand and the metal complexes. Similarly, the N—H deformation peak, which is an extremely weak band in the range 1650-1550 cm^{-1} [37], is impossible to detect because of the interference of the strong carboxylate stretching absorption that occurs in this region.

Several investigators [41-43, 48], studying similar aminocarboxylic acid ligands, have used the C—N—C out-of-phase stretching vibration as an indication of nitrogen-metal interaction. They found that this band shifted to lower frequency upon complexation of the nitrogen with several heavy metals. A similar shifting was found in the spectra of the complexes prepared in this research. The spectra show that the 1125 cm^{-1} peak of the sodium salt of the ligand disappears in all of the metal complexes. Furthermore, there is a distinct shoulder apparent at 1110-1105 cm^{-1} in the spectra of the metal complexes that cannot be observed in the spectrum of the sodium salt of the ligand. This is the same narrow spectral region in which Sawyer and Paulsen observed the shifted C—N—C peaks of the strontium, barium, zinc, cadmium, mercury, and lead chelates of EDTA. If it is accepted that this spectral shift is indicative of metal-nitrogen interaction, then it is implied that the metal complexes of N-(2-hydroxy-2-phenylethyl)aminoacetic acid made in this research are chelate in nature.

Another possible indication of chelate formation is found in the C—H stretching region [43, 48] of the metal complex spectra.

Whereas the C—H absorption bands are not well resolved, the bands as a whole and the estimated centers of the absorption maxima definitely increase in frequency on going from the sodium salt to the metal complexes.

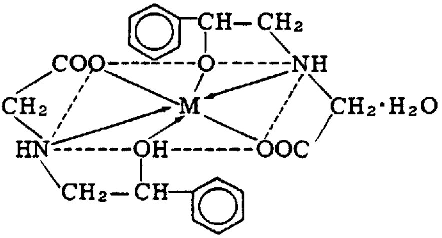
It was noted that while the profile and the position of the 3300 cm^{-1} peak remained essentially the same in the spectra of the ligand and the metal chelates, its intensity in the spectra of the rare earth chelates is noticeably less than in the sodium salt form of the ligand or in the copper chelate. This decrease in intensity is shown in a more quantitative way in Table 8.

TABLE 8. Intensity Ratios of the 3300 cm^{-1} Peak to the 3060 cm^{-1} Peak of the Metal Chelates of N-(2-Hydroxy-2-phenylethyl)aminoacetic Acid

Metal ion	Na	Cu(II)	Pr(III)	Ho(III)	Yb(III)
I_{3300}/I_{3060}	1.2	1.16	0.93	0.96	0.94

A similar decrease in intensity has been found in the 1350-1300 cm^{-1} region of the spectra of the metal complexes. This region has been shown to be associated with the alcoholic OH group of the ligand. There appears to be a definite decrease in absorption in this region in the spectra of the metal complexes as compared to the absorption found in the spectrum of the sodium salt of the ligand. These observations could be taken as indications of interaction between the alcoholic OH group of the ligand and the metal ion.

A close examination of all of the characterization data on the rare earth complexes, as well as a consideration of the electroneutrality requirements of the compounds, suggests Structure III.



III

Structure III, in which the alcoholic CO^- group of one of the ligands is considered to be bonded to the rare earth ion, is consistent with all of the accumulated data. While no attempt has been made to depict the over-all three-dimensional character of the chelate, space-filling models suggest that the two ligand molecules can bond to the metal ion in the proposed fashion without any unfavorable steric interaction or bond strain. The data for the copper chelate would then be consistent with either a square planar structure in which only the carboxylate and the amine groups were bonded to the metal, or a tetragonal structure in which the alcoholic —OH groups occupied the fifth and sixth coordination positions.

Several investigators [17, 49-51], studying the rare earths and ligands similar to N-(2-hydroxy-2-phenylethyl)aminoacetic acid, have proposed structures in which an alcoholic oxygen from the ligand acts as a donor. This same type of bonding has been noted in transition metal complexes of analogous ligands also [30, 52, 53]. Thompson and Loraas [49], investigating the rare earth chelates of 2-hydroxyethyliminodiacetic acid, suggested that this type of bonding should be more prevalent in the rare earth chelates than in the copper chelate. They attributed this to the more ready coordination of rare earths to oxygen donors and to the trivalent character of the rare earths. However, Krause [53] has reported that in the cobalt(II) and nickel(II) complexes of 2-hydroxyethyliminodiacetic acid the alcoholic group coordinates with the metal ions. He bases this conclusion upon the decreased intensity of the OH stretching peak at 3300 cm^{-1} and upon the appearance of a carboxyl peak at 1730 cm^{-1} in the ir spectra of the complexes. That the same ligand can coordinate in two different ways in a bis-chelate has also been proposed for rare earth chelates [54] as well as for transition metal chelates [30, 55]. In both of these examples, the difference in the bonding of the ligands in each bis-chelate was due to the participation or nonparticipation of an alcoholic OH group.

In order to confirm the proposed structure of the rare earth chelates, the stability constants of these compounds were determined. So that these values could be compared with those of the analogous aminoacetic acid chelates of the rare earths, the latter values were also determined under identical conditions. The results are given in Table 3.

On comparing the first stability constants of the aminoacetic acid-rare earth complexes with those of the corresponding N-(2-hydroxy-2-phenylethyl)aminoacetic acid—rare earth complexes, it appears that the latter ligand bonds in the same manner as does the bidentate aminoacetic acid ligand. However, if this were the case, it would be expected that the N-(2-hydroxy-2-phenylethyl)-aminoacetic acid chelates would be noticeably weaker than those of aminoacetic acid. This decreased stability would be expected because of the considerably decreased basicity of the nitrogen donor in the N-substituted ligand [pk_2 of N-(2-hydroxy-2-phenylethyl)aminoacetic acid is 8.52 whereas the pk_2 of aminoacetic acid is 9.96] and because of the increased steric hindrance in the N-substituted ligand [29]. Because the rare earth stability constants of these two ligands are of the same magnitude, it is suggested that there is an additional factor in the N-(2-hydroxy-2-phenylethyl)aminoacetic acid chelates that is adding to the over-all stability of these complexes. The proposed chelate structure, in which the ligand is acting as a tridentate ligand with the alcoholic oxygen atom being the third donor, is consistent with these findings.

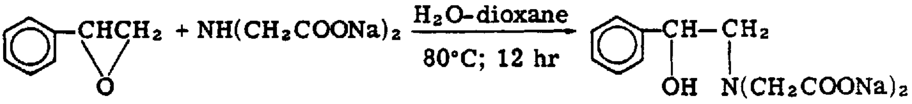
The additional chelate ring formed by such a ligand would easily explain the added stability. Chaberek and Martell [30] used the same type of reasoning when deducing the coordination of the alcoholic group in the 3-hydroxypropyliminodiacetic acid complexes of various di- and trivalent metals.

Another indication that the alcoholic group of N-(2-hydroxy-2-phenylethyl)aminoacetic acid is taking part in the chelation of the rare earth ions is the small difference in the magnitudes of the stability constants going across the rare earth series. It is seen that while the measured stability constants of the aminoacetic acid chelates increase by about 0.6 log units between praseodymium and ytterbium, those of N-(2-hydroxy-2-phenylethyl)aminoacetic acid increase by only 0.24 log units over the same interval.

The measured second stability constants of at least the holmium and the ytterbium complexes of N-(2-hydroxy-2-phenylethyl)aminoacetic acid suggest that in solution the second ligand that bonds to the metal ion may also act as a tridentate rather than a bidentate ligand. The much larger difference between the first and second stability constants of the praseodymium complex indicates that the second ligand may act as a bidentate ligand in this case. However, these results are somewhat questionable because the titration solutions had to be taken to pH values of from 6.6 to 7.5 before $\bar{n}$ values of 1.5 were reached. Hydrolysis, especially of the higher atomic numbered metal ions, could cause these measured values to be high.

Prototype Monomeric Compound N-(2-Hydroxy-2-phenylethyl)Iminodiacetic Acid and Its Metal Complexes

This ligand was prepared by the same procedure as that used to prepare its aminoacetic acid analog. The reaction can be summarized as in Eq. (3).



(3)

The composition of the isolated product was verified by measuring several of its physical and chemical properties. As with N-(2-hydroxy-2-phenylethyl)aminoacetic acid, the molecular weight of the product was measured by potentiometric titrations. The molecular weight, taken as the average value obtained from several such titrations, was 312. This is in good agreement with the theoretical molecular weight of 315 for disodium N-(2-hydroxy-2-phenylethyl)iminodiacetate monohydrate. A thermogravimetric analysis indicated that the product began to decompose at 280°C and contained about 5.5% (by weight) water. This amount of water is equivalent to one molecule of water of hydration. The elemental analysis of the isolated product was also in good agreement with that for disodium N-(2-hydroxy-2-phenylethyl)iminodiacetate monohydrate.

The first and second acid dissociation constants of the product were determined in the same manner as the corresponding values of the prototype N-(2-hydroxy-2-phenylethyl)aminoacetic acid. The measured values, along with those of some analogous compounds, are shown in Table 9. The first and second acid dissociation constants may be taken to be measures of the acidity of the carboxylate group and the basicity of the amine group, respectively.

A comparison of the various values in Table 9 reveals much of the same information that was found with the ligand N-(2-hydroxy-2-phenylethyl)aminoacetic acid and its analogs. Since this information was examined in detail with reference to that ligand, it will not be similarly re-examined here. One should be able to see, however, that the measured acid dissociation constants of N-(2-hydroxy-2-phenylethyl)iminodiacetic acid are consistant with the proposed structure of this ligand.

TABLE 9. Acid Dissociation Constants of Iminodiacetic Acid and N-Substituted Iminodiacetic Acids

Compound	Medium	Temp. (°C)	Ionic strength	pk_1	pk_2	Ref.
Iminodiacetic acid	Water	30	0.1 (KCl)	2.54	9.12	29
N-Methyliminodiacetic acid	Water	30	0.1 (KCl)	2.15	9.92	29
N-2-Hydroxyethyliminodiacetic acid	Water	30	0.1 (KCl)	1.96	8.78	29
N-3-Hydroxypropyliminodiacetic acid	Water	30	0.1 (KCl)	2.06	9.24	31
N,N-Bis(2-hydroxyethyl)aminoacetic acid	Water	30	0.1 (KCl)	2.00[a]	8.08	32, 33
Iminodiacetic acid	50% v/v dioxane-water	25	0.1 (KCl)	3.83	10.05	b
N-(2-Hydroxy-2-phenylethyl)iminodiacetic acid	50% v/v dioxane-water	25	0.1 (KCl)	3.62	8.83	b

[a] This value was obtained at 20°C in Ref. 32.

[b] This work.

The ir spectra of disodium N-(2-hydroxy-2-phenylethyl)iminodiacetate monohydrate and its deuterated product are quite consistent with those expected for the proposed compound. A comparison of these spectra with those of their aminoacetate analogs readily indicates the structural similarities of these two ligands. Table 5 contains several important band assignments that have been made for both of these ligands and their deuterated products. These assignments were made in a manner similar to that used in assigning the bands of sodium N-(2-hydroxy-2-phenylethyl)aminoacetate. Again, it should be remembered that some of these peaks are associated with more than the one mode assigned in the table.

The praseodymium(III), holmium(III), and ytterbium(III) complexes of N-(2-hydroxy-2-phenylethyl)iminodiacetic acid, prepared as described in the Experimental section, were analyzed in much the same way as their N-(2-hydroxy-2-phenylethyl)aminoacetic acid analogs. Because of the many similarities of the two ligands and also of their rare earth chelates, many of the results of these analyses were also quite similar and were interpreted similarly. Only a brief description of the results are given here.

All of the metal complexes of N-(2-hydroxy-2-phenylethyl)iminodiacetic acid were found to give negative chloride tests with silver nitrate. Carbon, hydrogen, and nitrogen analyses suggested identical compositions for each of the three metal complexes; namely, a 1:1 ligand-to-metal structure with one molecule of water per each molecule of complex. Thermogravimetric analysis indicated the presence of at least one molecule of water in each molecule of the rare earth complexes. The thermograms are shown in Figure 2. It is indicated the weights of the residues do not become constant even at temperatures of 900-950°C. Because of this, accurate metal analyses and molecular weight determinations were not possible from the thermogravimetric measurements.

The ir spectra of the three rare earth complexes were measured from 3900 to 600 cm^{-1}. Several important band assignments are listed in Table 10. The frequencies of these assigned bands represent estimated centers of the absorption maxima. As can be seen in Table 10, interaction between the rare earth ions and the ligand carboxylate groups is shown by the shifting of the antisymmetric and the symmetric carboxylate stretching peaks and of the carboxylate wagging peak. A further indication of the rare earth-carboxylate interaction in these complexes is shown by the positions of the peaks associated with the antisymmetric and symmetric carboxylate stretching vibrations relative to each other. The frequency separations of

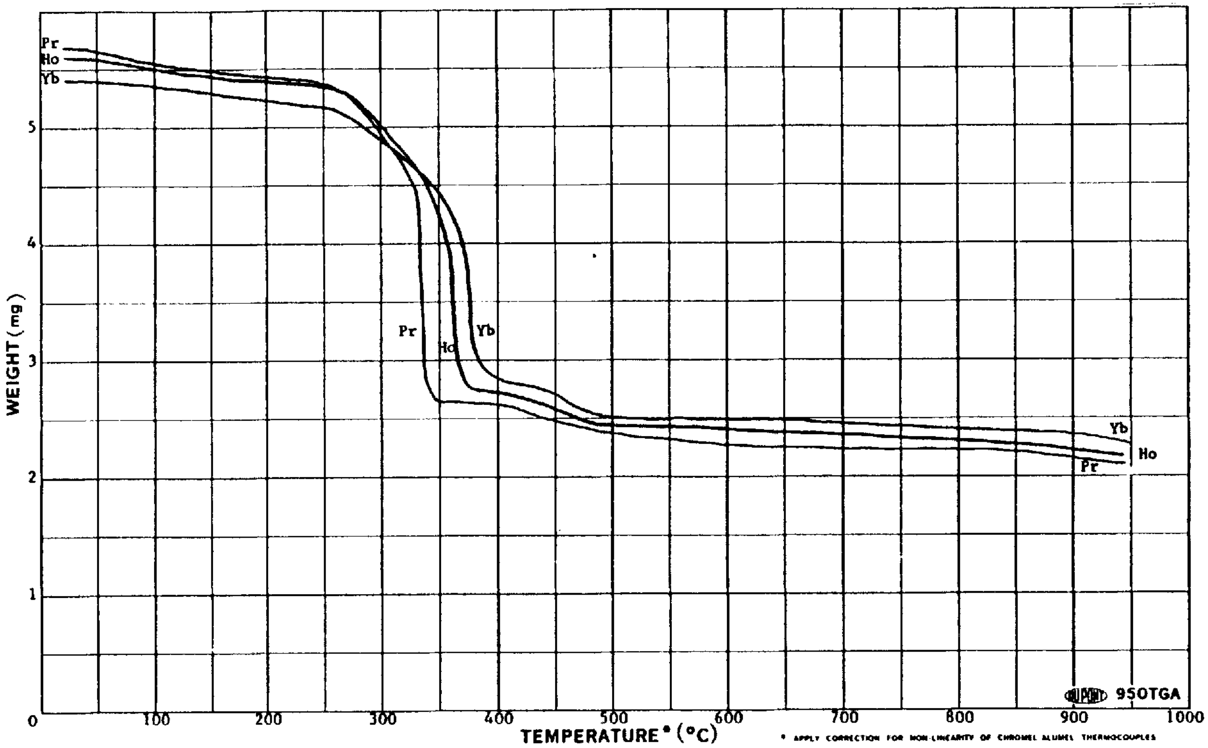


FIG. 2. TGA in air of metal complexes of N-(2-hydroxy-2-phenylethyl)iminodiacetic acid.

TABLE 10. Some Characteristic Infrared Absorption Frequencies (cm^{-1}) and Their Tentative Assignments for Various Rare Earth Chelates of N-(2-Hydroxy-2-phenylethyl)iminodiacetic Acid[a]

Rare earth			
Pr(III)	Ho(III)	Yb(III)	Assignments
3220 (S,VB)	3210 (S,VB)	3210 (S,VB)	OH stretching; NH stretching; H_2O
3060 (M) 3030 (M)	3060 (M) 3030 (M)	3060 (M) 3030 (M)	CH (aromatic) stretching
2940 (M) 2900 (M) 2850 (Sh)	2960-2910 (M) 2860 (Sh)	2960-2910 (M) 2860 (Sh)	CH (aliphatic) stretching
1580 (VS,B)	1595 (VS,B)	1600 (VS,B)	COO antisymmetric stretching
1405 (S)	1403 (S)	1403 (S)	COO symmetric stretching
1330 (M)	1330 (M)	1330 (M)	OH in-plane deformation
1105 (M)	1100 (M)	1100 (M)	CNC out-of-phase stretching
1060 (M)	1060 (M)	1063 (M)	CO stretching
635 (W)	641 (W)	645 (W)	COO wagging

[a] Abbreviations used in this table: S, strong; M, medium; W, weak; B, broad; V, very; Sh, shoulder.

these two peaks were measured as 175, 182, 192, and 197 cm^{-1} for the praseodymium complex, the disodium salt, the holmium complex, and the ytterbium complex, respectively. These results are very similar to those found for the N-(2-hydroxy-2-phenylethyl)aminoacetic acid chelates of the same metals. Again, they indicate that while the bonding between the carboxylate oxygen atoms and the metal ions is very ionic in all of the complexes, the degree of covalent bonding increases in the order Pr < Na < HO < Yb.

Interaction between the rare earth ions and the nitrogen atom of the N-(2-hydroxy-2-phenylethyl)iminodiacetic acid ligand is shown by the shifting of the C—N—C out-of-phase stretching vibration from 1125 cm^{-1} in the disodium salt to 1105-1100 cm^{-1} in the spectra of the metal complexes.

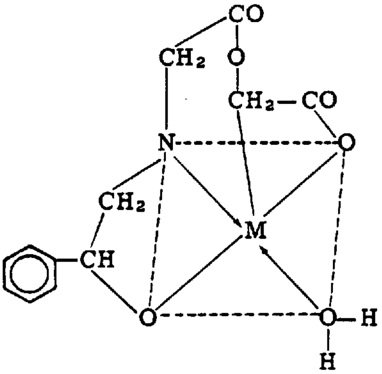
Another possible indication of chelate ring formation is found in the aliphatic C—H stretching peaks of the metal complex spectra. While these peaks are broad and not well resolved, the spectra clearly show that they shift to higher frequencies in going from the disodium salt of the ligand to the rare earth complexes.

Finally, as was found to be the case in the rare earth complexes of N-(2-hydroxy-2-phenylethyl)aminoacetic acid, the ir spectra of the rare earth complexes of N-(2-hydroxy-2-phenylethyl)iminodiacetic acid indicate the possibility of interaction between the OH group and the metal ions. This interaction is indicated in each of the chelates by the decrease in intensity of the peak associated with the OH stretching vibration (3250 cm^{-1}) and the peak associated with the OH in-plane deformation (1330 cm^{-1}). These interactions are shown in a more quantitative way in Table 11.

TABLE 11. Intensity Ratios of Peaks in the Infrared Spectra of the Rare Earth Chelates of N-(2-Hydroxy-2-phenylethyl)iminodiacetic Acid

Metal ion	I_{3250}/I_{3060}	I_{1400}/I_{1330}
Na	1.24	2.7
Pr(III)	1.01	3.9
Ho(III)	0.98	4.0
Yb(III)	0.98	4.5

Integrating all of the above analytical data for the rare earth complexes of N-(2-hydroxy-2-phenylethyl)iminodiacetic acid with the electroneutrality requirements of the complexes strongly suggests Structure IV.

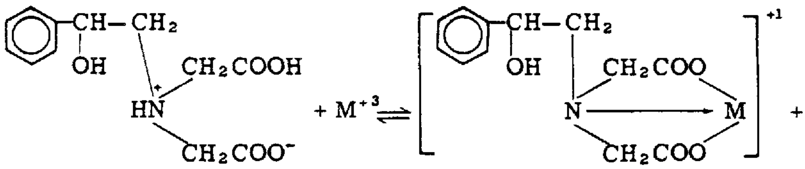


IV

In Structure IV the ligand is acting as a quadradentate chelating ligand. Assuming an octahedral structure, the fifth coordination position of the metal ion is occupied by a water molecule while the sixth coordination position is left unoccupied. It is possible that the sixth coordination position is filled by a carboxyl oxygen atom of an adjacent complex in the crystal lattice. This latter type of coordination has been proposed for other metal complexes of iminodiacetic acid [56] and N-substituted iminodiacetic acids [57, 58].

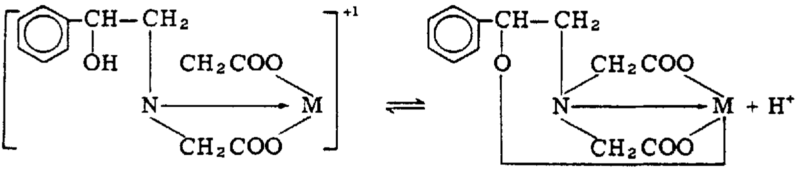
In order to substantiate the proposed structure, the stability constants of the praseodymium(III), holmium(III) and ytterbium(III) chelates of N-(2-hydroxy-2-phenylethyl)iminodiacetic acid were measured. So that these values could be compared to their corresponding values found for the iminodiacetic acid chelates, the stability constants of the same three metals with the latter ligand were also measured under the same conditions. All of the measurements were made using the same technique that was used in determining the stability constants of the metal chelates of N-(2-hydroxy-2-phenylethyl)aminoacetic acid. The results are given in Table 3.

An examination of Table 3 offers some very important insights into the type of bonding that takes place in the rare earth chelates of N-(2-hydroxy-2-phenylethyl)iminodiacetic acid. A comparison of the first rare earth stability constants of the above ligand with the corresponding values for the iminodiacetic acid chelates indicates that the former chelates are much more stable than the latter chelates. This is particularly revealing because the acid dissociation constants of iminodiacetic acid ($pk_1 = 3.83$ and $pk_2 = 10.05$) are higher than the acid dissociation constants of N-(2-hydroxy-2-phenylethyl)iminodiacetic acid ($pk_1 = 3.62$ and $pk_2 = 8.83$). The measured values are therefore taken to be indications that the hydroxy-ethyl group of N-(2-hydroxy-2-phenylethyl)iminodiacetic acid is forming an additional chelate ring to the metal ions. This additional chelate ring could easily account for the increased stability of the chelates of this prototype ligand over those of the tridentate iminodiacetic acid ligand [43, 45-47]. Furthermore, it is consistent with all of the other data that have been obtained for these chelates. This proposal is further substantiated by the shapes of the 1:1 titration curves shown in Fig. 3. The positions of the metal titration curves with respect to the ligand titration curve indicate that the 1:1 metal complexes are quite stable even in the strongly acid solution where the undissociated form of the ligand predominates. Furthermore, the inflection points at two moles of base per mole of ligand indicate that the first step in the complexation is probably as shown in Eq. (4).



(4)

However, because the titration curves show a pronounced buffer region between two moles of base per mole of ligand and a second inflection point at three moles of base per mole of ligand, they can also be interpreted to mean that a second step in the formation of the complex is as shown in Eq. (5).



(5)

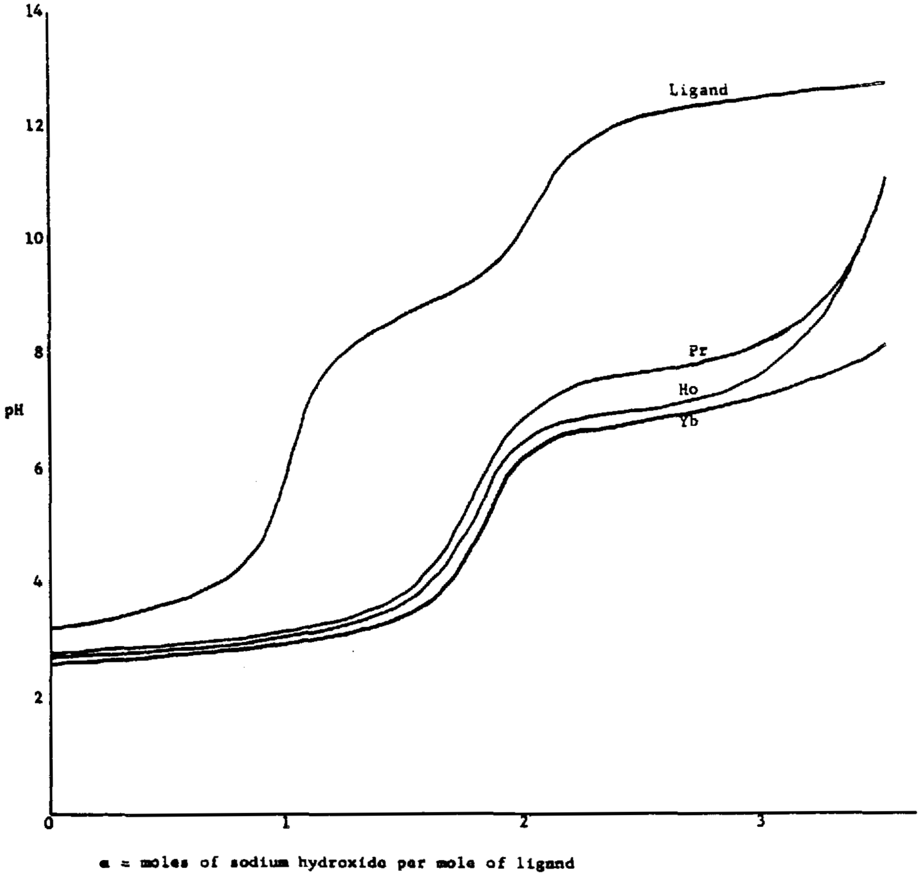


FIG. 3. Potentiometric titration curves of N-(2-hydroxy-2-phenylethyl)iminodiacetic acid in the absence of and in the presence of various metal ions. $C_A/C_M = 1$.

A similar interpretation was suggested by Chaberek et al. [30] for the chelates of several metals with N-2-hydroxyethyliminodiacetic acid.

Information concerning the structures of the 2:1 chelates that form between N-(2-hydroxy-2-phenylethyl)iminodiacetic acid and the tripositive rare earth ions can be obtained from the 2:1 titration curves shown in Fig. 4. These curves all show only a single inflection point at two moles of base per mole of ligand. This indicates that in the 2:1 chelates the metal is displacing the protons from only the carboxylate group and the amine group of each of the ligands to give a charged chelate of the type MA_2^-. Moeller and Horwitz [59] found a similar situation in the rare earth complexes

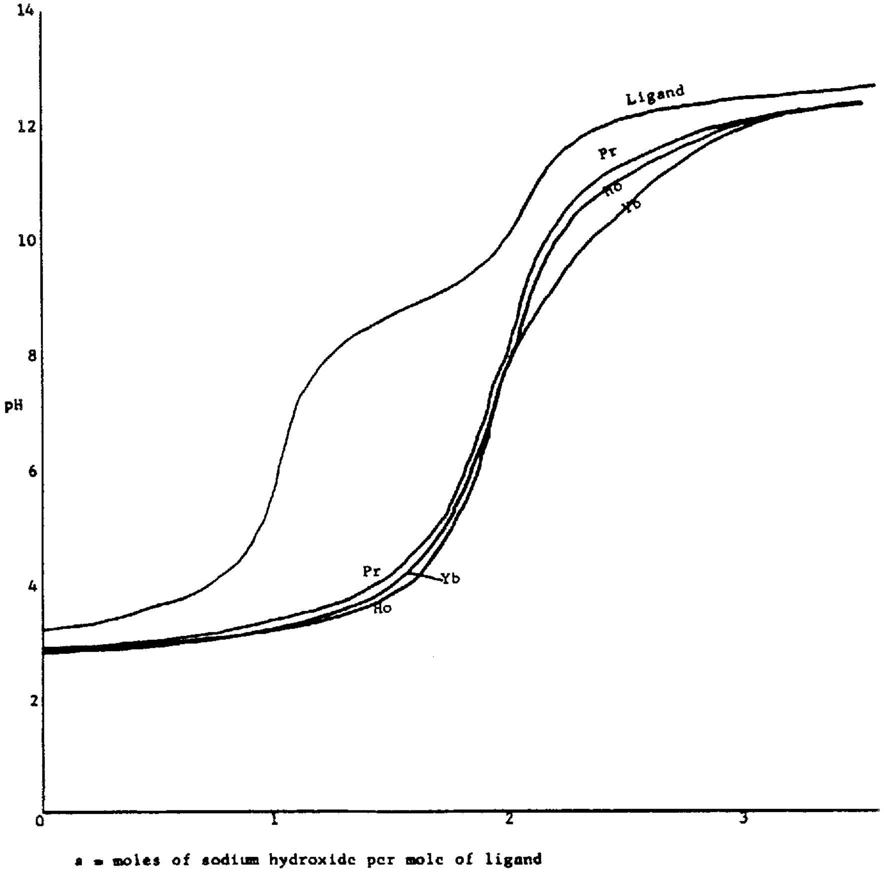


FIG. 4. Potentiometric titration curves of N-(2-hydroxy-2-phenylethyl)iminodiacetic acid in the absence of and in the presence of various metal ions. $C_A/C_M = 2$.

of hydroxyethyl-ethylenediaminetriacetic acid. In these complexes the three acetato groups neutralized the charge of the trivalent rare earth ion and the hydroxyethyl group remained unbound. That the inflection points of the present curves are somewhat skewed indicates that the various steps involved in the formation of the 2:1 chelates overlap one another.

The proposed structure of the 2:1 chelates is also consistent with the magnitudes of the calculated second stability constants as shown in Table 3. A comparison of these values with their corresponding first stability constants shows that for each of the metals the ratio of log K_1 to log K_2 is approximately 4. Such a large ratio would be expected if the second ligand molecule in the bis-chelates was acting as a tridentate rather than as a quadridentate ligand [49]. A final point that should be noted concerns the differences between the measured stability constants of each of the rare earth ions with N-(2-hydroxy-2-phenylethyl)iminodiacetic acid. As shown in Table 3, the difference between the first stability constants of the praseodymium and ytterbium chelates is about 0.5 log units. While this is twice as large as that found for the same metals with N-(2-hydroxy-2-phenylethyl)aminoacetic acid, it is only about half as large as the difference found in the stability constants of the iminodiacetic acid chelates. It should be remembered that this same leveling of the stabilities of the rare earth complexes of N-(2-hydroxy-2-phenylethyl)-aminoacetic acid was also observed.

In order to determine if this leveling effect had been found for rare earth complexes with analogous ligands, a literature search was undertaken. Nowhere in the literature could a discussion of such a trend be found. However, an interesting clue as to the cause of the observed trend was found when several independent data were combined. These data are shown in Fig. 5 as plots of the logarithm of the first stability constant versus atomic number for the rare earth complexes of several chelating ligands. These stability constants were all determined by potentiometric techniques at 20-25°C in aqueous media and at constant ionic strengths of 0.1 (KCl or KNO_3).

Using the nitrilotriacetic acid ligand, $N(CH_2COOH)_3$, as the parent compound, the plots in the figure clearly show the effect of substituting first one hydroxyethyl group for a carboxymethyl group to give N-2-hydroxyethyliminodiacetic acid, $HOCH_2CH_2N(CH_2COOH)_2$, and then substituting a second hydroxyethyl group for a carboxymethyl group to give N,N-bis(2-hydroxyethyl)aminoacetic acid,

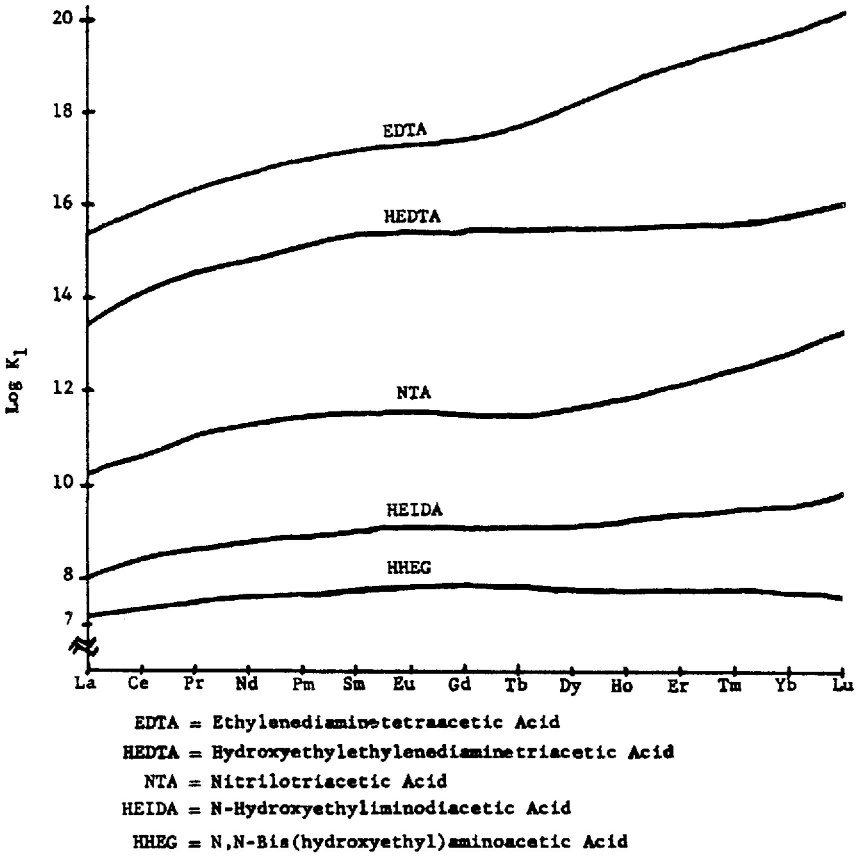


FIG. 5. Stabilities of various rare earth chelates.

$(HOCH_2CH_2)_2NCH_2COOH$. As the carboxymethyl groups are successively replaced by the hydroxyethyl groups, the differences in the stability constants of the rare earth complexes correspondingly decrease. This is dramatically seen in the case of the N,N-bis-(2-hydroxyethyl)aminoacetic acid complexes of the rare earths where there is practically no difference in stability in the entire rare earth series. A comparison of the stabilities of the rare earth complexes of EDTA and HEDTA shows that even replacing one of the four carboxymethyl groups of the former with a hydroxyethyl group results in a drastic leveling of the stability constants.

It therefore appears that the stability trends observed here with the rare earth complexes of the prototype compounds are the rule rather than the exception. Apparently the normally large differences in stability observed for the various rare earth chelates of a given aminocarboxylic acid [1] are reduced by the inclusion of an N-2-hydroxyethyl group in the chelate structure. Furthermore, this leveling effect appears to increase with an increase in the ratio of the N-2-hydroxyethyl groups to the carboxymethyl groups in the ligand.

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