[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, CLARK UNIVERSITY]

Stability of Metal Chelates. VII. N,N'-Ethylenediaminedipropionic Acid and N,N'-Ethylenediaminetetrapropionic Acid

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RECEIVED APRIL 29, 1953

The successive acid dissociation constants of N,N'-ethylenediaminedipropionic acid and of N,N'-ethylenediaminetetrapropionic acid and the stability constants of the 1:1 chelates of Cu(II), Ni(II), Co(II), Fe(II), Fe(III), Zn(II), Cd(II), Mn(II) and Mg(II) ions are reported. The results are compared with the corresponding stability constants of the analogous chelates of the ethylenediaminediacetate, ethylenediaminetetraacetate and ethylenediaminediacetatedipropionate anions. For all the metals investigated, the effect of replacement of an acetate group by a propionate group results in a decrease in affinity of the ligand for metal ions. The Fe(III) chelates differed from those of the divalent metals in that mono- and dihydroxy derivatives were formed.

In a recent report[2] of the synthesis of N,N'-ethylenediaminedipropionic acid and N,N'-ethylenediaminetetrapropionic acid, it was shown semiquantitatively that both substances form very stable complexes with copper(II) ion, but that the interaction with the calcium(II) ion is relatively weak. These compounds are related structurally to the corresponding α-amino acid derivatives, N,N'-ethylenediaminediacetic acid and N,N'-ethylenediaminetetraacetic acid, and differ only in that the acetic acid groups are replaced by propionic acid. Thus, both types of ligands form stable five-membered rings with metal ions through the basic ethylenediamine bridge, while the chelating agents of the present investigation are capable of forming six-membered chelate rings through the amino and acetate groups, rather than the five-membered rings characteristic of the bidentate α-amino acetate donor groups.

Little quantitative information has been published on the effect of chelate ring enlargement on the metal ion affinity of the ethylenediaminepolycarboxylic acids. In a recent publication[3] it was shown that the symmetrical substitution of two propionate groups for two acetate groups of the ethylenediaminetetraacetate ligand, resulted in a considerable decrease in the stability constants of the transition metal chelates. Since the resulting ethylenediamine-N,N'-diacetic-N,N'-dipropionic acid still contains two strongly chelating acetate groups, it was considered desirable to determine the metal ion interaction of some β-amino acids of ethylenediamine in which these groups are absent. The effect of complete substitution of propionate groups for acetate groups in N,N'-ethylenediaminedi- and tetraacetic acids upon chelation has not been previously reported.

Experimental

Apparatus and Procedure.—The experimental method used in this investigation is similar to that described in an earlier publication.[4] The temperature was 30 ± 0.05°, and the ionic strength was maintained at 0.10 with KCl. The amino acid concentration was very low—about 2×10^{-3} molar—so that its conversion to other ionic species during the course of the titration would have only a negligible effect upon the ionic strength. The titrations were carried out in a nitrogen atmosphere by the addition of small increments of potassium hydroxide solution. Although the *p*H was recorded by a Beckman Model G *p*H meter, the values corresponded to *p*H values determined by the hydrogen–silver–silver chloride cell, since the *p*H meter–glass electrode–calomel cell system was calibrated periodically against the hydrogen–silver–silver chloride cell under experimental conditions which were the same as those used in the metal titrations.

Materials.—The ethylenediaminetetrapropionic and N,-N'-ethylenediaminedipropionic acid dihydrochloride used in this investigation were original samples which were prepared and reported previously.[2] The potassium hydroxide employed was prepared in a carbonate-free condition by the interaction of silver oxide and 0.1 *M* potassium chloride solution.

Experimental Data.—The experimental measurements upon which the calculation of the equilibrium constants is based, are presented in graphical form in Figs. 1 and 2. The titration data were somewhat modified by conversion of volume of base to *a*, moles of base per mole of chelating agent present, in order that the resulting titration curves would be more readily interpreted. In all, these figures represent about a thousand potentiometric measurements.

Calculations.—The acid dissociation constants for ethylenediaminedi- and tetrapropionic acids were calculated by the method of Schwarzenbach and Ackermann,[5] while the metal stability constants were calculated by the algebraic and modified Bjerrum methods described in previous papers.[3,4] The general form of the final equation for the algebraic solution for an acid H_nA is

$$K = \frac{C_A - \beta(A^{-n})}{(A^{-n})[C_M + \beta(A^{-n}) - C_A]} \qquad (1)$$

where

K = chelate stability constant for the reaction

$$M^{+2} + A^{-n} \rightleftarrows MA^{n-2}$$

C_A = total acid concn.

C_M = total metal ion concn.

(A^{-n}) = concn. of the completely dissociated anion species.

For ethylenediaminetetrapropionic acid

$$(A^{-4}) = \frac{(4 - a)C_A - (H^+) + (OH^-)}{\frac{4(H^+)^4}{k_1k_2k_3k_4} + \frac{3(H^+)^3}{k_2k_3k_4} + \frac{2(H^+)^2}{k_3k_4} + \frac{(H^+)}{k_4}} \qquad (2)$$

and

$$\beta = \frac{(H^+)^4}{k_1k_2k_3k_4} + \frac{(H^+)^3}{k_2k_3k_4} + \frac{(H^+)^2}{k_3k_4} + \frac{(H^+)}{k_4} + 1 \qquad (3)$$

while for ethylenediaminedipropionic acid

$$(A^{-2}) = \frac{(2 - a)C_A - (H^+) + (OH^-)}{\frac{2(H^+)^2}{k_1k_2} \frac{(H^+)}{k_2}} \qquad (4)$$

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[2] A. E. Martell and S. Chaberek, Jr., THIS JOURNAL, **72**, 5357 (1950).

[3] S. Chaberek, Jr., and A. E. Martell, *ibid.*, **74**, 6228 (1952).

[4] S. Chaberek, Jr., and A. E. Martell, *ibid.*, **74**, 5052 (1952).

[5] G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **31**, 1029 (1948).

and

$$\beta = \frac{(H^+)^2}{k_1k_2} + \frac{(H^+)}{k_2} + 1 \qquad (5)$$

where k_1, k_2, k_3 and k_4 are the corresponding acid dissociation constants and "a" denotes moles of KOH added per mole of amino acid. With the exception of the Fe^{+3} and Cu^{+2} acid titration curves the terms involving $(H^+)^4$ and $(H^+)^3$ in equations 2 and 3 are negligible and may be neglected in the final equations, thus simplifying the calculations.

The first inflection point of the ethylenediaminedipropionic acid dihydrochloride titration curve, at $a = 2$ (Fig. 2) corresponds to the neutralization of the hydrochloride. Therefore, all calculations were performed in the region of $a = 2$ to $a = 4$, where the "free" amino acid is present.

Equilibria Involving Fe^{+3} Ion.—As will be shown below, the interaction of iron(II) ions with ethylenediaminetetrapropionic acid results in the formation of a hydroxy chelate, $FeAOH^{-2}$, in the acid pH region. This is converted to a dihydroxy complex, $FeA(OH)_2^{-3}$, at higher pH, accompanied by a well-defined inflection point between the two regions. Hence, the formation may be considered separately. The first step is defined as

$$Fe^{+3} + A^{-4} \underset{}{\overset{K_1}{\rightleftarrows}} FeA^-$$
$$K_1 = (FeA^-)/[(Fe^{+3})(A^{-4})] \qquad (6)$$

and

$$FeA^- + OH^- \overset{K_2}{\rightleftarrows} FeAOH^{-2}$$
$$K_2 = (FeAOH^{-2})/[(FeA^-)(OH^-)] \qquad (7)$$

For purposes of calculation, these reactions were considered to occur in the reverse direction. Thus, the chelate $FeAOH^{-2}$ would undergo a series of stepwise proton association processes, proceeding along the titration curve from $a = 5$ to $a = 0$. These hydrogen ion association reactions, and the corresponding mass action expressions, are

$$FeAOH^{-2} + H^+ \overset{K_1'}{\rightleftarrows} FeA^- + H_2O$$
$$K_1' = \frac{(FeA^-)(H_2O)}{(FeAOH^{-2})(H^+)} \qquad (8)$$

and

$$FeA^- + H^+ \overset{K_2'}{\rightleftarrows} Fe^{+3} + HA^{-3}$$
$$K_2' = \frac{(HA^{-3})(Fe^{+3})}{(FeA^-)(H^+)} \qquad (9)$$

Finally

$$a'C_A + (OH^-) - (H^+) = (FeA^-) + 2(HA^{-3}) \qquad (10)$$

The Bjerrum function, $\bar{n}$, is then defined by the relation

$$\bar{n} = \frac{a'C_H + (OH^-) - (H^+)}{C_M} \qquad (11)$$

where $a' = (5 - a)$ and a = moles of base added per mole of amino acid. From a plot of $\bar{n}$ vs. pH, it follows that at $\bar{n} = 0.5$, $(FeA^-) = (FeAOH^{-2})$, and

$$K_1' = (H_2O)/(H^+) \qquad (12)$$

At $\bar{n} = 1.5$, $(Fe^{+3}) = (FeA^-)$ and

$$K_2' = (HA^{-3})/(H^+) \qquad (13)$$

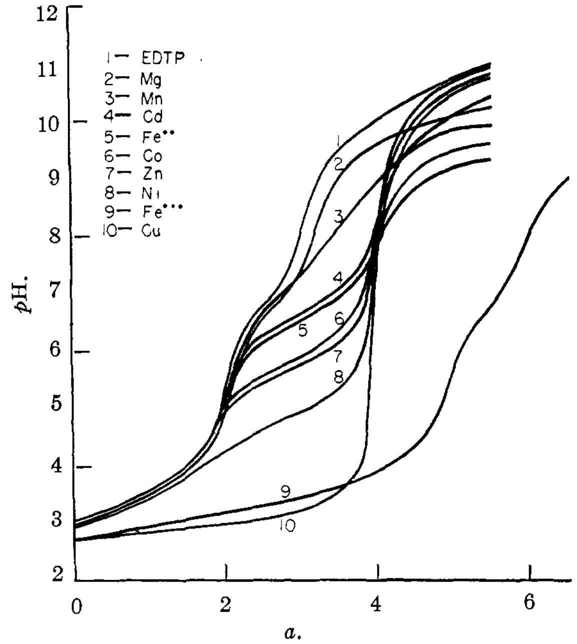


Fig. 1.—pH titration data for ethylenediaminetetrapropionic acid in the presence of equimolar amounts of metal ions as a function of a, the moles of KOH added per mole of amino acid present: 1, free acid; 2, Mg^{++}; 3, Mn^{++}; 4, Cd^{++}; 5, Fe^{++}; 6, Co^{++}; 7, Zn^{++}; 8, Ni^{++}; 9, Fe^{+++}; 10, Cu^{++}; $\mu = 0.1$; and $t = 25°$.

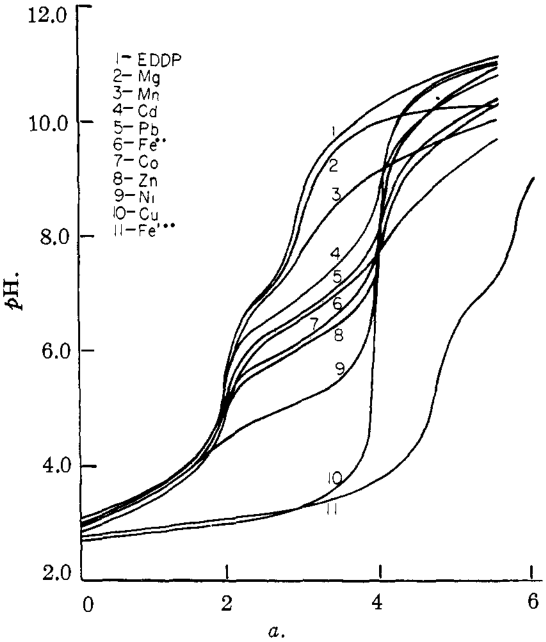


Fig. 2.—pH of ethylenediaminedipropionic acid dihydrochloride in the presence of equimolar amounts of metal ions as a function of a, the moles of KOH added per mole of amino acid: 1, free acid; 2, Mg^{++}; 3, Mn^{++}; 4, Cd^{++}; 5, Pb^{++}; 6, Fe^{++}; 7, Co^{++}; 8, Zn^{++}; 9, Ni^{++}; 10, Cu^{++}; 11, Fe^{+++}; $\mu = 0.1$ and $t = 25°$.

Since the unbound amino acid concentration at $\bar{n} = 1.5$ is $C_{A/2}$ and the acid dissociation constants are known, equations 12 and 13 may be solved for K_1' and K_2'. The formation constants K_1 and K_2 may be calculated from the following relations

$$K_2 = (H_2O)/K_1'k_w \qquad (14)$$

where k_w is the ion product constant of water and

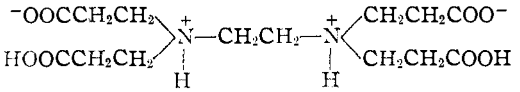
$$K_1 = 1/K'_2k_4 \qquad (15)$$

The relations involving ferric ion interaction with the symmetrical ethylenediaminedipropionic acid were developed in a similar manner, and therefore are not given here.

Discussion of Results

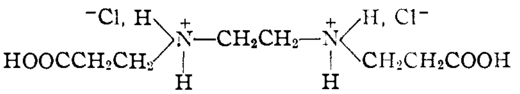
The first inflection in the titration curve of ethylenediaminetetrapropionic acid in the absence of metal ions (Fig. 1) corresponds to the formation of the dipotassium salt, and the second inflection corresponds to the formation of the tripotassium salt, as stable entities in solution There is no inflection point corresponding to the complete formation of the potassium salt of the tetranegative anion. This lack of inflection point may be interpreted to indicate the extensive hydrolysis of the completely dissociated form of the ligand in aqueous solution.

The free acid curve of ethylenediaminedipropionic acid dihydrochloride is very similar to that of the tetrapropionic acid derivative. Although this seems at first surprising, it may be explained on the basis of the fact that, although the ligands differ considerably in structure, the environment of the protons which dissociate is remarkably similar for these two compounds. Thus, in formulas I and II it is apparent that both substances contain two dissociable carboxyl hydrogens as well as two positive amino hydrogens, and that the only dissociating groups which interact appreciably, the positive amino nitrogens, are the same distance apart. The spacing of the basic nitrogens is also the same as that of ethylenediaminetetraacetic acid, and it is for this reason that the titration curves of the propionic acid derivatives in Figs. 1 and 2 are very similar to that of ethylenediaminetetraacetic acid between $a = 2$ and $a = 4$.



I

Ethylenediaminetetrapropionic acid



II

Ethylenediaminedipropionic acid dihydrochloride

Comparison of the free acid titration curve of Fig. 1 with the corresponding curves for the amino acid in the presence of an equivalent amount of metal ion indicates that in the region near *p*H 8, the following neutralization reaction takes place to an appreciable extent for all the metals investigated

$$HA^{-3} + M^{+2} + OH^- \rightleftarrows MA^{-2} + H_2O$$

However, the reaction is not nearly complete enough with Mg^{+2} and Mn^{+2} to give a sharp end-point, as measured by the *p*H (or *p*M) change which occurs. In the case of the dipotassium salt of the ligand, H_2A^{-2}, at *p*H 5–5.5, the neutralization reaction

$$H_2A^{-2} + M^{+2} + 2OH^- \rightleftarrows MA^{-2} + 2H_2O$$

occurs to an appreciable extent with only the divalent ions of Co(II), Zn(II), Ni(II) and Cu(II). Only in the case of Cu(II), however, is the reaction complete enough to give a sharp end-point. In fact the copper(II) chelate, CuA^{-2}, is so stable that the reaction with the pure acid occurs to a considerable extent at *p*H 3 and below.

$$Cu^{+2} + H_4A \rightleftarrows CuA^{-2} + 4H^+$$

Inspection of the titration curves in Fig. 2 indicates that the reactions discussed for the tripotassium salt of ethylenediaminetetrapropionic acid apply in general to the monopotassium potassium salt of ethylenediaminedipropionic acid, with the exception that the stabilities of the metal chelates are lower and the titration curves indicate generally less complete reactions. Thus, the monovalent anion HB^-, stable at a *p*H of about 8, may be considered to undergo the reaction

$$HB^- + M^{+2} + OH^- \rightleftarrows MB + H_2O$$

This reaction, however, occurs only slightly when M^{+2} represents Mg^{+2}, and incompletely with Mn^{+2} and Cd^{+2}. In the case of lead(II), iron(II), cobalt(II), zinc(II), nickel(II) and copper(II) ions, the reaction takes place completely at *p*H 8. Reactions with the "free" amino acid, stable in the *p*H range about 5, may be formulated as

$$H_2B + M^{+2} + 2OH^- \rightleftarrows MB + 2H_2O$$

In this case, however, the only divalent metal ion which reacts completely is the copper(II) ion, while of the remaining divalent metal ions investigated, there is no appreciable interaction with the exception of the nickel(II).

In the presence of ferric ions, inflection points are observed at five and six equivalents of base for both ethylenediaminetetrapropionic acid and the dihydrochloride of ethylenediaminedipropionic acid. This indicates that mono- and dihydroxy complexes are probably formed according to the following neutralizations

$$Fe(H_2O)_6^{+3} + H_4A + 5OH^- \longrightarrow FeA(H_2O)(OH)^{-2} + 9H_2O$$

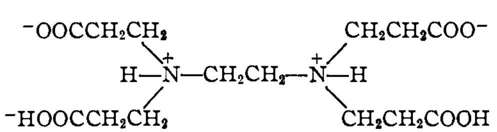
$$FeA(H_2O)(OH)^{-2} + OH^- \longrightarrow FeA(OH)_2^{-3} + H_2O$$

$$Fe(H_2O)_6^{+3} + H_2B\cdot 2HCl + 5OH^- \longrightarrow FeB(H_2O)(OH) + 9H_2O + 2Cl^-$$

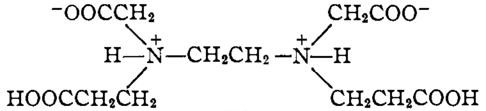
$$FeB(H_2O)(OH) + OH^- \longrightarrow FeB(OH)_2^- + H_2O$$

The use of additional base over the amount required by the divalent ion cannot be accounted for by hydrolysis of the ferric ion itself since precipitation of ferric hydroxide did not take place in the *p*H range of the iron(III) titration curves of Figs. 1 and 2.

Acid Dissociation Constants.—The acid dissociation constants of N,N′-ethylenediaminedipropionic acid (EDDP) and ethylenediaminetetrapropionic acid (EDTP) are listed in Table I, together with those of the related chelating agents N,N′-ethylenediaminediacetic acid (EDDA), ethylenediaminetetraacetic acid (EDTA) and ethylenediamine-N,N′-diacetic-N,N′-dipropionic acid (EDDPDA). It is interesting to note that pk_1 and pk_2 for the tetrapropionic and dipropionicdiacetic acids are approximately the same magnitude. This may be explained by similarity of the acid structures, as is indicated by formulas III and IV



III



IV

The first and second acid dissociation constants correspond to the ionization of the two nearly identical β-aminopropionic acid groups in each case.

The differences between pk_1 and pk_2 of ethylenediaminediacetic acid, ethylenediaminedipropionic acid, and between the analogous quantities, pk_3 and pk_4, of ethylenediaminetetrapropionic acid, are all quite close to three log units. This is approximately the same as the corresponding values of ethylenediamine, and corresponds to the electrostatic effect of one positive ammonium group on the dissociation constant of a similar group separated from it by two carbon atoms. The possible significance of the larger differences in pk_3 and pk_4 observed for ethylenediaminedipropionicdiacetic and for ethylenediaminetetraacetic acid has been discussed previously.[3]

The increasing values of pk_4 for the series ethylenediaminetetrapropionic, ethylenediaminedipropionicdiacetic and ethylenediaminetetraacetic acids may be a reflection of increasing concentration of negative charge toward the center of the anion (*i.e.*, toward the basic nitrogen atoms) resulting in an increase in binding energy for hydrogen ions. On the other hand, the reason for the slight reversal of this effect for ethylenediaminediacetic and ethylenediaminedipropionic acids is not readily apparent.

Metal Stability Constants.—The metal stability constants calculated for ethylenediamine-N,N′-dipropionic and ethylenediaminetetrapropionic acids are listed in Table I, together with the corresponding values for ethylenediaminediacetic, ethylenediaminediaceticdipropionic and ethylenediaminetetraacetic acids.

Table I

Comparison of Chelation Tendencies and Acid Dissociation Constants

$T = 30°$, $\mu = 0.1$, $\gamma_{H^+} = 0.78$

M^{+2}		EDDP	EDTP	EDDA[a]	EDDPDA[a]	EDTA[b]
		log K				
H^+	pk_1	6.87	3.00	6.42	3.00	2.00
	pk_2	9.60	3.43	9.46	3.79	2.67
	pk_3	...	6.77	...	5.98	6.13
	pk_4	...	9.60	...	9.83	10.26
Cu^{+2}		15.1	15.4	16.2	16.3	18.3
Ni^{+2}		9.3	9.7	13.5	15.5	18.4
Co^{+2}		7.3	7.6	11.2	14.9	16.1
Zn^{+2}		7.6	7.8	11.1	14.5	16.1
Fe^{+2}		6.3	6.2	...	...	14.3
Fe^{+3}		13.1[d]	14.4[e]	...	...	25.0
Cd^{+2}		5.6	6.0	8.8	11.8	16.4
Mn^{+2}		3.4	4.7	...	...	13.4
Mg^{+2}		1.6	1.8	3.9	6.9	8.7[c]

[a] Chaberek and Martell.[3] [b] G. Schwarzenbach and E. Freitag, *Helv. Chim. Acta*, **34**, 1503 (1951). [c] Schwarzenbach and Ackermann.[4] [d] $FeA + OH^- \rightleftarrows FeAOH^-$, $\log K_2 = 10.0$; $FeAOH^- + OH^- \rightleftarrows FeA(OH)_2^{-2}$, $\log K_3 = 7.0$. [e] $FeA^- + OH^- \rightleftarrows FeAOH^{-2}$, $\log K_2 = 9.9$; $FeAOH^{-2} + OH^- \rightleftarrows FeA(OH)_2^{-3}$, $\log K_3 = 7.1$.

The relative stabilities of the 1:1 metal complexes are the same for both acids investigated and are in agreement with those found for other chelating agents: $Cu^{+2} > Ni^{+2}, > Co^{+2}, Zn^{+2} > Fe^{+2} > Cd^{+2} > Mn^{+2} > Mg^{+2}$. It is of interest to note that with the exception of Mn^{+2}, the two additional propionate groups result in only a small increase in stability—approximately 0.3–0.4 log K unit. This increase is so small that the additional propionate groups are probably not involved in chelation of the metal. The effect is significant, however, in view of the agreement between the metals listed in Table I. That it cannot be due to a difference in basicity of the anions is indicated by the fact that the values of k_2 for ethylenediaminedipropionic acid and k_4 for ethylenediaminetetrapropionic acid, which may be taken as measures of basicity, are equal. Since at least two of the carboxylate ions are involved in metal binding, it is possible that the increase in stability of the tetrapropionate chelate is in part a statistical effect. The stability increase may also be the result of the effect of increased charge of the anion on metal binding.

The fact that the stability of the manganese(II) ethylenediaminetetrapropionate ion is much greater than that of the ethylenediaminedipropionate chelate indicates that the additional propionate ions are probably involved in the binding of this metal ion.

It should be noted that the buffer regions of the copper titration curve of ethylenediaminedipropionic acid occurs at such low pH that calculations must be made under conditions such that the mono- and dipositive forms contribute appreciably to the amino acid species present in solution. From the titration curve of the dihydrochloride of ethylenediaminedipropionic acid, two dissociation constants were calculated corresponding to the dissociation of protons bound to the carboxyl groups

$$H_4B^{+2} \rightleftarrows H_3B^+ + H^+ \quad pk'_1 = 3.0$$

$$H_3B^+ \rightleftarrows H_2B + H^+ \quad pk'_2 = 3.8$$

where H_2B has the same meaning as before. Thus these dissociation constants are the same as k_1 and k_2 for ethylenediaminetetrapropionic acid within the limits of experimental error. These positive forms of the amino acid need not be considered for the remaining metal chelates, excepting Fe^{+3}, since the calculations were made at pH values sufficiently high so that they did not contribute appreciably to the ligand species present.

Since the close similarities in the stability constants of the di- and tetrapropionic acid derivatives indicate that both probably behave as tetradentate chelating agents, it was decided to correct the stability constant, K_1, of the ferric–tetrapropionate chelate for hydrogen complexing.

A comparison of the chelation tendencies of the ethylenediaminepolycarboxylic acids with various divalent metal ions given in Table I indicates that replacement of the acetate groups of ethylenediaminediacetic acid by propionate groups results in a log K decrease of approximately 3–4 units. The effect is much less pronounced for the Cu^{+2} and Mg^{+2} chelates. It is particularly interesting to note that in the case of the tetracarboxylic acids, this effect is considerably greater. The symmetrical substitution of two acetate groups for propionate groups in ethylenediaminetetrapropionic acid results in a general increase in log K of 6–7 log K units. Further replacement by acetate groups (to ethylenediaminetetraacetic acid) results in a much smaller increase in stability constants. Again, the increase in the association constants of the Cu^{+2} and Mg^{+2} chelates is much smaller. The results constitute an excellent example of the greater stability of aliphatic five-membered rings over six-membered rings when the chelates are derived from α- and β-amino acids.

The effectiveness of ethylenediaminetetrapropionic acid in regulating the aqueous concentration of metal ions is illustrated in Fig. 3 for copper(II), Ni(II), Zn(II), Cd(II) and Mn(II) ions. The metal buffer system consists of an equimolar excess of ligand in each case. For all metals illustrated, the pM remains constant in the pH range above 10, since the ligand anion is fully dissociated in this region. Below pH of 10 all curves have a slope of unity, indicating that one hydrogen ion is displaced per metal ion chelated. In the case of the copper(II), nickel(II) and Zn(II) chelates, below pH 7, the slope of $\Delta p\text{M}/\Delta p\text{H}$ is two, indicating that the effective form of the chelating agent in this region is the divalent anion, H_2A^{-2}, and that two hydrogen ions are displaced per metal ion bound. The remaining metal ions are too weakly bound to show appreciable interaction in this pH range.

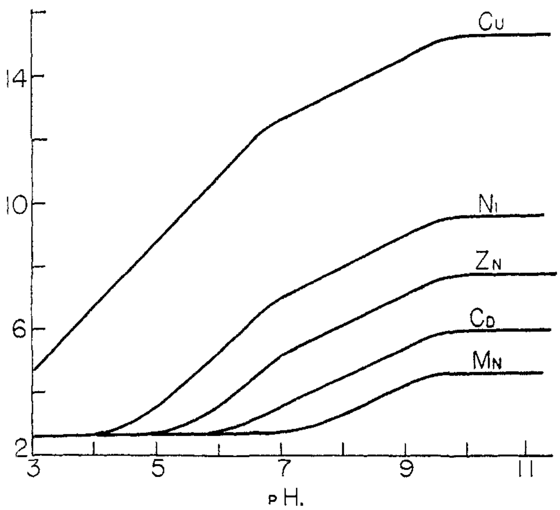


Fig. 3.—Effect of pH on regulation of metal ion concentration by an equimolar excess of ethylenediaminetetrapropionic acid; pM = log molar concentration of metal ion; $t = 20°$; $\mu = 0.1$; total concentration of metal species $= 2 \times 10^{-3}\,M$.

In addition to the difference in stability constants described above, ethylenediaminetetrapropionic acid and ethylenediaminetetraacetic acid show a striking difference in the correlation of chelate stability constants with second ionization potential of the metals of the first transition series. In Fig. 4 the stability constants of the transition metal chelates investigated and the corresponding values of the second ionization potential of the metal are plotted *vs.* the atomic number. In addition, the correlation of the stability constants of ethylenediamine, previously pointed out by Irving and Williams[6] is also shown. It is apparent that ethylenediaminetetraacetic acid chelates have a high order of stability, but that the ligand has a lower order of selectivity for these metals, than the other chelating agents listed. The close parallelism in the behavior of ethylenediaminetetrapropionic acid and of ethylenediamine indicate that the substitution of propionate groups has only a secondary influence on the metal affinity of ethylenediamine, and does not affect the selectivity at all. The correlation with second ionization potential indicates that both ligands are more nearly "normal" in their behavior toward metal ions than is the case with ethylenediaminetetraacetic acid.

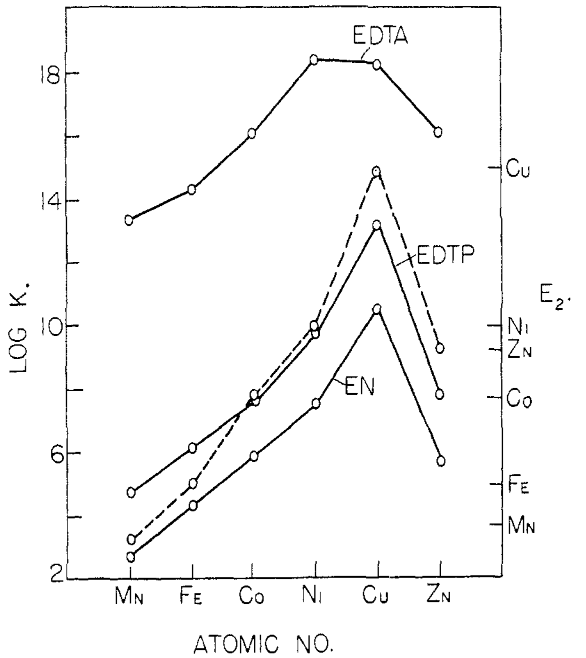


Fig. 4.—Correlation of chelate stability constants with second ionization potential of the metal: EDTP = ethylenediaminetetrapropionic acid; EDTA = ethylenediaminetetraacetic acid and EN represents ethylenediamine; solid lines designate stability constants, and broken lines represent second ionization potentials.

Acknowledgment.—The authors are indebted to the Bersworth Research Organization of Framingham, Massachusetts, for a research grant in support of this work.

Worcester, Mass.

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[6] H. Irving and R. Williams, *Nature*, **162**, 746 (1948).