mechanism involving absorption of light by the catalyst to produce the chain initiating free radical. The effect of catalyst concentration on the "take-off" point in the rate curve was also comparable to that of light intensity.

Acknowledgment.—The authors wish to thank Dr. A. W. Anderson and Dr. W. H. Stockmayer for many helpful discussions during the course of this work.

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[CONTRIBUTION OF DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

Stability of Metal Chelates. V. N,N-Dihydroxyethylglycine

BY S. CHABEREK, JR.,[1] R. C. COURTNEY AND A. E. MARTELL

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The acid dissociation constant and chelate stability constants for the interaction of Cu^{+2}, Ni^{+2}, Co^{+2}, Fe^{+2}, Mn^{+2}, Zn^{+2}, Cd^{+2}, Mg^{+2} and Fe^{+3} ions with N,N-dihydroxyethylglycinate ion have been determined by potentiometric *p*H titration measurements. The ligand was found to be less basic than the glycinate ion but showed equal or higher affinity for metal ions, indicating the participation of the hydroxyethyl groups in chelate formation. By means of the titration curves and related information, the divalent metal ions are shown to form chelates with 1 and 2 moles of ligand per metal ion, whereas the 1:1 Fe^{+3} chelate is proved to combine with excess ligand to give a chelate having a ratio of 3 ligands to 2 metal ions. The Fe^{+3} chelates differ from those of the divalent metals in that protons are also displaced from the hydroxyalkyl groups. The chelate stability constants are correlated with the second ionization potential of the metal, and the effect of *p*H on dissociation of the metal chelates is discussed.

Literature reports of the chelating tendencies of amino acids containing auxiliary hydroxyl groups have been limited to a description of N-hydroxyethyliminodiacetic acid given by Chaberek, *et al.*[2] Since this substance was found to have a much greater affinity for transition metal ions than did corresponding compounds without the hydroxyl group, it was concluded that the hydroxyl group is associated with the metal ions, and that the chelating agent is tetradentate. The compound reported in the present paper, containing one amino group, one carboxyl group, and two hydroxyl groups, was first developed by F. C. Bersworth as a special sequestering agent for the Fe^{III} ion,[3] and was kindly donated by him for investigational purposes. Because of its unusual properties, it was believed that special interactions might occur between this chelating agent and certain metal ions.

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 no more than a negligible effect on the ionic strength. The titration was carried out with potassium hydroxide in a nitrogen atmosphere. Although the *p*H was recorded by a *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 electrode system was calibrated periodically against the potential of the hydrogen, silver–silver chloride cell with the experimental solution as the electrolyte.

Materials.—The chelating agent, dihydroxyethylglycine was supplied through the courtesy of the Bersworth Chemical Company, Framingham, Mass. Since traces of inorganic salts were present in the original sample—a common impurity in amino acids of this type—it was further purified by successive recrystallizations from rather concentrated aqueous solutions.

Experimental Data.—The experimental measurements which were made are presented graphically in Figs. 1, 2 and 3. The ordinates represent *p*H measurements corrected as described above, and the abscissas are expressed in terms of the quantity m, the moles of base added per mole of metal ion in the solution. In Fig. 1 the number of moles of metal was arbitrarily set equal to the number of moles of amino acid present in the solution. Hence in this case m is also a, the number of moles of base added per mole of amino acid, and the titration curve of the amino acid itself is thus comparable with those of the metal chelates in the same graph. In addition to presentation of the data, these curves serve as evidence for the formulas of the metal chelates formed. Thus it is necessary to study the titration curves before the calculations can be set up for the determination of the stability constants. The reasoning involved in this process is described below in the discussion of results.

Calculations.—The single acid dissociation constant employed for this amino acid is defined by: $k_1 = [H^+][A^-]/[HA]$. The successive metal chelate stability constants are defined by: $K_1 = [MA^+]/[M^{+2}][A^-]$, and $K_2 = [MA_2]/[MA^+][A^-]$. In this paper brackets are employed to designate molar concentration. The calculations of the amino acid dissociation constant, and of the metal chelate stability constants were carried out by the modified Bjerrum method described previously.[4] By this method, the concentration of the anion of the chelating agent $[A^{-1}]$ was calculated algebraically with the aid of the acid dissociation constant. The average number of ligands bound per metal ion was then determined and plotted *vs.* *p*A, (log $1/[A^{-1}]$). The values of *p*A at $\bar{n} = 0.5$ and $\bar{n} = 1.5$ are then equivalent to log K_1 and log K_2, respectively. In practice it was found desirable to calculate log K_1 from titration data for which the concentration of metal ion was equal to the concentration of amino acid, while K_2 was best calculated from measurements on solutions for which the concentration of amino acid was two times that of the metal ion. The dissociation constant of the amino acid was calculated by plotting $\bar{n}$, the number of protons bound per mole of amino acid, *vs.* *p*H, the value of *p*H at $\bar{n} = 0.5$ being equivalent to pk_1.

Hydrolysis of Copper(II) Chelate.—Since the titration curves indicated that the hydroxyl complex of the cupric chelate was formed in the absence of appreciable amounts of other species, the calculation of this equilibrium constant is greatly simplified. If the acid form of the copper(II) chelate is represented by $CuA(H_2O)^+$ and the basic

(1) F. C. Bersworth Postdoctoral Fellow, Clark University.

(2) S. Chaberek, Jr., R. C. Courtney and A. E. Martell, THIS JOURNAL, **74**, 5057 (1952).

(3) The sodium salt of this substance is marketed as a special sequestering agent for trivalent metal ions by the Bersworth Chemical Company, Framingham, Mass. (patent pending).

(4) S. Chaberek, Jr., and A. E. Martell, THIS JOURNAL, **74**, 5052 (1952).

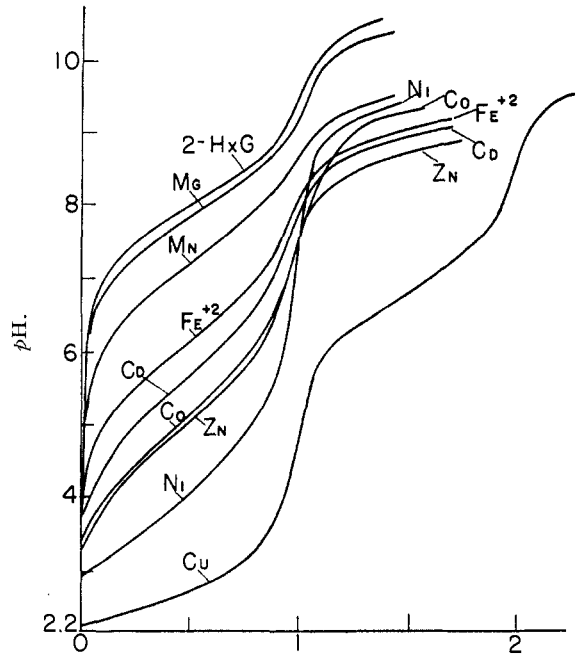


Fig. 1.—Titration of N,N-dihydroxyethylglycine (2-HxG): molar ratio of ligand to metal ion = 1:1; a = moles of base added per mole of acid.

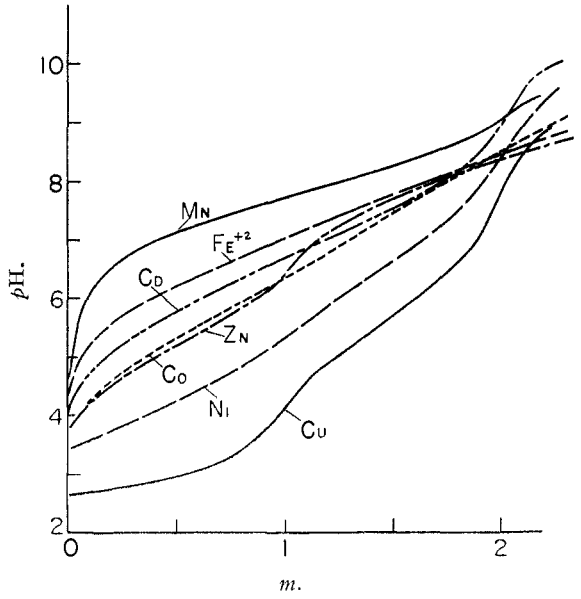


Fig. 2.—Titration curves of N,N-dihydroxyethylglycine (2-HxG): molar ratio of ligand to metal ion = 2:1; m = moles of base added per mole of metal ion.

form by CuA(OH), the equilibrium may be expressed by

$$CuA(H_2O)^+ \rightleftarrows CuA(OH) + H^+$$
$$k_d = [CuA(OH)][H^+]/[CuA(H_2O)^+] \quad (1)$$

The pH read directly from the 1:1 titration curve at $m = 1.5$ is equal to pK_d.

Equilibria Involving $Fe^{(III)}$ Ion.—In order to describe properly the $Fe^{(III)}$ chelate species present, it is desirable to represent the neutral amino acid by the formula $HA(OH)_2$, whereby the

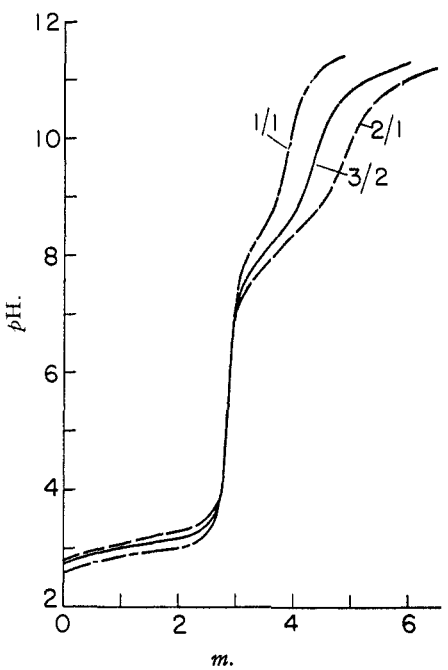


Fig. 3.—Titration of N,N-dihydroxyethylglycine (2-HxG) in the presence of Fe^{+3} ion: m = moles of base added per mole of metal ion.

OH groups indicate the condition of the hydroxyethyl groups. Thus, as will be shown below, the $Fe^{(III)}$ chelate species which may be considered present at low pH is $FeAO_2$, a neutral complex. This is converted to $Fe_2(AO_2)_3^{-3}$ at higher pH, with a well-defined inflection point between the two regions. Hence, the formation of each may be considered separately. The 1:1 chelate may be considered to combine with protons as ligand, and the resulting association constants may be calculated by the Bjerrum method

$$FeAO_2 + 2H^+ \xrightarrow{K'_1} FeA(OH)_2^{+2}$$
$$K'_1 = [FeA(OH)_2^{+2}]/[FeAO_2][H^+]^2 \quad (2)$$

$$FeA(OH)_2^{+2} + H^+ \xrightarrow{K'_2} Fe^{+3} + HA(OH)_2$$
$$K'_2 = [Fe^{+3}][HA(OH)_2]/[FeA(OH)_2^{+2}][H^+] \quad (3)$$

If it is assumed that all the metal is bound to the amino acid, $\bar{n}$, the average number of protons found per chelate molecule, is

$$\bar{n} = (a'C_A - [H^+])/C_M$$

where $a' = 3 - a$, C_A = total concentration of amino acid species, C_M = total concentration of metal ion species.

At $n = 1.0$, $2 \times p\text{H} = \log K'_1$. In actual practice, an attempt was made to determine both of the association steps implied in K'_1. The separation factor was so low, however, that only approximate equilibrium constants for the individual steps could be determined directly from the formation function. Hence, it was decided to report the product of the two, K'_1, which could be determined more accurately. At $n = 2.5$, $[Fe^{+3}] = [FeA(OH)_2^{+2}]$, and

$$K'_2 = [HA(OH)_2]/[H^+] \quad (4)$$

Also, it follows that $C_A/2 = [H_2A(OH)_2^+] + [HA(OH)_2]$.

If k' is defined by $k' = [H^+][HA(OH)_2]/[H_2A(OH)_2^+]$, and if the definition for k_1 given above is employed, equation (4) is transformed to

$$K'_2 = C_A \Big/ 2[H^+]\left(\frac{[H^+]}{k'} + 1\right) \qquad (5)$$

Thus K'_2 may be calculated from the pH at $\bar{n} = 2.5$ if k' is known. Since the term involving k' is the less important quantity in equation (5) at the experimental pH values, an approximate value of 4.5×10^{-3} calculated according to the method of Harned and Owen[5] will suffice. Also, it follows that K_1, the formation constant of the 1:1 chelate is expressed by the relationship $K_1 = 1/K'_2k_1$.

The second step in the chelation of ferric ion may be expressed in terms of the relationships

$$2FeAO_2 + A(OH)_2^- \rightleftarrows Fe_2(AO_2)_3^{-3} + 2H^+$$

$$K_3 = [Fe_2(AO_2)_3^{-3}][H^+]^2/[FeAO_2]^2[A(OH)_2^-] \qquad (6)$$

At the mid-point of the corresponding buffer region of the 3:2 curve, where $m = 3.75$, $2[Fe_2(AO_2)_3^{-3}] = [FeAO_2]$. Since the concentration of free metal ion is here negligible, it follows that

$$C_M = 2[Fe_2(AO_2)_3^{-3}] + [FeAO_2] \qquad (7)$$

and

$$C_M/2 = 2[Fe_2(AO_2)_3^{-3}] = [Fe(AO_2)] \qquad (8)$$

For the titration curve involving 1.5 moles of amino acid per mole of ferric ion, and at $m = 3.75$, the total unbound amino acid species may be expressed by the equation, $C_A/6 = [HA(OH)_2] + [A(OH)_2^-]$, since the concentration of $H_2A^+(OH)_2$ may be neglected at the higher pH involved. By substitution of the expression for k_1, this equation may be transformed to

$$[A(OH)_2^-] = C_A \Big/ 6\left(\frac{[H^+]}{k_1} + 1\right) \qquad (9)$$

From known values of pH, the concentration of $A(OH)_2^-$ from equation (9), and equation (8), it is possible to solve equation (6) directly for K_3.

Discussion of Results

Titration Curves—Composition of Metal Chelates Formed.—The titration curve of N-dihydroxyethylglycine in the absence of metal ions, shown in Fig. 1, is typical of a weak monobasic acid, with a buffer region around a pH of 8. The calculated value of the dissociation constant, $10^{-8.08}$, is somewhat surprising since it is very much larger than that of glycine, $10^{-9.78}$ (see Table I). The difference seems to be too large to be due to inductive electron attraction by the hydroxyl oxygens. Possibly the hydroxyl groups are able to form hydrogen bond with the basic nitrogen atom and thus assist in the dissociation of the ammonium hydrogen ion. It is significant, in view of the behavior of this amino acid with certain metal ions, that the hydroxyl hydrogens apparently do not dissociate even at pH values considerably above 10.

In the presence of an equivalent amount of metal ion (Fig. 1), the titration curves indicate that the normal 1:1 chelates with Mg^{+2}, Mn^{+2}, Fe^{+2}, Cd^{+2}, Co^{+2}, Zn^{+2}, Ni^{+2} and Cu^{+2} form with the displacement of a single proton from the amino group of the chelating agent. Thus, for all of these metals, it is possible to write the reaction

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

wherein the OH^- ion represents the base added during the titration.

It is interesting to note that the Cu^{+2} titration curve has an additional buffer region and inflection point at two moles of base per mole of amino acid. In such cases the additional interaction is either (1) formation of a chelate containing two moles of ligand per mole of metal ion, or (2) the removal of an additional proton from the chelate formed in the first step. In this case it is possible to eliminate the first alternative since, under the special conditions employed here, the higher chelate could form only by a disproportionation reaction to give an equivalent amount of copper(II) hydroxide. The fact that no precipitation occurred in this titration indicated that the reaction involved was merely the dissociation of an additional proton from the 1:1 chelate.

The iron(III) chelate titration curves of Fig. 3 offer an example of the usefulness of potentiometric data in the determination of the formulas of metal chelates formed in aqueous solution. Since phenomena of this type have never been described previously, they will be described in some detail here. The first inflection point of the 1:1 curve does not occur at $m = 1$, as is the case for the curves of Fig. 1, but rather at $m = 3$. This indicates that three moles of hydrogen ions are titrated per mole of amino acid in a one-step process. Thus, if the amino acid is represented by the formula $HA(OH)_2$, the first step for a 1:1 titration may be represented by

$$HA(OH)_2 + Fe^{+3} + 3OH^- \longrightarrow FeAO_2 + 3H_2O$$

In the next step of the 1:1 titration of Fig. 3, an inflection occurs at $m = a = 4$, and part of the iron is precipitated as iron(III) hydroxide. This step, which requires an additional mole of base per mole of metal ion, probably involves the reaction

$$3FeAO_2 + 3OH^- \longrightarrow Fe(OH)_3 + Fe_2(AO_2)_3^{-3}$$

The conclusion that the 3:2 chelate is formed is supported not only by the fact that the above equation fits the data, but also by the fact that it is not possible to write any other reactions involving partial precipitation of iron(III) hydroxide with an inflection at $m = 4$. For example, the precipitation of half of the iron(III) as hydroxide with the simultaneous formation of a 2:1 chelate would involve the titration reaction

$$2FeAO_2 + 3OH^- \longrightarrow Fe(OH)_3 + Fe(AO_2)_2^{-3}$$

Thus 1.5 additional moles of base would be required per mole of metal ion, and the second inflection in the titration curve would occur at $m = 4.5$ rather than at $m = 4$. The only other combination of reactions which would fit the titration curve is

$$FeAO_2 + OH^- + 2H_2O \longrightarrow Fe(OH)_3 + A(OH)_2^-$$

This involves complete precipitation of the iron(III) which is, of course, contrary to the observations.

Additional evidence for the formation of the $Fe_2(AO_2)_3^{-3}$ chelate lies in the shape of the titration curves of Fig. 3 for which the ratios of amino acid

(5) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 580.

to $Fe^{(III)}$ ion are 3:2 and 2:1. All three curves coincide at the first inflection point, because of the initial formation of the 1:1 chelate in all cases. The second inflection point for the 3:2 curve occurs at $m = 4.5$. If a 3:2 chelate is formed, it is seen that the additional 1.5 moles of base per mole of metal ion are exactly accounted for, according to the reaction

$$2FeAO_2 + HA(OH)_2 + 3OH^- \longrightarrow Fe_2(AO_2)_3^{-3} + 3H_2O$$

In the case of the 2:1 curve of Fig. 3, it is seen that the second step is complete at $m = 5$, and two additional moles of base are required per mole of metal ion. Here the formation of the same 3:2 chelate is accompanied by the neutralization of the excess chelating agent. The over-all reaction may be summarized by the chemical equation

$$2FeAO_2 + 2HA(OH)_2 + 4OH^- \longrightarrow Fe_2(AO_2)_3^{-3} + A(OH)_2^- + 4H_2O$$

Here again the experimental result is exactly accounted for on the basis of the 3:2 binucleate chelate. Since no other higher chelate can be postulated that will fit the experimental results, it is apparent that the formation of the 3:2 chelate has been demonstrated by means of titration curves. It is noteworthy that only qualitative observations of *p*H are sufficient to identify certain regions of the curves well enough that the formulas of the metal chelates formed could be determined from ratios of reactants.

The titration curves for the 2:1 ratios of moles of ligand per mole of metal ion, given in Fig. 2, are strikingly different from those for which the ratios were 1:1. In place of the inflection region at $a = 1$, the curves for Ni^{+2}, Co^{+2}, Cd^{+2}, Fe^{+2} and Mn^{+2} have long sloping buffer regions beginning with the formation of the 1:1 chelate. Only with Cu^{+2}, and to some extent with Zn^{+2} ions, is there a suggestion of a definite break at this point ($a = 1$). The absence of inflection points indicates a series of overlapping reactions, consisting of the formation of higher chelates. The formulas of the higher chelates, with the exception of that of Cu^{+2}, are not obvious from the titration data. Since none of these metals form 1:1 chelates of the type described for iron$^{(III)}$ it is believed that the compounds which form in the second step may involve two moles of ligand per mole of metal ion

$$MA(OH)_2^+ + HA(OH)_2 + OH^- \longrightarrow M[A(OH)_2]_2 + H_2O$$

The absence of sharp *p*H rise at $a = 2$ corresponding to the formation of a 2:1 chelate indicates that a further increase in *p*H results in dissociation of protons from the metal chelate. Such a reaction would carry the sloping region beyond $a = 2$, and this is seen to be the case for most of the metals in Fig. 2. This interpretation does not apply to the Mg^{+2} ion since chelation in this case is so weak that it is doubtful that the 2:1 chelate is formed to an appreciable extent.

Comparison of the copper$^{(II)}$ curves in Figs. 1 and 2 reveals that beyond the first inflection point, the *p*H values of the 2:1 titration curve are always considerably lower than those of the 1:1 solutions. Thus, while the curves appear to have similar shapes, quite different phenomena are involved. In the presence of a 2:1 ratio of ligand to metal, it is apparent that in the presence of excess ligand a reaction takes place which results in a greater *p*H decrease. This is evidence for the formation of a higher chelate rather than the hydroxy compound, as is indicated by the reaction given previously. The characteristic differences between the 2:1 Cu^{+2} curve and those of the other metals are due to the existence of a larger separation factor between the first and second chelates.

The formation functions shown in Fig. 4 represent the relative degrees of chelation of the various metals as a function of the concentration of ligand anion. The nearly straight line functions shown for Mn^{+2}, Fe^{+2}, Cd^{+2}, Co^{+2} and Ni^{+2} indicate considerable overlapping in the formation of the 1:1 and 2:1 chelates. In the cases of Cu^{+2} and Zn^{+2} it is seen that definite inflections are present and there is little overlapping in the formation of the successive chelates.

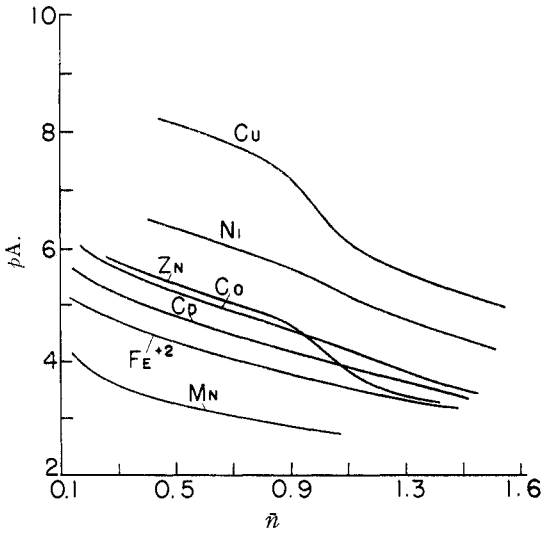


Fig. 4.—Formation functions of N,N-dihydroxyethylglycine (2-HxG): $\bar{n}$ = moles of amino acid bound per mole of metal ion; *p*A = negative logarithm of ligand anion concentration.

TABLE I

EQUILIBRIUM CONSTANTS

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

M	2-HxG			GLY[b]		2-HIMDA[d]	
	log K_1 (1:1)	log K_1 (2:1)	log K_2	log K_1	log K_1 + log K_2	log K_1	log K_2
H^+	$pk_1 = 8.08$			$pk_2 = 9.78$		$pk_2 = 8.78$	
Cu^{+2}	8.15	8.15	5.20	8.62	15.59	>10	4.23
Ni^{+2}	6.38	6.37	4.40	6.18	11.14	9.54	5.15
Co^{+2}	5.28	5.25	3.52	5.23	9.25	8.27	4.44
Zn^{+2}	5.36	5.38	3.26	5.52	9.96	8.57	4.10
Cd^{+2}	4.78	4.81	3.37	..	8.1[c]	7.12	5.12
Fe^{+2}	4.27	4.35	3.00	..	7.8[c]	..	..
Mn^{+2}	3.08	3.27	2.33[a]	3.44	5.5[c]	5.65	3.93
Mg^{+2}	1.15	..	..	..	3.44	3.54	..

[a] Calculated from value of (log K_1 + log K_2) at $\bar{n} = 1.0$. [b] Monk,[6] 25°, $\mu = 0$. [c] Albert,[7] 20°, $\mu = 0.1$. [d] Chaberek *et al.*,[2] same conditions as above.

(6) C. B. Monk, *Trans. Faraday Soc.*, **47**, 297 (1951), $T = 25°$, $\mu = 0$, unless specifically marked.

(7) A. Albert, *Biochem. J.*, **46**, Proc. of Soc. XXXIX (1950).

Stability Constants.—The calculated values of the stability constants of the 1:1 and 2:1 chelates listed in Table I show a striking resemblance to the chelate stability constants of the same metals with the glycinate anion in that the values listed for the 1:1 chelates are almost identical in all cases.

It would seem, therefore, that substitution of the two amino hydrogens of the glycinate ion with β-ethanol groups does not greatly enhance the metal chelating tendency of the ligand. This is a rather surprising observation, particularly in view of the fact that the ethanol group in the hydroxyethyliminodiacetate ion greatly increases the affinity of the ligand for metal ions over that observed for the iminodiacetate anion.[4] This apparent anomaly is resolved if it is remembered that the basicity of the amino nitrogen of the dihydroxyethylglycinate ion is much weaker than that of the glycinate ion, as measured by the pk_1 values listed in Table I. Calvin and Wilson[8] have demonstrated that similar ligands with different basicities vary considerably with respect to affinity for metal ions, and that normally the pk and log K values bear a linear relationship to each other. On this basis, one would expect the chelate stability constants of glycine to be much greater than those of dihydroxyethylglycine. Hence in spite of the similarities of the chelate stability constants of these substances it may be concluded that the hydroxyl groups enhance considerably metal chelate stability.

Another method of demonstrating the enhancement of chelating tendencies of the hydroxyethyl groups is illustrated in Fig. 5, in which are plotted a function (pM = log $1/[M^{+2}]$) of the concentration of the free metal ion *vs.* pH for 4:1 ratios of ligand to metal for the copper$^{(II)}$ ion. It is seen that, except for the very highest pH values, the chelating tendency of dihydroxyethylglycine is much greater than that of glycine, even though the stability constant of copper$^{(II)}$ glycinate, listed in Table I, is somewhat higher. Thus the relative values of the stability constants may be quite misleading as practical measure of chelating tendencies. The stability constants must be interpreted in the light of the pH, the relative basicities of the ligands, and the relative tendencies of the metal ions to hydrolyze or interact with other constituents of the solution.

In Fig. 6 the stabilities of the dihydroxyethylglycinate and glycinate chelates of the various metals listed in Table I are plotted as a function of the second ionization potential of the metal. It is seen that log K increases in a linear manner with increase in the ionization potential. This type of correlation was first observed by Calvin and Melchior[9] for transition metal chelates of salicylaldehyde derivatives, and was later pointed out by Schwarzenbach, Ackermann and Ruchstuhl[10] for the alkaline earth chelates of certain aminopolycarboxylic acids. The results of the present investigation add to the evidence in favor of using this property of the metal as a measure of the relative chelating tendencies of the corresponding ions.

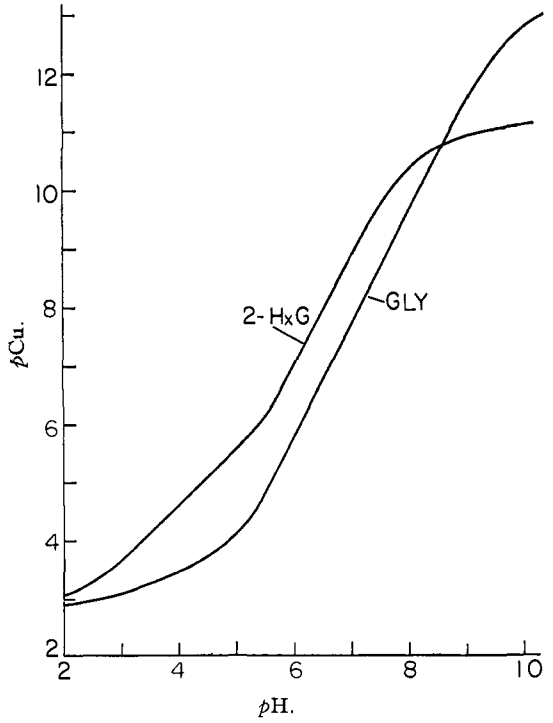


Fig. 5.—Metal ion control for glycine (GLY) and N,N-dihydroxyethylglycine (2-HxG): pCu = negative logarithm of cupric ion concentration; ratio of total concentration of ligand to that of metal ion = 4:1.

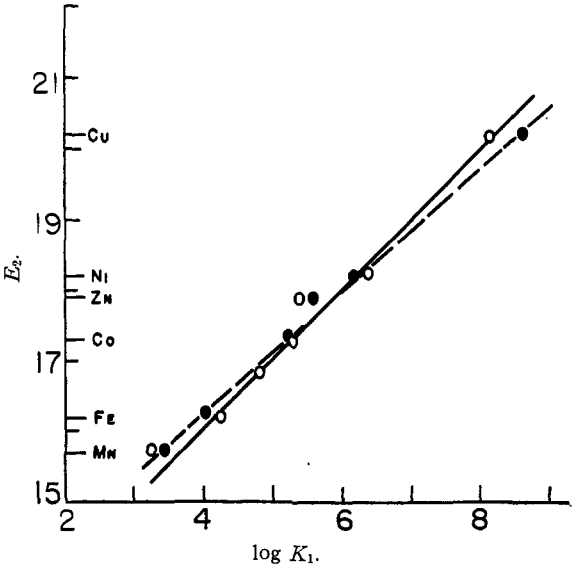


Fig. 6.—Correlation of dihydroxyethylglycinate and glycinate chelate stabilities as a function of the second ionization potential of the metal: E_2 = second ionization potential; log K_1 = logarithm of chelate stability constant; ● represents glycine and O represents dihydroxyethylglycine.

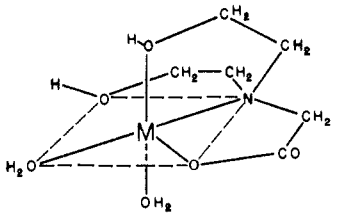
Chelate Structures.—The metal chelate stability constants listed in Table I for the dihydroxyethylglycinate ion represent two opposing tendencies. The decreased basicity tends to decrease the metal ion affinity compared to the glycinate ion, while the hydroxyethyl groups tend to increase the chelation

(8) M. Calvin and D. Wilson, THIS JOURNAL, **67**, 2003 (1945).

(9) M. Calvin and N. C. Melchior, *ibid.*, **70**, 3270 (1948).

(10) G. Schwarzenbach, H. Ackermann and P. Ruchstuhl, *Helv. Chim. Acta*, **32**, 1175 (1949).

tendencies. For this reason, it is suggested that the hydroxyethyl groups are definitely involved in chelation with the metal ion, and the chelate structure of a hexacovalent metal is illustrated by formula I.



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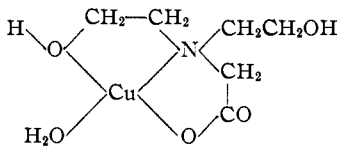
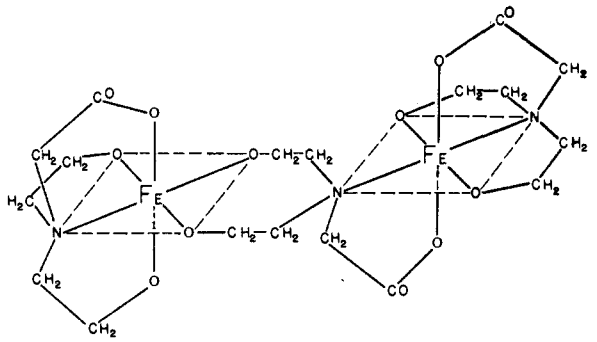
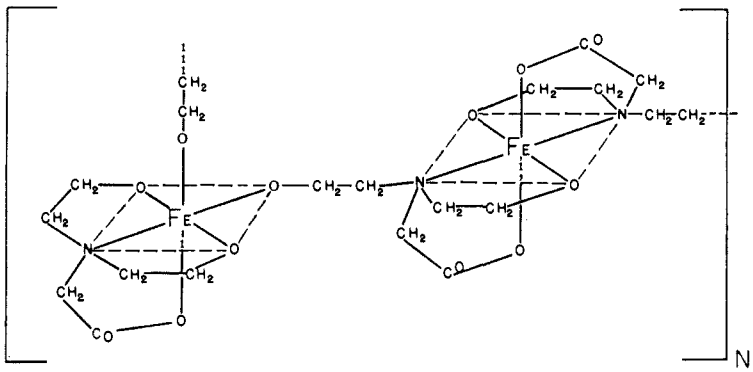


II



III



IV

For a square planar structure, such as that required by the Cu^{+2} ion, the use of molecular models indicates that only one hydroxyethyl group can be involved in chelate ring formation, and the ligand is therefore tridentate. In this connection, it is interesting to note that the Cu^{+2} chelate stability constants listed in Table I indicate relatively less increase in stability due to the hydroxyethyl groups, than is the case for the hexacovalent metals. The hydrolysis of the 1:1 copper(II) chelate (formula II) may involve dissociation of a proton from the hydroxyethyl group or from the coördinated water molecule. Such structures would bear a tautomeric relationship to each other, and the metal chelate may actually be an equilibrium mixture of both forms.

In view of the coördination requirements of the Fe^{+3} ion and the displacement of three protons from the ligand, it is apparent that the structure of the 1:1 chelate may be represented by formula I from which two additional protons have been removed. Here, too, there is the possibility of tautomerism involving proton shifts from the coördinated water molecules to the negative alkoxide groups attached to the metal.

The formulation of a 3:2 chelate, which has been demonstrated above on the basis of the titration curves, is interesting in that the coördination requirements of two Fe^{+3} ions are thereby exactly matched by the number of donor groups in three ligand anions. In this case the displacement of three protons from each ligand is evidence for its tetradentate character. In view of the facts, therefore, the 3:2 iron(III) chelate probably has a binucleate structure of the type pictured in formula III, wherein the two iron atoms are bound together by one of the ligand molecules. There is an additional possibility for the 3:2 chelate, a polynucleate structure of the type indicated by formula IV. Such a structure would be favored over III by the presence of one additional stabilizing five-membered metal chelate ring per mole of metal ion. The authors at present prefer III because of the very large electrical charge of IV and for other reasons. In this connection, measurements that would indicate ion size, such as electromigration studies, would be of interest.

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