[Contribution from The Dow Chemical Company, Eastern Research Laboratory and Clark University]

Chelating Tendencies of N,N'-Ethylenebis-[2-(*o*-hydroxyphenyl)]-glycine

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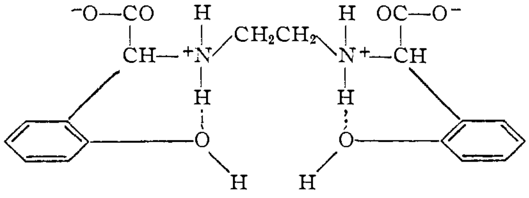
The acid dissociation constants and formation constants of the Cu(II), Ni(II), Zn(II), Cd(II), Mg(II) and Ca(II) chelates of N,N'-ethylenebis-[2-(*o*-hydroxyphenyl)]-glycine are reported. The Co(II) and Fe(II) ions are spontaneously oxidized by the ligand in the absence of oxygen, while the stabilities of the chelates formed by Co(III) and Fe(III) ions are too high for direct potentiometric determination. All of the metal ions except Fe(III), Ca(II) and Mg(II) combine initially with the ethylenediaminediacetic acid grouping of the ligand and undergo rearrangement of the two phenolic protons to give chelates of higher stability. The conversions from one form of chelate to the other are accompanied by characteristic changes in absorption spectra.

Recent investigations of a wide variety of chelate compounds as Fe(III) carriers in plant nutrition showed the Fe(III) chelate of N,N'-ethylenebis-[2-(*o*-hydroxyphenyl)]-glycine (EHPG) to be a very effective iron carrier in biological systems. Because of the remarkable properties of this new chelating agent, investigation of its affinity for Fe(III) and other metal ions seemed to be indicated. The structure of EHPG (I) differs from most of the common Fe(III) sequestering agents in that the hydroxyl groups are phenolic rather than aliphatic in nature.


I

Experimental

Apparatus and Procedure.—The interaction of EHPG with various metal ions was determined potentiometrically by a titration procedure. The hydrogen ion concentration was measured with a Beckman Model G *p*H meter with extension glass and calomel electrodes at a constant temperature of 25 ± 0.05°. The glass-calomel electrode system was calibrated directly in terms of hydrogen ion concentration at 0.1 ionic strength with the sodium acetate-acetic acid buffer system as a primary standard. The ionic strength was maintained constant by using a medium of 0.1 *M* potassium nitrate. This concentration of electrolyte was modified in solutions containing appreciable quantities of 2:1 electrolyte in order to maintain a constant total ionic strength of 0.1 *M*. Because of the large number of donor groups in the ligand, only 1:1 ratios of ligand to metal were investigated, except for the weakly bound Ca(II) and Mg(II) ions. For these metals both excess (10:1) and equivalent (1:1) curves were obtained. Similar procedures were not possible with the remaining metals, however, because of their tendency to precipitate in solutions above *p*H 5. During all titrations a stream of presaturated, CO_2-free nitrogen gas was passed through the reaction flask.

The visible and ultraviolet absorption spectra of the ligands and metal chelates were determined with a Cary Model 14 Recording Spectrophotometer.

Materials.—The preparation of the ligand, N,N'-ethylenebis-[2-(*o*-hydroxyphenyl)]-glycine (I), will be published at a later date; after recrystallization from boiling water it melted at 236–238° with decomposition. Its elementary analysis and infrared spectrum were in agreement with the structure as indicated in I. It is insoluble in cold water and organic solvents but soluble in strongly alkaline and strongly acidic aqueous solutions. The α,α'-ethylenediimino-di-*o*-cresol derivative, II, was prepared according to the method of Funke and Fourneau[1] and melted at 126° (lit.[1] 124°). Another related ligand, 2-(*o*-hydroxyphenyl)-glycine (IIIA), was prepared by a method similar to that described by Harvill and Herbst.[2] It melted at 193–194° with decomposition (lit.[2] 194–195° dec.). The standard metal salt solutions, having a concentration of about 3×10^{-2} *M*, were prepared from reagent grade nitrates and chlorides, and, except for Fe(II), were standardized according to the procedures outlined by Schwarzenbach,[3] which consists of direct titration with ethylenediaminetetraacetic acid in the presence of a suitable indicator. A solution of reagent grade ferrous chloride was standardized by titration with permanganate. Carbonate-free potassium hydroxide was used in all titrations. The concentrations of metal ions and ligands in the experimental solutions were 3×10^{-3} *M*, except for the excess curves, where ten times this concentration of metal was used.

Experimental Data

The potentiometric titration data obtained as described above are plotted in Fig. 1, for values of $-\log [H^+]$ *vs.* *a*, the moles of base added per mole of ligand. These titration curves were first used in a qualitative sense to deduce the various species of ligand and metal complexes which are formed in solution. On the basis of these preliminary conclusions, the interactions between metal ion and ligand were then expressed in terms of dissociation constants and chelate formation constants. Because of the tendency of EHPG to form metal complexes in which hydrogen ions are also present, it was not possible to calculate the metal chelate formation constants by conventional methods. The reasoning employed and the equations applied to elucidation of the equilibria occurring in these substances are described in the Discussion.

In the cases of the Mn(II), Fe(II) and Co(II) ions, meaningful titration curves could not be obtained because of irreversible oxidation of these metals in the presence of the ligand. This reaction was most apparent for the Fe(II) ion, since the deep red color characteristic of the ferric chelate rapidly developed even in the most acid solutions. In the case of cobalt, the color development was not as great, but the titration curve showed a sharp inflection at three moles of base per mole of metal ion and indicated qualitatively a much higher stability than that of the Cu(II) complex. Hence, formation of the trivalent cobalt complex seemed to be the most logical interpretation. In the case of the Mn(II) ion, oxidation at low *p*H did not take place and the initial part of the titration curve seemed normal. As the *p*H was raised, however, more base was required than was true of the other divalent metals, and the inflection did not occur at

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(1) A. Funke and J. P. Fourneau, *Bull. soc. chim.*, **9**, 806 (1942).

(2) D. K. Harvill and R. M. Herbst, *J. Org. Chem.*, **9**, 21 (1944).

(3) G. Schwarzenbach, "Die Komplexometrische Titration," Ferdinand Enke, Stuttgart, 1955.

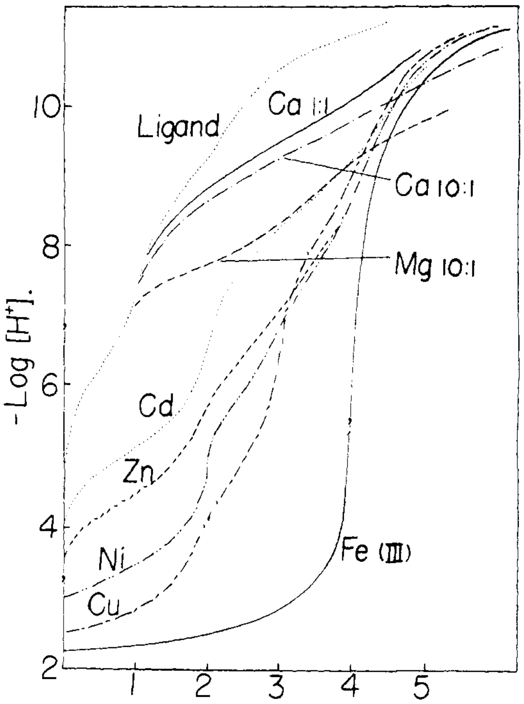
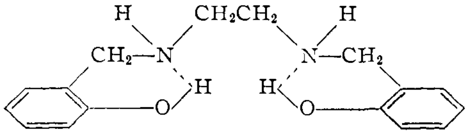


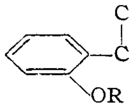
Fig. 1.—Potentiometric titration of various metal nitrates in the presence of equivalent quantities of EHPG; curves also given for 10:1. ratios of Ca(II) and Mg(II) salts to ligand. Abscissa, *a*, represents moles of base added per mole of ligand present.

the expected integral number of moles of base per mole of ligand. Moreover, oxidation proceeded steadily at high *p*H and reversal of the titration with acid did not reproduce the original curve. The possibility that interactions were occurring with trace oxygen impurities in the nitrogen was eliminated by repeating the titration in an atmosphere of hydrogen in the presence of suspended palladium catalyst. Under these conditions, the titration curves were essentially unchanged, and the oxidation of the divalent metal apparently occurs at the expense of decomposition of some of the ligand or of the solvent.

The absorption spectra of the ligand and its copper(II) and iron(III) chelates, measured over a wide *p*H range, are shown in Figs. 2 and 3. The *p*H values investigated were chosen in the case of Cu(II) so as to correspond to the inflection regions of the Cu(II) titration curves given in Fig. 1. Thus, each curve would characterize the successive compounds formed during the potentiometric titration.



II



IIIa, R = H
IIIb, R = CH_3

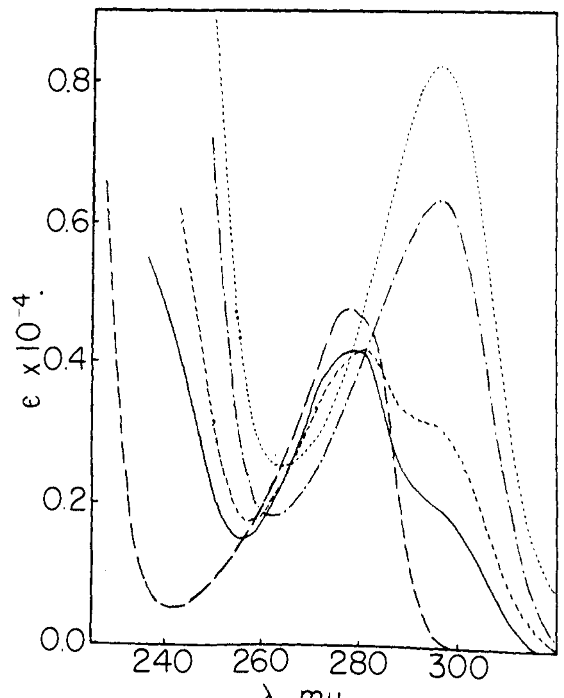


Fig. 2.—Ultraviolet absorption spectra of EHPG as a function of *p*H: - - - -, *p*H 2.1, ———, *p*H 8.5, --------, *p*H 10.2, —··—··—, *p*H 11.5 and ......, *p*H 12.5.

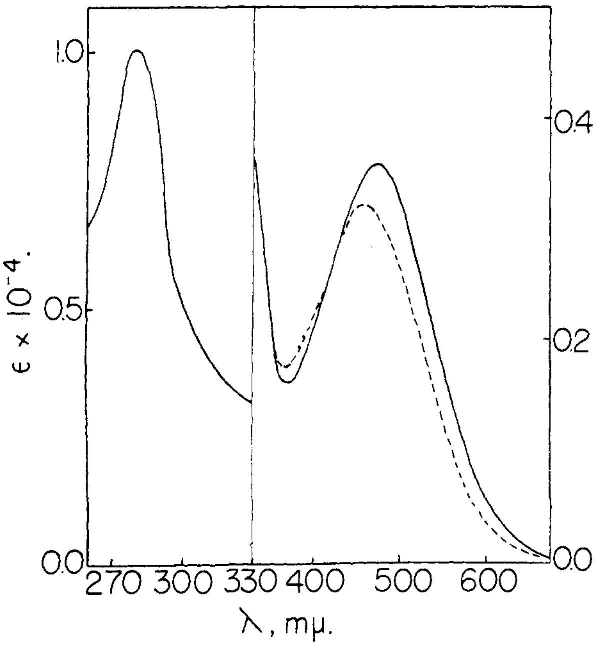


Fig. 3.—Ultraviolet and visible absorption spectra of the EHPG–Fe(III) chelate as a function of *p*H: ———, *p*H 4–10; --------, *p*H 12.

For the purpose of comparison, absorption spectra of α,α'-ethylenediiminodi-*o*-cresol (II), 2-(*o*-hydroxyphenyl)-glycine, (IIIa) and 2-(*o*-methoxyphenyl)-glycine (IIIb) (m.p. 161–162° in agreement with ref. 1) as well as their Cu(II) and Fe(III) chelates, were also determined as a function of *p*H.

Discussion

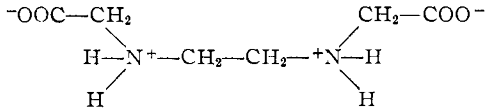
Calculation of the acid dissociation constants was complicated by the fact that only the first dissociation could be considered as taking place in a separate step. According to the titration curve of the pure ligand in Fig. 1, it is apparent that there is overlapping of the second, third and fourth dissociations with the consequent requirement of solving three simultaneous equations for K_2, K_3 and K_4. In order to obtain the best possible values for these dissociation constants, it is desirable to use the graphic solution employed previously by Schwarzenbach and Ackermann[4] for two overlapping dissociations. In order to avoid a three-dimensional graphic solution, it was assumed that in the range of a values from 1 to 2, the pH was low enough that no appreciable amount of fully dissociated ligand was present. From experimental points in this range, therefore, a graphic solution was carried out for pK_2 and pK_3. Similarly in the range of a values between three and four, it was assumed that no appreciable amount of the amino negative form of the ligand was present. From experimental points in this region of the titration curve, a graphic solution was carried out for pK_3 and pK_4. The validity of these assumptions was apparent in the comparison of the two values of pK_3 obtained by these graphic solutions. In this case the values agreed within experimental error. The acid dissociation constants thus obtained are listed in Table I, with the dissociation constants of the analogous ligand, ethylenediaminediacetic acid, IV.

TABLE I

ACID DISSOCIATION CONSTANTS

	EHPG[a]	EDDA[b]
pK_1	6.32	6.42
pK_2	8.64	9.46
pK_3	10.24	
pK_4	11.68	

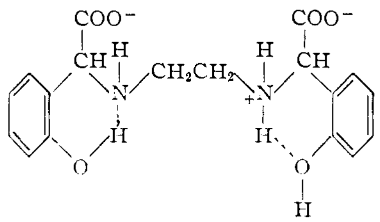
[a] This investigation, 25°, μ = 0.1 (KNO_3), = 0.78.
[b] From Chaberek and Martell,[5] 30°, μ = 0 1 (KCl), = 0.78.



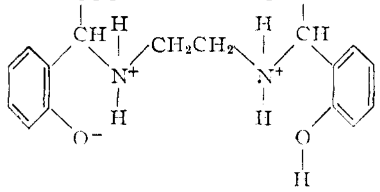
IV

It is apparent from the comparison of the structures of EHPG and of ethylenediaminediacetic acid (EDDA) that the factors which govern the first dissociation steps are similar for these two ligands. The value of pK_1 for EHPG is very nearly equivalent to that of EDDA. It is lower than pK_2 as a result of the inductive effect of one positive ammonium group on the other ammonium group two carbon atoms removed. Thus, the o-hydroxyphenyl groups have little effect on the acidity of the first quaternary ammonium group. Perhaps the tendency for hydrogen bonding in V to decrease pK_1 somewhat is balanced by hydrogen bonding with the phenolic group in the most acid form I.

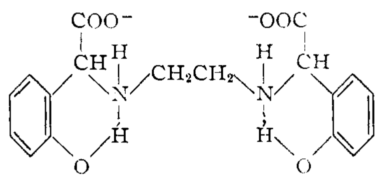
It is noted, however, that the second dissociation constant for EHPG is much larger than the corresponding value for EDDA. If the second dissociation constants indeed correspond in both cases to dissociation of the second ammonium group, it is apparent that the *ortho* phenolic groups have some influence on this dissociation step. A reasonable interpretation for intramolecular interaction between the phenolic group and the basic amino group is indicated in formula V as involving the formation of a hydrogen bond between the basic nitrogen and the phenolic group. On this basis it would be reasonable to expect an increase in acidity of the second quaternary ammonium group over that in IV, in view of the inductive effect of a hydrogen bonded proton on the adjacent nitrogen atom. Alternatively, it might be stated that interaction with the phenolic groups (through hydrogen bonding) would decrease the charge interactions of the positive nitrogen atoms and thus decrease the spread between pK_1 and pK_2 over that of EDDA. Evidence in favor of VII for the binegative anion of EHPG may be found in the fact that the increase in pK_2 of I over that of IV is only 0.8 rather than the much larger value that would be expected if the preliminary dissociations involve the phenolic linkages. Thus, if a structure such as that indicated by formula VI were formed in the first dissociation step, it is apparent on the basis of its structural relationship to EDDA, which contains two positively charged nitrogen atoms separated by an ethylene bridge, that pK_2 would be lower than the observed value by about two units. It seems, therefore, that the first two dissociation steps of the ligand are completely analogous to those of EDDA and that the last two dissociation steps correspond to the removal of protons from the hydrogen bonded phenolic groups of VII. This conclusion is further supported by the spectrophotometric evidence presented below.



V



VI



VII

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[4] G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1029 (1948).

[5] S. Chaberek and A. E. Martell THIS JOURNAL, **74**, 6228 (1952).

All of the transition metals which were successfully titrated gave an initial inflection (Fig. 1) when two moles of base per mole of metal ion had been added to the experimental solution. The initial reaction, therefore, may be considered to be a two-proton displacement, to form a metal chelate

$$M^{+2} + H_4A \longrightarrow MH_2A + 2H^+ \qquad (a)$$

of the type indicated by VIII. This is followed by a series of dissociation reactions in which as much as three additional moles of base are required per mole of metal chelate. In the case of Cu(II) and Ni(II) the third and fourth steps are separated and may be treated as individual dissociations of a weak acid. For Zn(II) and Cd(II) the last three dissociation steps overlap to give a single sloping buffer region.

The metal chelate stability constants for Cu(II), Ni(II), Zn(II) and Cd(II), calculated on the basis of equation a, are listed in Table II, along with the successive acid dissociation constants of these metal chelate compounds.

The titration curves of the alkaline earth metals present a rather more complicated picture as the result of weaker binding of these metals by the ligand and consequent simultaneous neutralization reactions of the ligand and partially formed metal chelate species. Thus in the region between $a = 1$ and $a = 4$, one may assume the presence of as many as three forms of the metal chelates MH_2A, MHA^- and MA^{-2} along with the four most basic forms of the ligand, H_3A^-, H_2A^{-2}, HA^{-3} and A^{-4}. In order to simplify the calculation of stability constants, the 10:1 excess curves were assumed as a first approximation to involve a constant concentration of free metal ion. If then the reasonable assumption is made that Ca(II) and Mg(II) are not effectively bound unless at least two protons are displaced from the ligand, the reactions represented by the excess curves may be considered as three successive overlapping dissociation steps

$$H_3A \rightleftarrows (H_2A + MH_2A) + H^+$$

$$K_1' = \frac{([H_2A] + [MH_2A])[H^+]}{[H_3A]} \qquad (1)$$

$$(H_2A + MH_2A) \rightleftarrows (HA + MHA) + H^+$$

$$K_2' = \frac{([HA] + [MHA])[H^+]}{[H_2A] + [MH_2A]} \qquad (2)$$

$$(HA + MHA) \rightleftarrows (A + MA) + H^+$$

$$K_3' = \frac{([A] + [MA])[H^+]}{[HA] + [MHA]} \qquad (3)$$

where K_n' are related to the metal chelate formation constants and normal acid dissociation constants by the following relationships:

$$K_1' = K_2\,(1 + K_{MH_2A}[M]) \qquad (4)$$

$$K_2' = K_3\left(\frac{1 + [M]K_{MHA}}{1 + [M]K_{MH_2A}}\right) \qquad (5)$$

$$K_3' = K_4\left(\frac{1 + [M]K_{MA}}{1 + [M]K_{MHA}}\right) \qquad (6)$$

where

$$K_{MH_2A} = \frac{[MH_2A]}{[M][H_2A]} \qquad (7)$$

$$K_{MHA} = \frac{[MHA]}{[M][HA]} \qquad (8)$$

$$K_{MA} = \frac{[MA]}{[M][A]} \qquad (9)$$

The three overlapping acid dissociation constants were determined in a manner similar to that described above for the ligand. For example, in the region of the curve between $a = 3$ and $a = 4$, values for K_2' and K_3' can be obtained from the relationship

$$(1/K_2')[H](2T_A - b) - K_3'b/[H] + T_A - b = 0$$

where

$T_A = [H_2A] + [HA] + [A] + [MH_2A] + [MHA] + [MA]$

b = total titratable acid = $(4 - a)T_A - [OH]$

a = moles of base added per mole of ligand or metal present.

This equation with two unknowns was solved graphically from a number of experimental points in order to obtain the best possible values of K_2' and K_3'. A similar procedure was employed for the portion of the titration curve between $a = 1$ and $a = 2$ where $T_A = [H_3A] + [H_2A] + [HA] + [MHA] + [MA]$. Values of K_1' and K_2' were then obtained. After adjustment of K_2' obtained by the two graphical plots, the formation constants were then calculated by equations 7, 8 and 9.

Since successive approximations obtained by this method gave some variation in the values of K_n', a modified Bjerrum method of calculation was attempted, in which the fully dissociated forms ($MA^{-2} + A^{-4}$) were considered to be the central ion, and the hydrogen ion was considered as the ligand. Thus a series of stepwise association constants corresponding to $1/K_3'$, $1/K_2'$ and $1/K_1'$ were obtained. These values were corrected by the convergence formulas of Carlson, *et al.*[6]

It is of interest to note that the stability constants for the formation of compounds corresponding to VIII are smaller than those of the analogous chelates of EDDA, XI. This may be in part a steric effect of the phenyl groups and in part a result of hydrogen bonding between the phenol groups in VII and the basic amino groups, a phenomenon which has no counterpart in the basic form of EDDA. The displacement of the hydrogen bonds in VII by metal chelate formation would be expected to decrease the tendency toward metal chelate formation.

TABLE II

CHELATE STABILITY CONSTANTS AND DISSOCIATION CONSTANTS; EHPG

Metal	log K_{MH_2A}	pK_a	pK_b	EDDA[a]
Cu(II)	>15	4.98	8.04	16.2
Ni(II)	11.40	6.03	7.63	13.5
Zn(II)	9.26	6.64	7.74	11.1
Cd(II)	7.77	7.86	8.70	8.8
	log K_{MH_2A}	log K_{MHA}	log K_{MA}	
Ca(II)	1.7	4.8	7.2	
Mg(II)	2.9	5.2	8.0	
Fe(III)	..	..	>30 (estimated)	

[a] Data obtained from Chaberek and Martell,[5] $\mu = 0.1$ (KCl), 30°.

The Fe(III) titration curve is unique in that four protons are displaced from the ligand in a single step, giving rise to the direct formation of a structure resembling XII at low pH. The pos-

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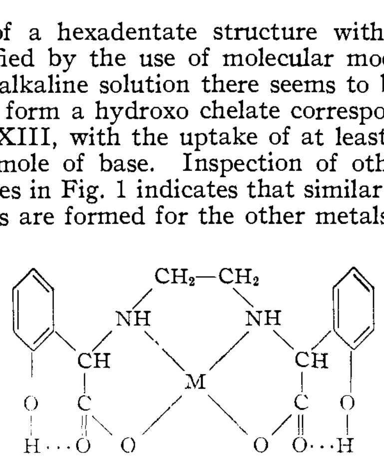
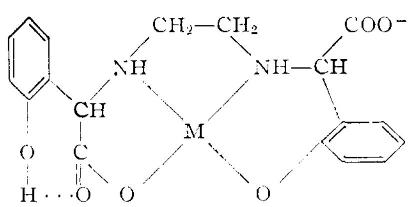
(6) G. A. Carlson, J. P. McReynolds and F. H. Verhoek, THIS JOURNAL, **67**, 1334 (1945).

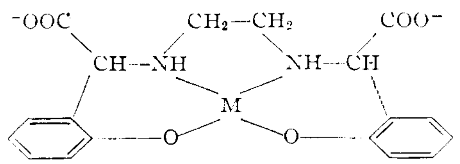
sibility of a hexadentate structure with Fe(III) was verified by the use of molecular models. In strongly alkaline solution there seems to be a tendency to form a hydroxo chelate corresponding to formula XIII, with the uptake of at least one additional mole of base. Inspection of other titration curves in Fig. 1 indicates that similar hydroxo complexes are formed for the other metals investigated.



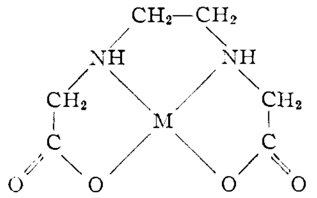
VIII



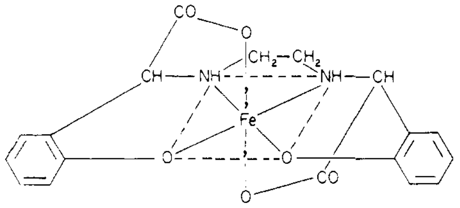
IX



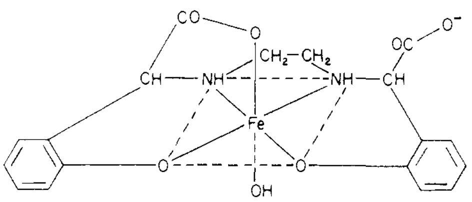
X



XI



XII



XIII

Absorption Spectra.—The ultraviolet spectra of EHPG (I), given in Fig. 2 show bands at 277 and 296 mμ. At low *p*H values, only one band is observed at 277 mμ, which is assigned to the unionized phenolic group. At intermediate *p*H a second band appears at 296 mμ as the result of the formation of the phenolate ion. At high *p*H (≅11) only the 296 mμ band is present indicating complete conversion of the phenolic hydroxyl to the phenolate ion. The longer wave length of the latter is in accord with its greater negative charge, which would be expected to result in a bathochromic shift.

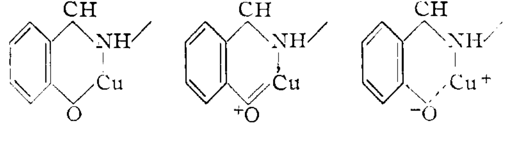
Of the two absorption bands of the Cu(II) chelate of EHPG, indicated in Table III, the position of the band at 375 mμ was found to be unaffected by an increase in *p*H and is assigned to the phenolate resonance, displaced toward the longer wave length region by combination with the Cu(II) ion, a shift which correlates with a degree of resonance interaction with the metal ion. A second band, at 275 mμ at low *p*H, is shifted to somewhat longer wave length with an increase in *p*H. This is apparently the absorption band of the acid form of the phenolic group (found at 277 mμ in the free ligand), which is shifted to longer wave length as the hydrogen ion is displaced by the Cu(II) ion. This shift is not nearly so great as that observed above for the sodium salt in accordance with a high degree of covalent character for the Cu(II)-phenolate bonds. These wave length shifts correlate with the two subsequent displacements of hydrogen ions observed in the Cu(II) titration curve in Fig. 1. Thus it is possible to conclude that the Cu(II) chelate initially formed has the structure indicated by VIII, which then undergoes two rearrangements to give IX and X, each of which involves the displacement of an additional hydrogen ion, as is indicated by the two successive buffer regions of the titration curve.

Table III

Absorption Bands of Cu(II)-EHPG Chelates

*p*H	λ_1, mμ	ϵ_1	λ_2, mμ	ϵ_2
2.97	647	181	..	..
3.97	645	183	..	..
5.05	645	161	..	..
5.98	640	146	..	..
7.18	645	139	375	271
8.00	650	127	375	381
9.05	650	123	377	667
10.02	650	157	375	685
12.00	650	154	374	733

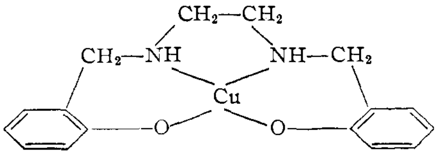
Below *p*H 6 the Cu(II)-EHPG chelate has the typical deep blue color normally associated with Cu(II)-amino acid chelates, characterized by a broad absorption band at about 645 mμ. As the *p*H is increased above 6, a second and much stronger (*i.e.*, K-type) band appears at 375 mμ, the intensity of which increases with increasing *p*H. When one considers the changes indicated by the Cu(II) titration curve in Fig. 1, it seems that this new band must be due to a resonating system involving the metal-phenolate linkages



and its interaction with the benzene ring. The tailing off of this new band in the visible results in increased blue absorption and a shift in color of the complex from blue to green. The longer wave length band of the Cu(II) ion is not greatly shifted by participation of phenolate groups in the binding of the metal.

The ultraviolet absorption spectrum of the Fe(III) chelate, illustrated in Fig. 3, is unique in that the *p*H-dependent phenol band of the ligand is replaced by a single band at 282 mμ (ε 5000) which is independent of *p*H. This strongly suggests that the phenol group is completely dissociated and is involved in binding of the Fe(III) ion over the entire *p*H range. The position of the Fe(III)–phenolate band is intermediate between the phenolic–OH band at 277 mμ and the phenolate band at 296 mμ, in accordance with partial covalent character of the Fe(III)–phenolate linkage, resulting in a lesser negative charge in the resonating phenolate system than would be present in the tetrasodium salt. The lack of a *p*H effect on the ultraviolet and visible absorption bands in the *p*H range 3–11 is an indication of the stability of this chelate compound. Since it is completely associated at *p*H 3, it is apparent that the stability constant cannot be calculated from the potentiometric titration curve. The decrease in extinction at high *p*H is attributed to the formation of a hydroxo complex of the type indicated by XIII.

The titration curve of the dihydrochloride of ethylenediiminodi-*o*-cresol (II) given in Fig. 4 is very similar to that of EHPG. The groups which dissociate first are therefore assumed to be the two basic ammonium groups one of which is more acidic than the other as the result of the interactions of their positive charges. The phenolic groups do not dissociate until a very high *p*H is reached. The 1:1 Cu(II) titration curve indicates a remarkable difference from the behavior of EHPG, in that the reaction takes place in a single step, with the displacement of four hydrogen ions, rather than the stepwise reaction noted above for VIII, IX and X. Thus in the absence of the carboxylate groups the intermediate chelates analogous to VIII and IX are not formed, and XIV is formed directly from the metal ion and the acid form of the ligand, H_4A. This one-step reaction at first seems puzzling since the chelate XIV is formed at a much lower *p*H than is the Cu(II) chelate of EHPG, X, although the latter is without doubt the more stable compound. However, a chelate compound such as VIII, initially formed from EHPG and Cu(II), cannot be formed from ethylenediiminodi-*o*-cresol. Thus the stepwise formation of X is due to the existence of stable intermediate chelates, VIII and IX, and not to any lower stability of the final product.



XIV

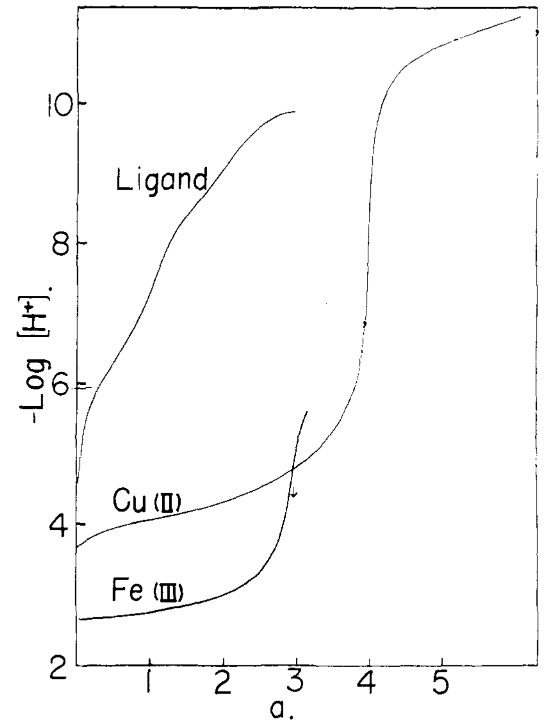


Fig. 4.—Potentiometric titrations of α,α'-ethylenediiminodi-*o*-cresol dihydrochloride in the absence of, and in the presence of, equivalent amounts of Cu(II) and Fe(III) nitrates at 25° and 0.1 μ (KNO_3). Abscissa, *a*, represents moles of base added per mole of ligand.

The precipitation of $Fe(OH)_3$ in the presence of II is interesting as an indication of the importance of the α-carboxylate linkages of EHPG in contributing to the high stability of the iron chelate.

The absorption spectrum of the Cu(II) chelate of II varies with *p*H as might be expected on the basis of the titration data. Two absorption bands, a Cu(II) band at 590 mμ and a Cu(II)–phenolate resonance band at 380 mμ, increase in intensity in the *p*H range 4–6 and remain constant in more alkaline solutions.

The low *p*H portions of the titration curves of IIIa, given in Fig. 5, are characterized by deep purple solutions corresponding to an absorption band at 546 mμ, characteristic of the phenol iron compounds. The intensity of this band increases at first with *p*H but drops off above *p*H 4.0 as the result of the formation of a precipitate of $Fe(OH)_3$. In the titration curve this change is characterized by the formation of a brown solution and by precipitation between *p*H 3.5 and 5.0, with the addition of exactly three moles of base per mole of metal, regardless of the molar ratio of ligand to metal ion. At higher *p*H (above 6.5 to 7) the precipitate redissolves to give a deep red solution similar in appearance to the Fe(III)–EHPG chelate. The family of Fe(III) titration curves in Fig. 5 indicates a high *p*H buffer region which at a ratio of two moles of ligand to one of metal ion results in the uptake of more than four equivalents of base. This effect is also apparent at higher ratios of ligand to metal but is due in part to neutralization of excess ligand. Thus it seems that the Fe(III) chelates of IIIa probably form hydroxo compounds

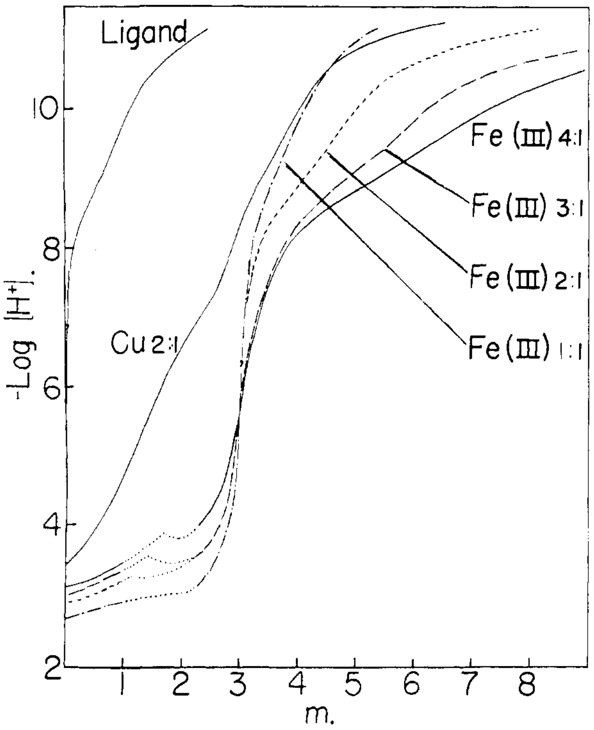


Fig. 5.—Potentiometric titration of *o*-hydroxyphenylglycine at 25° and 0.1 μ (KNO_3) in the absence of metal ions and in the presence of various amounts of Cu(II) and Fe(III) nitrates. Numbers indicate molar ratio of ligand to metal. Abscissa, *m*, represents moles of base added per mole of metal.

analogous to XIII. This effect is seen in the absorption spectra by a decrease in extinction coefficient of the Fe(III) chelate above *p*H 11.

The significant difference in the Fe(III) complexes of I and IIIa brought out by the titration and spectrophotometric data is the much greater stability of the former, in accordance with the fact that the IIIa chelate does not form until a relatively high *p*H is attained.

The absorption spectrum of the copper chelate of IIIa is quite similar to that of the corresponding EHPG chelate. In the ultraviolet region there is an absorption band at 238.5 mμ which increases in intensity with an increase in *p*H. This is apparently due to the copper phenolate linkage which is formed as the *p*H increases. There is also a band at 213 mμ at very low *p*H which disappears at and above the inflection point and which probably is due to the presence of the free phenolic group in acid solution.

In the visible region the similarity between the copper chelates of EHPG and IIIa are quite striking and the effects observed as a result of participation of the phenolic groups in complex formation are the same for both compounds.

Like EHPG, the ultraviolet spectra of α,α'-ethylenediiminodi-*o*-cresol (II) and of 2-(*o*-hydroxyphenyl)-glycine (IIIa) show a band at about 277 mμ (with ϵ of about 2000 per cresol group) which shifts at high *p*H to give a phenolate band at 292–6 mμ with ϵ of about 3000 per cresol group. In all three compounds the spectra indicate that the ionization of the phenol group is not complete until the *p*H is over 12. In the case of 2-(*o*-methoxyphenyl)-glycine (IIIb, not shown), this variation of spectra with *p*H does not occur, and the 273 mμ band remains at the same intensity (ϵ 2000) over the whole *p*H range.

Comparison of the ultraviolet spectra of II and IIIa with the spectra of their iron chelates indicates that no significant changes are introduced by combination with the metal ion. This is roughly in accord with the titration data, which indicate that a stable chelate between the Fe(III) ion and the ligand is not formed except perhaps at rather high *p*H.

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[CONTRIBUTION NO. 587 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE. WORK WAS PERFORMED IN THE AMES LABORATORY OF THE U. S. ATOMIC ENERGY COMMISSION]

The Acid Hydrolysis (Aquation) of the Trichloroammineplatinate(II) Ion

BY THOMAS S. ELLEMAN, JOHN W. REISHUS AND DON S. MARTIN, JR.

RECEIVED AUGUST 22, 1957

The acid hydrolysis of $[Pt(NH_3)Cl_3]^-$ in aqueous solution has been studied by spectrophotometric and potentiometric titration techniques in the temperature range of 0 to 35°. For the first hydrolysis: $[Pt(NH_3)Cl_3]^- + H_2O \underset{k_1}{\overset{k_{-1}}{\leftrightarrows}} [Pt(NH_3)Cl_2(H_2O)] + Cl^-$, k_1 is 3.6×10^{-5} sec.$^{-1}$ and k_{-1} is 2.5×10^{-3} l. moles^{-1} sec.$^{-1}$ at 25°. $\Delta H_1^{\ddagger}$ is 18.9 kcal. and $\Delta H_{-1}^{\ddagger}$ is 16.8 kcal. The existence of a second acid hydrolysis has been demonstrated: $[Pt(NH_3)Cl_2(H_2O)] + H_2O \underset{k_2}{\overset{k_{-2}}{\leftrightarrows}} [Pt(NH_3)Cl(H_2O)_2]^+ + Cl^-$. Approximate values, $K_2 = k_2/k_{-2} = 4 \times 10^{-5}$ mole/l. and $k_{-2} = 0.2$ l. mole^{-1} sec.$^{-1}$ at 24° were indicated.

Introduction

In an earlier publication[1] it was shown that the tetrachloroplatinate(II) ion undergoes a reversible acid hydrolysis reaction in aqueous solution for which rate constants and an equilibriun constant were presented. A similar aquation has been observed for *cis*-$[Pt(NH_3)_2Cl_2]$ and [Pt(en)Cl_2], (en is ethylenediamine) by Banerjea, Basolo and Pear-

[1] L. F. Grantham, T. S. Elleman and D. S. Martin, Jr., THIS JOURNAL, **77**, 2965 (1955).