

compound or some multiple having the same composition.

It is interesting to note that Feldman, *et al.*,^{5a} observed inflections in the *pH* range 5–8 when the ratio of moles of base added to moles of $\text{UO}_2(\text{VI})$ salt was equal to $1\frac{2}{3}$ plus the number of carboxyl groups present in the ligand in the cases of the 1:2 chelates of lactate, citrate, tartrate and malate. There is no evidence at this point, however, indicating that the reactions observed in this paper, and those of Feldman, *et al.*,^{5a} represent the same, or even related, phenomena.

$\text{MoO}_2(\text{VI})$.—In the reaction of a $\text{MoO}_2(\text{VI})$ salt with various ligands such as EDTA, HEDTA, 5-SSA and DNS, the titration data showed very little difference between the metal ion alone and metal solutions containing ligand. In all cases there is no evidence from the potentiometric data

that any reactions other than simple formation of the molybdate ion occurred along with neutralization of free ligand as base was added to the solution. In the case of PDS (Tiron), however, there was a definite *pH* effect indicating the formation of a stable chelate between some electropositive molybdenum species, such as MoO_2^{+2} , with one or more moles of ligand. The inflection corresponding to the formation of the molybdate anion in the case of the other titrations occurred at the same position in the presence of Tiron. Before definite conclusions can be drawn concerning the extent and the nature of the interaction of $\text{MoO}_2(\text{VI})$ with this ligand, it will be necessary to study the interaction by measuring other properties of this system such as ultraviolet absorption spectra.

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[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

Hydrolytic Tendencies of Metal Chelate Compounds. IV. Dimerization of Copper(II) Chelates¹

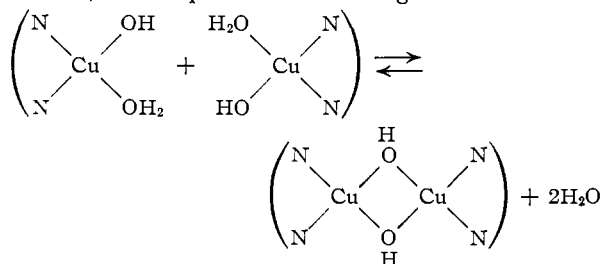
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The interactions of *N*-hydroxyethylethylenediamine (HEN), *N,N'*-dihydroxyethylethylenediamine (2-HEN), 1,3-diaminopropane (DAP), diethylenetriamine (DIEN) and triethylenetetramine (TRIE) with equivalent amounts of $\text{Cu}(\text{II})$ ion were investigated over the entire *pH* range. Chelate formation constants, chelate hydrolysis constants and chelate olation constants are reported for the chelate compounds formed with bidentate ligands, and hydrolysis constants are reported for the 1:1 $\text{Cu}(\text{II})$ chelates of DIEN and TRIEN. Hydrolytic tendencies of the chelates decrease with an increase in the number of donor groups in the ligands, while olation reactions occur with only the diamine chelates to form binuclear compounds.

In a recent publication² in which the hydrolytic tendencies of a large number of copper(II) chelates were compared, it was shown that the degree of formation of soluble hydroxo complexes generally increases with decreasing metal chelate stability, increasing charge of the central metal ion and decreasing number of donor groups associated with the ligand. Thus the $\text{Cu}(\text{II})$ chelate of ethylenediamine readily forms hydroxo complexes, while no measurable hydrolysis can be detected for the analogous chelate of ethylenediaminetetraacetic acid.

Since the formation of a monohydroxo complex may be considered to be the first step in dimer formation, which proceeds according to the reaction



it would seem logical to assume that the same general rules apply also to dimer formation as well.

(1) This paper reports work done under contract with the Chemical Corps, U. S. Army, Washington 25, D. C.

(2) A. E. Martell, S. Chaberek, Jr., R. C. Courtney, H. Hyytiäinen and S. J. Westerback, *THIS JOURNAL*, **79**, 3036 (1957).

In order to provide a comparison between analogous $\text{Cu}(\text{II})$ chelates having different numbers of free aquo positions attached to the metal ion, the interactions of $\text{Cu}(\text{II})$ nitrate with *N*-hydroxyethylethylenediamine (HEN), *N,N'*-dihydroxyethylethylenediamine (2-HEN), 1,3-diaminopropane (DAP), diethylenetriamine (DIEN) and triethylenetetramine (TRIE) were investigated. While DAP may function only as a bidentate chelating agent, the analogous chelates of HEN and 2-HEN could possibly act as tri- or tetradentate donors, provided that the hydroxyethyl groups take part in chelation. DIEN and TRIEN are normally considered to function as tri- and tetradentate ligands, respectively.

Experimental

Reagents.—A solution of J. T. Baker Analyzed Reagent cupric nitrate was standardized both by thiosulfate titration and by the method of Schwarzenbach³ in which standard disodium ethylenediaminetetraacetate was employed as a titrant with murexide as an indicator in ammoniacal solution. Results obtained by the two methods agreed within three parts per thousand. Samples of diethylenetriamine, triethylenetetramine, 1,3-diaminopropane, *N*-hydroxyethylethylenediamine and *N,N'*-dihydroxyethylethylenediamine were purified by fractional distillation and were then isolated as the corresponding hydrochlorides. Standardization of the aqueous solutions of these chelating agents was effected by means of potentiometric titration with standard carbonate-

(3) G. Schwarzenbach, "Die komplexometrische Titration," Ferdinand Enke, Stuttgart, 1955, p. 68.

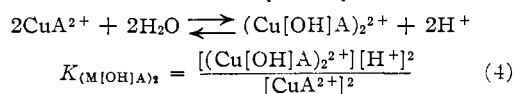
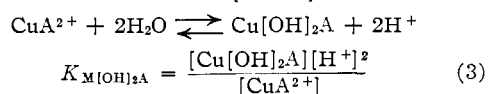
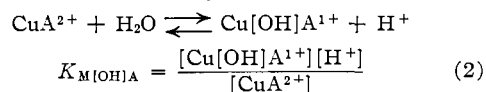
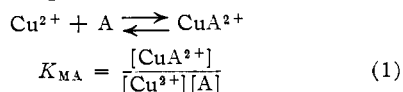
free potassium hydroxide, which was prepared by the method of Schwarzenbach and Biedermann.⁴

Potentiometric Titrations.—The calculation of the distribution of the various chelate forms as a function of pH and total metal ion concentration was carried out on the basis of titration curves obtained by measuring the change in pH of the metal chelate solution as a function of the amount of standard potassium hydroxide added. A Beckman Model G pH meter with extension glass and calomel electrodes was used to record the hydrogen ion concentration. The electrode system was calibrated with acetate buffer making use of data given by Harned and Owen.⁵ It was assumed that the "concentration constant," $[H^+][Ac^-]/[HAc]$, where HAc represents acetic acid, is the same in a 0.1 M potassium nitrate solution as the value given for a potassium chloride solution. Standardization at extremely high and low pH values was carried out using standard potassium hydroxide and hydrochloric acid, respectively. The titrations were carried out in a 200-ml. multi-necked flask designed to accommodate a mercury seal stirrer, gas inlet and outlet tubes, microburet delivery tube and electrodes. The ionic strength was maintained relatively constant by using an electrolyte medium of 0.1 M potassium nitrate and relatively low concentrations of copper chelate.

For each of the five chelate systems investigated, four to five titrations over approximately a tenfold range of concentration were carried out. In order to obtain a carbon dioxide-free system, presaturated nitrogen was bubbled through the solutions during the course of the titrations. All measurements were made at a temperature of $25 \pm 0.1^\circ$. When thermal equilibrium was obtained, increments of standard carbonate-free 0.1 M potassium hydroxide were added, and readings of $-\log[H^+]$ were recorded for each addition until values of 10.5–11.0 were obtained. In all cases, titration data were recorded for solutions containing equimolar concentrations of ligand and cupric ion.

Mathematical Treatment of Data

Solution Equilibria.—In most of the copper(II) chelate systems studied which contain equimolar concentrations of ligand and metal ions, four species have been shown to exist: a normal diaquo chelate, CuA^{2+} ; a monohydroxo compound⁶ $Cu[OH]A-(H_2O)^{1+}$; a dihydroxo species, $Cu[OH]_2A$; and a dimer, $(Cu[OH]A)_2^{2+}$. The solution equilibria may be defined by the equations



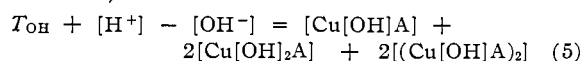
The amount and distribution of the various chelate species present under varying conditions of pH and total concentration may be calculated from the above equilibria and from the relationship between the total copper(II) content, the value of $-\log[H^+]$ and the amount of hydroxide added.

(4) G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 331 (1948).

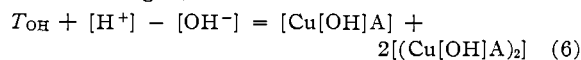
(5) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950.

(6) Brackets around OH within the formula of a coordination compound indicate a hydroxyl ion bound directly to the metal, whereas a set of brackets enclosing the entire formula indicates molar concentration.

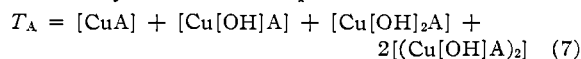
If T_{OH} represents the hydroxide added to a solution of the diaquo chelate, $[CuA]$, during the titration, then



In equation 5, charges of ions have been eliminated for achieving clarity. Since the concentration of the dihydroxo chelate is small in the region preceding the crossover point (intersection of curves in Fig. 1)



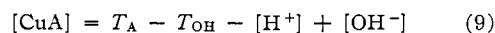
The total concentration of chelate species, T_A , is defined by the relationship



Therefore in the region preceding the crossover



and



Combination of equations 2, 4 and 6 gives the expression

$$\frac{T_{OH} + [H^+] - [OH^-]}{[CuA]/[H^+]} = \frac{K_{M(OH)A} + 2K_{(M(OH)A)_2} \frac{[CuA]}{[H^+]}}{[H^+]} \quad (10)$$

Thus if a dimer is formed, a straight line is obtained when $(T_{OH} + [H^+] - [OH^-])[H^+]/[CuA]$ is plotted against $[CuA]/[H^+]$, the slope of which is equal to $2K_{(M(OH)A)_2}$ and the intercept at $[CuA]/[H^+] = 0$ is equal to $K_{M(OH)A}$. It is of course possible that higher polymers of the form $(Cu[OH]A)_n^{n+}$ may be formed. For instance, if a trimer were formed, a straight line would be obtained when $(T_{OH} + [H^+] - [OH^-])[H^+]/[CuA]$ is plotted against $[CuA]^2/(H^+)^2$, the slope of which would be equal to $3K_{(M(OH)A)_3}$. In all cases studied in this investigation, the presence of a dimer was indicated.

$K_{M(OH)_2A}$ may be calculated from the value of $-\log(H^+)$ where the curves in Fig. 1 cross in accordance with the relationship

$$pK_{M(OH)_2A} = 2(-\log[H^+]) \quad (11)$$

since at this point it may be assumed that the concentrations of $Cu[OH]_2A$ and of CuA are equal. However, since it is difficult to locate with certainty the crossover point from titration curves having steep inflections, it was considered more desirable to calculate $K_{M(OH)_2A}$ algebraically using the values of $K_{M(OH)A}$ and $K_{(M(OH)A)_2}$, already determined. Combination of equations 2, 3, 4, 5 and 7 yields

$$K_{M(OH)_2A} = \frac{[H^+]^2(T_{OH} + [H^+] - [OH^-] - [Cu[OH]A] - 2[(Cu[OH]A)_2])}{2[CuA]} \quad (12)$$

The quantity $[CuA]$ may be determined by solving the quadratic equation

$$[CuA] = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (13)$$

where

$$a = 2K_{(M(OH)A)_2}/[H^+]^2$$

$$b = 2 + K_{M(OH)A}/[H^+]$$

$$c = T_{OH} + [H^+] - [OH^-] - 2T_A$$

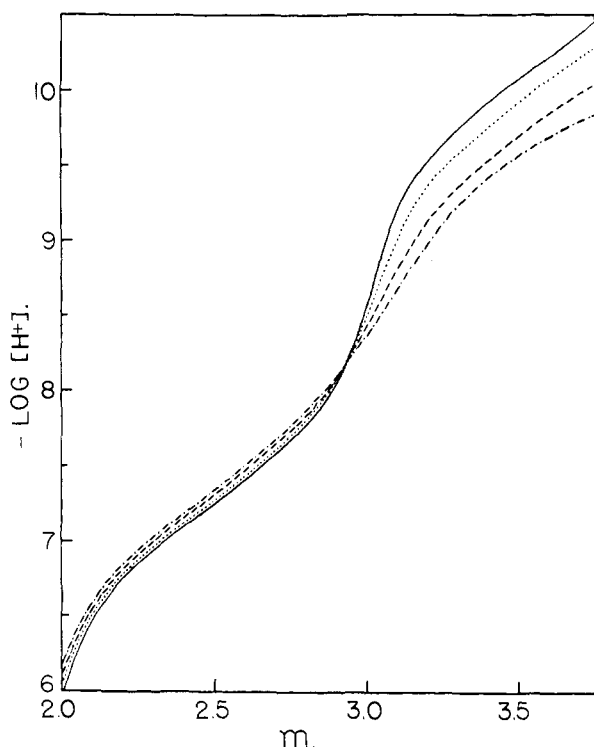


Fig. 1.—Potentiometric titration of 1:1 copper(II)-N-hydroxyethylethylenediamine chelates. Concentrations: —, $5.21 \times 10^{-3} M$; . . . , $2.61 \times 10^{-3} M$; ---, $1.04 \times 10^{-3} M$; - · - · -, $5.21 \times 10^{-4} M$; $t = 25.0^\circ$; $\mu = 0.10$ (KNO_3); m = moles of base added per mole of 1:1 chelate compound present.

Having determined the equilibrium constants associated with equations 2-4, the concentrations of the various metal chelate species present at a particular value of total concentration and pH may be calculated from the equation

$$\frac{2K_{M(OH)A_2}}{[H^+]} [CuA]^2 + \left[\frac{K_{M(OH)A}}{[H^+]} + \frac{K_{M(OH)A}}{[H^+]^2} + 1 \right] [CuA] - T_A = 0 \quad (14)$$

and equations 2, 3 and 4.

Results and Discussion

HEN, 2-HEN and DAP Chelates.—The titration curves illustrated in Fig. 1 for Cu(II)-HEN show that an increase in metal ion concentration results in a shift of the buffer regions to lower pH in the range of neutralization values from 2-3. The portion of the curves corresponding to " m " values from 0 to 2 (not shown in figure) indicates neutralization of the two moles of HCl present per mole of ligand. Beyond the crossover at $m = 3$, the second buffer region is displaced to higher pH values with a corresponding increase in the concentration of the metal chelate. Similar sets of titration curves were obtained for the copper(II) chelates of 2-HEN and DAP. The increased requirement of base at a particular pH with an increase in the concentration of metal chelate is an indication of the formation of a polymer of the type $(Cu[OH]A)_n^{n+}$.

As is shown graphically in Fig. 2, a plot of $(T_{OH} + [H^+] - [OH^-])[H^+]/[CuA]$ vs. $[CuA]/[H^+]$

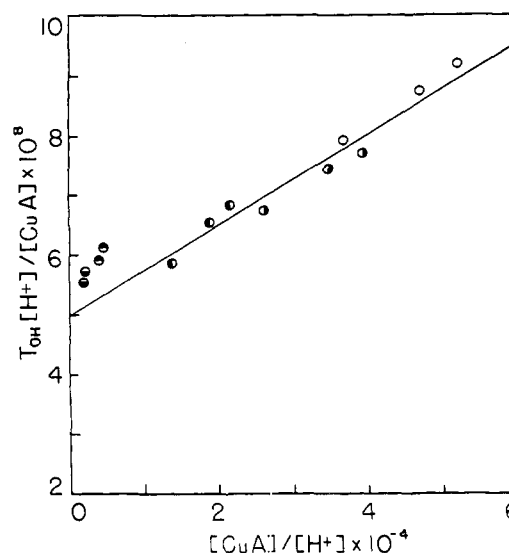


Fig. 2.—Graphical demonstration of dimer of mono-hydroxocopper(II)-N-hydroxyethylethylenediamine chelate. Concentrations: \circ , $7.82 \times 10^{-3} M$; \bullet , $5.21 \times 10^{-3} M$; \ominus , $2.61 \times 10^{-3} M$; $\omin�$, $5.21 \times 10^{-4} M$; $\omin�$, $2.61 \times 10^{-4} M$.

gives a straight line, which verifies the formation of the binuclear diolate chelate compound. Similar plots were obtained for the Cu(II)-2-HEN and Cu(II)-DAP chelates. Some scattering of the experimental points in Fig. 2 is apparent, especially for those calculated from data at the lower concentration levels. However, both the slope and intercept of the straight line may be determined with reasonable accuracy. On the basis of plots similar to that illustrated in Fig. 2, equilibrium constants involving the formation of mono-hydroxo and dimeric chelate species were determined for the interaction of Cu(II) with all three ligands. A summary of the equilibrium constants obtained is given in Table I. By use of these equilibrium constants in conjunction with equations 2, 3, 4 and 14 it was possible to determine the distribution of the various chelate species as a function of $-\log[H^+]$ and total metal chelate concentration. The sample distribution plot shown in Fig. 3 for a 7.82 millimolar solution of Cu(II)-HEN, indicates the successive replacement of CuA^{2+} by $Cu[OH]A^{1+}$, $(Cu[OH]A)_2^{2+}$ and $Cu[OH]_2A$ as the principal forms of the metal chelate compounds in solution.

Although the chelate stabilities of the Cu(II) chelates of HEN, 2-HEN and DAP are approximately equivalent, the tendency toward hydroxo chelate formation is somewhat greater for the hydroxyethyl substituted compounds. This may be an indication of the formation of chelates of types I and II of HEN and 2-HEN, respectively. For Cu(II)-HEN, the inflection at $m = 3$ may correspond to the complete conversion of the normal chelate I to a hydroxo complex III or to a compound such as IV in which a proton has been dissociated from the coordinated ethanolic group. Actually structures III and IV are tautomeric and no doubt are in rapid equilibrium in aqueous solution.

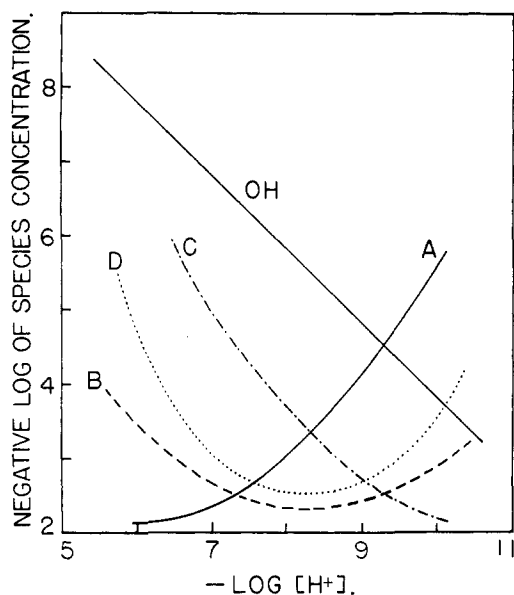
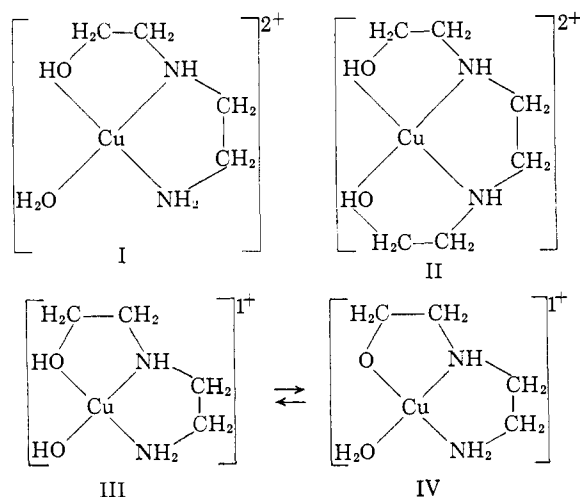


Fig. 3.—Distribution of copper(II)-N-hydroxyethylethylenediamine chelate species as a function of the hydrogen ion concentration: A, diaquo chelate, $[\text{CuA}^{2+}]$; B, monohydroxo chelate, $[\text{Cu}[\text{OH}]\text{A}^{+}]$; C, dihydroxo chelate, $[\text{Cu}[\text{OH}]_2\text{A}^0]$; D, dimer $[(\text{Cu}[\text{OH}]\text{A})_2^{2+}]$; OH, hydroxyl ion: $T_A = 7.82 \times 10^{-3} M$; $t = 25.0$; $\mu = 0.10$ (KNO_3).

The formation of compounds represented by structures I and II is supported by additional evidence. Although Basolo and Murmann⁷ have shown that the introduction of alkyl groups into the ethylenediamine molecule substantially lowers the stability of the resulting Cu(II) complex, only a slight difference between the corresponding chelates of HEN, 2-HEN and ethylenediamine is



observed. Also while the introduction of a second hydroxyethyl group into the HEN molecule results in a drop in basicity of the ligand of 0.6 pK unit, the resultant drop in chelate stability is only 0.2 $\log K$ unit. Metal chelate formation with these ligands therefore involves two opposing tendencies; decreased ligand basicity which tends to decrease the metal ion affinity and additional

(7) F. Basolo and F. Murmann, *THIS JOURNAL*, **74**, 5243 (1952).

TABLE I
EQUILIBRIUM CONSTANTS FOR COPPER(II) CHELATES
 $t = 25.0^\circ$; $\mu = 0.10$ (KNO_3)

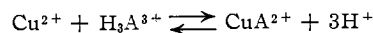
Ligand	$\log K_{MA}$	$pK_{M[\text{OH}]A}$	$pK_{M[\text{OH}]_2A}$	$pK_{(M[\text{OH}]A)_2}$	$\log \frac{K_D}{K_D}$
HEN	9.90	7.30	17.24	12.42	2.18
2-HEN	9.68	7.15	16.52	12.92	1.38
DAP ^a	9.81	7.70	19.05	12.84	2.56
DIEN	15.9 ^{b,c}	9.03
TRIEEN	20.5 ^d	10.8

^a No supporting electrolyte employed; k_w assumed to be 1.3×10^{-14} . ^b Det. at 20° , $\mu = 0.1 M$ (KCl). ^c J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 985 (1950). ^d G. Schwarzenbach, *ibid.*, **33**, 974 (1950).

weak coordination through the ethanolic groups which tend to increase the affinity.

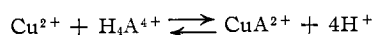
For a given metal ion and similar donor atoms in the chelate rings, it would seem logical to assume that an increase in the polar character of the A_xM-OH linkage would increase the tendency for olate bridging. The geometric arrangement of the chelate rings as well as steric repulsions between the groups attached to the nitrogen atoms of the ligands differ so greatly that valid comparisons cannot be made readily on the basis of variations of any one structural or constitutional feature. However, it may be noted that the dimerization tendencies of the monohydroxo species of the various chelates increase in the order 2-HEN < HEN < DAP. The decreased tendency toward diolate bridging in the former cases may again be partially explained by the presence of the hydroxyethyl groups which may occupy coordination sites on the central metal ion and/or prevent polymerization by means of steric repulsions.

DIEN and TRIEN Chelates.—The titration curves obtained for the cupric diethylenetriamine system are shown in Fig. 4. When the trihydrochloride of diethylenetriamine interacts with the Cu(II) ion, three moles of acid per mole of chelate may be titrated readily at low pH . This corresponds to the reaction



Between pH 8 and 10 there is a second buffer region which requires one mole of base per mole of metal chelate. The formation of a monohydroxo chelate seems to be the only possible conclusion that may be drawn from the potentiometric data, since no precipitation of metal hydroxide takes place and no excess of ligand is present.

The results of potentiometric studies of the 1:1 Cu(II) chelates of triethylenetetramine are given in Fig. 5. The titration curves of this compound are seen to be quite different from those of diethylenetriamine in that four moles of base are required per mole of metal chelate formed, and all the titration curves are characterized by a single step pH rise at $m = 4$. The formation of the metal chelate thus may be represented by the neutralization reaction



The high stability of the Cu(II) chelate of triethylenetetramine is apparent from the low pH at which the above reaction takes place. The shape of the high pH buffer region does not make it possible to

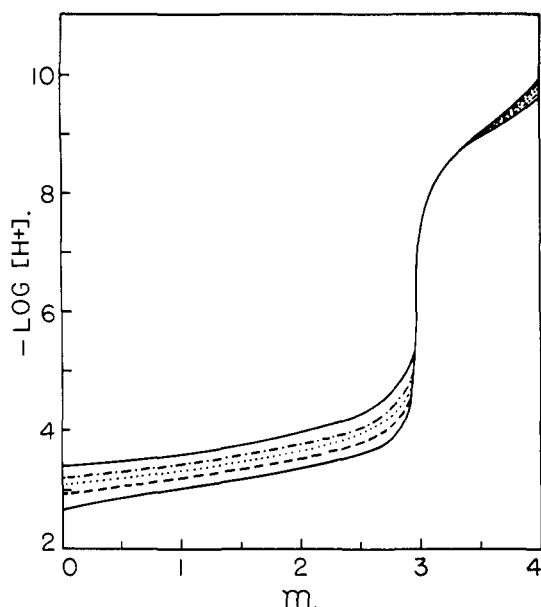
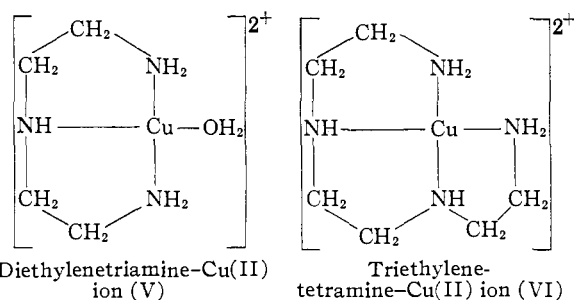


Fig. 4.—Potentiometric titrations of 1:1 copper(II)-diethylenetriamine chelates. Concentrations: — (lower left, upper right), $9.83 \times 10^{-3} M$; ----, $4.92 \times 10^{-3} M$;, $1.97 \times 10^{-3} M$; - - - -, $9.83 \times 10^{-4} M$; — (upper left, lower right), $4.92 \times 10^{-4} M$; $t = 25.0^\circ$; $\mu = 0.10$ (KNO_3).

draw conclusions concerning the possible formation of a hydroxo metal chelate, although it is apparent that no interaction of the normal chelate with base can take place below pH 9.

The difference in behavior between the Cu(II) chelates of diethylenetriamine and triethylenetetramine toward excess base is interesting in relation to the structures of these two chelate compounds, indicated in formulas V and VI.



It is apparent that the fourth position in V, which is occupied by the relatively weak ligand, H_2O , is more reactive toward hydroxyl ion than are any of the coordinated positions in VI. The formation of the monohydroxo derivative of V probably takes place, therefore, through the neutralization and removal of a hydrogen ion from the coordinated water molecule. Such a reaction is less likely in the case of VI since it would require the displacement of a strongly-bound amino group by a weaker coordinating group, H_2O .

The effect of concentration on the potentiometric titration data illustrated in Figs. 4 and 5 for Cu(II)-DIEN and Cu(II)-TRIEN, respectively, is so slight that no condensation of metal chelates to form higher molecular weight substances

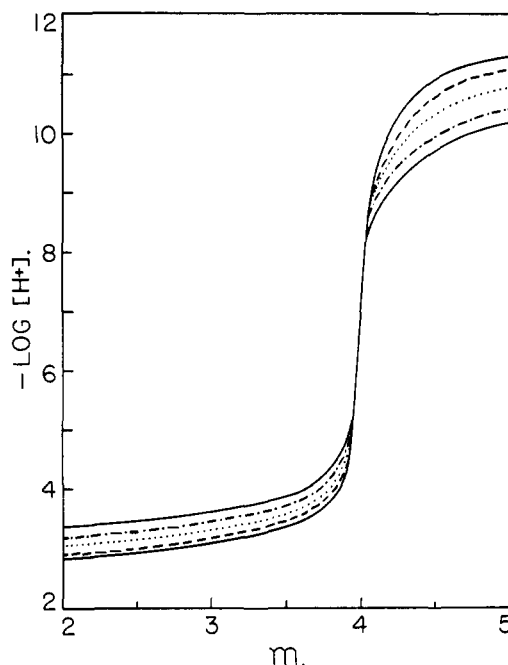
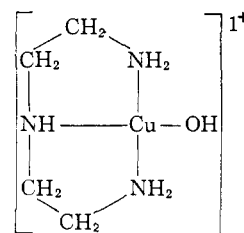


Fig. 5.—Potentiometric titration of (1:1) copper(II)-triethylenetetramine chelates. Concentrations: — (lower left, upper right), $6.08 \times 10^{-3} M$; ----, $3.04 \times 10^{-3} M$;, $1.52 \times 10^{-3} M$; - - - -, $7.59 \times 10^{-4} M$; — (upper left, lower right), $3.80 \times 10^{-4} M$; $t = 25.0^\circ$, $\mu = 0.10$ (KNO_3).

seems to occur. The spread of the low pH buffer regions seen in both figures can be accounted for entirely on the basis of variation of the degree of dissociation of acid forms as a function of concentration. The spread in the high pH buffer region of Cu(II)-DIEN is not significant until the pH approaches 10, and the shift that does occur in this region is accounted for on the basis of the free hydroxide ion present (*i.e.*, the spread is due primarily to the fact that different quantities of standard base were required to produce the same m value since the total concentrations of chelate differed considerably). Thus the principal species present above the high pH buffer region is monohydroxo chelate VII and no significant amount of polymerization is assumed to occur.



In the case of Cu(II)-TRIEN, formation of a monohydroxo chelate VI was indicated. Such an assumption would mean the opening of a portion of the chelate structure to allow coordination with the Cu(II) ion, since the number of strong coordination positions of copper(II) is four (VI, VII). This reaction is not without precedent, however, and is rendered more likely by the fact that tri-

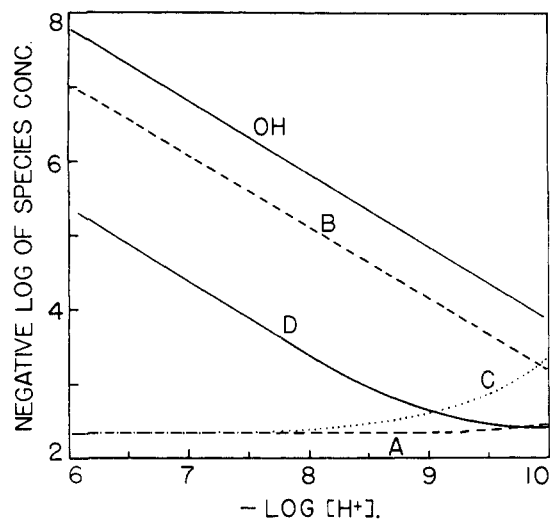
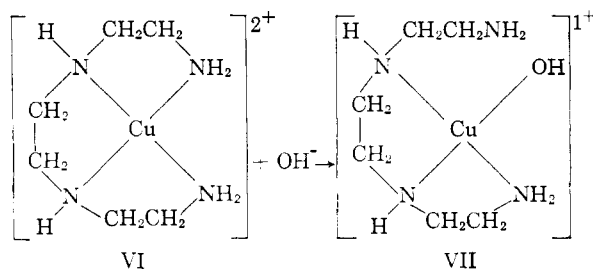


Fig. 6.—Distribution of copper(II)-diethylenetriamine and -triethylenetetramine chelate species as a function of the hydrogen ion concentration. A and B, normal and monohydroxy chelates, respectively, of triethylenetetramine; C and D, aquo and monohydroxo chelates, respectively, of diethylenetriamine; OH, hydroxyl ion. $T_A = 4.47 \times 10^{-3} M$; $t = 25.0^\circ$, $\mu = 0.10$ (KNO_3).

ethylenetetramine cannot quite conform to the square-planar structure indicated in formula VI with the result that some strain is introduced into the metal-ligand bonds.



For both chelate systems, therefore, the only species assumed to be present for calculation purposes are the normal chelate, CuA , and the monohydroxo chelate, $Cu[OH]A$. For reasons given above, the dimer and the dihydroxo chelate were

assumed to be absent. The values of $K_{M[OH]A}$ obtained for $Cu(II)$ -DIEN and $Cu(II)$ TRIEN over a range of total concentration are shown in Table II. These values remained essentially constant for the $Cu(II)$ DIEN system although a larger spread was observed for the latter system. In view of the difficulties usually encountered in the high hydroxide concentration range at which these constants were determined, the values listed may be considered to be essentially constant.

TABLE II
VARIATION OF $K_{M[OH]A}$ WITH TOTAL METAL CHELATE CONCENTRATION

T_A	$-\log[H^+]$	$K_{M[OH]A}$	$pK_{M[OH]A}$
Cu(II)-DIEN			
1.84×10^{-3}	9.04	9.6×10^{-10}	9.02
2.68×10^{-3}	9.07	9.5×10^{-10}	9.02
4.22×10^{-3}	9.09	9.2×10^{-10}	9.04
7.37×10^{-3}	9.05	9.4×10^{-10}	9.03
	Av.	9.4×10^{-10}	9.03
Cu(II)-TRIEN			
1.42×10^{-3}	10.32	1.9×10^{-11}	10.7
2.68×10^{-3}	10.59	1.0×10^{-11}	11.0
7.35×10^{-3}	10.16	2.2×10^{-11}	10.7
	Av.	1.7×10^{-11}	10.8

The success thus obtained in calculating the equilibrium constants $K_{M[OH]A}$ seems to strengthen somewhat the validity of the original assumptions involved. On the basis of these assumptions, therefore, the concentrations of various species present as a function of $-\log[H^+]$ and total concentration, T_A , were calculated. These concentrations are plotted as a function of $-\log[H^+]$ for both ligands in Fig. 6 for a single total concentration of metal chelate species. It is interesting to note that the concentrations of both normal metal chelates remain relatively constant through most of the range, but drop off somewhat at higher pH as the monohydroxo forms VII and VIII become more important. The latter effect occurs to a greater extent with the diethylenetriamine chelate since in this case the hydroxo chelate is formed at lower pH .

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