Equilibrium Studies of Polynucleating Ligands. I. The Interaction of Tetrakis(aminomethyl)methane with Copper(II) and Hydrogen Ions[1]
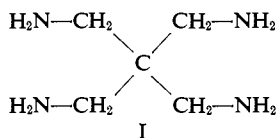
L. J. Zompa and R. F. Bogucki[2]

Contribution from the Department of Chemistry, Boston College, Chestnut Hill, Massachusetts. Received May 27, 1966

Abstract. The interactions of the polynucleating ligand tetrakis(aminomethyl)methane (tam) with Cu^{2+} and H^+ ions in aqueous solution have been investigated by potentiometric, spectrophotometric, and polarographic techniques. The four consecutive acid dissociation constants for the tetraprotonated ligand at 25° in 0.1 M KNO_3 are (as pK_a values) 3.03, 5.67, 8.17, and 9.89. The unique configuration of the ligand requires a bidentate behavior with the square-planar Cu(II) ion. In Cu:tam ratios of 1:2 and 2:1 the stable, soluble chelates $Cu(tam)_2{}^{2+}$ and $Cu_2(tam)^{4+}$ are formed at low pH values with formation constants of $10^{19.43}$ and $10^{17.59}$, respectively. The latter, binuclear chelate hydrolyzes to produce an insoluble coordination polymer $(OH)_2[Cu(tam)Cu(OH)_2]_x$, which contains both ligand bridging and μ-diol bridging, and in which x appears to have values in the range 10–20. In 1:1 ratio, an insoluble, violet solid separates which apparently has a one-dimensional, coordination polymeric structure of considerable length with the formula $[Cu(tam)(NO_3)_2]_n$. In chloride medium, the polymer is more soluble presumably because of shortened chains with chloro end groups. Many measured and derived association constants are reported which demonstrate the influence of electrostatic effects on association reactions in aqueous solution.

Recent studies[3,4] have demonstrated the ability of organic polyamines to act as polynucleating ligands through the process of coordination polymerization in which two or more separate metal ions are linked by coordination to separate donor atoms on the same ligand molecule. This type of polynucleation is distinct from μ bridging in which a single ligand atom serves as a donor to two or more separate metal ions.

For the present equilibrium study tetrakis(aminomethyl)methane (hereafter tam, structure I) was chosen as the polynucleating ligand. An inspection of a molecular model of this compound discloses that three

$$
\begin{array}{ccc}
H_2N-CH_2 & & CH_2-NH_2 \\
& \diagdown \;\; \diagup & \\
& C & \\
& \diagup \;\; \diagdown & \\
H_2N-CH_2 & & CH_2-NH_2 \\
& \text{I} &
\end{array}
$$

of the four amine groups are sterically able to occupy the three vertices of a triangular face of a single metal ion which has a tetrahedral or an octahedral coordination requirement, whereas only two of the four amine groups can be simultaneously bound to a metal ion which requires a square-planar arrangement of donors. In no case can all four amine groups be bound to a single metal ion. The structure of tam clearly suggests the possibility of forming extensively polynucleated metal chelates. In a recent paper, Oehmke and Bailar[4] reported the preparations and properties of solid compounds of tam with Co(III), Cu(II), Ni(II), and Pt(II) and concluded that most of the solids had a polymeric structure. The present study reports the measurement of equilibrium con-

stants of the detailed stepwise reactions which precede the formation of Cu(II)–tam polymers in aqueous solution, and an attempt to produce controlled-length polymers by introducing a bidentate ligand to act as a chain stopper.

Experimental Section

Procedures. The potentiometric measurements were made with a Radiometer PHM4 pH meter by a procedure which has been described previously.[5]

The polarograms were produced at $25 \pm 0.05°$ on a Leeds and Northrup Electrochemograph with an H-type cell. The values for the half-wave potentials (reproducible to ± 2 mv) and the reversibility of the electrode reactions were determined from plots of $(i_d - i)/i$ *vs.* E according to standard methods.[6]

Absorption spectra were recorded on a Perkin-Elmer Model 202 ultraviolet–visible spectrophotometer.

Materials. The tetraammonium sulfate salt of tam was prepared according to the method of Litherland and Mann.[7] The tetraammonium chloride salt, $C(CH_2NH_3)_4Cl_4$, was prepared by dissolving the sulfate salt in hot water and adding 12 M HCl. White crystals of the chloride salt separated upon cooling. The nitrate salt, $C(CH_2NH_3)_4(NO_3)_4$, was prepared in a similar manner by addition of 15 M HNO_3. Subsequent recrystallizations of the chloride salt from 6 M HCl, and the nitrate salt from 8 M HNO_3, produced pure products.

Anal. Calcd for $C(CH_2NH_3)_4Cl_4$: C, 21.6; H, 7.2; N, 20.2; Cl, 51.0. Found: C, 21.8; H, 7.2; N, 20.0; Cl, 50.9.

The molecular weight of the nitrate salt, which decomposes explosively upon ignition, was determined by potentiometric titration with standardized sodium hydroxide. The number of moles of base required between the first and second inflections was assumed to be equivalent to the number of moles of tam present. Agreement with the theoretical molecular weight was within 2 parts per thousand.

Stock solutions of copper(II) nitrate, chloride, and perchlorate were prepared from reagent grade salts, and the copper concentrations were determined both by electrodeposition and by iodometric titration. The concentration of free acid (added in some cases to inhibit hydrolysis) was determined by difference. Stoichiometric amounts of ethylenediaminetetraacetic acid or ethylenediamine dihydrochloride were added in precise ratios to complex all of the

(1) Abstracted from the doctoral dissertation of L. J. Zompa, Boston College, 1964; presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

(2) Correspondence should be directed to R. F. Bogucki, Chemistry Department, Purdue University, Lafayette, Ind., until June 1967.

(3) F. Louis, R. Green, K. Catchpole, and A. Phillip, *Inorg. Chem.*, 2, 597 (1963).

(4) R. W. Oehmke and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, 27, 2199 (1965).

(5) R. F. Bogucki and A. E. Martell, *J. Am. Chem. Soc.*, 80, 4170 (1958).

(6) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1952, pp 189–194.

(7) A. Litherland and F. Mann, *J. Chem. Soc.*, 1588 (1938).

metal ion present according to a known reaction. The excess acid in solution was then determined by subtracting the calculated number of moles of base required to reach the end point attributable to complex formation from the moles of base necessary to reach the experimental end point.

The titrant solutions of sodium hydroxide were prepared by diluting aliquots of saturated, carbonate-free NaOH solutions with boiled, distilled water and were standardized against potassium hydrogen phthalate.

Calculations. Equilibrium constants were calculated from the experimental data according to a general method described by Schwarzenbach and Heller,[8] in which chemical reactions deduced from the stoichiometries and the inflections in the titration curves are tested for consistency with the equilibrium quotients and with charge and mass-balance equations. Some of the calculations were programmed and performed on an IBM 1620 computer. The equilibrium constants are calculated for concentrations in moles/liter and refer to 25.0° and an ionic strength of 0.1 M, adjusted with potassium nitrate unless another supporting electrolyte is specified. Uncertainties in mathematical values are listed as standard deviations. Each subscripted equilibrium constant is defined as to its specific meaning in this paper when it first appears.

Results and Interpretation

Acid Dissociation Constants of H_4(tam)$(NO_3)_4$. A potentiometric titration of the tetraprotonated nitrate salt of tam with standard base yielded the experimental data shown as the smooth curve A in Figure 1. Well-defined inflections at $a = 1$ and $a = 2$ (a represents the number of moles of hydroxide ion added per mole of tam present in the solution) indicate that the first two protons are released in separate stepwise dissociations. The first two acid dissociation constants were readily evaluated from the titration data with the usual mass-balance and charge-balance relationships. The more poorly defined inflections at $a = 3$ and $a = 4$ suggest that the third and fourth protons are released in overlapping steps. This was confirmed by a small drift in the K_{a3} and K_{a4} values calculated with the simple one-step equations used for K_{a1} and K_{a2}. The method outlined by Martell and Calvin[9] for the determination of overlapping acid dissociation constants was therefore used to calculate K_{a3} and K_{a4}. The four consecutive acid dissociation constants are listed in Table II.

Cu(II)–tam (2:1). When standard solutions of Cu$(NO_3)_2$ and H_4(tam)$(NO_3)_4$ were mixed in ratio of 2 moles of metal per mole of ligand and titrated with standard NaOH, curve B in Figure 1 was obtained. The following, detailed analysis of titration curve B will exemplify the method used throughout the paper for all of the other reactions, for which, however, only the final results are given.

The significant lowering of the pH below that of the acid alone at corresponding a values indicates a strong interaction between the protonated ligand and Cu^{2+}, while the presence of a weak but readily discernible inflection at $a = 2$ reveals that the first step in this interaction involves the release of two protons. On the assumption that a stable amine complex of Cu^{2+} would occur at these low pH values only if a chelate is formed (i.e., only if two amine groups from the same molecule became bound to a single Cu^{2+} ion), a reasonable reaction for the region $a = 0$ to $a = 2$ is

$$Cu^{2+} + H_4L^{4+} \xrightarrow{\text{excess } Cu^{2+}} CuH_2L^{4+} + 2H^+$$
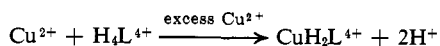
(8) G. Schwarzenbach and J. Heller, *Helv. Chim. Acta*, **34**, 119 (1951).
(9) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, pp 90–92.
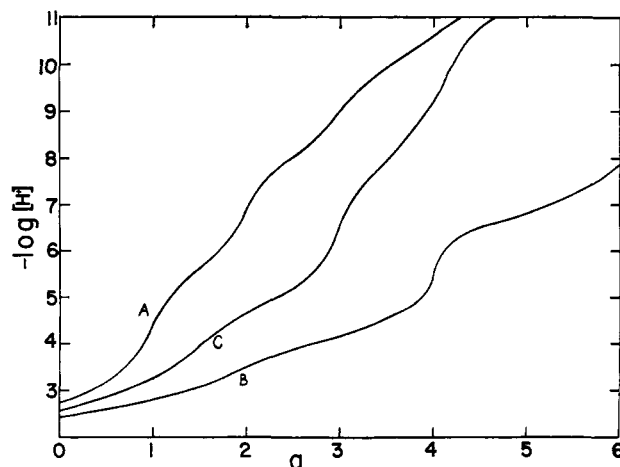
Figure 1. Titration curves for 6 × 10⁻³ M H_4(tam)$(NO_3)_4$ in the presence and absence of Cu^{2+} at 25° and in 0.1 M KNO$_3$. a represents the number of moles of NaOH added per mole of tam present in the solution: curve A, H_4(tam)$(NO_3)_4$ alone; curve B, Cu:tam ratio = 2:1; curve C, Cu:tam ratio = 1:2.

in which L represents tam, and for which the equilibrium quotient is

$$K_1 = \frac{[CuH_2L^{4+}][H^+]^2}{[Cu^{2+}][H_4L^{4+}]} \tag{1}$$

The mass-balance and charge-balance equations for this region are

$$T_L = [H_4L^{4+}]\alpha + [CuH_2L^{4+}]$$

$$T_M = 2T_L = [Cu^{2+}] + [CuH_2L^{4+}]$$

and

$$aT_L + [H^+] = [H_4L^{4+}]\beta + 2[CuH_2L^{2+}]$$

in which T_M and T_L represent the analytical (total) concentrations of metal ion and ligand, respectively, $\alpha = K_{a1}/[H^+] + 1$ and $\beta = \alpha - 1$. The terms α and β account for the amount of H_3L^{3+} which is present because of dissociation of the unbound H_4L^{4+}.

The material-balance equations may be solved simultaneously to yield the expressions

$$[H_4L^{4+}] = \frac{T_L((a/2) - 1) + [H^+]/2}{(\beta/2) - \alpha}$$

$$[CuH_2L^{4+}] = \frac{T_L(\alpha a - \beta) + \alpha[H^+]}{\alpha + 1}$$

and

$$[Cu^{2+}] = 2T_L - [CuH_2L^{4+}]$$

When these expressions for species concentrations are substituted into eq 1 along with the known values of T_L, a, and [H$^+$] taken from 16 experimental points at various a values and two different concentrations, a consistent value of $K_1 = 10^{-3.32 \pm 0.03}$ is obtained. This intermediate constant can be combined with the values for K_{a1} and K_{a2} to derive the formation constant for CuH$_2$L^{4+}

$$K_{CuH_2L} = \frac{[CuH_2L^{4+}]}{[Cu^{2+}][H_2L^{2+}]} = \frac{K_1}{K_{a1}K_{a2}} = 10^{5.38 \pm 0.04} \tag{2}$$

The second inflection at $a = 4$ indicates that a second step occurs which releases two additional protons.
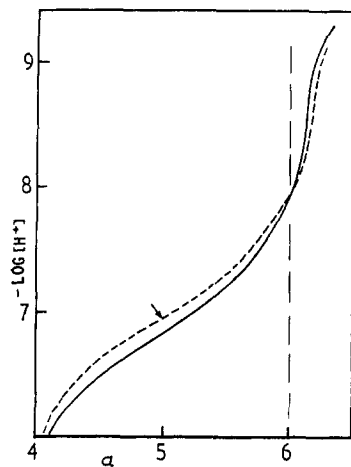
Figure 2. Expanded region of curve B in Figure 1 in the region $a = 4$ to $a = 6$, showing details of the concentration dependence of the buffer and inflection regions: dashed line, [tam] $= 3.08 \times 10^{-3}$ M; solid line [tam] $= 6.93 \times 10^{-3} M$.

The reaction for the region between $a = 2$ and $a = 4$ involves the coordination of the remaining two amine groups to the second Cu^{2+} ion

$$Cu^{2+} + CuH_2L^{4+} \longrightarrow Cu_2L^{4+} + 2H^+$$

The equilibrium constant for this reaction is designated K_2. The material-balance equations for this region are

$$T_L = [CuH_2L^{4+}] + [CuHL^{3+}) + [Cu_2L^{4+}]$$

$$T_M = 2T_L =$$
$$[CuH_2L^{4+}] + [CuHL^{3+}] + 2[Cu_2L^{4+}] + [Cu^{2+}]$$

and

$$a'T_L + [H^+] = [CuHL^{3+}] + 2[Cu_2L^{4+}]$$

where $a' = (a - 2)$. The species $CuHL^{3+}$ was included tentatively since the species CuH_2L^{4+} might be expected to undergo some degree of acidic dissociation in this pH range before all of it had reacted with the second Cu^{2+} ion. The value for $[CuHL^{3+}]$ can be introduced into the equations through the relationship

$$K_a(CuH_2L) = \frac{[CuHL^{3+}][H^+]}{[CuH_2L^{4+}]} = [H^+](\gamma - 1) \quad (3)$$

An algebraic combination of the material-balance equations with eq 3 produces the expression

$$K_2 = \frac{(T_L - [CuH_2L^{4+}]\gamma)[H^+]^2}{[CuH_2L^{4+}]^2\gamma} \quad (4)$$

where

$$[CuH_2L^{4+}] = \frac{(2 - a')T_L - [H^+]}{\gamma + 1}$$

In this case, in order to evaluate γ it was necessary to estimate the value of $K_a(CuH_2L)$. It is reasonable to expect the first acid dissociation constant of CuH_2L^{4+} to lie somewhere between $10^{-8.15}$, the dissociation constant for H_2L^{2+} alone, and 10^{-4}, below which value the acidity of CuH_2L^{4+} would obscure the inflection at $a = 2$, and only the inflection at $a = 4$ would be observed. Several values within these limits were esti-

mated for $K_a(CuH_2L)$ and inserted along with the experimental data into a programmed solution for K_2. The calculated mean value for K_2 was little affected by the choice of value for $K_a(CuH_2L)$, but the drift of values for K_2 vs. a and the standard deviation for K_2 were minimized for the set, $K_a(CuH_2L) = 10^{-6.0}$ and $K_2 = 10^{-5.85\pm0.03}$. (Precise calculations show that less than 1% of the total Cu(II) present exists as $CuHL^{3+}$.) The formation constant for the binuclear species Cu_2L^{4+} can thus be calculated as

$$K_{Cu_2L} = \frac{[Cu_2L^{4+}]}{[Cu^{2+}]^2[L]} = \frac{K_1K_2}{\beta_{a4}} = 10^{17.59} \quad (5)$$

where $\beta_{a4} = K_{a1}K_{a2}K_{a3}K_{a4}$.

Since all four of the protons from $H_4(tam)^{4+}$ have been released and neutralized at $a = 4$, the buffer region beyond $a = 4$ must represent the hydrolysis of Cu_2L^{4+}. The concentration dependence of the curves in this region indicates the formation of polynuclear, hydroxo-bridged species. Past $a = 5$, there appears in the titration cell a slight turbidity which increases, as more base is added, to a dense, finely divided, blue precipitate at the steep inflection. This solid appears to be an unusual polymer which is catenated by alternating links of organic polyamine and μ-diol bridges and which has the probable structure shown in II. The solid
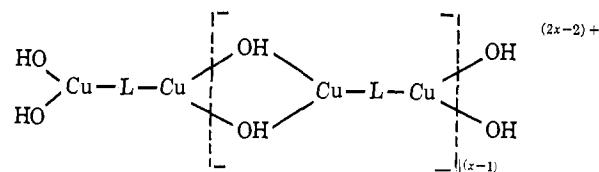
compound shows sharp infrared absorption peaks at $ca.$ 3200 and 3300 cm^{-1} and at 1630 cm^{-1}. Peaks in these regions were also observed for all other solid Cu(II)–tam and Cu(II)–en chelates prepared in this work and are presumably due to the N–H stretching and deformation vibrations, respectively. In addition, the polymeric solid shows an additional strong peak at 3500 cm^{-1}. This peak may reasonably be assigned to the O–H stretching frequency of the hydroxo-bridged OH on the basis of a similar assignment by Meek and Ehrhardt[10] of a strong absorption peak at 3530 cm^{-1} in di-μ-hydroxo-bis(N,N,N′,N′-tetramethylethylenediamine)dicopper(II) perchlorate.

Figure 2 shows an expanded view of the 2:1 titration curves in the region $a = 4$ to $a = 6$. The inflection positions are concentration dependent and occur between a values of 6.1 and 6.2. Table I lists the expected locations of inflections for various values of x in structure II. The effect of the hydroxo end groups

Table I. Location of Inflection for Values of x in Structure II

x	a (inflection)
1	8.0
2	7.0
3	6.7
10	6.2 ⎫ obsd
20	6.1 ⎭
100	6.0

(10) D. W. Meek and S. A. Ehrhardt, Inorg. Chem., 4, 584 (1965).

is very large for small values of x and is negligible for very large values of x. The observed inflections indicate average x values of 10 to 20 at the concentrations studied. It is reasonable that the more concentrated solution appears to have a higher value of x. Elemental analysis is consistent with a value of $x = 10$.

Anal. Calcd for $(Cu_2(OH)_2C_5H_{16}N_4)_{10}(OH)_2(NO_3 \cdot H_2O)_{18}$: C, 13.6; H, 5.0; N, 18.4. Found: C, 13.7; H, 5.0; N, 17.5.

Cu–tam (1:2). When the ratio of ligand to metal is 2:1, data represented by curve C in Figure 1 are obtained. The first, weak inflection at $a = 1.5$ indicates the completion of the reaction

$$Cu^{2+} + 2H_4L^{4+} \longrightarrow CuH_2L^{4+} + H_3L^{3+} + 3H^+$$

for which the equilibrium constant was determined from the data to be $K_3 = 10^{-6.36}$. The value for K_3 can be independently derived as the product of K_1 and K_{a1} which is seen to be $K_1K_{a1} = 10^{-6.35}$, and which is in excellent agreement with the above value for K_3.

Between $a = 1.5$ and $a = 3$, the over-all reaction

$$CuH_2L^{4+} + H_3L^{3+} \longrightarrow Cu(HL)_2^{4+} + 3H^+$$
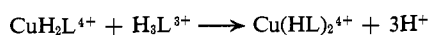
occurs, the equilibrium constant for which is designated as K_4. This constant is not readily determined by the usual method because of the prohibitively large number of possible intermediate protonated species (*e.g.*, CuH_2L^{4+}, $CuHL^{3+}$, $Cu(H_2L)_2^{6+}$, $Cu(H_2L)(HL)^{5+}$, $Cu(HL)_2^{4+}$, H_3L^{3+}, and H_2L^{2+}) which would have to be included in the material-balance equation. The value for K_4 was, however, derived indirectly as described below.

From $a = 3$ to $a = 4$, two overlapping acid dissociation reactions occur which are

$$Cu(HL)_2^{4+} \longrightarrow CuHL_2^{3+} + H^+$$

and

$$CuHL_2^{3+} \longrightarrow CuL_2^{2+} + H^+$$
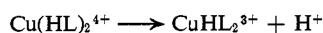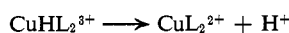
The equilibrium constants for these reactions are designated as K_5 and K_6, respectively, and are listed in Table II.

Table II

K	Reaction	Log K^a
K_{a1}	$H_4L^{4+} = H_3L^{3+} + H^+$	-3.03 ± 0.01
K_{a2}	$H_3L^{3+} = H_2L^{2+} + H^+$	-5.67 ± 0.01
K_{a3}	$H_2L^{2+} = HL^+ + H^+$	-8.17 ± 0.02
K_{a4}	$HL^+ = L + H^+$	-9.89 ± 0.03
K_1	$Cu^{2+} + H_4L^{4+} = CuH_2L^{4+} + 2H^+$	-3.32 ± 0.03
K_2	$Cu^{2+} + CuH_2L^{4+} = Cu_2L^{4+} + 2H^+$	-5.85 ± 0.03
K_3	$Cu^{2+} + 2H_4L^{4+} = CuH_2L^{4+} + H_3L^{3+} + 3H^+$	-6.36 ± 0.01
K_4	$CuH_2L^{4+} + H_3L^{3+} = Cu(HL)_2^{4+} + 3H^+$	-11.85 ± 0.08^b
K_5	$Cu(HL)_2^{4+} = CuHL_2^{3+} + H^+$	-7.55 ± 0.03
K_6	$CuHL_2^{3+} = CuL_2 + H^+$	-8.33 ± 0.04
K_{CuL_2}	$Cu^{2+} + 2L = CuL_2^{2+}$	19.43 ± 0.03
K_{Cu_2L}	$2Cu^{2+} + L = Cu_2L^{4+}$	17.59 ± 0.06^b

^{a} All constants refer to 25.0° and 0.1 M KNO$_3$. ^{b} Constants derived from the measured constants.

An independent determination of the over-all constant K_{CuL_2} for the reaction $Cu^{2+} + 2L \rightarrow CuL_2^{2+}$ was made by a polarographic method previously employed
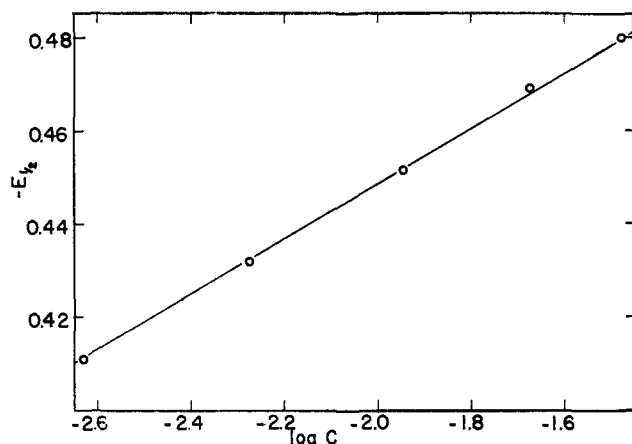

Figure 3. Plot of the half-wave potential $(E_{1/2})$ of solutions containing 8.16×10^{-5} M Cu(NO$_3$)$_2$ in 0.1 M KNO$_3$ medium as a function of the logarithm of the concentration of tam (log C).

by Laitinen.[11] In this method, the half-wave potential, $E_{1/2}$, is measured as a function of the concentration of the ligand while the Cu(II) concentration is held constant. In the equation

$$(E_{1/2})_c - (E_{1/2})_s = -0.0296 \log K_{CuL_p} - p(0.0296) \log C$$

the subscripts c and s refer to complexed and simple ions, respectively, C is the concentration of ligand, p is the number of ligands attached to each metal ion, and K_{CuL_p} is the formation constant for the reaction, $Cu^{2+} + pL \rightarrow CuL_p^{2+}$. Figure 3 demonstrates the linearity of the plot of $(E_{1/2})_c$ *vs.* log C and provides the value of $p = 2$. It is notable that at ligand-to-metal ratios as high as 200, there was no evidence for the association of a third ligand with the Cu(II). Log K_{CuL_2} was calculated from the data as 19.43 ± 0.03.

The previously by-passed constant K_4 can now be calculated indirectly as

$$K_4 = K_{CuL_2}(\beta_{a4})^2/K_1K_5K_6K_{a1}$$

Cu–tam (1:1). The behavior of the titration of equimolar amounts of Cu(II) and tam shows a marked dependence on the nature of the supporting electrolyte. The dashed line in Figure 4 shows a discontinuity beyond $a = 3$, where quantitative precipitation of Cu(II) in form of a finely divided, deep violet solid occurs when 0.1 M KNO$_3$ is the supporting medium. Continued titration of the remaining colorless solution results in a very sharp inflection at $a = 4$ indicating the completion of the reaction

$$xCu^{2+} + xH_4L^{4+} + 2xNO_3^- \longrightarrow (CuL)_x(NO_3)_{2x} + 4xH^+$$
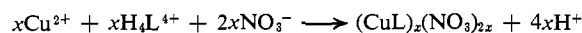
An elemental analysis of this violet solid clearly indicated a 1:1 ratio of Cu(II):tam but very precise percentages could not be obtained because of the somewhat explosive combustion of the solid. Solids also separated from solutions containing oxyanions such as ClO$_4^-$, SO$_4^{2-}$, and HPO^{2-} and are probably polymeric.

The solid line in Figure 4 represents a 1:1 titration with 0.1 M KCl as the supporting electrolyte. The titration proceeds smoothly with a more poorly defined inflection at $a = 4$ and with no precipitate forming

(11) H. Laitinen, E. Onstott, J. Bailar, and S. Swann, *J. Am. Chem. Soc.*, **71**, 1550 (1949).
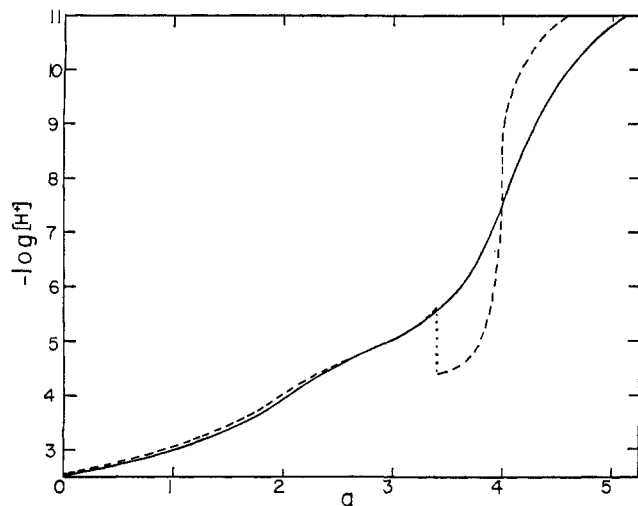
Figure 4. Titration curves for 6×10^{-3} M $H_4(tam)^{4+}$ with Cu^{2+} in a 1:1 ratio at 25°: dashed line, $H_4(tam)(NO_3)_4$ in 0.1 M KNO_3 medium; solid line, $H_4(tam)Cl_4$ in 0.1 M KCl medium.

at any time. Chloride ions are far better complexing ligands than nitrate ions and hence are more able to compete with amine donors for positions in the coordination sphere of Cu(II). This behavior is indicated by the broadening of the inflection region at $a = 4$ and by the lack of precipitation which is most likely due to the action of chloride ions as end groups or chain stoppers which limit the size of the coordination polymer. If, however, the solution was saturated with KCl, a blue solid was forced out which gave an analysis reasonably consistent with the general formula $[Cu^{II}\text{-}(tam)Cl_2\cdot 2H_2O]_n$. *Anal.* Calcd for $CuC_5H_{16}N_4Cl_2\cdot 2H_2O$: C, 19.8; H, 6.7; N, 18.5; Cl, 23.5. Found: C, 20.8; H, 6.0; N, 17.3; Cl, 23.9. The imprecision in the values probably reflects the effects of varying chain lengths and of chloro and aquo end groups.

Cu–tam–en (2:1:2). An attempt was made to produce a controlled-length polynuclear species with ethylenediamine (en) as an end group. With Cu(II) nitrate, tetraprotonated tam, and diprotonated en in the ratio 2:1:2 as the starting materials in 0.1 M KNO_3, a steep inflection in the titration curve at 4 moles of base added per mole of Cu(II) clearly indicates that each Cu(II) ion is coordinated to four amine nitrogen atoms. The general reaction may be written

$$2xCu^{2+} + 2xH_2(en)^{2+} + xH_4L^{4+} \longrightarrow$$
$$(x - 1)Cu(en)_2{}^{2+} + (en)[-Cu-L-]xCu(en)^{(2x+2)+} + 8xH^+$$
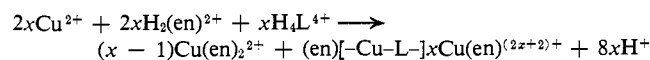
The absence of any precipitate from this mixed solution indicates that the value of x in the above equation is not very large, since 1:1 Cu–tam has already been shown to be very insoluble in 0.1 M KNO_3. Hence the ethylenediamine acts successfully to form mixed-ligand chelates and to restrict the length of the polymer chain.

A spectrophotometric measurement of individual solutions of $Cu(en)_2Cl_2$ and $Cu(tam)Cl_2$ in pure water yielded broad bands with absorption maxima at 552 and 583 mμ, respectively. When the incident light was passed successively through each of the above two solutions (of equal Cu(II) concentration, and in two cells of equal path length), a single summation band was observed at 570 mμ. When the same two cells were filled with a solution containing $CuCl_2$, tam, and

en in the ratio 2:1:2, a single absorption band was recorded at 563 mμ. This shift in wavelength again indicates the formation of mixed-ligand chelates. Although it is felt that the predominant species present is $(en-Cu-L-Cu-en)^{4+}$ (*i.e.*, that the value of x is 1), the breadth and proximity of the absorption bands do not allow a definite conclusion to be made.

Discussion

The unusually low pK_{a1} value of 3.03 for $H_4(tam)^{4+}$ reflects the very strong electrostatic repulsion of the leaving proton by the remaining three positive ammonium groups. The pK_a values increase in regular fashion as the residual positive charge decreases, and the fourth pK_a value of 9.89 is fairly typical for monoprotonated aliphatic amines.
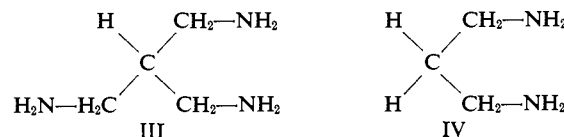
Many other interesting electrostatic effects can be observed in the equilibrium constants for the association reactions listed in Table III. For comparison purposes,

Table III. Approximate Association Constants for Various Cu(II)–tam Reactions

Eq	Reaction	Log K^a	Log K^b	Log K^c
6	$Cu^{2+} + L = CuL^{2+}$	11.0	10.9	9.8
7	$Cu^{2+} + HL^+ = CuHL^{3+}$	7.6	8.7	...
8	$Cu^{2+} + H_2L^{2+} = CuH_2L^{4+}$	5.4	3.6	...
9	$Cu^{2+} + CuL^{2+} = Cu_2L^{4+}$	6.6	...	...
10	$CuL^{2+} + H_2L^{2+} = Cu(HL)_2{}^{4+}$	6.3	...	...
11	$CuL^{2+} + HL^+ = CuHL_2{}^{3+}$	6.9	...	...
12	$CuL^{2+} + L = CuL_2{}^{2+}$	8.4	...	7.2
13	$CuHL^{3+} + L = CuHL_2{}^{3+}$	10.3	...	...
14	$CuH_2L^{4+} + L = Cu(HL)_2{}^{4+}$	11.9	...	...
15	$CuHL^{3+} + HL^+ = Cu(HL)_2{}^{4+}$	7.9	...	...
16	$Ni^{2+} + L = NiL^{2+}$	10.8	9.9	6.4
17	$Ni^{2+} + HL^+ = NiHL^{3+}$	8.5	5.6	...

[a] Values refer to tam, 25°, 0.1 M KNO_3. [b] Values refer to adap,[12] 20°, 0.1 M KNO_3. [c] Values refer to dap,[13] 25°, 0.1 M KCl.

this table includes some log K values for 2-aminomethyl-1,3-diaminopropane (adap, structure III)[12] and 1,3-diaminopropane (dap, structure IV),[13] both of which bear a structural resemblance to tam. Included also

$$\begin{array}{ccc} H & CH_2-NH_2 \\ & \diagdown \diagup \\ & C \\ & \diagup \diagdown \\ H_2N-H_2C & CH_2-NH_2 \\ & III \end{array} \qquad \begin{array}{ccc} H & CH_2-NH_2 \\ & \diagdown \diagup \\ & C \\ & \diagup \diagdown \\ H & CH_2-NH_2 \\ & IV \end{array}$$

are two values for Ni(II) from a preliminary investigation[14] which are pertinent to the discussion.

The log K values in Table III involving tam are all derived from the measured constants in Table II and from two estimated constants, $K_a(CuH_2L)$, previously discussed, and K_{CuL}, the first formation constant for the 1:1 Cu(II)–tam chelate. The latter constant was not directly measurable from the experimental data since the predominant species in a 1:1 solution are polynuclear. It was therefore assumed that the ratio of the formation constants for the addition of the first and second ligands is the same for tam as for dap which has been reported by Irving and co-workers[13] as $10^{2.6}$.

(12) G. Anderegg, *Helv. Chim. Acta*, **45**, 1303 (1962).

(13) H. Irving, R. J. P. Williams, D. J. Ferrett, and A. E. Williams, *J. Chem. Soc.*, 3494 (1954).

(14) L. J. Zompa and R. F. Bogucki, unpublished results.

Since the value for the simultaneous addition of two tam ligands to Cu(II), K_{CuL_2}, has been directly measured as $10^{19.4}$, the estimated value for K_{CuL} becomes $10^{11.0}$. Thus, although the derivations of the log K values for tam include two approximate constants and are probably not reliable to better than ± 0.5 log K unit, the trends are undoubtedly real and provide an interesting insight into the role played by electrostatic forces in association constants.

It is important to note that for every reaction of tam listed, there are at least two unprotonated nitrogen donors on the ligand available for coordination to two hydrated positions on the square-planar Cu(II) species so that direct displacement of protons by Cu(II) is not involved in any reaction.

The first formation constant represented by eq 6 is seen to increase in an expected manner as the number of available nitrogen donors on the ligand increases. The rapid drop in stability in the sequence 6, 7, and 8 is due to the increasing positive charge on the ligand which makes the approach of the ligand from the bulk solution into the inner coordination sphere of the Cu^{2+} increasingly difficult. The same effect is apparent for the addition of the second ligand in reactions 12, 11, and 10, although the drop in log K^a is less pronounced since the Cu(II) is already partially chelated with a first tam molecule. The displacement of water molecules by the more basic amine donor presumably causes the divalent charge on the complex to be somewhat less localized on the Cu(II).

Interestingly, the log K^a value for reaction 10 is actually larger than that for (8) since in (10) the incoming H_2L^{2+} group can transfer a proton to one of the remote (and more basic) nitrogen atoms on the already-bound tam molecule. This provides a more favorable distribution of positive charge and increases the stability of the resultant complex.

In reactions 12, 13, and 14, the same end products are produced as in the series 12, 11, and 10, viz., CuL_2^{2+}, $CuHL_2^{3+}$, and $Cu(HL)_2^{4+}$, respectively. However, whereas in the series 12, 11, 10, the association constants decrease, the series 12, 13, 14 shows a sharp increase in the association constants. In the latter series, the increasing positive charge resides not on the approaching ligand but on the Cu(II) complex, thus facilitating the approach of the uncharged, nucleophilic ligand into the coordination sphere of Cu(II).

The same combination of effects can be seen by comparing reactions 10, 15, and 14 all of which have the same end product, $Cu(HL)_2^{4+}$, but in which the positive charge shifts from the ligand to the complex and causes an increase in association constants.

A more subtle effect can be observed in reactions 8 and 9, in which the electrostatic repulsions between Cu^{2+} and the two dipositive species H_2L^{2+} and CuL^{2+} should be about the same with regard to approach from the bulk solution up to the coordination sphere. Once within bond-forming distance, however, the electrostatic resistance to the association of Cu^{2+} with H_2L^{2+} will be greater than with CuL^{2+} since in H_2L^{2+} the two positive charges are centered on the ammonium nitrogen atoms, while for CuL^{2+} the two charges are considerably more remotely centered predominantly on the Cu(II) atom. This effect is illustrated by structures V and VI,
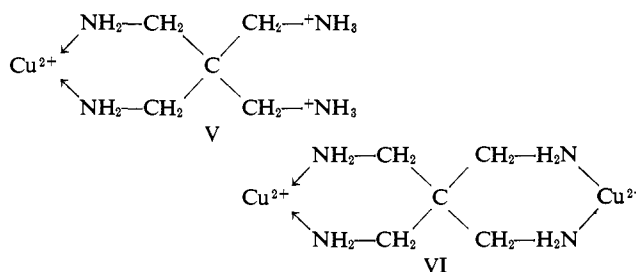
and is observed by the larger association constant for Cu^{2+} with CuL^{2+} than with H_2L^{2+}.

Finally, the values for reactions 16 and 17 clearly indicate that three amine groups of either tam or adap may be simultaneously bound to the three vertices of a triangular face of octahedral Ni(II). Further evidence for this arrangement is seen in the fact that $NiHL^{3+}$ is the most stable complex of Ni(II)–tam in acid solution. In contrast, the presence of CuH_2L^{4+} as the most stable acid complex in several Cu(II)–tam systems at various concentrations and in differing ratios demonstrates that any tendency to add a third amine nitrogen of tam to a tetragonally elongated axial position (predicted by the Jahn–Teller effect) is negligible, and the geometry of Cu(II) in this system is typically square planar.