actions were complete in 4–6 hr for R = C_6H_5 and R′ = CN or CF_3. The solubilities of the three species present at equilibrium were sufficiently different (with a suitable counterion) to allow a straightforward separation at room temperature of the desired products. However, the ligand-exchange reaction between $[NiS_4C_4(C_6H_5)_4]^-$ and $[NiS_4C_4(CN)_4]^-$ is complicated by the redox reaction

$$[NiS_4C_4(C_6H_5)_4]^- + [NiS_4C_4(CN)_4]^- \rightleftharpoons [NiS_4C_4(C_6H_5)_4] + [NiS_4C_4(CN)_4]^{2-}$$

which occurred very rapidly, as evidenced by the immediate precipitation of $[NiS_4C_4(C_6H_5)_4]$ on mixing. Polarographic studies of dilute (*ca.* 10^{-3} *M*) solutions in CH_2Cl_2 indicated that, while the redox equilibrium lay to the right, ligand exchange occurred gradually to give $[Ni\{S_2C_2(C_6H_5)_2\}\{S_2C_2(CN)_2\}]^-$. Because the redistribution reaction occurred extremely slowly (Table II) for R = CN and R′ = CF_3, a direct synthesis of the mixed species was attempted by the reaction of $[(C_6H_5)_3P]_2NiS_2C_2(CN)_2$ with excess bis(trifluoromethyl)-dithietene. However, it was not possible to obtain the mixed species completely free of $[NiS_4C_4(CF_3)_4]^{2-}$ even by repeated recrystallization. The complexes $[Ni(S_2C_2R_2)(S_2C_2R_2')]^z$, as expected, have properties intermediate to those of the corresponding symmetrical species. The polarograms of freshly prepared solutions of these new compounds exhibit only those waves which were attributed (Table I) to the mixed species in the exchange studies. However, if these solutions are allowed to stand, "scrambling" of the ligands occurs to give an equilibrium mixture of all three species. Thus the isolation and purification of the mixed species must be effected as rapidly as possible, preferably without heating the solutions.

Although there is no evidence that the nickel monoanions are associated in solution, single crystal X-ray diffraction studies[6] of $[(C_6H_5)_3(CH_3)P][NiS_4C_4(CN)_4]$ clearly demonstrate a pairwise interaction in the solid state. It is tempting to suggest that the transient intermediate in the ligand exchange reactions may be dimeric. It is evident that other dithiolato complexes should undergo these "scrambling" reactions, and further investigations are in progress.

Acknowledgment. Financial support by the National Science Foundation (Grant G.P. 3468) is gratefully acknowledged. E. T. S. was a Woodrow Wilson Fellow, 1964–1965, and a National Science Foundation Graduate Fellow, 1965–1967.

(6) G. J. Fritchie, Jr., *Acta Cryst.*, **20**, 107 (1966).

New Multidentate Ligands. V. Transition Metal Chelates of Triethylenetetraminehexaacetic Acid[1]

T. A. Bohigian, Jr.,[2a] and A. E. Martell[2b]

Contribution from the Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois.
Received March 30, 1966

Abstract: Further studies of the interactions of transition metal ions with triethylenetetraminehexaacetic acid (TTHA) have elucidated the equilibria between the mononuclear chelates and several protonated species. Equilibrium constants are reported for mono-, di-, tri-, and tetraprotonated mononuclear Cu(II), Ni(II), and Co(II) chelates, as well as the simple 1:1 chelates. The decadentate ligand TTHA is found to be unique in its ability to combine simultaneously with a metal ion and from one to four protons. Probable arrangements of coordinate bonding in the aqueous chelates are inferred.

In a recent publication, the formation of mono-, di-, and ternuclear alkaline earth chelates of triethylenetetraminehexaacetic acid was described, and the corresponding equilibrium constants were reported,[3] together with the acid dissociation constants of the ligand and dissociation constants of protonated alkaline earth chelates. Reasonable arrangements of donor-ligand bonds were suggested as an aid in the interpretation of the equilibrium data reported. Because of the unusual properties of this new ligand, further studies of metal complex formation equilibria seemed warranted. This paper describes a further extension of the earlier work to successive protonation equilibria of mononuclear transition metal chelates.

There are very little equilibrium data on this new ligand in the literature. The work of Pribil and coworkers[4–12] is restricted to analytical applications. The first equilibrium constants reported for TTHA were the acid dissociation constants of the free ligand,

---

(1) This work was supported by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-1020.

(2) (a) Abstracted from a thesis submitted by T. A. Bohigian to the Faculty of Illinois Institute of Technology in partial fulfillment of the requirements for the degree of doctor of philosophy, June 1966. (b) To whom inquiries should be addressed: Department of Chemistry, Texas A & M University, College Station, Texas.

(3) T. A. Bohigian and A. E. Martell, *Inorg. Chem.*, **4**, 1264 (1965).

(4) R. Pribil and V. Vesély, *Talanta*, **9**, 939 (1962).

(5) R. Pribil and V. Vesély, *ibid.*, **10**, 899 (1963).

(6) R. Pribil and V. Vesély, *ibid.*, **11**, 1545 (1964).

(7) R. Pribil and V. Vesély, *ibid.*, **11**, 319 (1964).

(8) R. Pribil and V. Vesély, *Chemist-Analyst*, **53** (3), 77 (1964).

(9) R. Pribil and V. Vesély, *Talanta*, **12**, 475 (1965).

(10) G. Conradi, M. Kopanica, and J. Koryta, *Collection Czech. Chem. Commun.*, **30**, 2029 (1965).

(11) M. Kopanitea, G. Conradi, and R. Pribil, *Zavodsk. Lab.*, **30**, 1181 (1964).

(12) G. Conradi and M. Kopanica, *Collection Czech. Chem. Commun.*, **29**, 1952 (1964).

determined by Frost.[13] Grimes, Huggard, and Wilford[14] studied the reactions of the alkaline earth metal ions with TTHA and some related ligands by potentiometric titration and reported equilibrium constants for the formation of mononuclear and binuclear chelates of TTHA with alkaline earth ions, as well as mono- and diprotonated forms of the mononuclear chelates. No stability data have been published for the transition metal chelates of this ligand, except for the mention of binuclear chelates in the previous report from these laboratories.[3]

Experimental Section

Potentiometric Measurements. The experimental method employed in this investigation consisted of potentiometric titration of the hexabasic acid TTHA in the absence and presence of the metal ion being studied. The ionic strengths of the media were maintained constant at 0.10 by the addition of potassium nitrate to the experimental solution. All potentiometric measurements were carried out in a double-walled titration cell of 100-ml capacity. The temperature of the solutions was maintained at 25.0 ± 0.05° by circulation of water thermostated at this temperature through the outer jacket of the potentiometric cell. A Radiometer Model PHM4 pH meter fitted with extension glass and calomel electrodes was calibrated so as to determine the hydrogen ion concentration directly. This was done by direct titration of dilute HCl with NaOH, and by titration of acetic acid with NaOH in such a way that the observed pH meter reading was compared with the actual hydrogen ion concentration determined on the basis of the data tabulated by Harned and Owen.[15]

Reagents. Triethylenetetraminehexaacetic acid (TTHA) was obtained through the courtesy of the Dow Chemical Co., Midland, Mich. The purity of TTHA was established by nitrogen, carbon, and hydrogen analysis and by potentiometric titration. Since the ligand contained an unspecified amount of water (characteristic of long-chain polyelectrolytic ligands), the equivalent weight was not defined by the inflection in the ligand curve alone. The equivalent weight was determined by titration of the ligand in the presence of somewhat more than two times the molar ratio of copper(II) ion. The curve for this titration indicated that the formation of the 2:1 Cu(II) chelate had a definite end point, and the excess Cu(II) ion then precipitated beyond the inflection at higher pH. Since all of the protons of the ligand must be displaced by the Cu(II) ions, this inflection occurs at 6 equiv. These results were also obtained using Ni(II) ion, thus providing confirmation of the method.

Results and Calculations

Potentiometric Data. Potentiometric equilibrium curves of 1:1 and 2:1 molar ratios of Cu(II), Ni(II), and Co(II) to TTHA are presented in Figure 1. The 1:1 curves are quite similar, indicating the formation of a protonated metal chelate, which then dissociates at relatively high pH to a simple chelate of the tetranegative ligand. In the case of Ni(II) the subsequent dissociation step, while it occurs, is not as clearly defined as in the case of Cu(II) and Co(II). In the lower buffer region, it is possible that more highly protonated species are formed, especially in view of the much lower pH of the low buffer region of the curves in which the molar ratio of the metal ion to the ligand is 2:1. As it turned out, it was necessary to assume the formation of four low pH protonated species, MH_4L, MH_3L^-, MH_2L^{2-}, and MHL^{3-}, in order to calculate equilibrium constants from the experimental data. Therefore the calculations outlined below are based on the only assumptions of metal chelate species that gave agreement with experimental data.

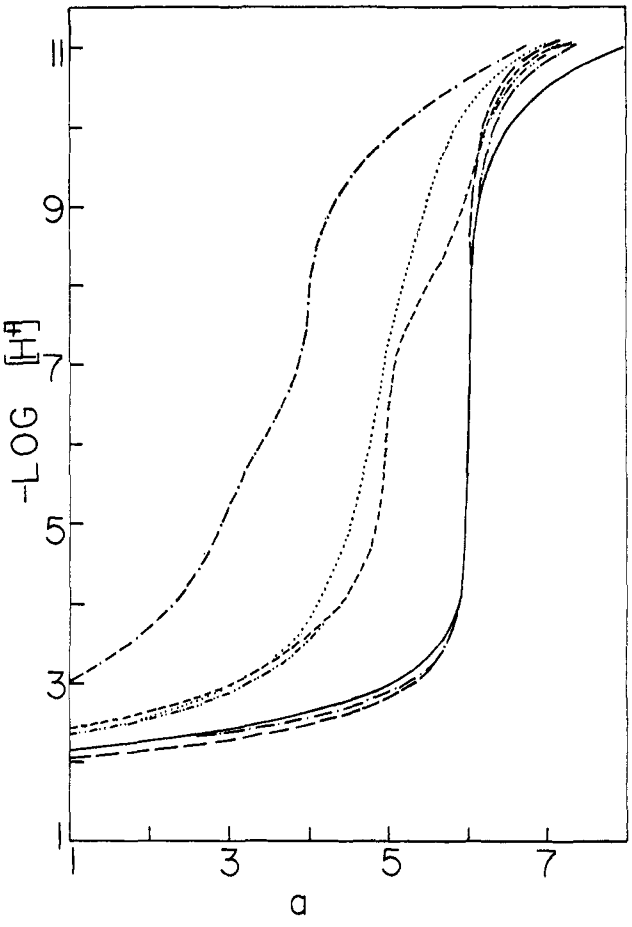


Figure 1. Potentiometric titration of Cu(II), Co(II), and Ni(II) chelates of TTHA at 25° in 0.1 M KNO_3 with the following molar ratios of metal ion to ligand: — — ·, ligand alone; – – – –, Cu (1:1); —··—, Co (1:1); · · · ·, Ni (1:1); ———, Cu (2:1); — · —, Co (2:1); — — —, Ni (2:1); T_L = 2.0 × 10^{-3} M.

In the presence of 2 moles of metal ion per mole of ligand, it is seen in Figure 1 that all of the available protons on the ligand are neutralized in a single step, with the formation of binuclear chelates. In this respect, the reactions of all three metal ions seem to be very similar, and the stabilities of the corresponding binuclear chelates are almost identical.

Calculations. In the mathematical treatment of data, the symbols employed are:

T_L = total analytical concentration of ligand in all forms.

T_M = total analytical concentration of metal ion in all forms.

T_{OH} = total molar concentration of base added to the experimental solution

a = number of moles of standard base added per mole of ligand.

H_nL = acid form of the ligand where n represents the number of equivalents of titratable hydrogens per mole of ligand.

K_n = proton association constant of the ligand. Log association constants previously determined are: K_1 = 10.19, K_2 = 9.40, K_3 = 6.16, K_4 = 4.16, K_5 = 2.95, K_6 = 2.42.

The potentiometric titration curve of a solution containing an equimolar amount of copper(II) ion and

---

(13) A. E. Frost, *Nature*, **178**, 322 (1956).

(14) J. H. Grimes, A. J. Huggard, and S. P. Wilford, *J. Inorg. Nucl. Chem.*, **25**, 1225 (1963).

(15) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed, Reinhold Publishing Corp., New York, N. Y., 1950, p 523.

Table I. Equilibrium Constants for the Formation of TTHA Chelates (μ = 0.1 (KNO$_3$), 25°)

Reaction	Log K				
	Cu^{2+}	Co^{2+}	Ni^{2+}	Ca^{2+} [3]	Mg^{2+} [3]
$M^{2+} + H_4L^{2-} \rightleftharpoons MH_4L$ [a]	7.3	6.9	6.7		
$MH_3L^- + H^+ \rightleftharpoons MH_4L$ [b]	2.04	1.57	1.15		
$MH_2L^{2-} + H^+ \rightleftharpoons MH_3L^-$ [c]	2.86	2.63	2.74		
$MHL^{3-} + H^+ \rightleftharpoons MH_2L^{2-}$ [d]	4.05	4.03	4.86	4.87	4.65
$ML^{4-} + H^+ \rightleftharpoons MHL^{3-}$ [d]	7.96	7.97	9.11	8.23	7.55
$M^{2+} + L^{6-} \rightleftharpoons ML^{4-}$ [a]	20.3	20.6	18.8	9.89	8.43
$2M^{2+} + L^{6-} \rightleftharpoons M_2L^{2-}$ [a]	27.6	28.0	29.5	14.2	13.9

[a–d] Probable errors of equilibrium constants in log K units: [a] ± 0.1; [b] ± 0.05; [c] ±0.03; [d] ±0.01.

TTHA (Figure 1) shows a well-defined inflection at $a = 5$, corresponding to the dissociation of five protons from the ligand and to the formation of a protonated metal chelate. The protonated complex dissociates subsequently at higher pH, and there is a second inflection at $a = 6$ corresponding to the formation of the normal mononuclear chelate.

The reactions which may be taking place in the first buffer region in the course of the neutralization of up to 5 equiv of base per mole of ligand involve the initial formation of a tetraprotonated complex, MH$_4$L, followed by the stepwise dissociation of this species to the monoprotonated form, MHL. The dissociation steps were first determined by an adaptation of the method of Carlson, *et al.*,[16] which was previously utilized in determining the acid dissociation constants of the ligand. Three overlapping steps involving further association of the protonated chelate, MHL, with hydrogen ions in the region $a = 2$ to 5 were considered according to the following equilibria.

$$MHL^{3-} + H^+ \rightleftharpoons MH_2L^{2-}$$

$$K_2' = \frac{1}{K^H{}_{MH_2L}} = \frac{[MH_2L^{2-}]}{[MHL^{3-}][H^+]} \tag{1}$$

$$MH_2L^{2-} + H^+ \rightleftharpoons MH_3L^-$$

$$K_3' = \frac{1}{K^H{}_{MH_3L}} = \frac{[MH_3L^-]}{[MH_2L^{2-}][H^+]} \tag{2}$$

$$MH_3L^- + H^+ \rightleftharpoons MH_4L$$

$$K_4' = \frac{1}{K^H{}_{MH_4L}} = \frac{[MH_4L]}{[MH_3L^-][H^+]} \tag{3}$$

The average number of moles of hydrogen ion bound per mole of ligand is related to the concentration of protonated chelate species by the following expression

$$\bar{n} = \frac{T_H - [H^+]}{T_L} = \frac{[MH_2L^{2-}] + 2[MH_3L^-] + 3[MH_4L]}{[MHL^{3-}] + [MH_2L^{2-}] + [MH_3L^-] + [MH_4L]} \tag{4}$$

where T_H is defined as the total analytical concentration of free or bound hydrogen ion. In terms of added base, T_{OH}, T_H is defined as

$$T_H = 5T_L - T_{OH}$$

Solution of eq 4 for K_2', K_3', and K_4', respectively, results in eq 5, 6, and 7. Values for K_2', K_3', and

$$K_2' = \frac{1}{[H^+]} \times \left[\frac{\bar{n}}{(1 - \bar{n}) + K_3'[H^+](2 - \bar{n}) + K_3'K_4'[H^+]^2(3 - \bar{n})}\right] \tag{5}$$

$$K_3' = \frac{1}{[H^+]}\left[\frac{\bar{n} - 1 + (\bar{n}/K_2'[H^+])}{(2 - \bar{n}) + [H^+]K_4'(3 - \bar{n})}\right] \tag{6}$$

$$K_4' = \frac{1}{[H^+]}\left(\frac{\bar{n} - 2 + \dfrac{\bar{n} - 1}{K_3'[H^+]} + \dfrac{\bar{n}}{K_2'K_3'[H^+]^2}}{3 - \bar{n}}\right) \tag{7}$$

K_4' were obtained by means of successive approximations based on three sets of experimental data. The values obtained for the three dissociation constants are listed in Table I.

The three dissociation constants calculated above were then utilized in calculating the formation constant of the MH$_4$L species.

$$M^{2+} + H_4L^{2-} \rightleftharpoons MH_4L \quad K_{MH_4L} = \frac{[MH_4L]}{[M^{2+}][H_4L^{2-}]} \tag{8}$$

Combination of the appropriate material balance relationships with eq 8 results in the following expression for K_{MH_4L}.

$$\begin{aligned} K_{MH_4L} = \Bigg\{ & \frac{[H^+]}{K^H{}_{MH_2L}}[4T_M + [HL^{5-}]Y + [OH^-] - 4[M^{2+}] - \\ & [H^+] - T_{OH}] - T_{OH} - [H^+] + [OH^-] - 5[M^{2+}] + 5T_M + \\ & [HL^{5-}]Y - \frac{[H^+]^2}{K^H{}_{MH_3L}K^H{}_{MH_2L}}[T_{OH} + [H^+] - \\ & [OH^-] + 3[M^{2+}] - 3T_M - [HL^{5-}]Y]\Bigg\} \times \\ & \left\{\frac{[M^{2+}][HL^{5-}][H^+]^3}{K_3K_4K_5}\left[\frac{2[H^+]}{K^H{}_{MH_2L}} + \frac{[H^+]^2}{K^H{}_{MH_3L}K^H{}_{MH_2L}} + 3\right]\right\}^{-1} \end{aligned} \tag{9}$$

where

$$Y = \frac{[H^+]^4}{K_2K_3K_4K_5} + \frac{2[H^+]^3}{K_3K_4K_5} + \frac{3[H^+]^2}{K_4K_5} + \frac{4[H^+]}{K_5} + 5 \tag{10}$$

and

$$\begin{aligned} [HL^{5-}] = \Bigg\{ & \frac{[H^+]^2}{K^H{}_{MH_3L}K^H{}_{MH_2L}}[T_{OH} + [H^+] - [OH^-] - \\ & 3T_M + \frac{[H^+]}{K^H{}_{MH_4L}}(T_{OH} + [H^+] - [OH^-] - 2T_M)] + \\ & T_{OH} + [H^+] - [OH^-] - 5T_M + \\ & \frac{[H^+]}{K^H{}_{MH_2L}}(T_{OH} + [H^+] - [OH^-] - 4T_M)\Bigg\} \times \end{aligned}$$

---

[16] G. A. Carlson, J. P. McReynolds, and F. H. Verhoek, *J. Am. Chem. Soc.*, 67, 1335 (1945).

$$\left\{Y + \frac{[\mathrm{H^+}]}{K^{\mathrm{H}}{}_{\mathrm{MH_2L}}}\left[4X + Y + \frac{3[\mathrm{H^+}]X}{K^{\mathrm{H}}{}_{\mathrm{MH_3L}}} + \frac{[\mathrm{H^+}]Y}{K^{\mathrm{H}}{}_{\mathrm{MH_3L}}} + \frac{2[\mathrm{H^+}]^2X}{K^{\mathrm{H}}{}_{\mathrm{MH_4L}}K^{\mathrm{H}}{}_{\mathrm{MH_3L}}} + \frac{[\mathrm{H^+}]^2Y}{K^{\mathrm{H}}{}_{\mathrm{MH_4L}}K^{\mathrm{H}}{}_{\mathrm{MH_3L}}}\right]\right\}^{-1} \tag{11}$$

and

$$[\mathrm{M^{2+}}] = [\mathrm{HL^{5-}}]X \tag{12}$$

X is given by the expression

$$X = \frac{[\mathrm{H^+}]^5}{K_1K_2K_3K_4K_5} + \frac{[\mathrm{H^+}]^4}{K_2K_3K_4K_5} + \frac{[\mathrm{H^+}]^3}{K_3K_4K_5} + \frac{[\mathrm{H^+}]^2}{K_4K_5} + \frac{[\mathrm{H^+}]}{K_5} + 1 \tag{13}$$

Values for $K^{\mathrm{H}}{}_{\mathrm{MH_2L}}$, $K^{\mathrm{H}}{}_{\mathrm{MH_2L}}$, and $K^{\mathrm{H}}{}_{\mathrm{MH_4L}}$ (calculated from eq 5, 6, 7) were used in the determination of $K_{\mathrm{MH_4L}}$. The values of this constant are listed in Table I.

The dissociation constant for the region $a = 5$ to 6 was calculated using the following equilibrium.

$$\mathrm{MHL^{3-}} \rightleftharpoons \mathrm{ML^{4-}} + \mathrm{H^+} \tag{14}$$

$$K^{\mathrm{H}}{}_{\mathrm{MHL}} = \frac{[\mathrm{ML^{4-}}][\mathrm{H^+}]}{[\mathrm{MHL^{3-}}]}$$

The value for this constant is given in Table I. A combination of several constants was used to determine the formation constant for the normal mononuclear copper(II)–TTHA chelate species. This determination was accomplished by utilization of the following equation.

$$K^{\mathrm{M}}{}_{\mathrm{ML}} = K^{\mathrm{M}}{}_{\mathrm{MH_4L}}K^{\mathrm{H}}{}_{\mathrm{MH_4L}}K^{\mathrm{H}}{}_{\mathrm{MH_3L}}K^{\mathrm{H}}{}_{\mathrm{MH_2L}}K^{\mathrm{H}}{}_{\mathrm{MHL}}\frac{1}{K_3K_4K_5K_6} \tag{15}$$

The value of K_{ML} is listed in Table I. In Figure 1 it is shown that the 1:1 cobalt(II)–TTHA and nickel(II)–TTHA systems behave very similarly to the 1:1 copper(II)–TTHA system except that in the nickel(II) titration, the dissociation step following the formation of the monoprotonated chelate is not as well defined as in the case of the Cu(II)- and Co(II)–TTHA systems. The same methods of calculation were used successfully for these two cases and the values obtained are presented in Table I.

When 2 moles of copper(II), nickel(II), or cobalt(II) is combined with TTHA, the resulting titration curves presented in Figure 1 show that all of the available protons on the ligand are neutralized in a single step and binuclear chelates of the respective metal ions are formed. All three systems have sharp inflections at $a = 6$. A value for $K_{\mathrm{M_2L}}$ was determined for the following equilibrium.

$$2\mathrm{M^{2+}} + \mathrm{L^{6-}} \rightleftharpoons \mathrm{M_2L^{2-}} \quad K_{\mathrm{M_2L}} = \frac{[\mathrm{M_2L^{2-}}]}{[\mathrm{M^{2+}}]^2[\mathrm{L^{6-}}]} \tag{16}$$

Combination of eq 16 with appropriate material balance equations yields an expression for $K_{\mathrm{M_2L}}$ defined as

$$K_{\mathrm{M_2L}} = \frac{T_{\mathrm{L}} - [\mathrm{L^{6-}}]X'}{4[\mathrm{L^{6-}}]^3X'^2} \tag{17}$$

where

$$[\mathrm{L^{6-}}] = \frac{6T_{\mathrm{L}} - T_{\mathrm{OH}} - [\mathrm{H^+}] + [\mathrm{OH^-}]}{6X' - Y'} \tag{18}$$

$$X' = \frac{[\mathrm{H^+}]^6}{K_1K_2K_3K_4K_5K_6} + \frac{[\mathrm{H^+}]^5}{K_2K_3K_4K_5K_6} + \frac{[\mathrm{H^+}]^4}{K_3K_4K_5K_6} + \frac{[\mathrm{H^+}]^3}{K_4K_5K_6} + \frac{[\mathrm{H^+}]^2}{K_5K_6} + \frac{[\mathrm{H^+}]}{K_6} + 1 \tag{19}$$

$$Y' = \frac{(\mathrm{H^+})^5}{K_2K_3K_4K_5K_6} + \frac{2[\mathrm{H^+}]^4}{K_3K_4K_5K_6} + \frac{3[\mathrm{H^+}]^3}{K_4K_5K_6} + \frac{4[\mathrm{H^+}]^2}{K_5K_6} + \frac{5[\mathrm{H^+}]}{K_6} + 6 \tag{20}$$

Equilibrium Constants. The equilibrium constants calculated from the above equations are given in Table I. All of the protonated constants listed for the 1:1 metal–ligand systems are necessary parameters for agreement with the potentiometric data.

Discussion

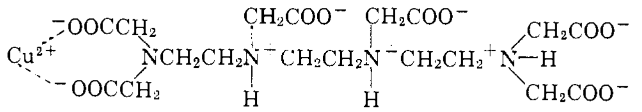
Mononuclear Chelates. The presence of mono-, di-, tri-, and tetraprotonated metal chelate species in aqueous solution has not been previously reported for any other system. The binding of the metal ion to the ligand in the tri- and tetraprotonated forms ($\mathrm{MH_3L^-}$ and $\mathrm{MH_4L}$) probably occurs through a terminal iminodiacetate group at the end of the molecule, as indicated by I for $\mathrm{CuH_3L^-}$. The additional proton in the tetraprotonated form may become attached to one of the two carboxylate ions at the end of the ligand opposite to that at which the metal ion is coordinated. The remaining three protons must be bound to the most basic free donor groups of the ligand, the nitrogen atoms, as indicated in I.

As the pH of the solution in which I occurs is increased, there is a series of overlapping dissociations that terminate in the formation of a stable monoprotonated species. The coordinate bonding in this form may be that indicated by II, analogous to the arrangement in a similar Ca(II) chelate, $\mathrm{CaHL^{3-}}$, suggested previously.[3] Another, and perhaps more probable, arrangement would involve coordination of the metal ion by the three unprotonated nitrogen atoms, and three adjacent carboxylate groups, the proton remaining on a terminal nitrogen atom.

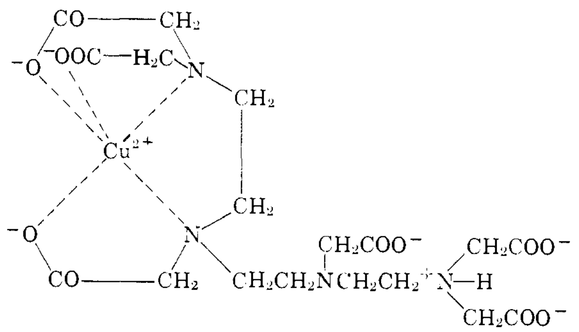
Binuclear Chelates. For the 2:1 metal–ligand system, the potentiometric data indicated that no protonated metal chelate species are formed under the reaction conditions employed. A reasonable structure for all three complexes is illustrated by III for the binuclear Cu(II) chelate. This arrangement is considered highly probable since it shares the basic nitrogens and negative charges of the ligand equally between the two metal ions present.

Equilibrium Constants. The successive dissociation constants listed in Table I, as well as the corresponding titration curves, reveal a steady increase of stability with pH in the 2–4 pH range. This series of protonated complexes of rapidly increasing stability is quite unique in the field of coordination chemistry, and to the knowledge of the authors has not been described previously in published form.

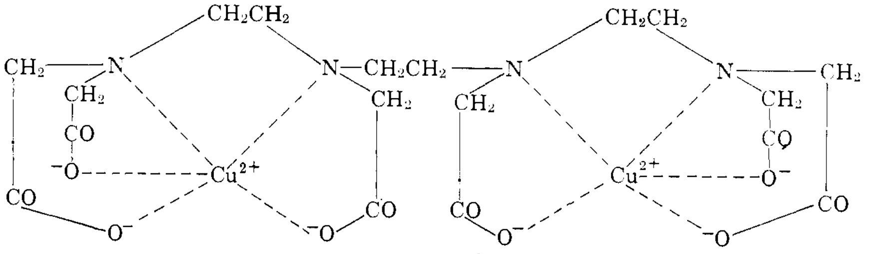
It is interesting to note that, in spite of the large number of donor groups on the ligand, the stabilities of



I, CuH_3L^-



II, $CuHL^{3-}$



III, Cu_2L^{2-}

the deprotonated chelates (relative to free metal ion and completely dissociated ligand) are not markedly greater than the corresponding EDTA or cyclohexanediaminetetraacetic acid (CDTA) chelates. This effect must certainly be due to the inability of these metal ions to expand their coordination numbers beyond 6 and thus take advantage of the ten donor groups of the ligand.

The increment of stability in going from the mono- to the binuclear chelate is quite small, in accordance with the interpretation that coordinate bonds must be broken in converting the 1 : 1 to the 2 : 1 chelate.

The protonation constants of the Ca(II) and Mg(II) chelates listed in Table I indicate that the usual relationships governing relative stabilities of protonated chelate compounds (a form of polynuclear chelate) do not seem to apply to chelates of TTHA. Thus the much stronger interactions of the transition metal ions with the ligand, compared to the interactions of the alkaline earths, do not result in the expected decrease in the residual proton affinity of the uncoordinated groups of the ligand. Although the reasons for detailed variations in the proton association constants are not apparent from the limited data available, the lack of a marked difference in behavior of the transition and alkaline earth chelates must be due to the presence of remote donor sites on the ligand that are only slightly (or not at all) influenced by the single coordinated metal ion.

A comparison of the Co(II), Ni(II), and Cu(II) chelates of the series EDTA, DTPA, and TTHA, given in Table II, shows interesting trends that may be rationalized on the basis of the coordination numbers of the metal ions. Thus as the number of coordinating groups of the ligand increases, the stabilities of the Co(II) chelates continue to increase. In the case of Cu(II) and Ni(II), however, the stability constant reaches a maximum with DTPA and decreases with TTHA. This difference in behavior must be due to the lower coordination number of the Cu(*II*) ion, and its consequently lesser ability to take advantage of the presence of larger numbers of electron donor groups of the ligand. In the case of Ni(II), there may also be some tendency of the metal ion toward tetragonal bonding with its stronger coordination tendencies directed toward the corners of a square. The increasing trend observed for Co(II) cannot be easily rationalized. Further understanding of the stabilities of these metal chelates will require measurement of heats and entropies of reaction.

Table II. Formation Constants of EDTA and DTPA Chelates of Transition Metal Ions (μ = 0.10 (KNO_3), 25°)

Ligand (L)	Log K_{ML}		
	Cu^{2+}	Ni^{2+}	Co^{2+}
EDTA[a,b]	18.8	18.6	16.2
DTPA[c]	21.1	20.2	18.4
TTHA	20.3	18.8	20.6

[a] μ = 0.10 (KCl), 20°. [b] G. Schwarzenbach, R. Gut, and G. Anderegg, *Helv. Chim. Acta*, **76**, 358 (1954). [c] S. Chaberek, A. E. Frost, M. A. Doran, and N. J. Bicknell, *J. Inorg. Nucl. Chem.*, **11**, 184 (1959).