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The Formation Constants and Composition of Tetraethylenepentamineheptaacetato Nickel(II) Complexes measured by a Potentiometric Titration Method

Yoshitaka Masuda, Yukiko Hirai, and Eiichi Sekido
Department of Chemistry, Faculty of Science, Kobe University, Nada-ku, Kobe

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Stability constants for nickel(II) complexes of tetraethylenepentamineheptaacetic acid (TPHA: H_7L) were determined by the pH titration method. In an aqueous solution ($\mu=0.1$) three uninuclear complex species, NiH_2L, NiHL, and NiL, and a binuclear compound, Ni_2L seem to exist. The structures of uni- and bi-nuclear chelates are discussed with their visible absorption spectra. Formation of the hydroxo complex was not observed on the titration curves. In the present investigation no evidence was found for species of Ni_2HL either. The formation constants of the complexes stated above have been calculated as follows, (at 25±0.1°C). $\log K_{ML}=16.18$, $\log K_{MHL}=10.00$, $\log K_{MH_2L}=6.16$, $\log K_{M_2L}=17.35$ and $\log K_{ML_2}=27.78$.

Ethylenediaminetetraacetic acid (EDTA) and many related polyaminopolycarboxylic acids form metal complexes which exist over a wide pH range, and have high stability constants. Among them, triethylenetetraminehexaacetic acid (TTHA, H_6L) has been shown as an interesting complexing agent by some workers. Přibil and co-workers[1] studied its analytical usefulness as a titrant for many metal ions. It is noteworthy that the equilibrium of complexation for mono- and diprotonated forms of uni-nuclear chelates have been investigated by Martell and Bohigian.[2] They also reported that there are some differences between the structure of the complex of alkaline-earth metals and that of transition metals. Further, Koryta and Kopanica[3] have undertaken the investigation of the polarographic behavior of cadmium(II)-TTHA complex. They reported that CdH_2L^{2-} species exists over a wide pH range and the logarithm of its formation constant is given as 10.36 at 25°C.

Recently, it has been found further that a new multi-dentate ligand,[4] TPHA (tetraethylenepentamineheptaacetic acid H_7L) forms complexes with many transition metals. However, there are few equilibrium data for this new ligand in the literature. The acid dissociation constants of free TPHA have been first determined by Dyatrova[5] by a potentiometric titration method. Aihara, Kida, and Misumi[6] studied the reactions of the lanthanide(III) ion with TPHA. No stability constant data have been published for the transition metal chelates of this ligand. In this paper, are reported the stability constants of nickel(II)-TPHA complexes determined potentiometrically by a similar method to Bohigian and Martell's[2] and by deriving new equations for calculation.

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[1] R. Pribil and V. Vesely, *Talanta*, **10**, 939 (1962); R. Pribil and V. Vesely, *Talanta*, **11**, 319 (1964).

[2] T. A. Bohigian, Jr., and A. E. Martell, *J. Amer. Chem. Soc.*, **89**, 832 (1967); T. A. Bohigian, Jr., and A. E. Martell, *Inorg. Chem.*, **4**, 1264 (1965).

[3] G. Conradi, M. Kopanica, and J. Koryta, *Collect. Czechoslov. Chem. Commun.*, **30**, 2029 (1965).

[4] I. Murase, T. A. Bohigian, and A. E. Martell, "Preparations of Complexes and Reaction Properties of ligands," ed. by S. Nakahara and M. Shibata, Nankodo, Kyoto (1970), p. 126.

[5] N. M. Dyatrova, Yu. E. Belugin, and V. Ya. Temkima, *Chem. Abstr.*, **62**, 2288c (1965).

[6] S. Misumi, S. Kida, and M. Aihara, *Coord. Chem. Rev.*, **3**, 189 (1968); S. Misumi *Nippon Kagaku Zasshi*, **89**, 723 (1968).

Experimental

Hitachi-Horiba model P pH meter fitted with extension glass and calomel electrode was calibrated with standard buffer solutions of pH 4.10 and 7.00. Actual hydrogen ion concentration was determined on the basis of the data tabulated by Harned and Owen.[7]

Reagent. The chemical formula of synthesized TPHA ligand[4] was given by $C_{33}H_{27}N_5O_{14}\cdot 4HCl\cdot 2H_2O$. The TPHA solution was standardized by the titration with a standard thorium nitrate solution. Standard carbonate-free potassium hydroxide solution was prepared as follows. G. R. potassium hydroxide (7.0 g) and G. R. barium chloride (2 g) were dissolved in demineralized water. The solution was set aside for a few days at ordinary temperature in a 1000 m*l* Erlenmyer flask. Excess of barium chloride in the solution was removed by passing the solution through a column of potassium-type cation exchange resion "Dowex 50-X12" (100—200 mesh). The resulting carbonate free potassium hydroxide solution was stored in a polyethylene bottle and protected from the atmosphere by a soda lime tube.

The potassium hydroxide solution was standardized by potentiometric titration with potassium phthalate solution. The solution of nickel nitrate was standardized titrimetrically by the EDTA procedure,[8] and was stored under pure nitrogen gas. Potassium nitrate was used to make the ionic strength to 0.1. Demineralized water free from carbonate was used in all the titrations.

Procedure. The experimental method consists of potentiometric titration of the hepta basic acid, TPHA, with potassium hydroxide solution in the absence and the presence of the nickel(II) ion at 1:1, 2:1, 1:2, and 3:1 molar ratios of metal ion to ligand. All titrations were carried out in a double walled glass titration cell of 200 m*l* capacity. The temperature was controlled to 25±0.1°C by circulating water through the double wall cell and the ionic strength of the solution were maintained constant at 0.10. Nitrogen free from carbon dioxide was continuously passed through the system in the titration cell. After each addition of aliquots of alkali titrant (0.05 m*l*), the solution was stirred with a magnetic stirrer and was allowed to stand for 3 min to attain equilibrium. The titrations were carried out from an initial pH 2.5 to 10.5.

Calculations

The values of the dissociation constants of TPHA (H_7L) obtained by Dyatrova[5] were used in this work, namely, pK_1, 9.95; pK_2, 8.85; pK_3, 5.56; pK_4, 3.82; pK_5, 2.79. The calculations were carried out in the range of a=3—6, where a is the equivalent base added per mole of ligand (above pH 2.9). The influence of pK_6 and pK_7 was not observed at all. The equations can be derived by modifying Martell's.[2] The following equilibria were considered for the calculation of stability constants for the ligand, H_7L and the metal ion, M^{2+}.

$$\mathrm{M} + \mathrm{L} \rightleftharpoons \mathrm{ML} \qquad K_{\mathrm{ML}} = [\mathrm{ML}]/[\mathrm{M}][\mathrm{L}] \tag{1}$$

$$\mathrm{M} + \mathrm{HL} \rightleftharpoons \mathrm{MHL} \qquad K_{\mathrm{MHL}} = [\mathrm{MHL}]/[\mathrm{M}][\mathrm{HL}] \tag{2}$$

$$\mathrm{MHL} \rightleftharpoons \mathrm{ML} + \mathrm{H} \qquad K^{\mathrm{H}}_{\mathrm{MHL}} = [\mathrm{ML}][\mathrm{H}]/[\mathrm{MHL}] \tag{3}$$

$$\mathrm{M} + \mathrm{H_2L} \rightleftharpoons \mathrm{MH_2L} \qquad K_{\mathrm{MH_2L}} = [\mathrm{MH_2L}]/[\mathrm{M}][\mathrm{H_2L}] \tag{4}$$

$$\mathrm{MH_2L} \rightleftharpoons \mathrm{MHL} + \mathrm{H} \qquad K^{\mathrm{H}}_{\mathrm{MH_2L}} = [\mathrm{MHL}][\mathrm{H}]/[\mathrm{MH_2L}] \tag{5}$$

$$\mathrm{M} + \mathrm{H_3L} \rightleftharpoons \mathrm{MH_3L} \qquad K_{\mathrm{MH_3L}} = [\mathrm{MH_3L}]/[\mathrm{M}][\mathrm{H_3L}] \tag{6}$$

$$\mathrm{MH_3L} \rightleftharpoons \mathrm{MH_2L} + \mathrm{H} \qquad K^{\mathrm{H}}_{\mathrm{MH_2L}} = [\mathrm{MH_2L}][\mathrm{H}]/[\mathrm{MH_3L}] \tag{7}$$

Equations describing the total analytical concentration of metal ion (T_{M}), total ligand concentration (T_{L}), and electroneutrality can be written as follows.

$$T_{\mathrm{L}} = \sum_{j=1}^{7}[\mathrm{H}_j\mathrm{L}] + [\mathrm{L}] + [\mathrm{MHL}] + [\mathrm{MH_2L}] \tag{8}$$

$$T_{\mathrm{M}} = [\mathrm{M}] + [\mathrm{MHL}] + [\mathrm{MH_2L}] \tag{9}$$

$$T_{\mathrm{H}} = (7-a)T_{\mathrm{L}} = [\mathrm{H}] - [\mathrm{OH}] + \sum_{j=1}^{7} j[\mathrm{H}_j\mathrm{L}] + [\mathrm{MHL}] + 2[\mathrm{MH_2L}] \tag{10}$$

From Eqs. (2), (3), (4), (5), (8), (9), and (10), Eqs. (11) and (12) are obtained.

$$[\mathrm{H_2L}] = \frac{\{(6-a)T_{\mathrm{L}}-[\mathrm{H}]+[\mathrm{OH}]\}K^{\mathrm{H}}_{\mathrm{MH_2L}}+\{(5-a)T_{\mathrm{L}}-[\mathrm{H}]+[\mathrm{OH}]\}[\mathrm{H}]}{(P-S)K^{\mathrm{H}}_{\mathrm{MH_2L}}+[\mathrm{H}](P-2S)} \tag{11}$$

$$K_{\mathrm{MH_2L}} = \{(6-a)T_{\mathrm{L}}-[\mathrm{H}]+[\mathrm{OH}]-[\mathrm{H_2L}](P-S)\}/[\mathrm{H_2L}]^2\cdot S \tag{12}$$

where

$$P = 2 + K_2{}^{\mathrm{H}}/[\mathrm{H}] + \sum_{i=1}^{5}(i+2)[\mathrm{H}]^i/\prod_{z=3}^{i+2}K_z{}^{\mathrm{H}}$$

and

$$S = 1 + K_2{}^{\mathrm{H}}/[\mathrm{H}] + K_1{}^{\mathrm{H}}K_2{}^{\mathrm{H}}/[\mathrm{H}]^2 + \sum_{i=1}^{5}[\mathrm{H}]^i/\prod_{z=3}^{i+2}K_z{}^{\mathrm{H}}$$

K^{H}_z may be defined as the zth acid dissociation constant of the TPHA ligand. $K^{\mathrm{H}}_z=[\mathrm{H}_{z-1}\mathrm{L}][\mathrm{H}]/[\mathrm{H}_z\mathrm{L}]$, $z=1, 2,\cdots, 7$.

The calculation of the stability constants of MHL and ML was made by a graphical method. A series of values for p$K^{\mathrm{H}}_{\mathrm{MHL}}$ were assumed and corresponding values for K_{MHL} calculated from the following equations.

$$[\mathrm{HL}] = \frac{[\mathrm{H}]\{(6-a)T_{\mathrm{L}}-[\mathrm{H}]+[\mathrm{OH}]\}+K^{\mathrm{H}}_{\mathrm{MHL}}\{(7-a)T_{\mathrm{L}}-[\mathrm{H}]+[\mathrm{OH}]\}}{[\mathrm{H}](Y-X)+Y\cdot K^{\mathrm{H}}_{\mathrm{MHL}}} \tag{13}$$

$$K_{\mathrm{MHL}} = \{(7-a)T_{\mathrm{L}}-[\mathrm{H}]+[\mathrm{OH}]-[\mathrm{HL}]\cdot Y\}/[\mathrm{HL}]^2X \tag{14}$$

where

$$X = 1 + K_1{}^{\mathrm{H}}/[\mathrm{H}] + \sum_{i=1}^{6}[\mathrm{H}]^i/\prod_{z=2}^{i+1}K_z{}^{\mathrm{H}}$$

and

$$Y = 1 + \sum_{i=1}^{6}(i+1)[\mathrm{H}]^i/\prod_{z=2}^{i+1}K_z{}^{\mathrm{H}}$$

When the resulting values of log K_{MHL} are plotted against the assumed values of p$K^{\mathrm{H}}_{\mathrm{MHL}}$, intersecting lines are obtained. The fact that all the lines obtained from different points on the titration curve intersect at one point indicates the existence of a set of unique values for log K_{MHL} and p$K^{\mathrm{H}}_{\mathrm{MHL}}$, which will satisfy the assumed reaction at any point along the titration curve in a certain range of a values. The values for log K_{ML} are calculated from Eq. (15).

$$K_{\mathrm{ML}} = K^{\mathrm{H}}_{\mathrm{MHL}}\cdot K_{\mathrm{MHL}}/K_1 \tag{15}$$

where K_1 is the first acid dissociation constant of the

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7) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solution," Reinhold, New York (1958), pp. 634, 712.

8) K. Ueno, "Chelatometric Titration" (reprinted 12), Nankodo, Kyoto, (1967), p. 287.

ligand TPHA. The value of K_{MHL} is obtained in the same fashion on the process of the log K_{ML}. In a similar fashion, equations for the stability constant of the triprotonated TPHA complex can be obtained. The following equations for stability constant of the binuclear chelate compounds are derived.

$$[\mathrm{L}] = \{(7-a)T_{\mathrm{L}} - [\mathrm{H}] + [\mathrm{OH}]\}/Y' \tag{16}$$

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

where

$$X' = 1 + \sum_{i=1}^{7}[\mathrm{H}]^i/\prod_{z=1}^{i}K_z^{\mathrm{H}}$$

and

$$Y' = \sum_{i=1}^{7}i[\mathrm{H}]^i/\prod_{z=1}^{i}K_z^{\mathrm{H}}$$

To calculate the formation constants of hydroxo complexes, the average number of hydroxide ions bound to the metal ion is described by

$$\bar{n}_{\mathrm{OH}} = \frac{T_{\mathrm{OH}} - [\mathrm{OH}]}{T_{\mathrm{M}}} = \frac{[\mathrm{M(OH)L}] + 2[\mathrm{M(OH)_2L}]}{[\mathrm{ML}] + [\mathrm{M(OH)L}] + [\mathrm{M(OH)_2L}]} \tag{18}$$

T_{OH} represents concentration of the hydroxide ion added to any point along the titration curve. The relationship between $\bar{n}_{\mathrm{OH}}$ and [OH] was equivalent to that between $\bar{n}_{\mathrm{L}}$ and the free ligand concentration [L].[9] From a plot of $\bar{n}_{\mathrm{OH}}$ *vs.* pOH, the formation constant of mono hydroxide complex was calculated as first approximation ($\bar{n}_{\mathrm{OH}}=0.5$).

The extent of 1:2 chelate formation can be characterized by the complex formation function or the average co-ordination number introduced by Bjerrum.

$$\bar{n}_{\mathrm{L}} = \frac{[\mathrm{ML}] + 2[\mathrm{ML_2}]}{[\mathrm{M}] + [\mathrm{ML}] + [\mathrm{ML_2}]} = \frac{K_{\mathrm{ML}}[\mathrm{L}] + 2K_{\mathrm{ML_2}}[\mathrm{L}]^2}{1 + K_{\mathrm{ML}}[\mathrm{L}] + K_{\mathrm{ML_2}}[\mathrm{L}]^2} \tag{19}$$

[L] can be obtained by Eq. (16).

From some points along the titration curve, the values for $\bar{n}_{\mathrm{L}}$ are plotted against [L]. log K_{ML} and log $K_{\mathrm{ML_2}}$ may be determined from values of pL at $\bar{n}_{\mathrm{L}}$ values of 0.5 and 1.5 on the plot of $\bar{n}_{\mathrm{L}}$ *vs.* pL.

Results and Discussion

Potentiometric pH Curves. The potentiometric titration curves of TPHA and of mixtures of nickel(II) and TPHA (1:2, 1:1, 2:1, and 3:1) are shown in Fig. 1. The titration curve of the acid (TPHA) points out two steps, that is, it appears as a well-defined inflextion at a between 4 and 5 involving the dissociation of the acid species, H_3L and H_2L and as a less distinction inflextion at a above 5 involving the dissociation of HL acid species. It is seen that this small inflextion is due to the least mutual electrostatic repulsion between the protonated amino groups. A 1:1 mixture of nickel(II) and acid (TPHA) exhibits a well-defined inflextion at $a=5.75$, whereas a 2:1 mixture shows one steep inflextion at $a=6.75$. In the case of a 1:1 mixture of nickel(II) and TPHA, inflextion is not seen exactly at $a=5$, $a=6$, and $a=7$. Although an explanation for this fact is not found, it may be suggested that sites of nickel(II) are not saturated for arrangement of TPHA ligand. The titration curve of 3:1 mixture of nickel(II) and TPHA is similar to the 2:1 curve up to $a=6.75$. This shows that metal ions more than two can't be bound to one TPHA molecule. Further addition of potassium hydroxide results in the formation of nickel hydroxide. The buffer region for $a>6.75$ is consistent with the pH region where the nickel(II) hydroxide is precipitated. This was checked by separate titrations of the corresponding nickel nitrate solutions in absence of TPHA.

The 1:1 curve indicates the formation of a protonated nickel chelate below $a=4.5$ and the formation of the hydroxo complex was not observed on those curves. These experiments indicate the presence of the complexes; MH_3L, MH_2L, MHL, ML, M_2L, and ML_2. From the knick of the titration curves at $a=4$, the following reaction is considered.

$$\mathrm{Ni^{2+} + H_7L + 4OH^- \rightleftharpoons NiH_3L + 4H_2O}$$

At $a=5$ and $a=6$, the following reactions take place.

$$\mathrm{Ni^{2+} + H_7L + 5OH^- \rightleftharpoons NiH_2L + 5H_2O}$$

$$\mathrm{Ni^{2+} + H_7L + 6OH^- \rightleftharpoons NiHL + 6H_2O}$$

Above $a=6$, the following reaction takes place.

$$\mathrm{NiHL + OH^- \rightleftharpoons NiL + H_2O}$$

In the 2:1 mixtures a binuclear complex is obviously predominant:

$$\mathrm{2Ni^{2+} + H_7L + 7OH^- \rightleftharpoons Ni_2L + 7H_2O}$$

The Ionization of TPHA. Figure 2 shows the percentage of variously dissociated forms of the ligand, TPHA, at various pH's. The percentages have been calculated from Eq. (20) and by using Dyatrova's data of the dissociation constants[5] of TPHA. It has been assumed that pK_7 and pK_6 should be 2.0 and 2.5, respectively.

$$T_{\mathrm{L}} = [\mathrm{H_7L}] + [\mathrm{H_6L}] + [\mathrm{H_5L}] + [\mathrm{H_4L}] + [\mathrm{H_3L}] + [\mathrm{H_2L}] + [\mathrm{HL}] + [\mathrm{L}] \tag{20}$$

For the sake of simplicity for calculation, a parameter D was introduced (Eq. (21)).

$$D = [\mathrm{H}]^7/\alpha_7 + [\mathrm{H}]^6/\alpha_6 + [\mathrm{H}]^5/\alpha_5 + [\mathrm{H}]^4/\alpha_4 + [\mathrm{H}]^3/\alpha_3 + [\mathrm{H}]^2/\alpha_2 + [\mathrm{H}]/\alpha_1 + 1 \tag{21}$$

which α's indicate dissociation constants of TPHA ligand. Each of the distribution ratio may be represented by Eq. (22).

$$\begin{aligned} &[\mathrm{L}]/T_{\mathrm{L}} = 1/D && [\mathrm{HL}]/T_{\mathrm{L}} = [\mathrm{H}]/D\alpha_1 \\ &[\mathrm{H_2L}]/T_{\mathrm{L}} = [\mathrm{H}]^2/D\alpha_2 && [\mathrm{H_3L}]/T_{\mathrm{L}} = [\mathrm{H}]^3/D\alpha_3 \\ &[\mathrm{H_4L}]/T_{\mathrm{L}} = [\mathrm{H}]^4/D\alpha_4 && [\mathrm{H_5L}]/T_{\mathrm{L}} = [\mathrm{H}]^5/D\alpha_5 \\ &[\mathrm{H_6L}]/T_{\mathrm{L}} = [\mathrm{H}]^6/D\alpha_6 && [\mathrm{H_7L}]/T_{\mathrm{L}} = [\mathrm{H}]^7/D\alpha_7 \end{aligned} \tag{22}$$

Below pH 3 three species, H_7L, H_6L, and H_5L are present in the solution in the absence of metal ions. In the range of pH 3.0 to 4.0, H_4L species is obviously predominant and in the range of pH 3.8 to 5.5, H_3L species is predominant. The percentage of H_2L species attained maximum value, 96% at the pH 7.0. The H_2L and HL species exist over the wide range from 4.5 to 9.8 and from 7.0 to 10.0 respectively. At pH≥ 8.0, the percentage of the L species increased with increasing pH. In this range of pH, TPHA acts as a

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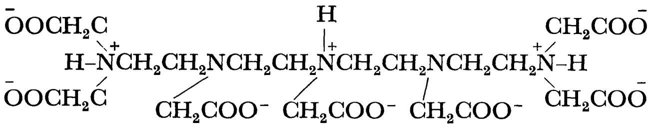
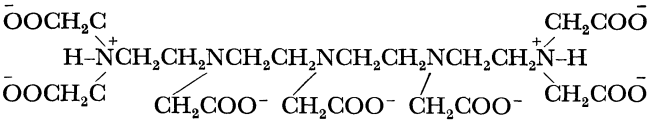
[9] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," E. Christensen, 2nd ed., P. Hasse and Son, Copenhagen (1957), p. 123.

diprotic acid. According to the diagram previously described, the species H_3L and H_2L, exist in a wide pH range. From infrared studies with respect to the structures of EDTA and DTPA,[10] the structures of the species, H_3L and H_2L will be inferred as follows.



H_3L



H_2L

Graphical Solution for Stepwise Equilibrium Constants, K_{MHL} and $pK^{\mathrm{H}}_{\mathrm{MHL}}$, K_{MHL} and $pK^{\mathrm{H}}_{\mathrm{MH_2L}}$. The resulting values of log K_{MHL} were plotted against the assumed values of $pK^{\mathrm{H}}_{\mathrm{MHL}}$ to give the intersecting curves shown in Fig. 3. (refer to Eqs. (13) and (14)). All curves obtained from the different points on one titration curve for the 1:1 Ni(II)-TPHA system intersect at one point, as shown in Fig. 3. This fact indicates the existence of a set of unique values for K_{MHL} and $pK^{\mathrm{H}}_{\mathrm{MHL}}$. The values for log$K_{\mathrm{MHL}}$ and $pK^{\mathrm{H}}_{\mathrm{MHL}}$ are found to be 9.90_0 and 3.77_5, respectively.

In a similar fashion the value of log $K_{\mathrm{MH_2L}}$ was also determined (refer to Eqs. (11) and (12)). From the graphical determination of $pK^{\mathrm{H}}_{\mathrm{MH_2L}}$ and log $K_{\mathrm{MH_2L}}$, intersection of the resulting curves gives the values of

TABLE 1. STABILITY CONSTANTS OF NICKEL-TPHA COMPLEXES AT 25°C, $\mu=0.1$

Complex	Value	
ML	log K_{ML}	16.18
MHL	log K_{MHL}	10.00 (±0.03)
MH_2L	log $K_{\mathrm{MH_2L}}$	6.16 (±0.10)
MH_3L	log $K_{\mathrm{MH_3L}}$	5.26
M_2L	log $K_{\mathrm{M_2L}}$	17.35
ML_2	log $K_{\mathrm{ML_2}}$	27.78 (11.6)[a]

[a] The second consecutive formation constant.

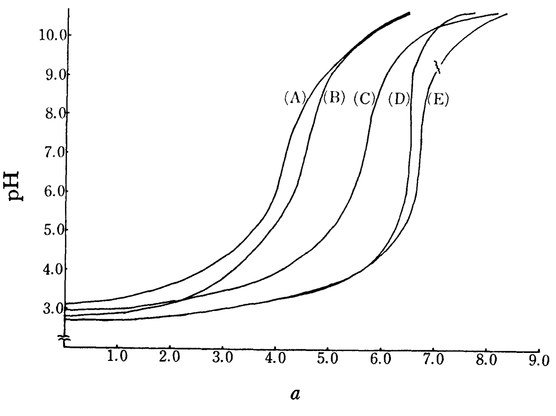


Fig. 1. Titration curves of 5×10^{-4}M TPHA(A) and 1:2(B) 1:1(C), 2:1(D), and 3:1(E) mixtures of Ni(II) and TPHA.

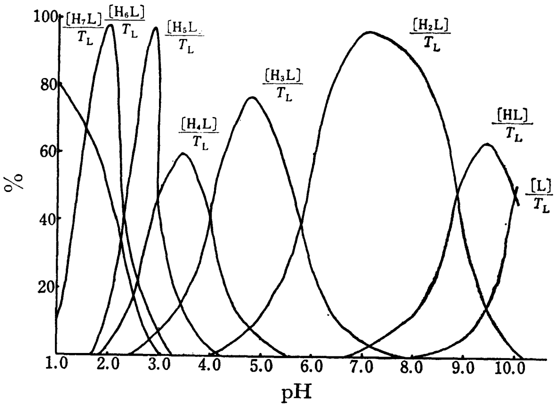


Fig. 2. Distribution diagram for the species of TPHA not containing metal.
The percentages are relation to total ligand.

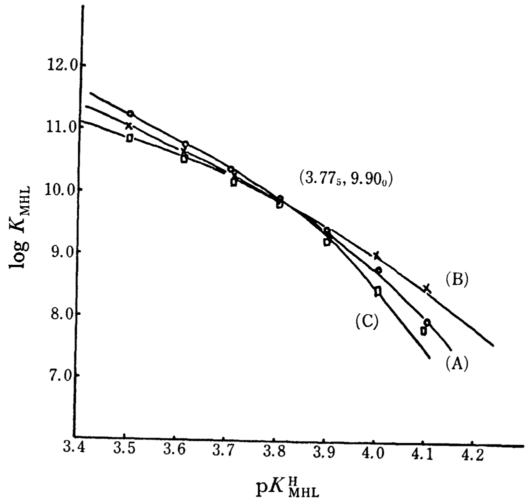


Fig. 3. Plots of log K_{MHL} *vs.* $pK^{\mathrm{H}}_{\mathrm{MHL}}$ for 1:1 nickel chelates of TPHA.
a=3.7(A), a=3.9(B), a=4.1(C)

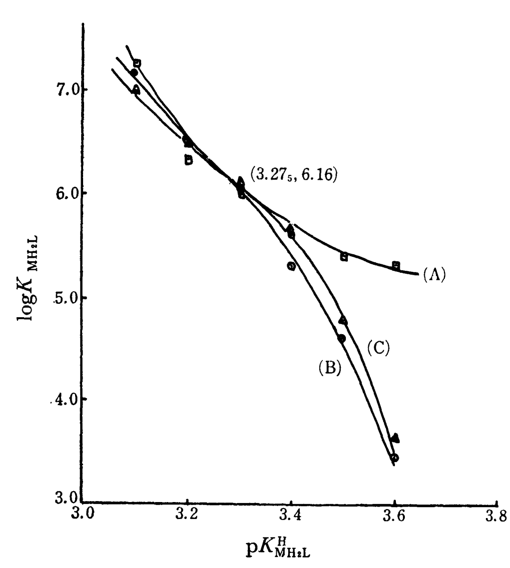


Fig. 4. Plots of log $K_{\mathrm{MH_2L}}$ *vs.* $pK^{\mathrm{H}}_{\mathrm{MH_2L}}$ for 1:1 nickel chelates of TPHA.
a=3.1(A), a=3.0(B), a=2.9(C)

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[10] K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Amer. Chem. Soc.*, **85**, 309 (1963).

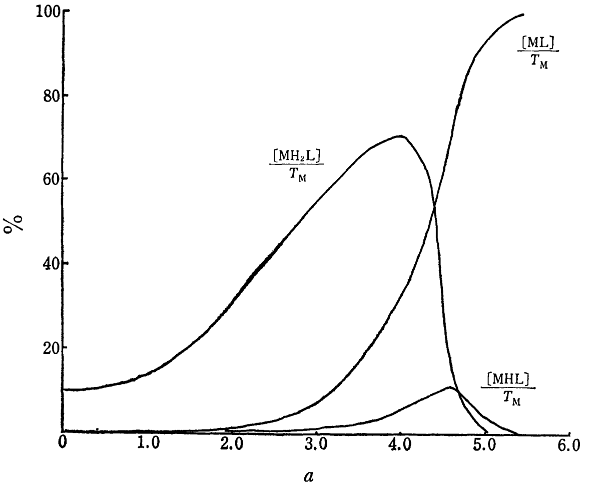


Fig 5. Distribution diagram of NiH_2L (1), NiHL (2), and NiL (3) drawn as a function of a for a 1:1 mixture of nickel(II) and TPHA (5×10^{-4} mol).
The percentages are relative to total metal.

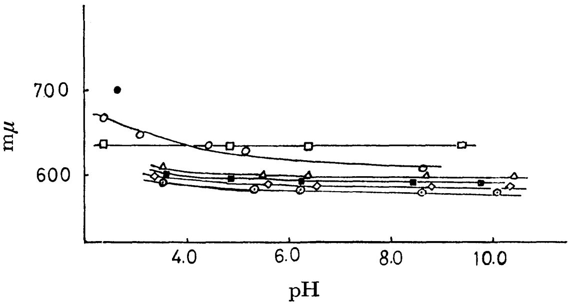


Fig. 6. Displacement of absorption maximum of nickel(II)-polyaminocarboxylic acid chelates (1:1) as a function of pH. polyaminocarboxylic acid; (□) NTA, (○) IDA, (△) EDTA, (■) TPHA, (◇) TTHA, (⊙) DTPA.
(●) nickel(II) perchlorate solution.

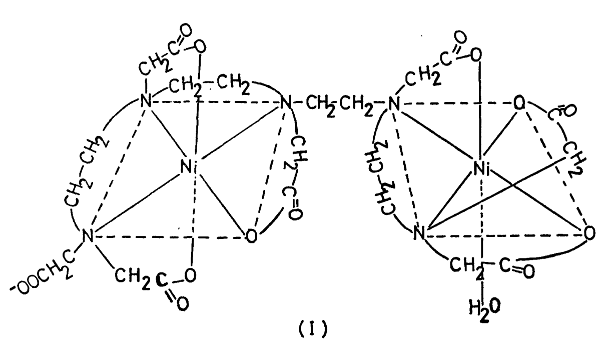
the equilibrium constants. For nickel(II), the values, $pK^{H}_{MH_2L}=3.275$ and $\log K_{MH_2L}=6.16$ were found (see Fig. 4). The value, $\log K_{MH_2L}=5.40$ calculated by using Eqs. (21) and (20) was less than the value of graphical solution. The disagreement between calculated and graphical solutions is due to the presence of species other than MH_2L and MHL complexes assumed for stepwise equilibrium constants. The value of $\log K_{MH_3L}$, 5.26 on the limiting range of pH measurement (3.0) was obtained.

Stability Constants of log K_{M_2L} and log K_{ML_2}. The stability constants of the complexes were calculated as described above (refer to Eqs. (16) to (17) and to Eq. (19)). The results are also given in Table 1.

The Percentages of the Species. Nickel(II) and TPHA form a normal and protonated complexes as described above. In Fig. 5. the percentages of the species, MH_2L, MHL, and ML in the solution of 1:1 mixtures of nickel(II) and the ligand, TPHA, are plotted as a function of a. Figure 5 clearly demonstrates the difference in the stabilities of MH_2L, MHL, and ML. It was shown that the MH_2L complex is present in the range between $a=1.0$ and $a=5.0$. The percentage of this species has a maximum value (70%) at $a=3.8$, while the MHL species is present from $a=2.0$ to $a=5.5$, although a maximum value at $a=4.6$ is only 11 pecent. However, the ML species predominated at $a \geq 5.0$. An intersecting point of lines representing the species MH_2L and ML was observed at $a=4.4$. A similar behaviour is indicated for lines representing the species MHL, and MH_2L, too. Below $a=3$, the species other than MHL, MH_2L, and ML, such as triprotonated species, also exists. In the present investigation no evidence was found for species of M_2HL and ML(OH).

Stability Constants and the Structures of Nickel(II)-TPHA Complexes. The stability constants of the uninuclear nickel(II)-complexes with EDTA, DTPA, and TTHA were reported by several authors.[2,11,12] Table 1 shows the stability constants of nickel(II) complexes with TPHA. The stability constant of the 1:1 nickel(II)-TPHA normal complex is lower than the corresponding constants of the EDTA, DTPA, and TTHA chelates by 2—3 logarithmic units. The chelate effect of 1:1 nickel(II)-TPHA complex may be lowered by the following reasons: 1) the presence of a number of ligand atoms which do not bind to nickel(II), 2) the steric forces of some kinds, that is, steric strain, and 3) diminution of the degree of freedom in molecular rotation of the ligand molecules by chelation.

The stability constants of di- and mono-protonated complex are also calculated (refer to Table 1). As nickel(II) has the co-ordination number of six in spite of TPHA having twelve open positions for the co-ordination, polynuclear chelates may be formed. It is found that TPHA ligand does not bind to metals more than two and that binuclear hydrogen or hydroxo complex does not exist as the results of potentiometric titration under the given condition. The normal binuclear complex is more stable than uninuclear one. Possible structure of M_2L is indicated as follows. This fact may be explained in terms of binding of the functional donor groups in TPHA ligand inlayed with sites of two nickel(II) in the binuclear complex.



(I)

Six donor groups combined with nickel(II) are arranged in an octahedral configuration. Nickel(II)-TPHA complex can involve carboxylate and nitrogen donors combination, which satisfy co-ordination sites of nickel(II). In the extreme case, three different arrangements for the normal uninuclear complex are

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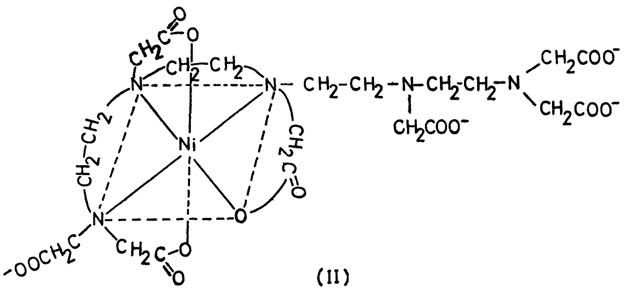
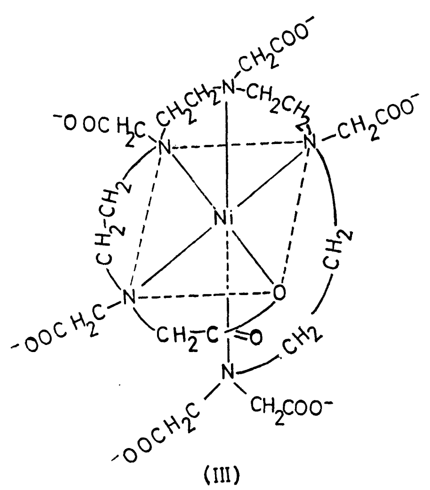
11) G. Schwarzenbach, R. Gut, and G. Anderegg, *Helv. Chim. Acta*, **76**, 358 (1954).

12) S. Chaberek, A. E. Frost, M. A. Doran, and N. J. Bicknell, *J. Inorg. Nucl. Chem.*, **11**, 184 (1959).

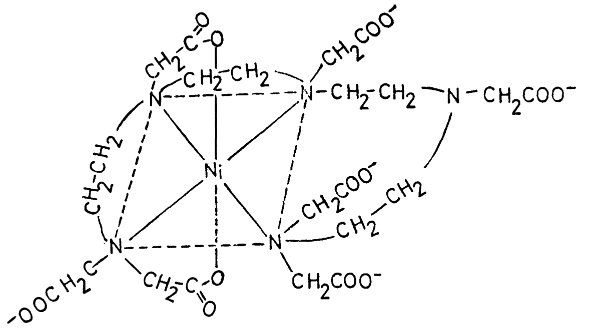
considered as formulae II, III, and IV. In formula II, nickel(II) is co-ordinated with three nitrogen and three carboxylate donors, in formula III with five nitrogen donors and in formula IV with three nitrogen atoms and remote nitrogen donor having the high basicity.



(II)



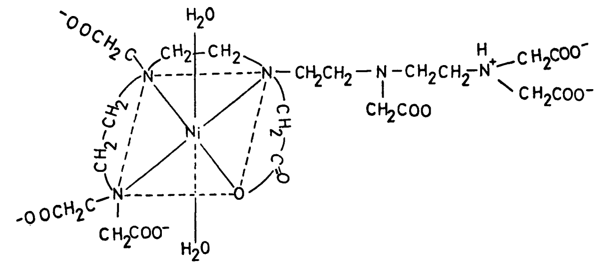
(III)



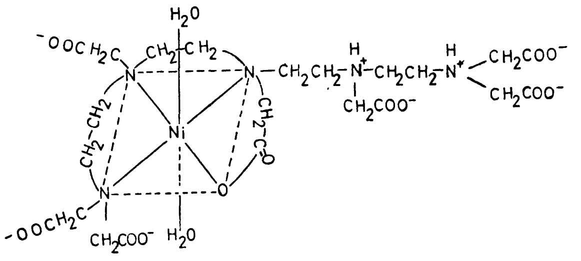
(IV)

A comparison of the visible absorption spectra of nickel(II)-polyaminocarboxylic acid complexes shows that the maxima are shifted to shorter wavelength as the number of co-ordinated nitrogen atoms increases. This fact suggests that the ligand field effect becomes powerful as the number of co-ordinated nitrogen atoms increases. However, for the nickel(II)-TPHA complex, the shift of the absorption maximum to shorter wavelength is smaller than for the DTPA complex with a rearrangment of donor groups involving three nitrogens and three caboxylate groups. It may be considered that the structure (II) is most probable one and is consistent with the reason mentioned before. On account of the ligand field strength and potential basicity of nitrogen atom of remote terminal amino group, the structure (IV) may be also present.

The following structures for mono- and diprotonated complexes may be suggested. More probable arrangements would involve co-ordination of metal ion by three nitrogen atoms and one carboxylate donor group, and un-co-ordinated groups exist in the structure as a terminal nitrogen atom remaining a proton and as carboxylate ion (refer to V and VI).



(V)



(VI)

Details concerning both the lack of a marked difference in behavior of the transition metal complexes and general validity of the Irving-William order will be reported in subsequent papers.

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