# Nickel(II), Copper(II) and Zinc(II) Complexes of 1,1,1-Tris(aminomethyl)propane. A Calculation Procedure of Stepwise Formation Constants and Their Standard Errors from the Values Obtained for the Cumulative Equilibria

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*The reactions of $CH_3CH_2C(CH_2NH_2)_3$ (tamp) with $H^+$, $Ni^{2+}$, $Cu^{2+}$ and $Zn^{2+}$ have been investigated at 298 K in aqueous solution (0.5 M $KNO_3$) using potentiometric techniques. The protonation constants have been determined and compared with those previously reported for similar triamines. The transition metal ions are able to form a large number of complexes with tamp, where the metal/ligand ratio is 1:1 or 1:2. The stability constants of the complexes have been calculated using a modified version of the program MINIQUAD. The equilibrium constants pertaining to stepwise equilibria were obtained by combining the cumulative constants: the errors associated with the stepwise constants have been calculated taking into account the standard deviations of the constants, which have been combined, and their correlation coefficients.*

## Introduction

The 1,1,1-tris(aminomethyl)alkalanes of general formula:
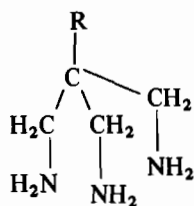


are tripod ligands which have been studied both by examining metal complex formation in solution [1–3] and by isolating and characterizing solid metal complexes [1, 4]. The results from these types of investigation appear to be contradictory: whilst the presence in aqueous solution of complex ions having metal/ligand ratios of 1:2 has not been verified, such complexes are the only ones to be isolated in the solid state. This fact led us to carry out a more extensive investigation of the complex formation equilibria in aqueous solution between the nickel(II), copper(II)

and zinc(II) ions and 1,1,1,-tris(aminomethyl)ethane (tame) adopting various metal/ligand ratios. The results of this study which identified the chemical model for the equilibria studied have already been published elsewhere [5]. The problem of the selection of species was solved by means of the computer program MINIQUAD using statistical criteria based on the agreement factor R and on the evaluation of the extent to which the distribution of residuals is normal [5–7].

The present work is concerned with the triamine 1,1,1-tris(aminomethyl)propane (tamp), where an ethyl group replaces the methyl group in the previously investigated ligand tame. Comparing the basicity and metal formation constants for the two ligands, it will be possible to ascertain the influence of the different apical substitution.

In the present work we have examined the relative stability of various metal complexes of both ligands with the aim of obtaining information about their structure and also about the coordinating ability of the ligands. In a study of this kind it is customary to compare the constants for different types of equilibria of formation. We present a correct method for obtaining the errors associated with the constants for these different equilibria from the values for the cumulative equilibria found in the calculation.

## Experimental

### Preparation of the Ligand

Tamp·3HCl was prepared as follows: 1,1,1-tris(chloromethyl)propane was prepared in 80% yield by the reaction of 1,1,1-tris(hydroxymethyl)propane with $SOCl_2$ in pyridine.

8.7 g of 1,1,1-tris(chloromethyl)propane were mixed with 100 ml of concentrated aqueous ammonia solution in which 1.5 g of NaI had previously been dissolved. The reaction mixture was placed in an autoclave, heated at 150 °C for two days with stirring, the cooled reaction mixture was then concentrated under reduced pressure to a thick paste. 10 g

of KOH were added to the cooled reaction mixture and the product was extracted by refluxing three times with 50 ml of benzene for two hours each time. The benzene solution was dried over KOH and then shaken with three 40 ml portions of HCl.

The combined solution was decolourised with animal charcoal and evaporated to the point of crystallisation and 100 ml of hot methanol were added to this solution. The white precipitate was filtered and washed with aqueous methanol. The solid was dried over silica gel under vacuum (35% yield). *Anal.* Calcd for $C_6H_{20}N_3Cl_3$: C, 29.95; H, 8.38; N, 17.47; Cl, 44.21%. Found: C, 30.39; H, 8.35; N, 18.03; Cl, 43.89%.

### Materials

A concentrated solution of NaOH (50%) was prepared and allowed to stand for three weeks. The clear supernatant liquid was siphoned off and suitably diluted in order to obtain about 0.3 $M$ $CO_2$-free solutions of NaOH. These solutions were kept in polythene bottles provided with soda-lime guard tubes. The bottles were directly connected to a piston burette. The concentration of these solutions was determined by means of a pH-metric titration against standard HCl solution and was periodically checked using the same method. Inspection of the Gran plots [8] obtained from these titrations allowed the amount of protolytic impurities contained in the solutions to be determined. This had a tendency to increase with time, in spite of the precautions taken to avoid contact with the external atmosphere. When the concentration of impurities exceeded 0.5% of the concentration of NaOH the solution itself was discarded. Aqueous solutions of nickel, copper and zinc chlorides were obtained by dissolving the solid hydrated salts (C. Erba, analytical purity) in water. The concentration of metal ion was determined gravimetrically by standard methods. Commercial potassium nitrate (C. Erba) was recrystallised several times from water. Gran plots obtained from strong acid–strong base titrations in 0.5 $M$ solutions of this salt showed that three recrystallisations were necessary to obtain a sufficiently pure product. A 0.5 $M$ stock solution of $KNO_3$ purified in this way was prepared and used as the ionic medium for emf measurements.

### Emf Measurements

The potentiometric titrations were carried out using an Orion model 801 digital pH/mV meter, an Orion 91-01 glass electrode, a 0.5 $M$ silver/silver chloride electrode and a salt bridge containing 0.5 $M$ $KNO_3$ solution. The titration vessel used was a seven-necked 150 ml flask. The solution in the vessel was stirred continuously by means of a magnetic stirrer. A stream of nitrogen, presaturated with water vapour by bubbling it through a 0.5 $M$ $KNO_3$ solution, was passed over the surface of the solution. The

entire cell was thermostatted at 25.0 ± 0.1 °C. For the determination of the basicity constants of tamp the cell was filled with about 100 ml of 0.5 $M$ $KNO_3$ containing 0.14–0.24 mmol of tamp·3HCl and *ca.* 0.15 mmol HCl in excess. For the complex formation experiments the solution also contained varying quantities of the appropriate metal chlorides. For the titrations the NaOH solution was dispensed from a Metrohm Multidosimat piston burette graduated to a hundreth of a milliliter. Equilibrium was reached almost instantaneously in all the systems. The experimental values of the emf have not been corrected for the liquid junction potential or for the potential drift of the electrode during the measurements. Preliminary acid–base titrations carried out under the same experimental conditions showed that the corrections due to the above effects are negligible in the pH range investigated.

The ionic product of water was determined in 0.5 $M$ $KNO_3$ at 25 °C. The value found ($pK_w = 13.74$) is in good agreement with that reported previously [9].

The concentration of hydrogen ion was calculated from the experimental emf values E (expressed in mV) by means of the formula:

$$[H^+] = \exp(E - E°)/25.693$$

The standard potential of the cell, $E°$, was calculated for each titration by applying Gran's method to the initial part of the curve where only neutralisation of excess acid is involved. Later Gran plots obtained at the end of the curve were used to check the analytical concentrations of the reagents for internal consistency.

The initial concentrations of the reagents and the range of pH explored for each titration curve are shown in Table I*.

### Calculations and Results

The computer program MINIQUAD [7] was used to calculate the equilibrium constants. The criteria adopted in the procedure for selecting the species formed at the equilibrium in the system under investigation have already been reported [5].

The types of cumulative equilibria which were taken into consideration are shown in Table II. This table also shows the symbols which we have used in the text and in later tables for the cumulative equilibrium constants considered and for the standard deviations of the logarithms of these constants.

The standard output of the program MINIQUAD furnishes, as a result of the least squares refinement, the values of the cumulative formation constants, their logarithms to the base 10, the standard deviations of these latter quantities and the matrix of the

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*See paragraph at the end of the paper regarding supplementary material.

TABLE I. Experimental Details of the Emf Measurements.

| Curve | Ion | Initial Concentrations (mM) | | | pH Range | Number of Data Points |
|---|---|---|---|---|---|---|
| | | MCl$_2$ | Tamp·3HCl | HCl | | |
| 1 | H$^+$ | | 1.801 | 1.900 | 4.9–10.9 | 22 |
| 2 | H$^+$ | | 1.277 | 1.351 | 5.1–10.9 | 28 |
| 3 | H$^+$ | | 2.380 | 2.986 | 4.8–11.1 | 31 |
| 4 | Cu$^{2+}$ | 1.703 | 1.809 | 1.922 | 3.5–7.6 | 19 |
| 5 | Cu$^{2+}$ | 1.434 | 2.757 | 2.925 | 3.4–10.2 | 32 |
| 6 | Cu$^{2+}$ | 0.310 | 1.341 | 1.422 | 3.5–10.2 | 20 |
| 7 | Cu$^{2+}$ | 2.825 | 2.720 | 2.892 | 3.3–7.6 | 23 |
| 8 | Cu$^{2+}$ | 0.300 | 3.650 | 2.751 | 3.4–10.8 | 21 |
| 9 | Ni$^{2+}$ | 2.586 | 2.779 | 2.940 | 3.5–5.6 | 19 |
| 10 | Ni$^{2+}$ | 1.940 | 2.840 | 3.008 | 3.9–7.9 | 29 |
| 11 | Ni$^{2+}$ | 0.657 | 0.952 | 1.008 | 4.5–9.4 | 18 |
| 12 | Ni$^{2+}$ | 0.385 | 1.385 | 1.467 | 3.5–11.0 | 21 |
| 13 | Ni$^{2+}$ | 0.643 | 1.862 | 1.972 | 3.7–11.0 | 26 |
| 14 | Zn$^{2+}$ | 3.616 | 3.716 | 3.935 | 3.7–6.9 | 43 |
| 15 | Zn$^{2+}$ | 2.691 | 5.328 | 5.641 | 3.8–11.0 | 63 |
| 16 | Zn$^{2+}$ | 0.895 | 1.815 | 1.923 | 4.1–10.9 | 23 |
| 17 | Zn$^{2+}$ | 1.758 | 8.705 | 9.210 | 3.6–10.7 | 24 |

TABLE II. Cumulative Formation Equilibria of the Species Present in the System Investigated and Symbols Used for the Equilibrium Constants and for the Standard Deviations of the Logarithms of These Constants[a].

| Equilibrium | Chemical Equation | Equilibrium Constant | Standard Deviation of log $\beta$ |
|---|---|---|---|
| (1) | H$^+$ + L $\rightleftarrows$ HL$^+$ | $\beta_{HL}$ | $\sigma_1$ |
| (2) | 2H$^+$ + L $\rightleftarrows$ H$_2$L$^{2+}$ | $\beta_{H_2L}$ | $\sigma_2$ |
| (3) | 3H$^+$ + L $\rightleftarrows$ H$_3$L$^{3+}$ | $\beta_{H_3L}$ | $\sigma_3$ |
| (4) | H$_2$O $\rightleftarrows$ H$^+$ + OH$^-$ | $\beta_{OH}$ | $\sigma_4$ |
| (5) | M$^{2+}$ + L $\rightleftarrows$ ML$^{2+}$ | $\beta_{ML}$ | $\sigma_5$ |
| (6) | M$^{2+}$ + 2L $\rightleftarrows$ ML$_2^{2+}$ | $\beta_{ML_2}$ | $\sigma_6$ |
| (7) | M$^{2+}$ + H$^+$ + L $\rightleftarrows$ MHL$^{3+}$ | $\beta_{MHL}$ | $\sigma_7$ |
| (8) | M$^{2+}$ + H$^+$ + 2L $\rightleftarrows$ MHL$_2^{3+}$ | $\beta_{MHL_2}$ | $\sigma_8$ |
| (9) | M$^{2+}$ + 2H$^+$ + 2L $\rightleftarrows$ MH$_2$L$_2^{4+}$ | $\beta_{MH_2L_2}$ | $\sigma_9$ |
| (10) | M$^{2+}$ + L + H$_2$O $\rightleftarrows$ M(OH)L$^+$ + H$^+$ | $\beta_{M(OH)L}$ | $\sigma_{10}$ |
| (11) | M$^{2+}$ + L + 2H$_2$O $\rightleftarrows$ M(OH)$_2$L + 2H$^+$ | $\beta_{M(OH)_2L}$ | $\sigma_{11}$ |

[a]M = metal, L = tamp.

correlation coefficients between the logarithms of the constants. For example, the results of the refinement of the ligand protonation constants, obtained from curves 1, 2, and 3 of Table I, are shown in Table III. In order to interpret and discuss the values of the equilibrium constants it is worthwhile examining appropriately chosen values pertaining to specific equilibria obtained by combining cumulative formation equilibria. The logarithms of the constants of these specific equilibria can be found by linear combination of the logarithms of the cumulative

constants. For example, the chemical equation for the stepwise equilibrium

$$H^+ + HL^+ \rightleftharpoons H_2L^{2+}$$
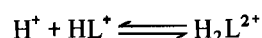
is found by subtracting equation (1) from equation (2) of Table II. The logarithm of the constant $K$ is given by

$$\log K = \log \beta_{H_2L} - \log \beta_{HL}$$

The error associated with log $K$ is obtained from the errors $\sigma_1$ and $\sigma_2$, estimated respectively for log $\beta_{HL}$

TABLE III. Logarithms of the Cumulative Formation Constants of the Species not Containing Metal, Their Standard Deviations and Correlation Matrix[a].

| Formation Constant | $\log \beta$ | Correlation Matrix | | | |
|---|---|---|---|---|---|
| $\beta_{HL}$ | $10.2304 \pm 0.0012$ | 1 | 0.47 | 0.27 | 0.70 |
| $\beta_{H_2L}$ | $18.4011 \pm 0.0021$ | | 1 | 0.55 | 0.34 |
| $\beta_{H_3L}$ | $23.9297 \pm 0.0036$ | | | 1 | 0.20 |
| $\beta_{OH}$ | $-13.7424 \pm 0.0005$ | | | | 1 |

[a]For the symbol of the formation constants see Table II. Only the upper triangular part of the square symmetric correlation matrix is reported.

and $\log \beta_{H_2L}$, and from their correlation coefficient $\rho_{1,2}$ *:

$$\sigma = \sqrt{\sigma_1^2 + \sigma_2^2 - 2\rho_{1,2}\,\sigma_1\sigma_2}$$

Using the values reported in Table III, we obtain

$$\sigma = \sqrt{0.0012^2 + 0.0021^2 - 2\cdot0.47\cdot0.0012\cdot0.0021}$$
$$= 0.0019$$

In the case of the correlation coefficient not being known, the value of $\sigma$ is usually obtained by simply summing the two standard deviations:

$$\sigma = \sigma_1 + \sigma_2 = 0.0012 + 0.0021 = 0.0033$$

This value is greater than the value obtained with the previous formula and, consequently, can be considered as a pessimistic estimate of the error. It is well known that correlation coefficients must lie within the range of $-1$ to $+1$ [10]; only if $\rho_{1,2}$ were equal to $-1$, would the values of $\sigma$ calculated using the two different formulae be coincident. Another method commonly followed in this type of calculation implies the formula

$$\sigma = \sqrt{\sigma_1^2 + \sigma_2^2} = \sqrt{0.0012 + 0.0021} = 0.0024$$

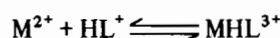where the correlation coefficient is assumed equal to zero or, in other words, the two parameters are assumed not to be linearly correlated**.

The constant for the equilibrium

$$M^{2+} + HL^+ \rightleftharpoons MHL^{3+}$$

is found by combining the cumulative constants $\beta_{MHL}$ and $\beta_{HL}$ defined in Table II

$$\log K = \log \beta_{MHL} - \log \beta_{HL}$$

The error $\sigma$ associated with this $\log K$ is given by

$$\sigma = \sqrt{\sigma_7^2 + \sigma_1^2 - 2\rho_{1,7}\sigma_1\sigma_7}$$

where $\sigma_7$ and $\sigma_1$ are the standard deviations defined in Table II and $\rho_{1,7}$ is the correlation coefficient between $\log \beta_{MHL}$ and $\log \beta_{HL}$.

When the equilibrium being considered is obtained by combining more than two cumulative equilibria, as in

$$ML^{2+} + HL^+ \rightleftharpoons MHL_2^{3+}$$
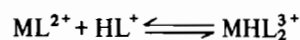
obtained by combining equations (1), (5) and (8) of Table II, we have

$$\log K = \log \beta_{MHL_2} - \log \beta_{ML} - \log \beta_{HL}$$

and using the following equation:

$$\sigma = \left( \sigma_8^2 + \sigma_5^2 + \sigma_1^2 - 2\rho_{5,8}\sigma_5\sigma_8 - 2\rho_{1,8}\sigma_1\sigma_8 + 2\rho_{1,5}\sigma_1\sigma_5 \right)^{1/2}$$

the associated error is obtained.

*The general formula for computing the standard deviation associated with a quantity which is obtained by linear combination of parameters, say $ax + by + cz$ is given by

$$\sigma = \left( a^2\sigma_x^2 + b^2\sigma_y^2 + c^2\sigma_z^2 + 2ab\rho_{xy}\sigma_x\sigma_y + 2ac\rho_{xz}\sigma_x\sigma_z + 2bc\rho_{yz}\sigma_y\sigma_z \right)^{1/2}$$

where $\sigma_x$, $\sigma_y$, $\sigma_z$ are the standard deviations of the parameters x, y, z, and $\rho_{xy}, \rho_{xz}, \rho_{yz}$ are the corresponding correlation coefficients. See, for example, W. C. Hamilton, "Statistics in Physical Sciences", The Ronald Press, New York (1964) p. 31.

**The knowledge of the correlation coefficients is an important point for a correct estimate of the standard deviation of quantities obtained by combining the least squares parameters. If the correlation coefficients are not available, the standard deviation of the new quantities usually is approximated either by the sum of standard deviations of the parameters involved in the linear combination, or by the square root of the sum of the squares of the same values. The first method leads obviously to a pessimistic estimate of the error, whilst the other method implies the assumption that the parameters are not correlated: the value obtained by this way can be greater or lower than the true value, depending on the contribution of the correlation terms.

TABLE IV. Logarithms of the Cumulative Formation Constants of the Species Present in the System Nickel(II)–Tamp, Their Standard Deviations and Correlation Matrix[a].

| Formation Constant | log $\beta$ | Correlation Matrix | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $\beta_{HL}$ | 10.2336 ± 0.0020 | 1 | 0.43 | 0.28 | 0.63 | 0.27 | 0.25 | 0.08 | 0.05 |
| $\beta_{H_2L}$ | 18.4034 ± 0.0037 | | 1 | 0.61 | 0.29 | 0.59 | 0.56 | 0.16 | 0.12 |
| $\beta_{H_3L}$ | 23.9221 ± 0.0058 | | | 1 | 0.18 | 0.93 | 0.71 | 0.63 | 0.27 |
| $\beta_{OH}$ | −13.7401 ± 0.0007 | | | | 1 | 0.18 | 0.16 | 0.05 | 0.03 |
| $\beta_{ML}$ | 10.468 ± 0.006 | | | | | 1 | 0.66 | 0.45 | 0.08 |
| $\beta_{ML_2}$ | 17.973 ± 0.013 | | | | | | 1 | 0.47 | 0.38 |
| $\beta_{MHL}$ | 15.378 ± 0.021 | | | | | | | 1 | 0.42 |
| $\beta_{MHL_2}$ | 24.316 ± 0.067 | | | | | | | | 1 |

[a]For the symbol of the formation constants see Table II. Only the upper triangular part of the square symmetric correlation matrix is reported.

TABLE V. Logarithms of the Cumulative Formation Constants of the Species Present in the System Copper(II)–Tamp, Their Standard Deviations and Correlation Matrix[a].

| Formation Constant | log $\beta$ | Correlation Matrix | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $\beta_{HL}$ | 10.2326 ± 0.0026 | 1 | 0.46 | 0.27 | 0.68 | 0.17 | 0.18 | 0.25 | 0.21 | 0.21 | 0.12 |
| $\beta_{H_2L}$ | 18.4008 ± 0.0045 | | 1 | 0.56 | 0.33 | 0.34 | 0.39 | 0.51 | 0.41 | 0.42 | 0.25 |
| $\beta_{H_3L}$ | 23.9280 ± 0.0077 | | | 1 | 0.20 | 0.63 | 0.66 | 0.94 | 0.71 | 0.78 | 0.57 |
| $\beta_{OH}$ | −13.7409 ± 0.0010 | | | | 1 | 0.12 | 0.14 | 0.18 | 0.15 | 0.15 | 0.08 |
| $\beta_{ML}$ | 11.168 ± 0.013 | | | | | 1 | 0.43 | 0.67 | 0.38 | 0.50 | 0.03 |
| $\beta_{ML_2}$ | 19.315 ± 0.024 | | | | | | 1 | 0.64 | 0.76 | 0.78 | 0.25 |
| $\beta_{MHL}$ | 18.429 ± 0.008 | | | | | | | 1 | 0.70 | 0.76 | 0.50 |
| $\beta_{MHL_2}$ | 27.540 ± 0.021 | | | | | | | | 1 | 0.80 | 0.36 |
| $\beta_{MH_2L_2}$ | 34.566 ± 0.021 | | | | | | | | | 1 | 0.41 |
| $\beta_{M(OH)L}$ | 3.200 ± 0.017 | | | | | | | | | | 1 |

[a]For the symbols of the formation constants see Table II. Only the upper triangular part of the square symmetric correlation matrix is reported.

For the last two examples the errors associated with the log $\beta$'s for the formation of the metal complexes and for the protonated forms of the ligand have been combined together. In general, when it is desired to calculate the constants and their errors for equilibria which involve simultaneously both metal complexes and either protonated forms of the ligand or the hydroxide ion, it is necessary to have the errors associated with the log $\beta$'s of formation for *all* the species which appear in the equilibria and also their correlation coefficients. These data can be obtained only if simultaneous refinement of the constants for all the cumulative equilibria involved in the system under investigation (formation of complexes, protonation of the ligand and dissociation of water) is being carried out. This implies the use in the calculation of data relative to the protonation of the ligand and to the formation of the complexes.

The program MINIQUAD is not capable of dealing simultaneously with the curves for simple protona-

tion (2 mass balance equations) and the curves for the formation of the complexes (3 mass balance equations). Hence it has been necessary to modify MINI-QUAD so that it can treat curves having a different number of mass balance equations simultaneously.

For each system containing the metal we have added the data relative to simple protonation of the ligand (curves 1, 2, and 3 in Table I) to the potentiometric data from the titration curves for complex formation.

The results obtained from the refinement process are shown in Table IV, V and VI. It can be seen that the ligand protonation constants and the constant for the dissociation of water obtained from each system do not differ by more than three standard deviations and these values are virtually identical to those obtained by considering only the data relative to the protonation curves (Table III). The same calculation has been applied to the potentiometric data on the protonation and the complex formation of tame. The

TABLE VI. Logarithms of the Cumulative Formation Constants of the Species Present in the System Zinc(II)–Tamp, Their Standard Deviations and Correlation Matrix[a].

| Formation Constant | $\log \beta$ | Correlation Matrix | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $\beta_{HL}$ | $10.2460 \pm 0.0046$ | 1 | 0.42 | 0.40 | 0.66 | 0.29 | −0.13 | 0.25 | 0.46 | 0.20 |
| $\beta_{H_2L}$ | $18.3854 \pm 0.0064$ | | 1 | 0.90 | 0.27 | 0.89 | 0.62 | 0.38 | 0.51 | 0.76 |
| $\beta_{H_3L}$ | $23.9017 \pm 0.0070$ | | | 1 | 0.26 | 0.84 | 0.56 | 0.52 | 0.53 | 0.72 |
| $\beta_{OH}$ | $-13.7381 \pm 0.0020$ | | | | 1 | 0.17 | −0.12 | 0.17 | 0.33 | 0.03 |
| $\beta_{ML}$ | $6.889 \pm 0.008$ | | | | | 1 | 0.68 | 0.45 | 0.41 | 0.76 |
| $\beta_{ML_2}$ | $11.225 \pm 0.027$ | | | | | | 1 | 0.22 | −0.04 | 0.78 |
| $\beta_{MHL}$ | $13.557 \pm 0.018$ | | | | | | | 1 | 0.57 | 0.44 |
| $\beta_{M(OH)L}$ | $-1.834 \pm 0.016$ | | | | | | | | 1 | 0.41 |
| $\beta_{M(OH)_2L}$ | $-12.334 \pm 0.018$ | | | | | | | | | 1 |

[a]For the symbols of the formation constants see Table II. Only the upper triangular part of the square symmetric correlation matrix is reported.
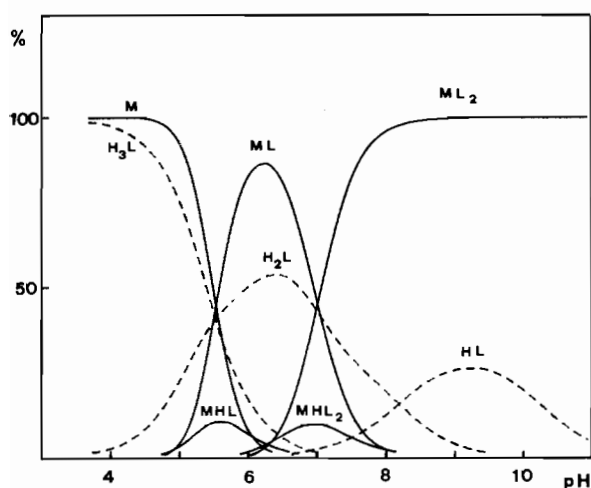


Figure 1. Distribution diagram for the system Ni$^{2+}$–tamp. The percentages have been calculated from the data of curve 13 in Table I. Broken lines show species not containing metal and the percentages are relative to total ligand; full lines show species containing metal and the percentages are relative to total metal.
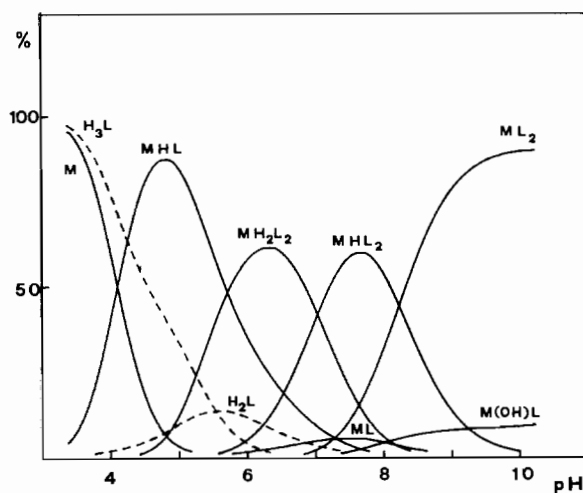


Figure 2. Distribution diagram for the system Cu$^{2+}$–tamp. The percentages have been calculated from the data of curve 5 in Table I. Broken lines show species not containing metal and the percentages are relative to total ligand; full lines show species containing metal and the percentages are relative to total metal.

stepwise equilibrium constants and the relative standard deviations, obtained by the above procedure are reported in Tables VII and VIII together with the corresponding values for tamp.

## Discussion

### Basicity Constants

The values of stepwise protonation constants of tamp and tame are shown in Table VII. As expected, only a slight difference in basicity was found between these two triamines. In the first step tamp is the

TABLE VII. Logarithms of the Stepwise Protonation Constants at 25 °C in 0.5 $M$ KNO$_3$[a].

| Reaction | $\log K$ | |
|---|---|---|
| | L = tamp | L = tame |
| $H^+ + L \rightleftarrows HL^+$ | 10.230(1) | 10.157(1) |
| $H^+ + HL^+ \rightleftarrows H_2L^{2+}$ | 8.171(2) | 8.253(2) |
| $H^+ + H_2L^{2+} \rightleftarrows H_3L^{3+}$ | 5.529(3) | 5.853(3) |

[a]Values in parentheses are standard deviations on the last significant figure.

TABLE VIII. Logarithms of the Equilibrium Constants for Reactions of Complex Formation at 25 °C in 0.5 $M$ KNO$_3$[a].

| | L = tamp | | | L = tame | | |
|---|---|---|---|---|---|---|
| | M = Ni | M = Cu | M = Zn | M = Ni | M = Cu | M = Zn |
| $M^{2+} + L \rightleftarrows ML^{2+}$ | 10.468(6) | 11.17(1) | 6.899(8) | 10.149(6) | 10.97(1) | 6.615(6) |
| $ML^{2+} + L \rightleftarrows ML_2^{2+}$ | 7.50(1) | 8.15(2) | 4.35(2) | 7.12(1) | 7.72(2) | 4.25(6) |
| $MHL^{3+} + L \rightleftarrows MHL_2^{3+}$ | 8.94(6) | 9.11(2) | | 8.52(6) | 8.66(1) | |
| $M^{2+} + HL^+ \rightleftarrows MHL^{3+}$ | 5.14(2) | 8.196(8) | 3.31(2) | 5.38(2) | 8.234(5) | 3.37(3) |
| $ML^{2+} + HL^+ \rightleftarrows MHL_2^{3+}$ | 3.61(7) | 6.14(2) | | 3.75(7) | 5.92(2) | |
| $MHL^{3+} + HL^+ \rightleftarrows MH_2L_2^{4+}$ | | 5.91(2) | | | 5.82(1) | |
| $ML^{2+} + H^+ \rightleftarrows MHL^{3+}$ | 4.91(2) | 7.26(1) | 6.67(2) | 5.38(2) | 7.42(1) | 6.91(3) |
| $ML_2^{2+} + H^+ \rightleftarrows MHL_2^{3+}$ | 6.34(6) | 8.22(2) | | 6.78(6) | 8.35(1) | |
| $MHL_2^{3+} + H^+ \rightleftarrows MH_2L_2^{4+}$ | | 7.03(1) | | | 7.32(1) | |
| $ML^{2+} + OH^- \rightleftarrows M(OH)L^+$ | | 5.77(2) | 5.02(1) | | 5.51(2) | 4.98(1) |
| $M(OH)L^+ + OH^- \rightleftarrows M(OH)_2L$ | | | 3.24(2) | | | 3.46(1) |

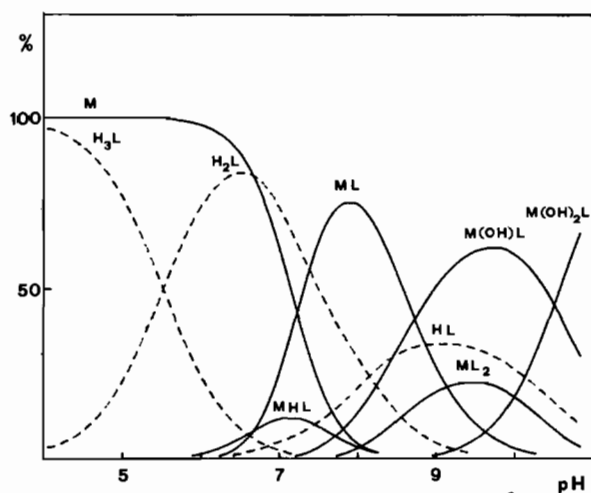[a]Values in parentheses are standard deviations on the last significant figure.



Figure 3. Distribution diagram for the system Zn$^{2+}$–tamp. The percentages have been calculated from the data of curve 16 in Table I. Broken lines show species not containing metal and the percentages are relative to total ligand; full lines show species containing metal and the percentages are relative to total metal.

slightly more basic ligand: this can be explained by the greater inductive effect of the ethyl group in the apical position. Tamp on the other hand is less basic than tame in the two successive steps, particularly the third one. This behavior can be explained by two effects, both working simultaneously. In the first, the greater size of ethyl group in tamp forces the protonated amino groups to be closer together than they are in tame by mutual repulsion. In the second, the increasing size of the hydrocarbon chain, going from tame to tamp, is associated with a decrease in the local dielectric constant, resulting in an increase in

the repulsion between the protonated amino groups. On the basis of this interpretation one can predict that 1,1,1-tris-(aminomethyl)methane (tamm), in which one hydrogen atom replaces the apical alkyl group, should be appreciably more basic than both tamp and tame, at least for the third protonation step. The literature values, albeit determined in different conditions of temperature and ionic strength (log $K$ = 6.90 at 22 °C in 1 $M$ KNO$_3$ [1] and log $K$ = 6.43 at 20 °C in 0.1 $M$ NaNO$_3$ [2]), are in agreement with the above hypothesis.

*Complex Formation Constants*

In Table VIII are shown the logarithms of the equilibrium constants for reactions specifically chosen to allow us to examine and discuss the relative stability of the complexes and the coordinating ability of the two ligands. As shown by the data reported in Table VIII analogous complexes formed by the two ligands exhibit only small differences in stability. In particular it should be noticed that the addition of the ligand L to the free metal or to the metal complexes is more favoured in the case of tamp. This result can be ascribed to the inductive effect of the apical alkyl group.

As shown by the data reported for the simple complexes ML$^{2+}$ and ML$_2^{2+}$ in Table VIII, the stepwise stability constants decrease regularly in going from the first to the second stage of complex formation. Surprisingly, the stability constants for the complexes CuL$^{2+}$ and CuL$_2^{2+}$ are only a little larger than those for the corresponding nickel complexes. This must be related to the fact that the tripod structure of the ligand imposes a *fac* coordination of the three amine groups, an arrangement which is particularly unfavourable for the copper ion. The same effect is ob-

served when a molecule of ligand is added to the protonated complex MHL.

For the addition reactions of the protonated ligand HL⁺, which can only coordinate as a bidentate ligand, the equilibrium constants for the copper complexes are, as expected, much higher than those for the other two metals.

The values of the constants discussed above leave us in some doubt as to whether tamp and tame behave as tridentate ligands towards the copper(II) ion. In order to establish whether or not the ligand in a polyamine complex has an uncoordinated nitrogen atom one can examine the protonation constants for the coordinated ligand. According to Schwarzenbach [11] if these constants do not differ appreciably from the basicity constants of the ligand, corrected if need be for the statistical term, it can reasonably be assumed that the amine group being protonated is not coordinated to the metal. The highest values of these constants are found in Table VIII for the copper complexes. While in the case of the species Cutamp$_2^{2+}$ (log $K$ = 8.22) and Cutame$_2^{2+}$ (log $K$ = 8.35) it can be inferred that one of the amine groups is not coordinated, this cannot be stated with the same degree of certainty for the other copper complexes. It is probable that the amine group in the axial position is only weakly bound to the copper(II) ion. As far as the nickel(II) and zinc(II) complexes are concerned the relatively low values of the protonation constant for the coordinated ligand are consistent with a fully coordinated ligand.

According to previous results reported for polyamine complexes [12, 13], nickel(II) does not form hydroxy species. However, the value of the equilibrium constant for the reaction involving the addition of a hydroxide ion to the complex CuL$^{2+}$, is about an order of magnitude greater than the corresponding values found with linear aliphatic triamines [12]. This is probably due to the different structures of the complexes involved. The values found for the analogous reaction of the zinc(II) complex of tamp and tame are similar to those found with linear triamines [12]. The literature contains very few values for the formation of dihydroxy complexes of zinc.

The formation constants for the species Zn(OH)$_2$L are of the same order as that found for the species Zn(OH)$_2$(2,4-tri), where 2,4-tri is a linear triamine of formula NH$_2$(CH$_2$)$_2$NH(CH$_2$)$_4$NH$_2$ [13].

## Supplementary Data

Listings of the computer output containing the experimental data are available from the Editor upon request.

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