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Potentiometric Determination of the Formation Constants of Complexes of 3,3′,4″-Triaminodipropylbutylamine with Co(II), Ni(II), Cu(II) and Zn(II)

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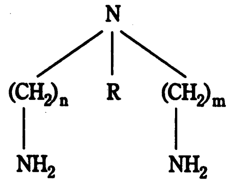
The tripodal 3,3,4-tetraamine ligand $N\{(CH_2)_3NH_2\}_2(CH_2)_4NH_2$ (L = ppb) has been investigated for the first time as asymmetrical tetraamine chelating agent for cobalt(II), nickel(II), copper(II) and zinc(II). The protonation constants of ppb and formation constants of its complexes have been determined potentiometrically in 0.1 M KCl at 25°C. The successive protonatoin constants (log K_n) are: 10.69, 10.12, 9.49, 6.72 (n = 1–4). Two complexes having the formulae ML, MHL (where L = ppb) are common to all the four metal ions for which the formation constants {log β_{ML}, M = Co^{2+}, $Ni,^{2+}$ Cu^{2+}, Zn^{2+}} are: 6.70, 6.79, 12.98 and 9.37 and {log β_{MHL}, M = Co^{2+}, Ni^{2+}, $Cu,^{2+}$ Zn^{2+}} are: 14.94, 16.09, 22.20 and 17.24 respectively. In addition to the simple and protonated complexes, cobalt(II), copper(II) and zinc(II) give the hydroxo complexes and nickel(II) gives the ML_2 complexes. The nickel(II) complex, $Ni(ppb)\cdot(ClO_4)_2\cdot 1.5H_2O$ and zinc(II) complex, $Zn(ppb)\cdot(ClO_4)_2\cdot H_2O$, have been isolated.

Key words: Potentiometric, determination, formation constants, Co(II), Ni(II), Cu(II), Zn(II), complexes.

INTRODUCTION

Polyamine ligands have attracted much attention not only because they form very stable complexes with metals but also because of possible analogies with amino acids[1]. In recent years, tripodal ligands have been of interest, and many combinations of donor sets have assembled and their protonation constants and formation constants of their complexes with some metal ions have been determined potentiometrically. We are investigating a range of amines, both for their own interest and also because of the possibilities of extending them by formation of open-chain and macrocyclic Schiff bases[2]. We have devised improved syntheses for tpt and related ligand[3, 4]; recently we described the synthesis of an asymmetrical, 3,3,4-tripodal ligand and crystal structure of its copper(II) complex[5].

The purpose of the present work was to measure the protonation constants of this asymmetrical tripodal ligand (ppb) and formation constants of its complexes with copper(II), nickel(II), cobalt(II) and zinc(II) at 25°C in 0.1 M KCl. This enabled us to make a comparison with corresponding values under the same condition for some symmetrical tripodal ligands such as tpt[6] and tren[7].



	n	m	R
ppb	3	3	$-(CH_2)_4-NH_2$
tpt	3	3	$-(CH_2)_3-NH_2$
dpt	3	3	H
bpt	3	4	H

EXPERIMENTAL

The ligand ppb was prepared as a perchlorate salt according to a published procedure[1]. Ampoule potassium chloride, used as supporting electrolyte, was also obtained as reagent material (BDH). Carbon-free solutions of 0.1 M NaOH were prepared from diluted (R) ampoules and standardized with potassium phthalate. Metal-chloride stock solutions were standardized by EDTA titration (xyleol orange)[8].

$[Ni(ppb)](ClO_4)_2 \cdot 1.5H_2O$*

$Ni(ClO_4)_2 \cdot 6H_2O$ (1 mmol, 0.365 g), $ppb \cdot 4HClO_4 \cdot H_2O$ (1 mmol, 0.622 g) and MeONa (7 mmol, 0.378 g) were dissolved in absolute MeOH (70 cm^3). The solution was stirred at 60°C for 20 min and allowed to stand. A blue solid precipitated slowly; yield: 60% (Found: C, 24; H, 6; N, 11.3 and Ni, 11.9%. $C_{10}H_{29}N_4O_9Cl_2Ni$ requires: C, 24.6; H, 5.4; N, 11.5 and Ni, 12%).

$[Zn(ppb)](ClO_4)_2.H_2O$

This compound was obtained analogously as a white powder; yield: 60%; (Found: C, 24.8; H, 5.7; N, 11.5 and Zn, 13.2%; $C_{10}H_{28}N_4O_9Cl_2Zn$ requires: C, 25.2; H, 5.5; N, 11.2 and Zn, 13.65%).

Potentiometric Measurements

Each calibration and potentiometric determination was measured in a 100 mL jacketed cell thermostated at 25°C by a refrigerated circulating water bath. The ionic strength was maintained through the addition of KCl to each solution to achieve 0.1 M. Anaerobic conditions were maintained through the use of pre-purified humidified nitrogen as an inert atmosphere. A Jenway 3010 pH meter was used with glass and calomel electrodes. A 10 mL capacity Mettler DV 11 piston burette was used which delivered standard sodium hydroxide solution directly into the sealed cell through a capillary burette tip which was attached to

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***Caution:** Perchlorate salts can be dangerously explosive. The compounds described here have never detonated in our hands, but they should be treated with care.

the cell cap. The apparatus was calibrated on a day to day basis by a one-point calibration of dilute strong acid at 0.1 M ionic strength (KCl) in order to measure the hydrogen ion concentration directly.

Procedure

In each system under investigation, the starting volume was 50 mL, pH measurements were recorded after reagents were added and NaOH was added in 0.1 mL increments to the sealed system. All titrations were carried out by addition of bases to the acid forms of the ligand. pK_w for H_2O at $\mu = 0.1$ M (KCl) at 25°C was found to be 13.78 .

The program BEST was used to calculate the equilibrium constants[9, 10]. Species distribution diagrams were computed from the equilibrium constants through the use of the programs SPE and the diagrams were plotted on a laser printer with program SPEPLOT[9].

RESULTS AND DISCUSSION

In the absence of added metal ions, the potentiometric equilibrium curve of ppb tetrahydroperchlorate is shown in Fig. 1. Two inflection points are seen at a = –4, –3 (where a is the number of moles of base added per mole of neutral ligand). The buffer region from a = –4 to a = 0 involves the equilibria for four deprotonation steps. All of these deprotonation steps are found to occur in a pH range that is suitable for protonation constants to be calculated directly from the potentiometric data. Analysis of the curve yields the successive protonation constants (defined in eqs. (1) and (2) which are shown in Table-1 along with values for related polyamines.

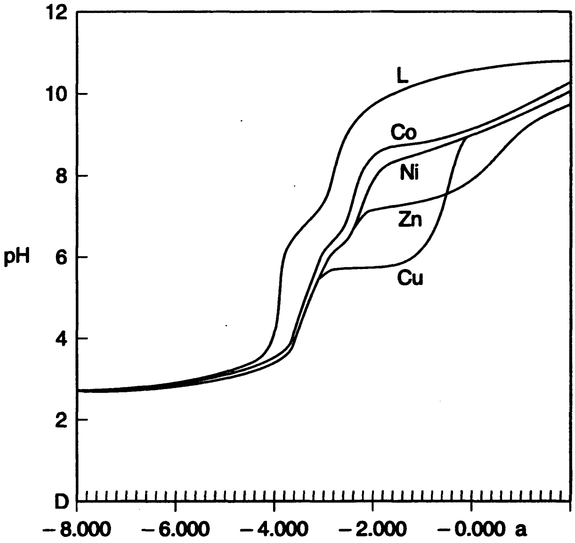

Fig. 1. Potentiometric equilibrium curves for ppb (L) and for the 1 : 1 M^{2+} : ppb system; 25°C, $\mu = 0.100$ M (KCl)

$$H_{n-1}L^{(n-1)+} + H^+ \Leftrightarrow H_nL^{n+} \quad (1)$$

$$K_n = [H_nL^{n+}]/\{[H_{n-1}L^{(n-1)+}][H^+]\} \quad (2)$$

TABLE-1
PROTONATION CONSTANTS FOR ppb AND RELATED POLYAMINES

	ppb[a]	tpt[b]	tren[c]	dpt[d]	pbt[e]
log K_1	10.69	10.511	10.14	10.65	10.81
log K_2	10.12	9.814	9.43	9.57	9.81
log K_3	9.49	9.129	8.41	7.72	8.34
log K_4	6.72	5.615	–	–	–

[a] This work; 25°C, μ = 0.100 M (KCl). [b] 3,3′,3″-triaminotripropylamine, Ref. 6.
[c] 2,2′,2″-triaminotriethylamine, Ref. 7. [d] 3,3′-diaminodipropylamine, Ref. 11.
[e] sperimidine, Ref. 12.

Comparison with corresponding constants for tpt and tren shows that the value for each stage is less than the previous stage might have been expected on the bases both of statistical factors and of electrostatic repulsion between the hydrogen ion and the ligand molecule which in successive stages of protonation becomes progressively more positively charged. Thus, for four stages of neutralization the constants lie in the order ppb > tpt > tren. The tertiary nitrogen is largely protonated in ppb and tpt, while in tren it is not; this is obviously due to smaller electrostatic repulsion exerted by the three positive poles which are further from the tertiary nitrogen in the above order. Similar trends are seen for all the polyamine ligands.

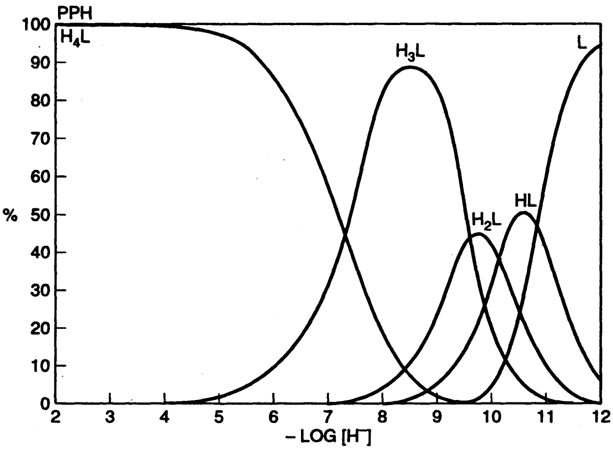

Fig. 2. Distribution curves for the protonated ppb (L) species as a function of pH. [ppb] = 0.995 mM, 25°C, μ = 0.100 M (KCl)

Fig. 2 shows the distribution curve for the various protonated forms of ppb as a function of pH in the absence of metal ions. Over a wide range below pH 5, the solution contains essentially tetraprotonated form.

Formation Constants

The potentiometric equilibrium curves for 1 : 1 mol ratio of M : L (M = Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) are shown in Fig. 1. Complex formation begins at pH 6–9, showing that all four metals are complexed. As usual the order of binding is $Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ with strong discrimination in favour of Cu^{2+}. Analysis of the curves shows that two complexes having the formulae ML, MHL are common to all the four metal ions. In addition to the simple and protonated complexes copper(II), cobalt(II) and zinc(II) also give the hydroxo complexes. Analysis of potentiometric data obtained for two ligands to one metal ion system indicated that only nickel(II) has significant concentration of ML_2 complex; therefore, the experiment was only repeated for nickel(II) at ratios L : M, 2 : 1. Analysis of all the curves allowed formation constants (β, see Eqs. (3)–(6)) to be derived for ML and MHL, MLOH and ML_2 complexes. The data are given in Table-2, where they are set against those for complexes of related ligand.

$$M^{2+} + L \Leftrightarrow ML^{2+} \qquad \beta_{ML} = [ML^{2+}]/[M^{2+}][L] \qquad (3)$$

$$M^{2+} + HL^{+} \Leftrightarrow MHL^{3+} \qquad \beta_{MHL} = [MHL^{3+}]/[M^{2+}][H^{+}][L] \qquad (4)$$

$$ML^{2+} + OH^{-} \Leftrightarrow MLOH^{+} \qquad \beta_{MLOH} = [MLOH^{+}]/[M^{2+}][L][OH^{-}] \qquad (5)$$

$$ML^{2+} + L \Leftrightarrow ML_2^{2+} \qquad \beta_{ML_2} = [ML_2^{2+}]/[M^{2+}][L]^2 \qquad (6)$$

Comparisons of log β for the formation of the normal complexes with ppb, tpt, tren and dpt (Table-2) indicate that in spite of lower basicity of tren relative to tpt and ppb it forms most stable complexes. In fact the order of stability of complexes with the exception of cobalt(II) is $M(tren)^{2+} > M(tpt)^{2+} > (ppb)^{2+}$. The reason for this order must be that tpt complexes have three six-membered chelate rings and ppb complexes have two six- and one seven-membered chelate rings and it is well known that seven-membered chelate rings are less stable than six-membered rings and both are less stable than analogous five-membered rings. Like $M(tpt)^{2+}$, the $M(ppb)^{2+}$ complexes are with the exception of that of zinc(II) slightly less stable than those of dpt. This is surprising considering that dpt has one less donor amine group. Thus it may be suspected that only three nitrogen atoms in ppb were involved in coordination (two primary and one tertiary), but in this case the values of equilibrium constants for $M(ppb)^{2+} + H^{+} \Rightarrow M(Hppb)^{3+}$ should be very close to the first basicity constant of the free amine. However, the values observed for cobalt(II) and zinc(II) (log K_s are 8.24 and 7.87 respectively) are too low to justify such a hypothesis, while for Ni(II) and Cu(II) (logK_s are 9.30 and 9.22 respectively) such a conclusions may be drawn ($\beta_{MHL} = K_{MHL} \cdot K_1$).

Species distribution curves

The formation constants allow calculation of the distribution curves for the various complexes as a function of pH, which are shown in Figs. 3–7.

For copper(II) complexes, in the presence of equivalent amount of metal and ligand, the titration curves show a jump at a = –1 suggesting the possible formation of monoprotonated copper complex (Fig. 1). Consequently, the distribution curve (Fig. 3) shows that hydroxo complexes Cu(ppb)(OH)$^+$ are present as well as mono-protonated and normal copper(II) complexes. Metal complex formation with ppb occurs even at pH = 5.

TABLE-2
FORMATION CONSTANTS OF METAL(II) COMPLEXES

M^{2+}	ppb[a]			tpt[b]			tren[c]			dpt[d]		
	$\log \beta_{MHL}$	$\log \beta_{ML}$	$\log \beta_{MLOH}$	$\log \beta_{MHL}$	$\log \beta_{ML}$	$\log \beta_{MLOH}$	$\log \beta_{MHL}$	$\log \beta_{ML}$	$\log \beta_{MLOH}$	$\log \beta_{MHL}$	$\log \beta_{ML}$	$\log \beta_{MLOH}$
Co	14.94	6.70	3.14	–	6.360	9.350	–	12.80	–	–	6.92	–
Ni	16.09	6.79	–	15.781	8.702	–	19.14	14.80	–	–	9.19	–
Cu	22.20	12.98	15.67	21.262	13.117	–	–	18.80	–	–	14.34	18.34
Zn	17.24	9.37	9.03	–	10.702	–	–	14.65	–	–	7.92	13.15

[a]This work; 25°C, μ = 0.100 M (KCl); [b]Ref. 6; [c]Ref. 7; [d]Ref. 11.

And while it is possible to obtain the protonated or hydroxo complexes alone in solution, the normal complex is always present together with one of the above two (Fig. 3). The copper protonated complex is very stable and sharply reduces the concentration of triprotonated ligand in solution.

Distribution curves for cobalt(II) and zinc(II) complexes (Figs. 4 and 5) show that the complex formation starts at pH 8 and 7 for Co and Zn, respectively. In both cases normal complex never exists alone but is always found with monoprotonated or with hydroxo complexes.

Distribution curves for Ni(II) complexes (1 : 1 and 1 : 2 metal : ligand ratios,

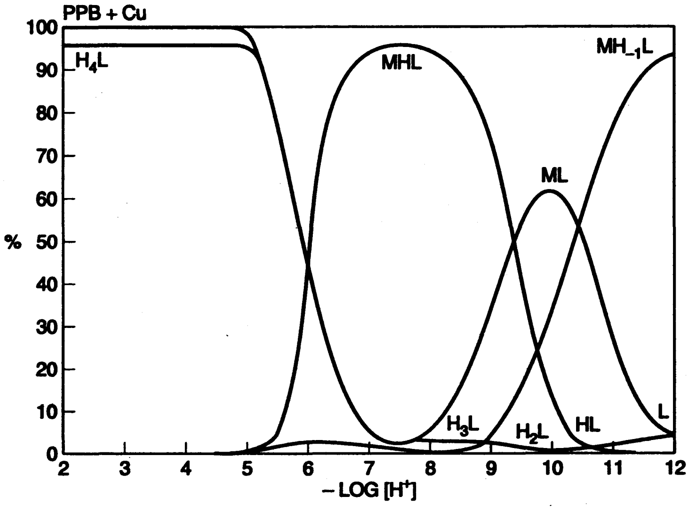

Fig. 3. Distribution curves for the Cu^{2+}-ppb system as a function of pH. 1 : 1, $[ppb]_{tot}$ = 0.989 mM, $[Cu^{2+}]_{tot}$ = 0.947 mM

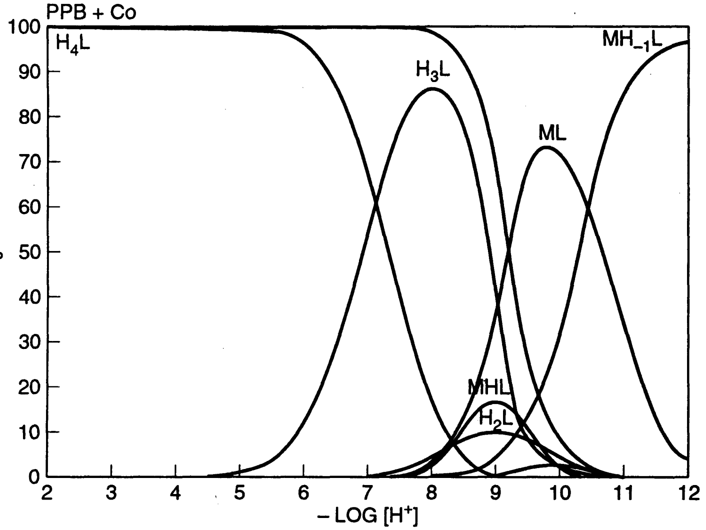

Fig. 4. Distribution curves for the Co^{2+}-ppb system as a function of pH. 1 : 1, $[ppb]_{tot}$ = 0.989 mM, $[Co^{2+}]_{tot}$ = 0.945 mM

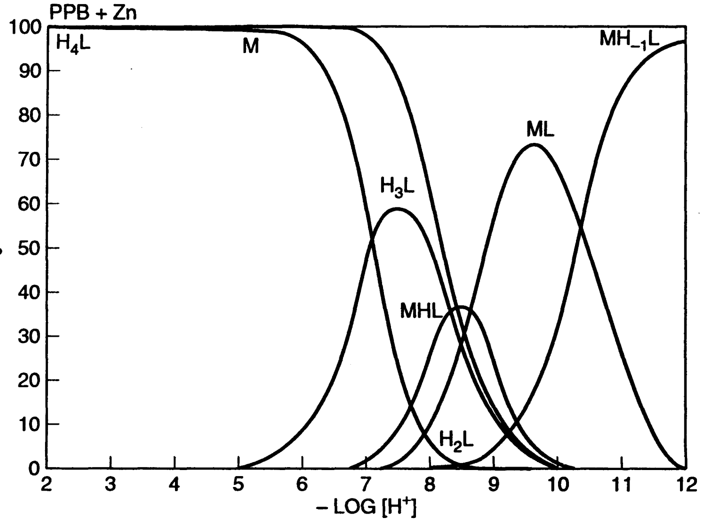

Fig. 5. Distribution curves for the Zn^{2+}-ppb system as a function of pH. 1 : 1, $[ppb]_{tot}$ = 0.989 mM, $(Zn^{2+}]_{tot}$ = 0.948 mM

Figs. 6 and 7) show that the complex formation starts from pH 7.5 and also the normal complex always exists together either with mono-protonated complex or with $[Ni(ppb)_2]^{2+}$.

The formation of mono-protonated and normal complexes was confirmed by the isolation of copper complex $[CuCl_2(Hppb)]ClO_4$,[5] nickel complex $Ni(ppb)\cdot(ClO_4)_2\cdot 1.5H_2O$ and zinc complex $Zn(ppb).(ClO_4)_2\cdot H_2O$.

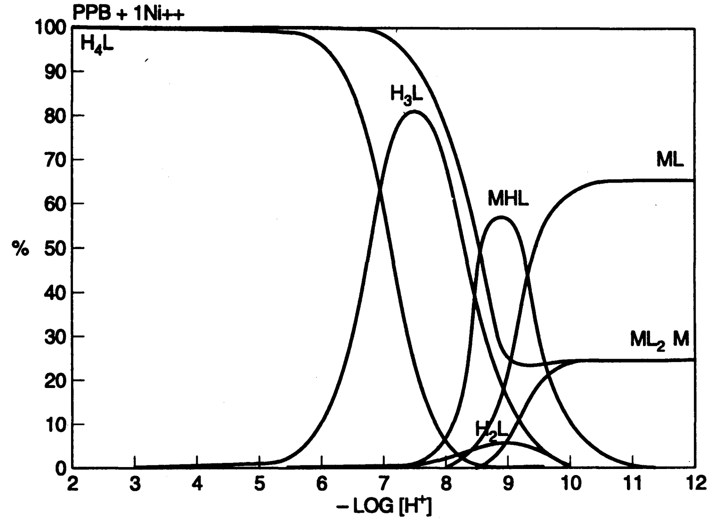

Fig. 6. Distribution curves for the Ni^{2+}-ppb system as a function of pH. 1:1. $[ppb]_{tot}$ = 0.989 mM, $[Ni^{2+}]_{tot}$ = 0.940 mM

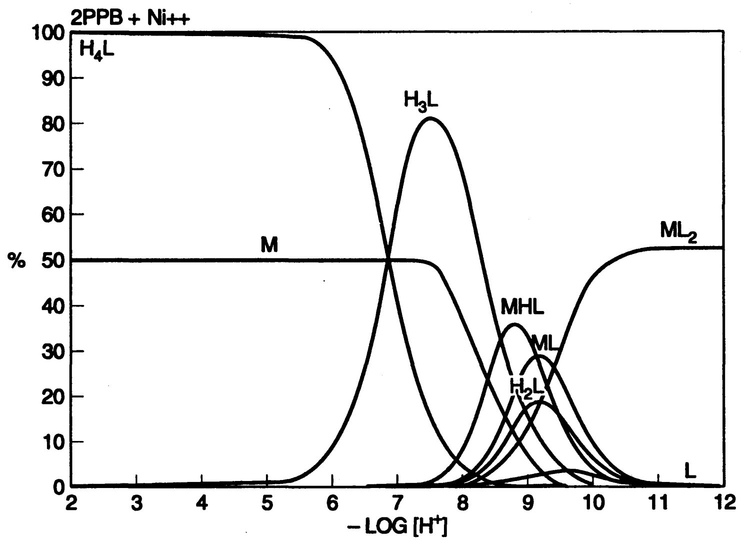

Fig. 7. Distribution curves for the Ni^{2+}-ppb system as a function of pH. 2 : 1, $[ppb]_{tot}$ = 0.989 mM, $[Ni^{2+}]_{tot}$ = 0.470 mM

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