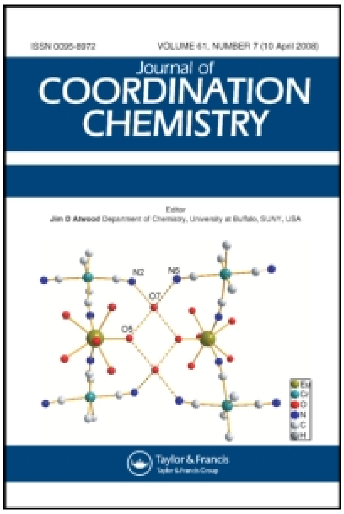

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POTENTIOMETRIC INVESTIGATION OF TERNARY COMPLEXES OF NICKEL, COPPER, ZINC AND CADMIUM WITH *L-α*-ALANINEHYDROXAMIC ACID AND ETHYLENEDIAMINE

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Mixed-ligand complex formation of M(II) (M = Ni, Cu, Zn and Cd) with *l-α*-alaninehydroxamic acid (α-Alaha) as primary ligand (A) and ethylenediamine (en) as secondary ligand (B) have been determined potentiometrically [298K, $\mu = 0.2$ (KCl)]. Formation constants for binary systems involving *L-α*-alaninehydroxamic acid or ethylenediamine were determined under identical experimental conditions and pH-titration data were analysed using the SUPERQUAD computer program. The relative stability of each ternary complex was compared with that of the corresponding binary complexes in terms of Δlog K and log X values.

KEYWORDS: nickel, copper, zinc, cadmium, *L-α*-alaninehydroxamic acid, ethylenediamine, ternary complexes, stability constants, potentiometry

INTRODUCTION

This paper is the second concerning our studies of chemical models relevant to the various species present in aqueous solutions containing transition metals and an aminohydroxamic acid [A] as a primary ligand and ethylenediamine [B] as a secondary ligand.

The chemistry and, in particular, biochemistry of hydroxamic acids are attracting increasing interest owing to the fact that the oxidized CON(OH) group is present in a number of substances produced by molds, fungi and yeasts.[1,2] Some inhibit proteolytic enzymes, some act as sequestering agents in metal overload, and some act as agents for lowering blood ammonia levels in some mammals. It has been also reported that low molecular weight monohydroxamic acids can be used therapeutically as urease inhibitors in hepatic coma.[3]

A cellular membrane transport system is specific for metal-bound hydroxamic acids. Since ternary system are somewhat better models for complex biological systems, the importance of studying ternary complexes containing aminohydrox-

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amic acids as primary ligand is clearly established. Because a neutral ligand seems to have a decisive influence on the biological activity of the metal complexes and the presence of the amino group (NH_2) is necessary to influence a receptor[4] we have chosen ethylenediamine as a secondary ligand.

The aim of the present work was to determine the stepwise stability constants of complexes formed in NI(II), Cu(II), Zn(II) or Cd(II) systems with L-α-alaninehydroxamic acid (α-Alaha) and ethylenediamine (en) and to evaluate of statistical parameters $\Delta\log K$, $\Delta\log \beta$ and $\log X$. Protonation constants of the free ligands, the stoichiometry of binary and ternary complexes and their formation constants were computed by analysing pH-titration data with the SUPERQUAD[5] computer program.

EXPERIMENTAL

Materials

L-α-alaninehydroxamic acid (α-Alaha) was prepared *via* the methyl ester of *L*-α-alanine as previously described.[6] The ligand ethylenediamine (en; Sigma, St. Louis) was dried over KOH, distilled ($T_f = 390$ K) and protected against moisture prior to use. Exact concentrations of ligand stock solutions were determined by Gran's method.[7] $NiCl_2$, $CuCl_2$ and $ZnCl_2$ solutions were purchased from Merck and $CdCl_2$ from POCh Gliwice, Poland. The metal ion stock solutions were standardized by EDTA titration.[8]

Carbonate-free KOH (the titrant) was prepared and standardized against standard potassium hydrogen phtalate solution. The concentration of the KOH solution was 0.1642 mol dm^{-3}.

Potentiometric measurements

The ligand protonation constants and stability constants of binary and ternary complexes were determined in water solutions in the pH range 2–11. Data for binary complexes can be found in the literature,[9–12] but for comparison we had to determine all of the data under the same conditions. For the M(II)-*L*-α-Alaha (ligand A) and M(II)-en (ligand B) binary systems, 1:2, 1:4 and 1:6 metal to ligand ratios were employed. The concentration of the ligand in the experimental solution was 4×10^{-3} mol dm^{-3}. For the determination of the stability constants of the mixed ligand complexes the metal(II) concentration in all samples was 2×10^{-3} mol dm^{-3}, and the concentration ratios of metal : ligand A : ligand B were 1:1:1, 1:1:2, 1:2:1, 1:2:2, 1:2:4 and 1:4:2. The titrations were carried out at 298K and ionic strength (KCl) 0.2 mol dm^{-3}.

All the pH-metric titrations were carried out with carbonate-free KOH solution. KOH solution was added from a ABU-80 microburette (Radiometer), the initial sample volume being 20 cm^3. The pH-metric titrations performed under argon in a water-thermostatted beaker using a Radelkis OP-208/1 pH meter equipped with OP7183 glass and OP830 calomel electrodes. The electrodes system was calibrated by periodic titrations of an HCl solution (5×10^{-2} mol dm^{-3} in KCl) against standard KOH solution. Titration emf data were used to calculate the hydrogen ion concentration, $[H^+]$.[13]

RESULTS AND DISCUSSION

Potentiometric titration data suggest the formation of ternary complexes. Mixed ligand curves were different to the composite curves (Figure 1). For all systems, the ternary complex curve was superimposed on the 1:4 MA curve in the lower pH region. Such an observation is consistent with the stability constants given in Table 1.

Factor $\Delta\log K_{MAB}$ given by expression (*1*)

$$\Delta\log K_{MAB} = \log\beta_{MAB} - (\log K_{MA} + \log K_{MB}) \qquad (1)$$

is measure of the tendency to forming ternary complexes by stepwise addition according to (*2*)–(*3*) or (*4*)–(*5*); charges are omitted.

$$M + A = [MA] \qquad (2)$$

$$[MA] + B = [MAB] \qquad (3)$$

$$M + B = [MB] \qquad (4)$$

$$[MB] + A = [MAB] \qquad (5)$$

The concentrations of $[MA_2]^{\circ}$ and $[MB_2]^{2+}$ are substantially high and thus their disporportionation according to the (*6*) seems to be a very probable way to form mixed ligand complexes (see Scheme 1 and Scheme 2).

$$[MA_2]^{\circ} + [MB_2]^{2+} = 2[MAB]^{+} \qquad (6)$$

The tendency for such disproportionation can be expressed by a factor $\log X_{MAB}$, given by expression (*7*).

$$\log X_{MAB} = 2\log\beta_{MAB} - (\log\beta_{MA_2} + \log\beta_{MB_2}) \qquad (7)$$

Since statistical effects are important for mixed ligand complex stabilization, we

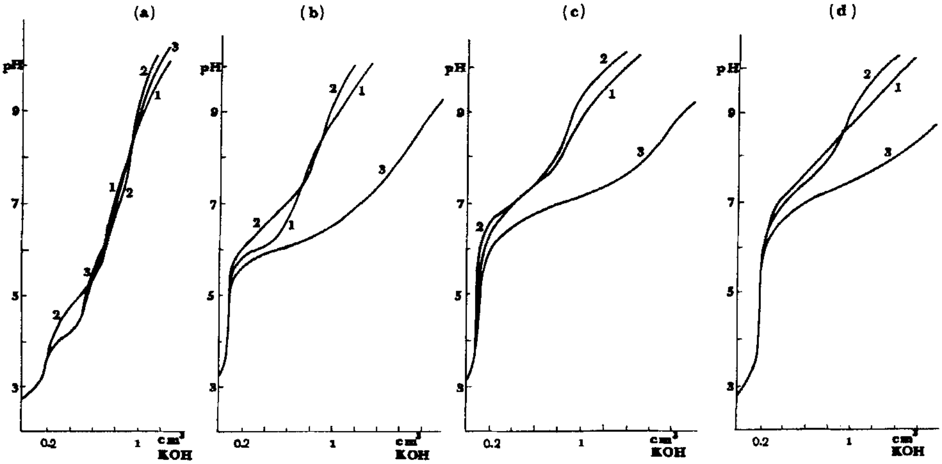


Figure 1 Titration curves for M(II)-α-Alaha (1), M(II)-en (2) and M(II)-α-Alaha-en (3) systems, where M(II) = Ni(II) (a), Cu(II) (b), Zn(II) (c), Cd(II) (d). Metal-to-ligand molar ratios are 1:4 for binary systems and 1:2:2 for the ternary systems.

Table 1 Overall stability constants for the M(II)-α-Alaha(A)-en(B) system, where M(II) = Cu(II), Ni(II), Zn(II) and Cd(II). Values in parentheses are standard deviations. Ionic charges are omitted.

Species	$\log\beta^{calc.}$
[NiAB]	14.06(5)
NiABH$_{-1}$]	5.06(6)
[CuAB]	20.57(3)
[CuABH$_{-1}$]	9.94(7)
[ZnAB]	11.15(2)
[ZnABH$_{-1}$]	1.72(2)
[CdABH]	17.46(2)
[CdAB]	9.01(2)
[CdABH$_{-1}$]	−0.60(3)

have calculated statistical stability constants (*8*).

$$\log \beta_{MAB}^{stat.} = \log 2 + 1/2(\log \beta_{MA_2} + \log \beta_{MB_2}) \qquad (8)$$

The $\Delta\log \beta_{MAB}$ value given by (*9*)

$$\Delta \log \beta_{MAB} = \log \beta_{MAB}^{calc.} - \log \beta_{MAB}^{stat.} \qquad (9)$$

is a measure of additional influences, other than statistical one, of ligands on the stability of mixed complexes. All calculated values are summarized in Table 2.

Ni(II)-α-Alaha-en and Cu(II)-α-Alaha-en systems

Stability constants for the ternary complexes were calculated using the data found for the binary M-α-Alaha and M-en systems (M = Ni(II) or Cu(II)). Titration data fit satisfactorily on the basis of the ternary complexes [MAB] and [MABH$_{-1}$]. Stability constants are given in Table 1.

A species distribution pattern for the Ni(II)-α-Alaha-en system (Figure 2), indicates formation of binary and ternary complexes above pH 5. The Ni(II)-en 1:1 complex reaches ca 50% of the total; at pH 7.5 the [NiAB] complex reaches 95%; the next ternary complex [NiABH$_{-1}$], observed from pH 8 to 11, reaches a maximum (about 90%) above pH 10.

From the results presented in Table 2 it can be seen that the Δlog K value for [NiAB] is abnormally high. However, since ternary mixed species are coexistent with binary species in solution, the tendency to form ternary complexes MAB from MB and MA will be influenced by that of forming MB_2 and MA_2, respectively, from

Table 2 Characteristic parameters for the stability of ternary complexes of the [MAB] type. Ionic charges are omitted.

Species	$\log\beta^{calc.}$	$\log\beta^{stat.}$	$\Delta\log\beta$	ΔlogK	log X
[NiAB]	14.06(5)	13.93	0.13	−0.18	0.86
[CuAB]	20.57(3)	20.13	0.44	−0.86	1.48
[ZnAB]	11.15(2)	10.09	1.06	0.26	2.72
[CdAB]	9.01(2)	8.31	0.70	−0.31	2.01

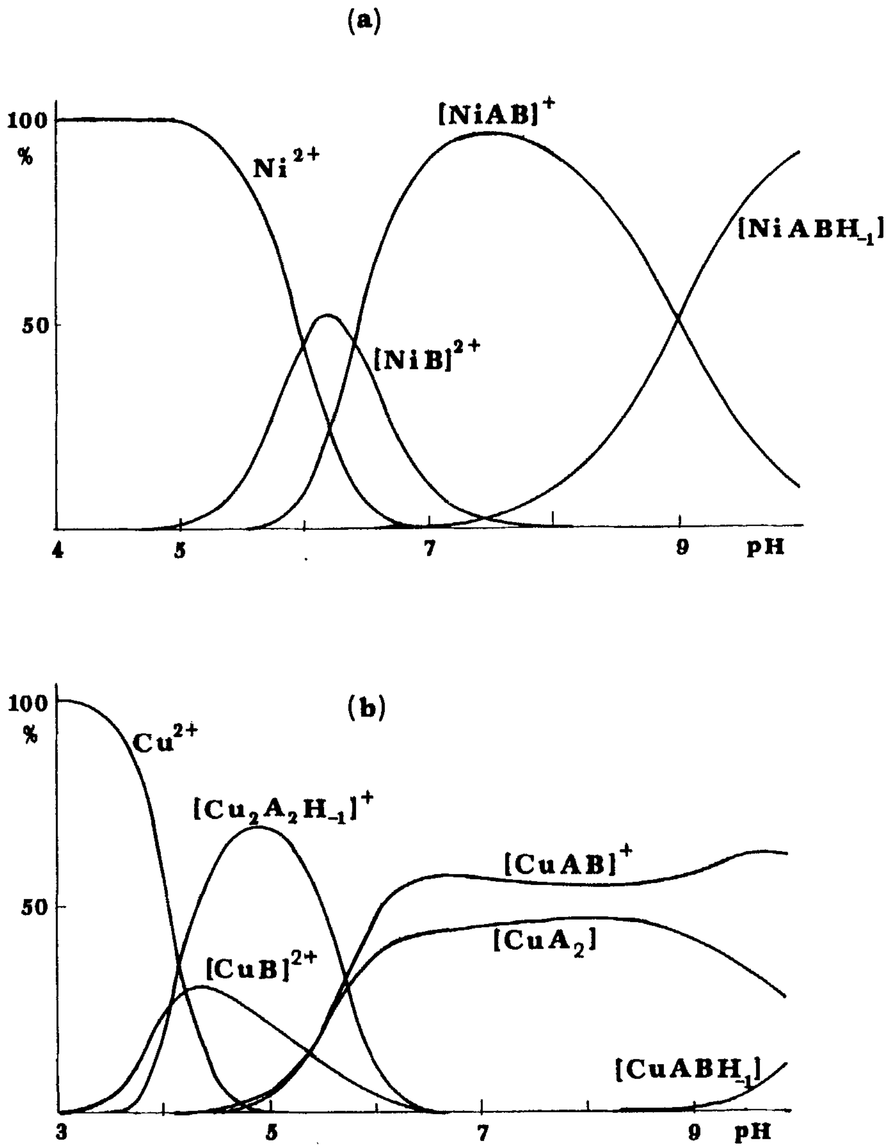
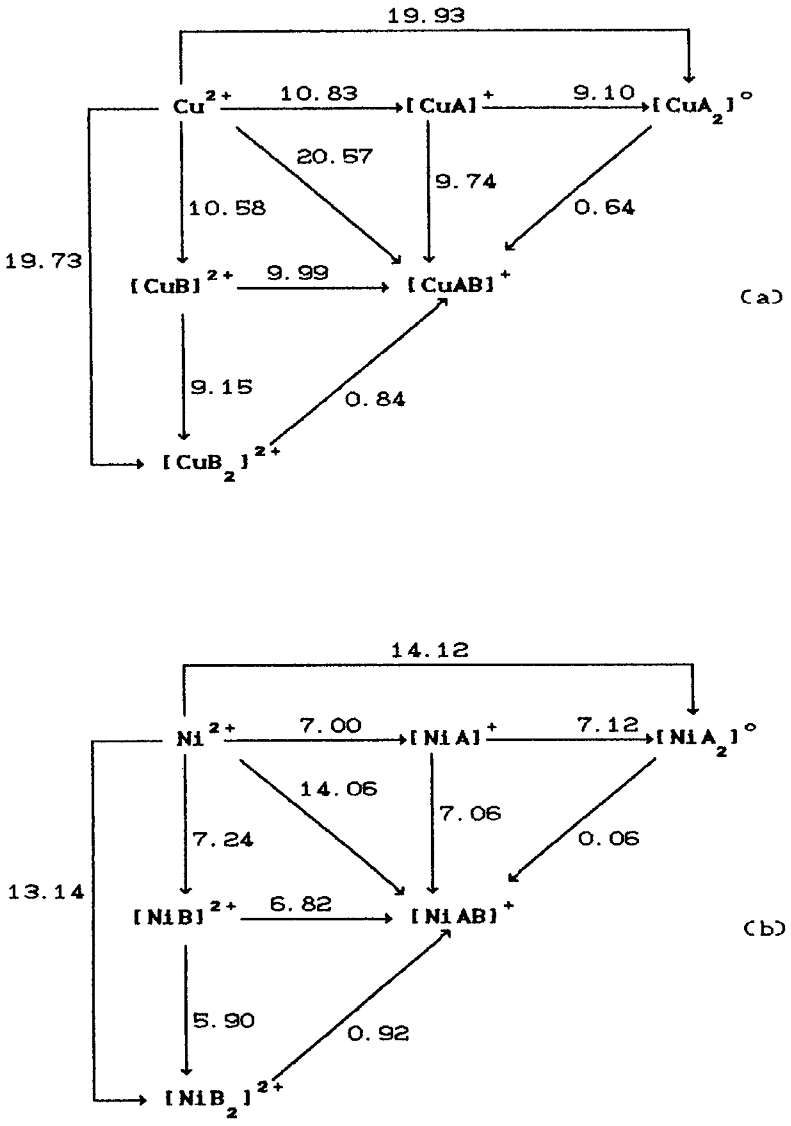


Figure 2 SUPERQUAD computed species distributions with pH for ternary sytems of Ni(II) (a) and Cu(II) (b). Metal-to-ligand mol ratios of 1:2:2 were chosen.

MB and MA (Scheme 1). This means that the magnitudes of log K^{MA}_{MAB} and log K^{MB}_{MBA} depend not only on MA + B = MAB and MB + A = MBA equilibria, but also on the magnitudes of log $K^{MA}_{MA_2}$ and log $K^{MB}_{MB_2}$.

Although coordination of many binary complexes deviates from statistical regularity and the extent of the deviation is different for particular binary



Scheme 1 Equilibria between mixed-ligand species and log K values for (a) the Cu(II)-α-Alaha-en system and (b) the Ni(II)-α-Alaha-en system.

complexes,[14] these factors still will influence the actual size of Δlog K, even though its definition does not include the second equilibrium constants for the binary complexes. The greater the opportunities of forming MA_2 or MB_2 from MA or MB, the chance of forming MAB from the same species will statistically augment the corresponding Δlog K values.[14] Thus it is expected that the abnormally high Δlog K value for [NiAB] is due to the high log $K^{MA}_{MA_2}$ value for Ni(α-Alaha)$_2$.

The pH-metric results strongly suggest that the *bis* complex, with 4N coordination and planar geometry, as is found in the solid state, is especially favoured.[15] It can be calculated from the complex stabilities that the formation of octahedral [NiA] species in this system is unfavourable (log K_{NiA}/K_{NiA_2} is -0.12). Otherwise, there is strong theoretical evidence[16] that the central nickel atom is strongly involved in the π system of the hydroxamato nitrogen atoms. This effect is an additional favourable factor.

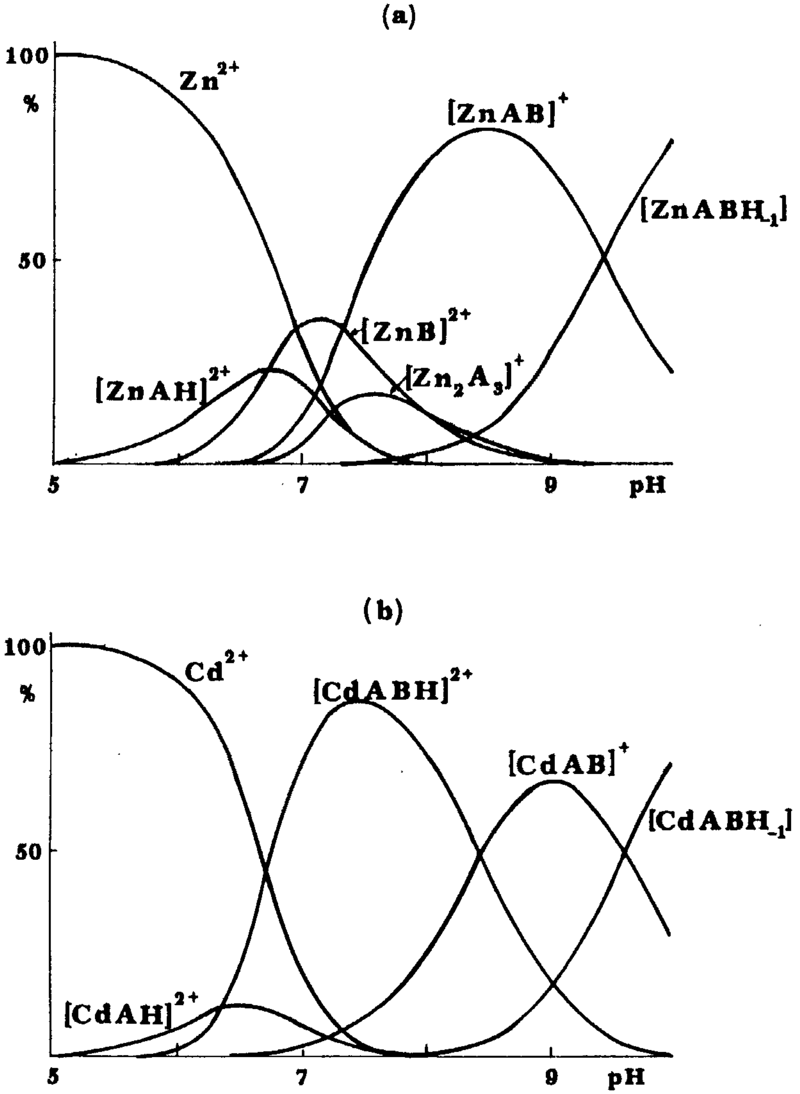
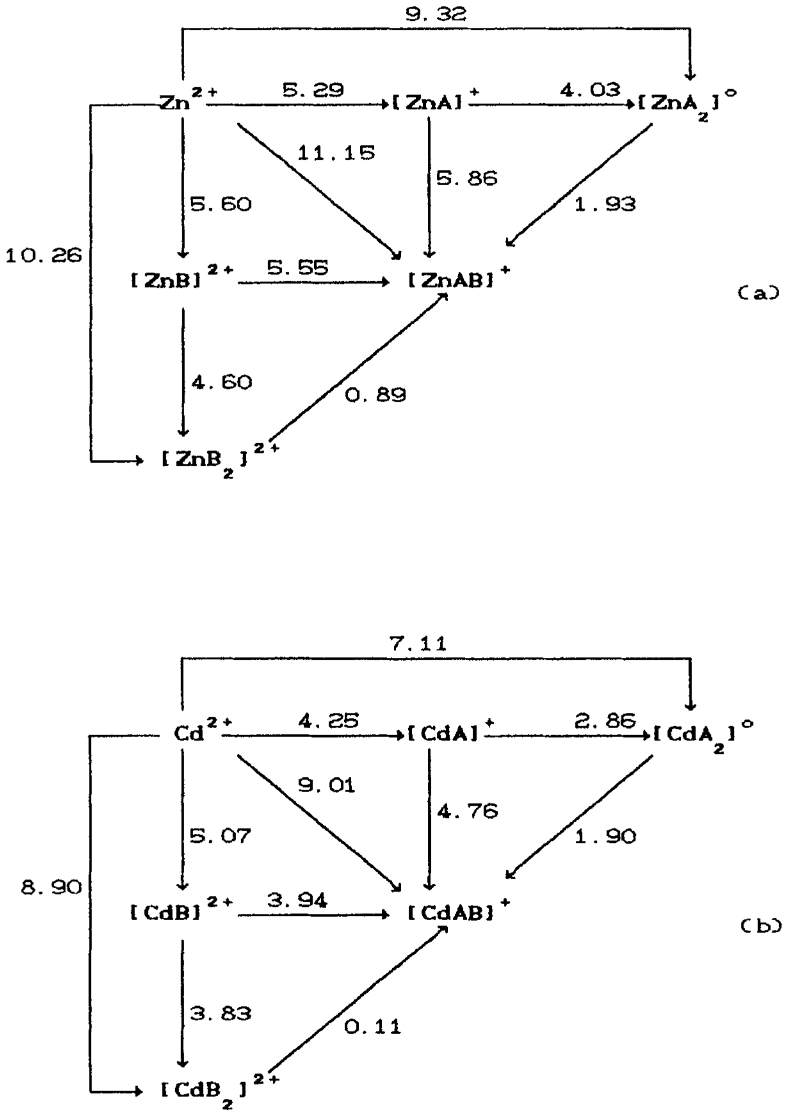


Figure 3 SUPERQUAD computed species distributions with pH for ternary systems of Zn(II) (a) and Cd(II) (b). Metal-to-ligand mol ratios of 1:2:2 were chosen.

Positive values of log X for [NiAB] and [CuAB] greater than the statistical value of 0.6) show that the formation of ternary complexes is favoured by equilibrium (*6*) or, in other words, binary species are less stable than the ternary ones. This seems to be caused by neutralization of ion charge during disproportionation. Positive values of Δlog β_{1110} also show higher stability for the 1:1:1:0 mixed-ligand species as compared with binary cases.



Scheme 2 Equilibria between mixed-ligand species and log K values for (a) the Zn(II)-α-Alaha-en system and (b) the Cd(II)-α-Alaha-en system.

Zn(II)-α-Alaha-en and Cd(II)-α-Alaha-en systems

Species distribution patterns for the Zn(II)-α-Alaha-en and Cd(II)-α-Alaha-en systems (Figure 3), indicate formation of the ternary complexes at pH > 6.5 and 6, respectively. At pH 7.5 [CdABH] reaches 85% of the metal content in solution (no observed protonated complexes in the Zn(II)-α-Alaha-en system). The ternary complexes [ZnAB] and [CdAB], had maximum concentrations above pH 8.5 and 9, respectively.

At very basic pH value, [$ZnABH_{-1}$] and [$CdABH_{-1}$] complexes predominate. Figure 3 shows that the presence of en strongly suppresses the formation of the polymeric Zn_2(α-Alaha)$_3$ complex.

From the values of Δlog K in Table 2, it can be seen that the ternary complexes in both systems have been an enhanced stability, with Δlog K values distinctly higher than the corresponding, statistically expected values (- 0.6 for tetragonal configuration, - 0.8 for tetrahedral configuration, - 0.4 for octahedral and -0.9--0.3 for distorted octahedral).[17] The Δlog K value for [CdAB] is negative (- 0.31) but for [ZnAB] it is positive (0.26).

Sigel[17–19] has noted that statistical values of Δlog K should be negative; positive values have been generally considered as evidence of some enhanced stability involving the π back-donating effects,[17,20] intramolecular ligand-ligand interactions[19,21,22] and hydrophobic effects.[19,23] As can be seen in Table 1 protonated ternary complex is formed only in the Cd(II)-α-Alaha-en system. Taking into account the appropriate protonation constants of α-Alaha, hydroxamate type (0,0) coordination can be supposed for this species. Concerning the zinc ternary complexes, the similar set of complex species as indicated in the copper and nickel systems indicates the 2N coordination of α-Alaha (in the Zn(α-Alaha)$_2$ species one of the ligands involve amino nitrogen in metal ion coordination[24]) and suggests that the central zinc atom is strongly involved in the π system of hydroxamato nitrogen atoms (*vide supra* for nickel complexes). The secondary ligand will thus exert an important effect on the formation of the ternary zinc complex. Positive Δlog β_{ZnAB} and Δlog β_{CdAB} values (1.06 and 0.75, respectively) also indicate a higher stability for the mixed ligand species as compared to binary ones (Scheme 2).

Log X_{ZnAB} and log X_{CdAB} values (2.72 and 2.01, respectively) are larger than that expected on statistical grounds (0.6), and this too seems to be caused by the neutralization of ionic charge during disproportionation, as for nickel and copper complexes (see above). The stability of the ternary complexes decreased in the order Ni ≪ Cu ≫ Zn > Cd, in line with the normal Irving-Williams Series. This rule also holds well for the binary complexes.

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