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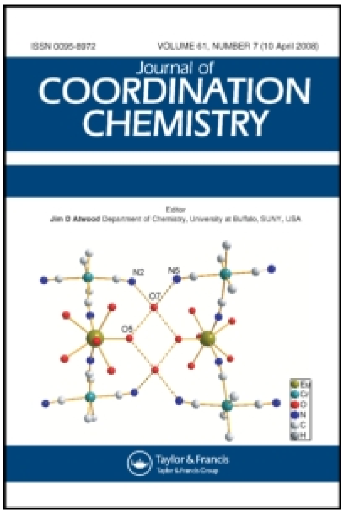

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NICKEL(II) AND ZINC(II) COMPLEXES OF β-ALANINEHYDROXAMIC ACID

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NOTE

NICKEL(II) AND ZINC(II) COMPLEXES OF β-ALANINEHYDROXAMIC ACID

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Potentiometric and spectrophotometric studies of Ni(II) coordination to β-alaninehydroxamix acid (β-Alaha) have shown 4N coordination of β-Alaha for 1:2 species and their planar geometry. The geometry of the species formed in the nickel(II)-β-Alaha below *ca.* pH 7 is octahedral. The differences between the stabilities of zinc(II)-β-Alaha and zinc(II)-α-alaninehydroxamic acid complexes can be explained by the terdentate coordination of the β-alaninehydroxamic acid.

KEY WORDS: Nickel, zinc, β-alaninehydroxamic acid, complexes, potentiometry, stability constants.

INTRODUCTION

β-Alaninehydroxamic acid (β-Alaha) contains NH_2 and hydroxamic acid groups β to each other. Thus 6-membered (N,N) chelate (*via* the amino and hydroxamate nitrogens) or 5-membered (O,O) rings (through the two hydroxamate oxygens) can be formed with various metal ions. Results recently published on copper(II)-β-Alaha[1] show that the stabilities of the above chelates are quite comparable. A very stable pentanuclear species $[(Cu_5L_4H_{-4}]^{2+}$ was found both in the solid state and in solution with alternating (N,N) and (O,O) chelates in it.

In the present work the nickel(II) and zinc(II) complexes of β-Alaha have been studied by pH-metric and spectrophotometric methods. Results as compared both to results for complexes of acetohydroxamate (Aha) and those formerly published[2] for α-Alaha have also been evaluated.

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EXPERIMENTAL

β-Alaha was prepared as described in ref. 1. Aha was purchased from Sigma. The purity of β-Alaha and the exact concentration of stock solutions made from the ligands was determined by Gran's method.[3]

Solutions containing metal ions were made from nickel chloride and zinc(II) oxide (Reanal) by dissolving the appropriate amount in doubly distilled water or hydrochloric acid of known concentration, respectively. Concentrations of stock solutions were checked gravimetrically *via* precipitation of the appropriate 8-hydroxyquinolinate.

For pH-metric titrations the metal-ligand ratios were in the range of 1:1–1:6 (five different ratios). The maximum concentration of β-Alaha and Aha was 5×10^{-3} mol dm^{-3}.

The ionic strength was adjusted to 0.2 mol × dm^{-3} with KCl. Titrations were carried

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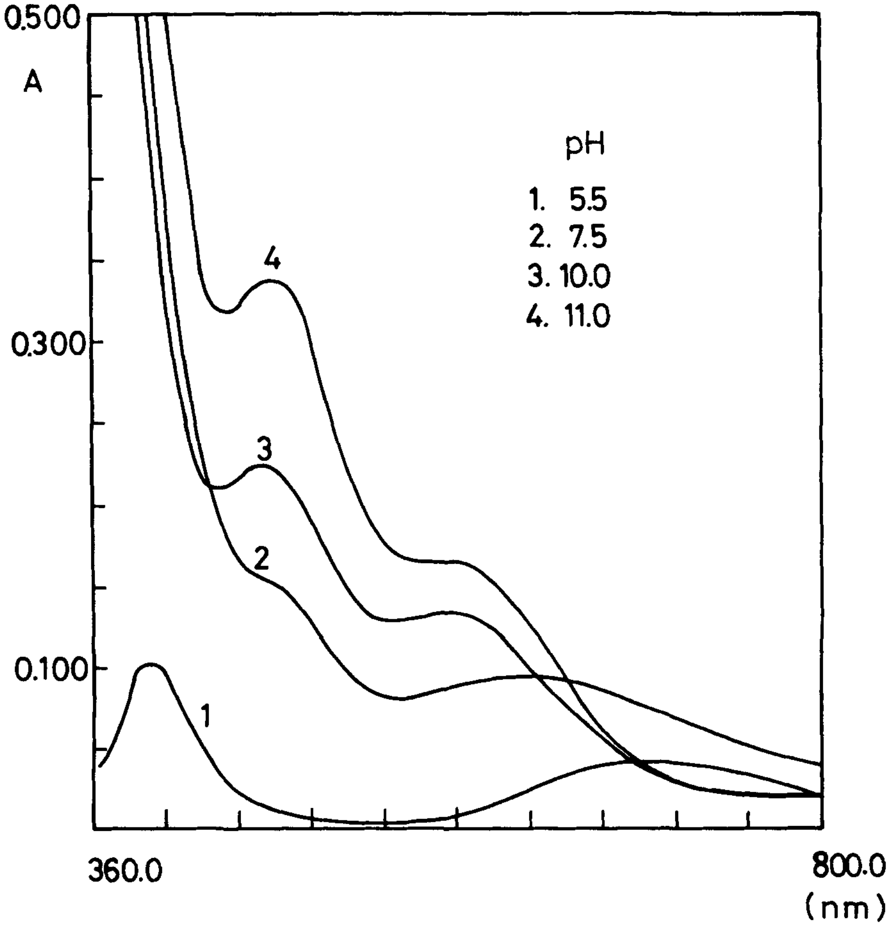

Figure 1 Visible spectra recorded for nickel(II)-β-Alaha; $c_L = 3 \times 10^{-2}$ mol dm^{-3}; $c_M = 1 \times 10^{-2}$ mol dm^{-3}.

out at 297K, with carbonate-free KOH solutions of known concentration (*ca* o.2 mol dm^{-3}). All measurements were made under an argon atmosphere.

A radiometer PHM 84 pH meter with an ABU 13 burette and a GK 2421C combined electrode was used. The electrode system was calibrated by the method of Irving *et al.*[4] so that readings could be converted into hydrogen ion concentrations. The calculations were performed with the aid of the PSEQUAD computer program.[5]

The absorption spectra of nickel(II)-β-Alaha samples were recorded on a Varian DMS100 double-beam recording spectrophotometer over the range 360–800 nm at metal-ligand ratios of 1:3 and 1:5.

RESULTS AND DISCUSSION

The acid-base chemistry of β-Alaha was studied in an earlier paper[6] in which the dissociation macroconstants were determined by pH-metric titrations and microconstants by combined pH-^{13}C NMR titrations. The results showed that the hydroxamic group is somewhat more acidic in β-Alaha than the -NH_3^+ fragment.

Ni(II) and Zn(II) complexes of β-Alaha

A comparison of the experimental findings with those for α-Alaha[2] revealed some differences: whereas only complexes with planar geometry are formed with nickel(II)-α-Alaha,[2] the geometry of species formed with nickel(II)-β-Alaha below *ca* pH 7 is (are) octahedral as it can be seen from Fig. 1.

While precipitation occurred in all samples in the zinc(II)-α-Alaha[2] system above pH 7.5–8.0, samples made with β-Alaha were titrated wthout precipitation if the metal-ligand ratios were higher than 1:2.

Models that provided the best fit with pH-metric data and the refined formation constants together with data (used as reference) for metal ion-α-Alaha[2] and metal ion-Aha systems are given in Table 1. Data for metal ion-Aha complexes can be found in the literature,[7] but for comparison we had to determine all of the data under the same conditions.

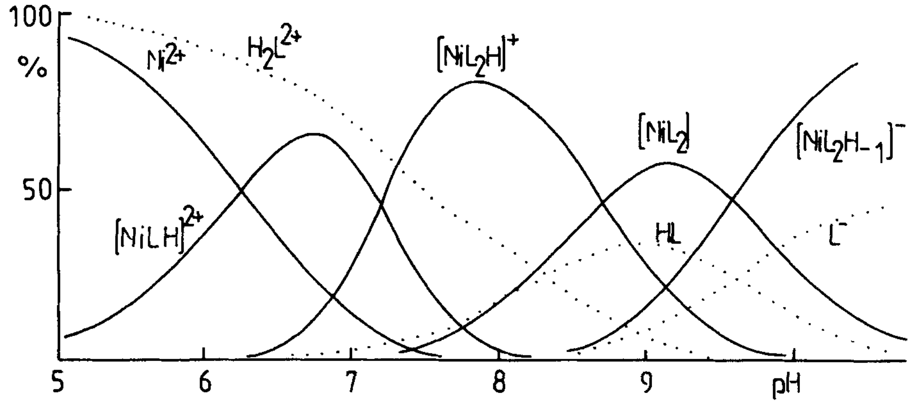

Figure 2 Species distribution for nickel(II)-β-Alaha system as a function of pH: $c_L = 4 \times 10^{-3}$ mol dm^{-3}; $c_M = 1 \times 10^{-3}$ mol dm^{-3}. Percentage of species refers to total metal except for the metal-free forms, which refer to total ligand.

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Table 1 Stability constants (log β) for H^+, Ni^{2+} and Zn^{2+} complexes formed with β-Alaha, α-Alaha and Aha; T = 298 K, I = 0.2 mol × dm^{-2} (KCl)

	log β		
Species	β-Alaha	α-Alaha[a]	Aha
[HL]	9.59	9.16	
[H_2L]	8.32	7.34	
[NiLH]	14.12		
[NiL]		6.76	5.15
[$NiLH_{-1}$]			−4.35
[NiL_2H]	20.26		
[NiL_2]	11.57	14.13	9.18
[NiL_2H_{-1}]	1.99	5.47	
[NiL_3]			11.68
[ZnLH]	14.16	12.27	
[ZnL]		5.29	5.18
[$ZnLH_{-1}$]		−2.26	
[ZnL_2H_2]	27.59		
[ZnL_2H]	19.65		
[ZnL_2]	10.85	9.32	9.45
[ZnL_2H_{-1}]	1.05		
[ZnL_3]			11.57
[Zn_2L_3]		18.77	

[a] See ref. 2. Charges are omitted for simplicity.

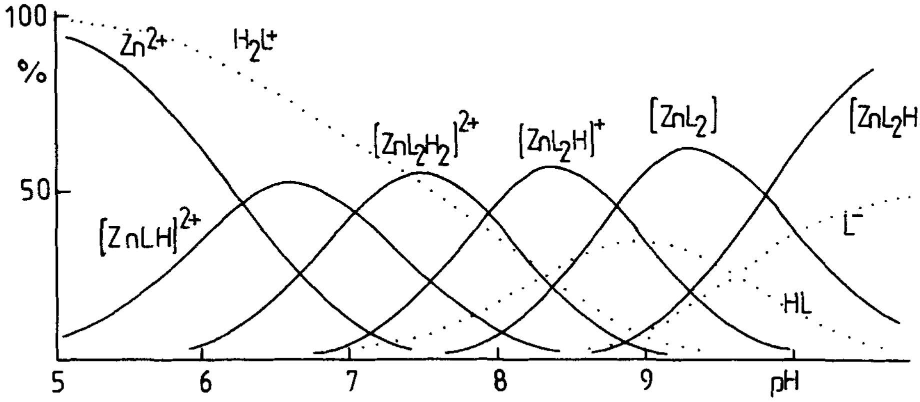

Figure 3 Species distribution for zinc(II)-β-Alaha system as a function of pH; $c_L = 4 \times 10^{-3}$ mol dm^{-3}; $c_M = 1 \times 10^{-3}$ mol/dm^{-3}. Percentage of species refers to total metal except for the metal-free forms, which refer to total ligand.

As can be seen in Table 1 protonated complexes are formed in metal ion-β-Alaha systems. Taking into account the appropriate protonation constant of β-Alaha, hydroxamate type (O,O) coordination can be supposed for all protonated species. The formation of complexes with planar geometry in the nickel(II)-β-Alaha system above pH 7 (see Fig. 1) is very surprising. In that pH range 1:2 species ([NiL_2H]$^+$, [NiL_2], [NiL_2H_{-1}]$^-$) are formed as can be seen in Fig. 2.

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A comparison of the data for nickel(II)-*β*-Alaha 1:2 species with those for nickel(II)-*α*-Alaha and nickel(II)-Aha indicates the 4N coordination of *β*-Alaha. The differences between the stabilities of nickel(II)-*α*-Alaha and nickel(II)-*β*-Alaha complexes can be explained by the fact the formation of a 6-membered chelate ring is less favoured than that of a 5-membered one. Steric factors may favour planar geometry with the two 6-membered (N,N) chelates rings in the nickel(II)-*β*-Alaha complexes.

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