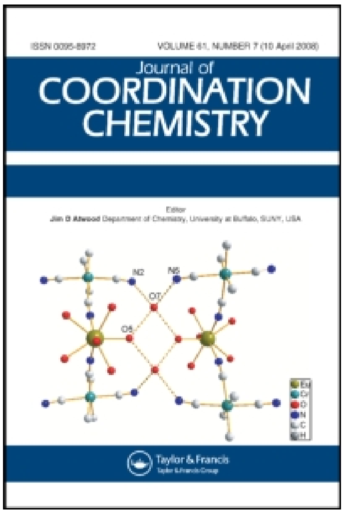

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# Coordination of Cadmium(II) by β-Alaninehydroxamic Acid. Potentiometric, Polarographic and Proton NMR Studies

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# COORDINATION OF CADMIUM(II) BY β-ALANINEHYDROXAMIC ACID. POTENTIOMETRIC, POLAROGRAPHIC AND PROTON NMR STUDIES

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Potentiometric, polarographic and NMR studies of Cd(II) coordination to β-Alaninehydroxamic acid have shown that aminohydroxamic acid ligands can be very effective chelating agents for this ion. The formation of oligonuclear species with involvement of most donor atoms seems to be a characteristic feature of aminohydroxamic acids having amino and hydroxamic groups to each other.

**Keywords:** Cadmium, β-alaninehydroxamic acid, stability constants, polarography, potentiometry

## INTRODUCTION

β-Alaninehydroxamic acid (β-Alaha, $NH_2CH_2CH_2CONHOH$) was found to be a very effective ligand for Cu(II) and Zn(II).[1,2] The possibility of different coordination modes derives from two strong donor sets *i.e.*, $NH_2$ and hydroxamic (CONHOH) groups. The amino and hydroxamic group nitrogen atoms may form a very stable 6-membered chelate ring while the two hydroxamic oxygen atoms, involved in the $\pi$ bond system of the CONHOH unit, would form another effective 5-membered chelate ring. Due to this arrangement, β-Alaha forms an unusually stable pentameric complex with Cu(II).[1] With Zn(II), β-Alaha forms stronger complexes than its α-amino acid analogue, α-Alaninehydroxamic acid.[3] The unique properties of the aminohydroxamic acid donors cause the coordinating ability of β-Alaha to be much more potent than with similar ligands which form complexes with a sequence of alternating five- and six-membered rings, *e.g.*, linear aliphatic tetraamines[4–6] or linear aliphatic triamines.[7]

Hydroxamic acids are powerful ligands of biological importance, due to their complexing properties.[8,9] It was thus interesting to follow their binding ability towards a set of toxic metal ions like cadmium, to which relatively little attention has been given. In this work we report the stabilities and binding modes for Cd(II) β-Alaha complexes.

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## EXPERIMENTAL

### *Potentiometric measurements*

β-Alaninehydroxamic acid was prepared by a method described earlier.[1] The ligand concentrations in solutions studied were determined potentiometrically. Ionic strength was maintained at 0.2 mol dm$^{-3}$ using KCl. The measuring system was kept at 25°C. Titrations were carried out with carbonate-free KOH solution of known concentration (*ca* 0.2 mol dm$^{-3}$). Small amounts of base were added using a micropipette; pH-metric titrations were performed over the pH range 2.0–11.0 using 20.0 cm$^3$ samples. The concentration of ligand was $5 \times 10^{-3}$ mol dm$^{-3}$, with metal-to-ligand mol ratios in the range 1:1–1:6. Measurements were carried out using an OP-208/1 pH-meter (Radelkis) equipped with OP 7183 glass and OP 830 saturated calomel electrodes. The electrode system was calibrated by the method of Molina *et al.*[10] Resulting titration data were used to calculate hydrogen ion concentrations from the potential readings. Formation constants were calculated using the SUPERQUAD computer program.[11]

Standard deviations quoted were computed by SUPERQUAD and refer to random errors only. They give, however, a good indication of the importance of the particular species in the equilibrium.

### *Polarographic measurements*

Measurements were carried out with a three-electrode system. A dropping or hanging mercury drop electrode (DME or HMDE), a saturated calomel electrode (SCE) and a platinum wire served as working, reference and auxiliary electrodes, respectively. All measurements (differential pulse polarography-DPP, normal pulse polarography-NPP) were performed with a PA-4 instrument (Laboratorni Pristroje-Praha) with an x–y recorder (ENDIM 200.02). Experiments were carried out under an argon atmosphere at 25°C in a medium of constant ionic strength (0.2 M $KNO_3$ and 0.2 M $Na_2SO_4$) with a pH range 6.5–9.5. Aqueous solutions containing $1 \times 10^{-4}$ Cd(II) or $5 \times 10^{-5}$ M Cd(II) were titrated with 100 μl to 1600 μl of a $1 \times 10^{-2}$ M solution of β-Alaha. The metal-to-ligand mol ratios ranged from 0.5:1 to 1:32. To distinguish between monomeric and polymeric species, dilution experiments were performed in which $c_L/c_M$ was maintained constant at 5:1 with a starting ligand concentration of $c_L = 5 \times 10^{-3}$ M.

### *NMR measurements*

Proton NMR measurements were carried out on a 400 MHz Bruker spectrometer with the same ligand concentration as in the potentiometric study for a metal-to-ligand ratio of 1:2.

## RESULTS AND DISCUSSION

In the measurable pH range, the fully protonated form of β-Alaha ($H_2L^+$) can release two protons in an overlapping process, one from the amino group and the other from the hydroxamic acid group. The dissociation micro-constants characteristic of the acidity of the particular groups were determined by selective monitoring of the dissociation of the $NH_3^+$ group *via* the $^{13}C$ chemical shift data relating to the closest β-carbon atom.[12] According to these results the NHOH group was shown to be more acidic than the $NH_3^+$ group.

Calculations based on the potentiometric data have indicated the formation of the [MLH], $[M_2L_2]$ and $[MLH_{-1}]$ species with the stability constants as shown in Table I. The calculated species distribution curves (Figure 1) indicate that coordination begins at pH 5.5 with the formation of CdLH. It is the major complex at pH 7.5 (55% of total metal concentration). The dinuclear complex $[Cd_2L_2]$, present from pH 7.5 to 10.0, reaches a maximum concentration (above 70%) at pH 8.5. At very basic pH $[CdLH_{-1}]$ predominates and it most likely results from the hydrolysis of the dinuclear complex. Its real formula should actually be presented as [CdLOH].

TABLE I

Stability constants ($\log\beta_n$) for the complexes $M_pL_qH_r$; M = Cd, L = β-Alaninehydroxamate ion, in 0.2 KCl at 25°C. Standard deviations are given in parentheses.

| | Potentiometric method | | Polarographic method | |
|---|---|---|---|---|
| Species | pH-metric method | ion selective method | NPP | DPP |
| $[CdLH]^{2+}$ | 13.46(4) | 13.41(10) | 14.07(14) | 13.79(5) |
| $[Cd_2L_2]^{2+}$ | 14.05(6) | | | 13.82(30) |
| $[CdLH_{-1}]$ | −3.70(11) | | | |

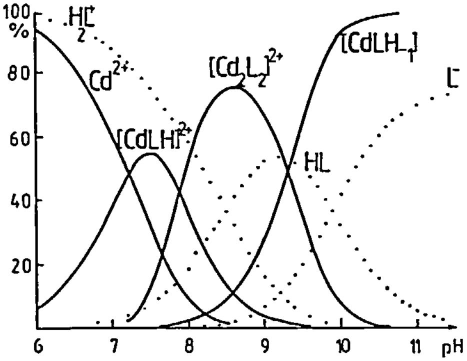


FIGURE 1 Species distribution curves for Cd(II)–β-Alaha for a metal concentration of $1.5 \times 10^{-3}$ mol dm$^{-3}$ and a 1:4 metal-to-ligand mol ratio. Percentages of species refer to total metal except for the metal-free forms, which refer to total ligand.

In order to obtain additional evidence for the model obtained from the potentiometric data calculations, polarographic measurements were also performed. NPP and DPP techniques were used to establish free metal ion concentrations. Assuming that at pH 7.6 the major complex is an equimolar species as indicated in Figure 2, the stability constant [CdLH] was calculated; it is very close to that obtained from potentiometric measurements (Table I). The free metal concentration was also evaluated with a cadmium ion-selective electrode and this procedure leads to similar

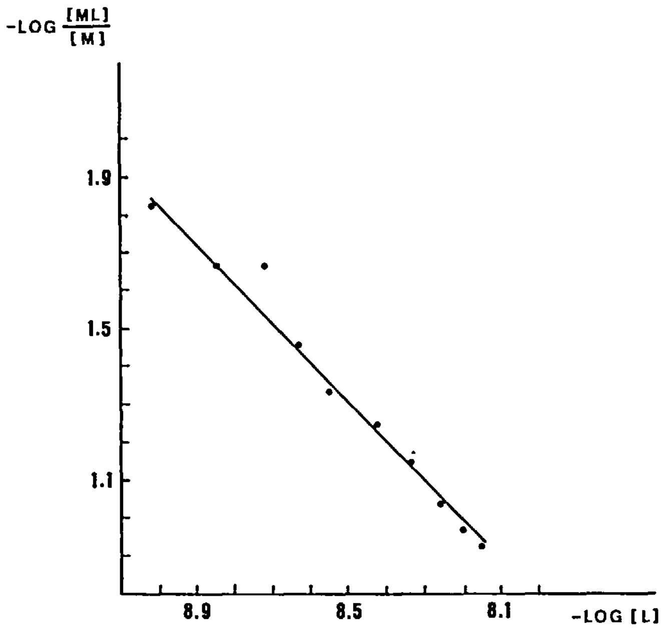


FIGURE 2 Dependence of log[ML]/[M] on log[L] for the Cd(II)–β-Alaha system. [ML] corresponds to the concentration of CdLH species. [M] is a free metal concentration and [L] is a free ligand concentration. The slope corresponds to equimolar species.

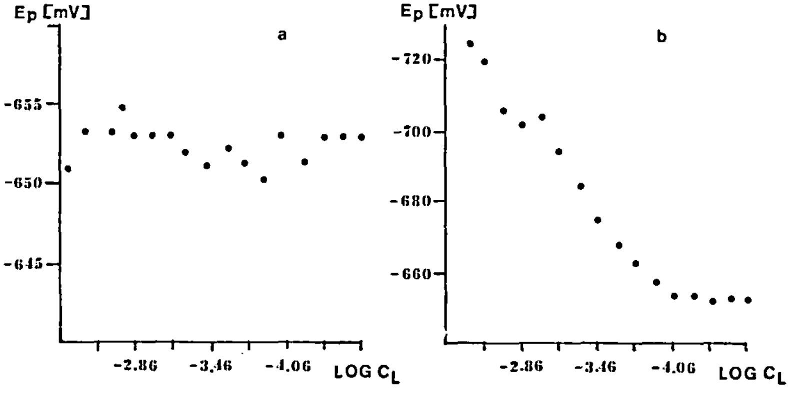
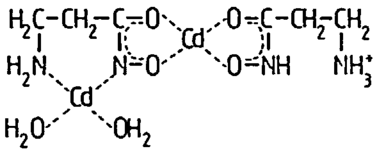


FIGURE 3 Dependence of $E_p$[mV] on log $c_L$ for Cd(II)–β-Alaha solutions for a constant metal-to-ligand mol ratio of 1:5 at pH 7.5 (a) and pH 9.5 (b). $E_p$ is the metal reduction peak potential and $c_L$ is the total ligand concentration.

result (Table I). Variation of $E_p$ ($E_p$ is the DPP peak potential for $Cd^{2+}$ reduction) observed during the experiment, in which the ligand-to-metal ratio is kept constant (5:1) while the total concentration changes, is characteristic for each particular species.[14] This behaviour was checked for the species formed at pH, [CdLH], and 9.5, [$Cd_2L_2$]. The results obtained (Fig. 3) clearly indicate that both complexes are distinctly different. The potential of metal ion reduction in the monomeric complex is independent of the dilution process and it is centred around −0.653 V. Dilution of the solutions at pH 9.5, however, causes an increase of reduction potential from −0.725 to −0.653 V. The latter potential is characteristic of the monomeric unit (Fig. 3). Since dilution would destabilize oligomeric species,[13] the results in Figure 3 strongly indicate the presence of the dinuclear complex suggested by potentiometric data calculations. Assuming that this species has the formula the potentiometric data suggests, *i.e.*, $[Cd_2L_2]$, the stability constant evaluated from polarographic data is close to that obtained from potentiometry (Table I).

Proton NMR spectra consisted of two triplets corresponding to α- and β-$CH_2$ protons at 2.665 and 3.365 ppm, respectively. The formation of the [CdLH] species causes only very slight changes in chemical shifts ($<0.03$ ppm) indicating that in this species the binding sites are far away from the methylene protons (*i.e.*, the cadmium ion binds only the hydroxamic group oxygens, $\{O^-, CO\}$, while the amino group remains protonated.[14] Formation of the dinuclear species causes a high-field chemical shift in both methylene group signals by 0.1 ppm (pH 9.2) as compared to the free ligand at the same pH. This suggests the involvement of both hydroxamic and amino group donors in metal ion coordination. The most likely structure of this complex is given below. This coordination mode seems to be characteristic for oligonuclear complexes as found by X-ray structural methods for the pentameric copper(II) complex.[1]



$[Cd_2L_2]^{2+}$

β-Alaninehydroxamic acid is found to be a very effective ligand for Cd(II) ions. Coordination of metal ion begins with hydroxamic group oxygen atoms at about pH 6.0. The presence of two potent binding sets, *i.e.*, $\{CO, O^-\}$ and $\{NH_2, N^-\}$, leads to the formation of a very stable dinuclear complex which is dominant at high pH. Although aminohydroxamic acids form less stable complexes than thiol-containing amino acids, they are very effective chelating agents for heavy metal ions.

## ACKNOWLEDGEMENTS

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