# Solution Properties of Cu(II)–L-α-leucinehydroxamic Acid

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## Abstract

Species distributions and relevant stability constants of species present in aqueous solutions of Cu(II) with bidentate L-α-leucinehydroxamic acid ($(CH_3)_2CHCH_2CH(NH_2)CONHOH$ = HL) have been obtained by analytical potentiometry at 25 °C and $I = 0.1$ M ($NaClO_4$). Together with ESR of frozen solutions measurements, these results show the existence of four different complex copper(II) species, one of which is a dimeric one.

The solution electronic spectra are reported too. The experimental curve was resolved into precise-positioned absorption bands by Gaussian analysis for the bis(L-α-leucinehydroxamato)copper(II) species. These data were used in a weak tetragonal ligand field model to calculate ligand field parameters.

The structures of the complexes are discussed and conclusions are drawn based on absorption and ESR spectra.

## Introduction

This paper is the second part of a series devoted to making a choice of chemical models on the basis of results of aqueous solutions potentiometric titration of some transition metals with aminohydroxamic acid and to determining the stability constants of the various species present in those solutions.

The pioneering work of Bjerrum [1] on metal ion–ammine complexes showed how the 'degree of formation', $\bar{n}$, could be used in the calculation of stepwise equilibrium constants for mononuclear metal complexes. Subsequently, methods based on $\bar{n}$ functions [2] have been used to obtain most of the published metal complex stability data. Because of the convenience of such methods it has become customary to interpret pH titration data for solutions in terms of the formation of the metal complexes

$ML, ML_2, ..., ML_n$. With the recent development of computer programs [3] for refining equilibrium constant values, it has become possible to examine the contributions of hydrolysed metal ions and complexes, polynuclear complexes and metal ion-protonated ligand complexes.

We have applied the computer program SCOGS [4] to pH titration data. In calculations of equilibrium constant values we have used the refinement program to test all species which might reasonably be expected to be present.

## Experimental

### Reagents and Materials

L-α-leucinehydroxamic acid (HL) was prepared by mixing ice-cold methanol solutions of L-α-leucine methyl ester (0.1 mol) and hydroxylamine (0.1 mol). When the mixture was cooled, HL crystallized easily. Recrystallization from methanol/aqueous solution of acetic acid (1%) gave pure crystals: yield 48%. *Anal.* Calc.: C, 49.30; H, 9.65; N, 19.16. Found: C, 49.29; H, 9.93; N, 18.96%.

Bidistilled water was used throughout and all titrations were carried out under an atmosphere of purified argon. All reagents were of analytical grade. Stock solution of copper(II) perchlorate (0.1 mol) was prepared by dissolving a proper amount of copper(II) perchlorate hexahydrate in water. The exact concentration of the solution was determined by the iodometric method.

### Potentiometric Titrations

Measurements of pH were carried out on OP-208 pH-meter (Radelkis) with a digital readout, equipped with OP 7183 glass and OP 830 saturated calomel (containing NaCl) electrodes. The electrode system was calibrated by periodic titrations of perchloric acid solution (0.1 M in $NaClO_4$) with standard sodium hydroxide solution. The resulting titration data was used to calculate the standard electrode potential $E°$ and the dissociation constant for water.

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Potentiometric titrations were carried out on a series of solutions (20 ml total volume) 0.1 M in $NaClO_4$ and sufficient $HClO_4$ to bring the starting pH close to 2.5. The measuring system was thermostated at $25 \pm 0.1$ °C. Small amounts of base were added with the use of a micropipette.

Ligand titrations were performed in the absence of copper ions (in this case, titration curves were obtained by varying the initial concentration of L-$\alpha$-leucinehydroxamic acid at $1.0 \times 10^{-2}$, $5.0 \times 10^{-3}$ and $2.5 \times 10^{-3}$ M, respectively) and in the presence of copper ions ($1.0-0.2 \times 10^{-3}$ M) (in this case, the concentration ratios of ligand to metal ions varied in the range of 2.5:1 to 5:1). Formation constants were calculated using Bjerrum method [1] and a modified version of the computer program SCOGS [4]. Species distribution as a function of pH was determined with the COMICS [5] computer program.

### ESR Measurements

The ESR spectra were obtained using a JES-ME X-band spectrometer, proton magnetometer and ESR standards, at 170 K. The samples were prepared from a stock solution containing 0.1 M $NaClO_4$, $4 \times 10^{-3}$ M copper(II) ions and $1.0 \times 10^{-2}$ M L-$\alpha$-leucinehydroxamic acid in bidistilled water. The pH was adjusted with 1.0 M NaOH solution.

### Spectrophotometric Measurements

Absorptions in the region 400–900 nm were obtained on a SPECORD M-40 (C. Zeiss, Jena) spectrophotometer and solutions were scanned at a series of pH values from pH 2.5–6.5 by using 3 cm quartz cells and from pH 6.5–12.0 by using 5 cm quartz cells. The former stock solution was 0.08 M in $NaClO_4$, $5 \times 10^{-4}$ M in Cu(II), $2.5 \times 10^{-3}$ M in HL and $5 \times 10^{-3}$ M in $HClO_4$ and the latter 0.1 M in $NaClO_4$, $2 \times 10^{-4}$ M in Cu(II), $1 \times 10^{-3}$ M in HL and $2 \times 10^{-3}$ M in $HClO_4$. The pH was adjusted by adding 1.0 M NaOH solution.

## Results and Discussion

L-$\alpha$-leucinehydroxamic acid (HL) is able to coordinate an additional proton to the amino group (pK = 7.14) and contains one ionizable proton in its hydroxamic acid group (p$K_a$ = 9.10).

Evaluation of the $\beta_{pqr}$ constants, using the computer program SCOGS, led us to include a fourth copper(II) species. The calculated concentrations of four copper(II) species, as a function of pH, in solution containing $1 \times 10^{-3}$ M Cu(II) and $2.5 \times 10^{-3}$ M L-$\alpha$-leucinehydroxamic acid indicate that under these conditions the $CuL^+$ species is not more than 27% of the total copper content in solution, while the dimeric species, at pH = 5, almost reaches 83%. The

TABLE I. Logarithmic Stability Constants (log $\beta_n$) of Complexes Species $M_pH_qL_r$ (M = Cu, L = L-$\alpha$-Leucinehydroxamate Ion) in 0.1 $NaClO_4$ at 25 °C (standard deviations given in parentheses)

| p | q | r | Numerical method (SCOGS) | Bjerrum method |
|---|---|---|---|---|
| 0 | 1 | 1 | 9.104(5) | 9.12 |
| 0 | 2 | 1 | 16.245(6) | 16.26 |
| 1 | 0 | 1 | 10.83(9) | 11.26 |
| 2 | -1 | 2 | 21.09(5) | |
| 1 | 0 | 2 | 19.51(3) | 19.32 |
| 1 | -1 | 2 | 9.98(6) | |



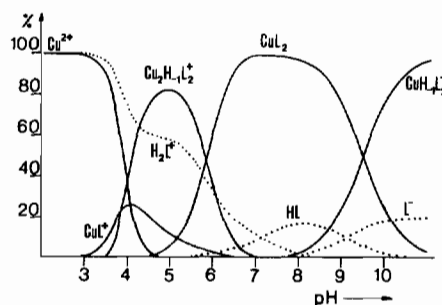Fig. 1. Species distribution in the Cu(II)/L-$\alpha$-leucinehydroxamic acid system as a function of pH, $c_M = 1.0 \times 10^{-3}$ M; $c_L = 2.5 \times 10^{-3}$ M. Percentage of the species refer to total metal except for the metal-free forms, which refer to total ligand.

species $CuL_2$, from pH = 7 to 8, corresponds to over 98%, with a maximum of 99% at pH about 7.5. The resulting formation constants are given in Table I and the species distribution is given in Fig. 1. Similar results were obtained for the Cu(II)/glycinehydroxamic acid system [6] and the Cu(II)/L-$\alpha$-alaninehydroxamic acid system [7].

### Electron Spin Resonance Spectra

Due to the small concentration of Cu(II)–L-$\alpha$-leucinehydroxamic acid complexes in water solution, their room temperature ESR spectra are not distinguishable. On the other hand, this concentration is sufficient to record the well resolved frozen solution spectra.

The changes of ESR spectra as a function of pH (Fig. 2) reveal that, in general, similar complexes arise as described for the Cu(II)/L-$\alpha$-analinehydroxamic acid system [7]. At the lowest pH (2.56) the ESR spectrum is typical for Cu(II) ions surrounded by $H_2O$ molecules. The new spectrum appears at pH = 3.40 indicating the formation of the $CuL^+$ complex (in equilibrium with Cu(II) aquoions) predicted on the basis of potentiometric titration. The values of its ESR parameters (Table II) suggest $N_2O_2$ coordination. The gradual change of the spectrum assigned to
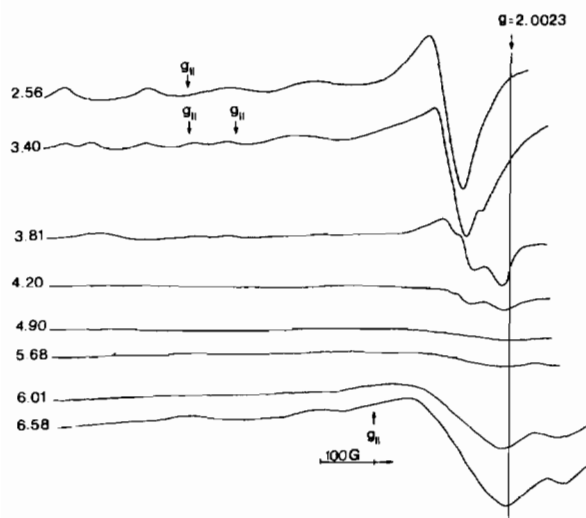
Fig. 2. ESR spectra of Cu(II)/L-α-leucinehydroxamic acid as a function of pH, $c_M = 4.0 \times 10^{-3}$ M; $c_L = 1.0 \times 10^{-2}$ M; solvent, $H_2O$; temperature, 170 K; microwave frequency, 9.186 GHz.

TABLE II. The Parameters of the ESR Spectra

| | pH | | | |
|---|---|---|---|---|
| | 2.56 | 3.40 | 4.90 | 6.58 |
| Form | Cu(II)aquo | CuL+ | Cu2H−1L2+ | CuL2 |
| $g_{\parallel}$ | 2.401 | 2.330 | | 2.170 |
| $\lvert A_{\parallel} \rvert$ $(10^{-4}$ cm$^{-1})$ | 146 | 168 | | 220 |

CuL+ complex with further increase of pH (from pH = 3.81 to pH = 4.20) is associated with an increasing contribution of the dimeric Cu2H−1L2+ complex in the solution. The complete disappearance of the spectrum is reached at pH = 4.90, which corresponds to the maximum concentration of the dimeric complex. The new spectrum reappears at pH = 5.68 and achieves a better resolution at pH = 6.58. This spectrum is characteristic of Cu(II) coordinated by four nitrogen donor group [7] supporting the formation of the CuL2 complex. It is not possible to obtain the ESR spectra above pH = 6.58 due to partial precipitation of the complexes, which occurs in the case of the used concentrations of the reagents.

*Electronic Spectra/pH Profile*

The absorption spectra of Cu(II)–L-α-leucine-hydroxamic acid exhibit, in general, approximately the same changes with increasing pH to those stated for Cu(II)–glycinehydroxamic acid [6] and Cu(II)–L-α-alaninehydroxamic acid [7]. Some differences are observed in the energy of the characteristic absorption maxima.
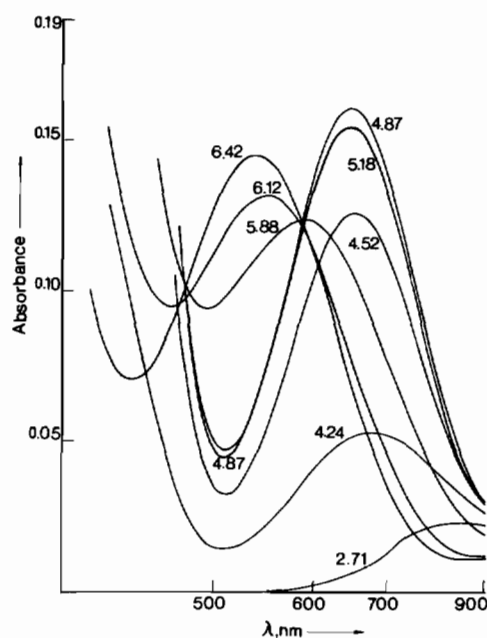


Fig. 3. Visible spectra of Cu(II)/L-α-leucinehydroxamic acid as a function of pH, pH range 2.7–6.4; $c_M = 5.0 \times 10^{-4}$ M; $c_L = 2.5 \times 10^{-3}$ M (3 cm cells).

TABLE III. Spectrophotometric Data for CuL2 Species as a Function of pH (pH range 6–9)

| pH | Band maxima (nm) | Absorption |
|---|---|---|
| 5.959 | 454 | 0.156 |
| 6.224 | 540 | 0.139 |
| 6.568 | 530 | 0.135 |
| 6.912 | 530 | 0.136 |
| 7.154 | 530 | 0.140 |
| 7.516 | 530 | 0.140 |
| 7.856 | 530 | 0.140 |
| 7.872 | 530 | 0.140 |
| 7.976 | 530 | 0.140 |
| 8.150 | 530 | 0.144 |
| 8.517 | 530 | 0.146 |
| 8.773 | 530 | 0.148 |
| 9.139 | 532 | 0.150 |

The formation of the complexes between Cu(II) and the investigated ligand begins at a low pH value (Fig. 3). The maximum of the broad spectrum near the infrared region shifts towards the visible region with increase of pH. At pH 4.87 the maximum occurring at 649 nm corresponds to the greatest concentration of the dimeric complex (Fig. 1). The characteristic isosbestic point seen at 595 nm is associated with an equilibrium between the Cu2H−1L2+ and CuL2 complexes. The maximum at 530 nm does not change its energy from pH = 7 to 8 (Table III),
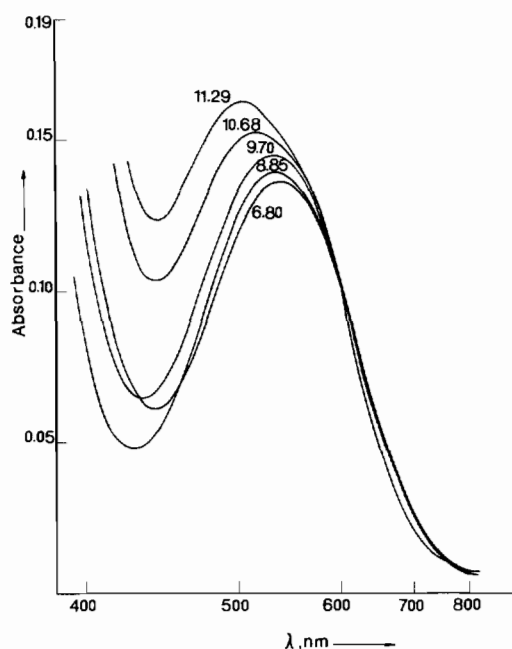
Fig. 4. Visible spectra of Cu(II)/L-α-leucinehydroxamic acid as a function of pH, pH range 6.8–11.3; $c_M$ = 2.0 × $10^{-4}$ M; $c_L$ = 1.0 × $10^{-3}$ M, (5 cm cells).

which corresponds to the predominant concentration of the $CuL_2$ complex in this pH range. The next shifting of the maximum with further increase in pH above 9.5 is consistent with the formation of the new $CuH_{-1}L_2^{-1}$ complex (Fig. 4).

The position of the absorption maximum for Cu(II) complexes in water solution depends on the number of Cu–N bonds [7]. Since, the dinuclear complex $Cu_2H_{-1}L_2^+$ exhibits $\lambda_{max}$ at 649 nm, it is possible to conclude that one copper cation is coordinated by two nitrogen atoms of the ligand.

Studies of the equilibria existing between Cu(II) ion and glycinchydroxamic acid have indicated the presence of an $OH^-$ in the dinuclear species [6]. This one $OH^-$ ion acts as a bridging group. Similar bridging of $CuL^+$ units by $OH^-$ groups is postulated in the $Cu_2H_{-1}L_2^+$ complex.

The appearance of the absorption maximum at 530 nm in the case of the studied Cu(II)/HL system suggests the coordination of one copper cation by two ligands forming two five-membered rings and supports its $CuL_2$ formula. In this complex the coordination is realised by two nitrogens of α-amino and -NHOH group [7].

### Interpretation of Spectra of the $CuL_2$ Species

In the first paper [7] the general principles of the method for determination of tetragonal ligand field parameters were presented. The method combines closely the ligand field theory with numerical resolu-

tion of spectra of the complexes in solutions. Unfortunately, the solution spectra at room temperature do not provide sufficient resolution for consideration of the lower symmetry. Fundamentally the procedure, which proceeded from Gaussian curve analysis, through assignment of the bands, to calculation of the ligand field parameters, is based on two assumptions: (1) the effective symmetry about the metal ion is $D_{4h}$; (2) the ligand field model is adequate for the deduction of spectral parameters.

Gaussian analysis was performed on electronic spectrum discussed herein using a dump least-squares computer program [7]. The experimental curve was resolved into precise-positioned absorption bands by Gaussian analysis assuming $D_{4h}$ (three bands) and $O_h$ (one band) symmetry. The results of both analysis were different in terms of root-mean-square deviations (RMS%) of calculated from observed spectral values: 0.99 for $D_{4h}$ and 1.11 for $O_h$ symmetry. Although both analysis are similar in terms of RMS% values, fine detail of spectral shape is reproduced more faithfully in former. On the other hand this difference is not so big as in bis(L-α-alaninehydroxamato)copper(II) complex [7].
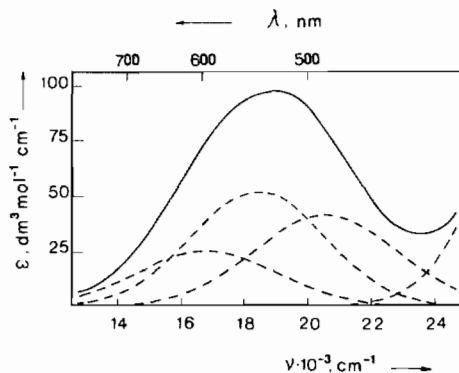


Fig. 5. Absorption spectrum of $CuL_2(H_2O)_2$: —— experimental bands; – – – composite bands.

Figure 5 shows the experimental spectrum and component bands obtained from spectral resolution. Table IV summarizes the results of resolution, parameters of component bands, their oscillator strength values and root-mean-square deviations.

For assumed $D_{4h}$ symmetry three spin-allowed transitions from the $^2B_{1g}$ ground state to the excited doublet states are to be expected and their energies in terms of $Dq$, $Ds$ and $Dt$ parameters are known [7, 8]. The ligand field parameters $Dq$, $Ds$ and $Dt$ derived from the set of equations are: $Dq = v_2/10$, $Ds = (v_2 - v_1 - v_3)/7$, $Dt = (4v_3 - 4v_2 - 3v_1)/35$. On the basis of transition energies and band assignments included in Table IV the ligand field parameters for the [$CuL_2$-

TABLE IV. Parameters of the Composite Bands Resulting from Gaussian Analysis of the Absorption Spectrum of $[CuL_2(H_2O)_2]$ (L = L-α-leucinehydroxamate Ion)[a]

| Assignment | $\epsilon$ (dm$^3$/mol cm) | $\nu$ (cm$^{-1}$) | $TW$ (cm$^{-1}$) | $f$ |
|---|---|---|---|---|
| $^2B_{1g} \longrightarrow {}^2A_{1g}$ | 25.734 | 16820.4 | 5119.6 | $6.057 \times 10^{-4}$ |
| $^2B_{1g} \longrightarrow {}^2B_{2g}$ | 53.571 | 18382.3 | 4861.7 | $1.197 \times 10^{-3}$ |
| $^2B_{1g} \longrightarrow {}^2E_g$ | 42.472 | 20490.9 | 5211.2 | $1.017 \times 10^{-3}$ |
| Unassigned band | 913.398 | 31772.3 | 6657.6 | $2.796 \times 10^{-2}$ |

[a]RMS% = 0.99; region of spectrum: 12 000–25 000 cm$^{-1}$.

$(H_2O)_2]$ complex were calculated. Derived values are as follows: $Dq = 1838$ cm$^{-1}$, $Ds = -2704$ cm$^{-1}$ and $Dt = -1201$ cm$^{-1}$.

## Conclusions

The above ESR and spectroscopic results have shown that L-α-leucinehydroxamic acid coordinates to Cu(II) via the α-amino nitrogen and the nitrogen atom of the -NHOH group. In the pH range 4–6 aqueous solutions contain dimeric species. In the pH range 7–8 only the $CuL_2$ species is suggested.

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