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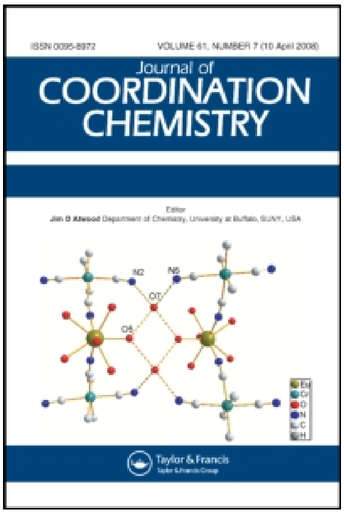

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Potentiometric and Spectroscopic Studies of Binary and Ternary Copper(II) Complexes with Histidinehydroxamic Acid

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POTENTIOMETRIC AND SPECTROSCOPIC STUDIES OF BINARY AND TERNARY COPPER(II) COMPLEXES WITH HISTIDINEHYDROXAMIC ACID

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Because the results concerning the Cu(II)-histidinehydroxamic acid (Hisha) system are somewhat controversial, we have performed a new study of the Cu(II)–Hisha binary system, using potentiometry and e.p.r. techniques. Since the occurrence of ternary complexes in natural systems is very probable, we have also undertaken potentiometric and spectroscopic studies of the Cu(II)–Hisha–His ternary system, where His is histidine.

Keywords: Copper, histidinehydroxamic acid, histidine, complexes, stability constants

INTRODUCTION

Great interest has recently been shown in the family of organic ligands containing a hydroxamic acid group. This class of compounds has been found to exhibit different biological activities as antibiotics, growth factors, antibiotic antagonists, tumour inhibitors and chelating agents in biological systems.[1-6] The hydroxamic acids and their aminoacid analogues have considerable coordinating abilities.[4,7] Aminohydroxamic acids are very effective ligands for Cu(II), due to the amino- and hydroxamate-nitrogens, which bind metal ions very strongly.[8-11] Histidine (His) itself is a basic aminoacid involved in the chelation of metal ions by peptides of various molecular weights. Hence, it is of interest to understand the binding ability of the hydroxamic acid analogue of this residue.

The Cu(II)-histidinehydroxamic acid (Hisha) system has been studied previously,[12,13] but the reported results are somewhat controversial. To render the situation relating to this system more comprehensive, and to acquire more reliable data, we have performed a new study of the Cu(II)–Hisha binary system, using potentiometry and e.p.r. methods. Since the occurrence of ternary complexes in natural systems is very probable, we have also undertaken potentiometric and spectroscopic studies of the Cu(II)–Hisha–His ternary system.

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EXPERIMENTAL

Materials

Details of the preparation of Hisha have been given earlier.[13,14] The ligand His (Fluka, purum) was used as purchased. The exact concentrations of the ligand stock solutions were determined by the Gran method.[15] $CuCl_2$ was purchased from Reanal. The metal ion stock solution was standardized gravimetrically *via* precipitation of the oxinate.

Potentiometric measurements

The protonation constants of the ligands and the stability constants of the parent and mixed complexes were determined potentiometrically. In the Cu(II)–Hisha (ligand A) system, 1:1, 1:2, 1:4 and 1:5 metal-ligand ratios were employed. The concentration of the ligand in the experimental solution was $4 \times 10^{-3} - 6 \times 10^{-3}$ mol dm^{-3}. Details of the measurements and the stability constants of the Cu(II)–His (ligand B) system have been reported previously.[16]

For the determination of the stability constants of the mixed complexes, the Cu(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, 1:2:1, 1:1:2 and 1:2:2. The titrations were carried out at 25°C and at 0.2 mol dm^{-3} ionic strength (KCl). The measurements were performed with a Radiometer pHM64 instrument, with G2040B glass and K4040 calomel electrodes, using a TTA80 titration unit. The method of Irving *et al.*[17] was used to eleminate the deviations arising from the diffusion potential differences and to transform the pH readings into values of $-\log [H^+]$. The calculations on the pH-metric data were performed with the aid of the PSEQUAD computer program.[10]

Spectroscopic measurements

E.p.r. spectra were recorded on a JES-ME X-band (9.3GHz) spectrometer at 120 K. The concentrations were the same as used in the potentiometric titrations.

RESULTS AND DISCUSSION

Cu(II)–Hisha system

The protonation constants found for the Hisha ligand in this work are similar to those obtained previously, as can be seen in Table I, where the stability constants for the proton and copper(II) complexes of Hisha are given together with earlier published data.

Only the lowest pK (5.43) can be unambiguously assigned (to proton dissociation from the imidazole nitrogen). The other two values are the macroscopic constants (9.07 and 7.14) and their assignment to deprotonation of the amine and hydroxamic groups is not direct.[11,14] The stability constants of the Cu(II) complexes and models of the species obtained in Refs 12 and 13 and in this work are, however, different. The major difference between the results concerns the formation of dimeric complexes; according to the present findings, these exist in three forms: $[Cu_2A_2H]^{3+}$, $[Cu_2A_2]^{2+}$ and $[Cu_2A_2H_{-1}]^{+}$. The last of these species was proposed earlier,[13] but

TABLE I

Overall stability constants for the Cu(II)–Hisha system.

p	*q*	*r*	Ref. 12	Ref. 13	this work
0	1	1	8.94	9.17	9.07(1)
0	1	2	16.00	16.33	16.21(1)
0	1	3	21.40	21.57	21.64(1)
1	1	2			20.4 (1)
1	1	1	16.92	17.75	17.46(3)
1	1	0	10.70		
2	2	1			34.03(3)
2	2	0			29.45(6)
2	2	−1		27.27	23.07(6)
1	2	2	29.15	33.36	33.53(3)
1	2	1	22.08	28.58	27.36(4)
1	2	0	13.73	21.46	20.23(4)
1	2	−1	3.34	10.85	10.31(6)

p q r refers to the $M_pA_qH_r$ species; values in parentheses are standard deviations.

with a different stability constant (Table I). To check on this dimer formation and the calculation of species distributions from potentiometric data, we have performed measurements of the e.p.r. spectra and correlated them with the complex concentration distribution presented in Figure 1b.

In the pH region 3.7–5.0, the intensity of the e.p.r. spectrum is only about half of the original intensity recorded at pH 2.1. This clearly indicates the formation of dinuclear e.p.r.-silent species[10] in the system. The presence of the dimeric species indicated by the e.p.r. spectra fits the results presented in Figure 1b very well. The correlation of spectroscopic and potentiometric data (Table I) lends strong support to the computed model of the species presented in this work.

With regard to the results for the dimeric species formed in the copper(II)–α-alaninehydroxamic acid system, the suggested bonding modes for the copper(II)–Hisha dimeric species are depicted in Scheme I.

Our assumption relating to the bonding modes in other complexes formed in the copper(II)–Hisha system is the same as that published previously.[13]

Cu(II)–Hisha–His system

The stability constants of the ternary complexes were calculated by using the data for the binary Cu(II)–His complexes obtained by Sóvágó *et al.*,[16] and those found for the Cu(II)–Hisha system in this work. The titration data are fitted satisfactorily to the assumption of the presence of the ternary complexes $[CuABH_2]^{2+}$, $[CuABH]^+$, [CuAB] and $[CuABH_{-1}]$. The stability constants obtained for the mixed complexes are given in Table II.

Concentration distribution curves are presented in Figure 2.

Figure 2 indicates the formation of ternary complexes above pH 3.2. The e.p.r. spectra of frozen solutions of *L*-Hisha and His in the presence of copper(II) at pH = 2.1 are typical of those for copper(II) ions surrounded by aquo molecules ($g_{\parallel}$ = 2.400; $A_{\parallel}$ = 146 G.) The intensities of signals in the e.p.r. spectra of the frozen solutions in the pH range 3.7–4.7 is less but not so much as in the binary system and agrees with the presence of the dimeric complexes $[Cu_2A_2H]^{3+}$, $[Cu_2A_2]^{2+}$ and

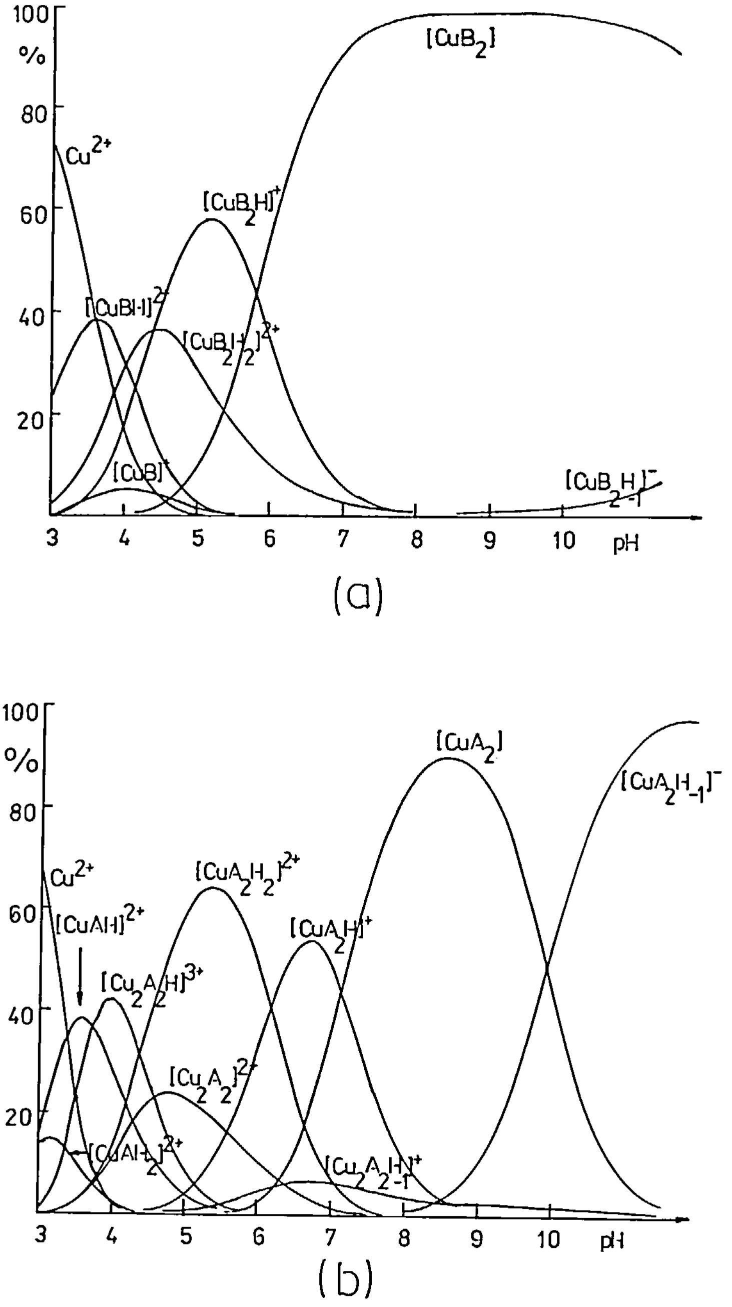


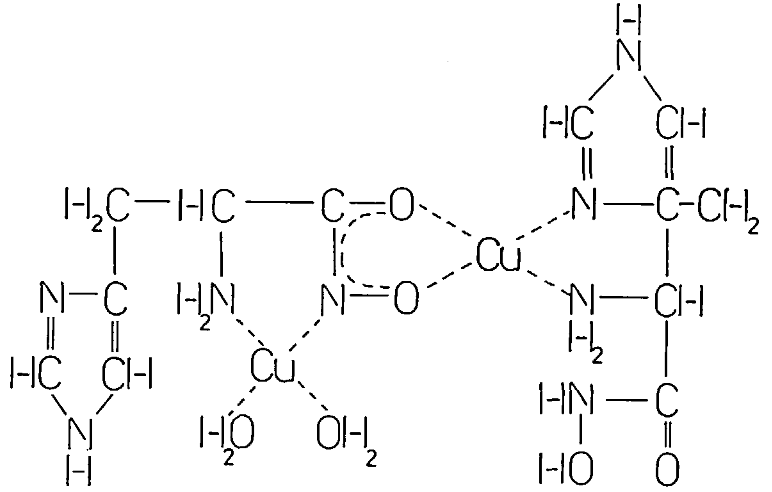
FIGURE 1 Species distribution patterns for Cu(II) complexes of His (a), and Hisha (b); [Cu(II)] = 2×10^{-3} mol dm^{-3}; [A] = [B] = 4×10^{-3} mol dm^{-3}.

TABLE II

Overall stability constants for the Cu(II)-Hisha (A)-His (B) system.*

Species	log β
$[CuABH_2]$	31.20(7)
$[CuABH]$	26.36(5)
$[CuAB]$	19.79(5)
$[CuABH_{-1}]$	9.50(8)

*Values in parentheses are standard deviations.



$[Cu_2A_2]^{2+}$

$[Cu_2A_2H_{-1}]^+$ postulated on the basis of the potentiometric titration data (Fig. 2). Additionally, Figure 2 shows that the presence of His suppresses the formation of dimeric Cu(II)-Hisha complexes in the ternary system. The e.p.r. parameters of the spectra for frozen solutions in the pH range 6.3–11 (Table III) resemble quite closely the values for CuN_4 centres ($g_\parallel = 2.212$; $A_\parallel = 195$ g).[10,13] Cu(II)-Hisha 1:2 complexes are formed in rather high concentrations at copper(II)-ligand A-ligand B ratios of 1:2:2. In contrast, Cu(II)-His binary complexes are not formed in any measurable concentration.

TABLE III

E.p.r. spectral parameters for the Cu(II)-Hisha-His system at 120 K.

pH	2.1	3.87	5.45	6.30–10.55
$g_\parallel$	2.400	2.211	2.211	2.212
$A_\parallel$(G)	146	180	180	195

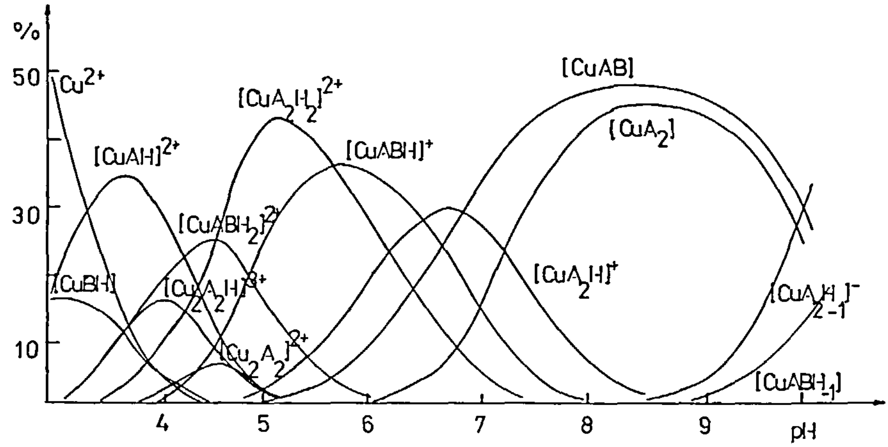


FIGURE 2 Species distribution patterns for the ternary system Cu(II):Hisha:His = 1:2:2; [Cu(II)] = 2×10^{-3} mol dm^{-3}; [A] = [B] = 4×10^{-3} mol dm^{-3}.

The results detailed above can be understood in the light of the great difference between the stabilities of copper(II)-Hisha and copper(II)-His(bis) complexes (*e.g.* log $\beta_{Cu(Hisha)_2} = 20.23$ (Table I), log $\beta_{Cu(His)_2} = 17.82$ (Ref. 16)) and the unfavoured formation of Cu(II)-His$_2$ (log $K_{Cu(II)-His}/K_{Cu(II)-His_2} = 2.23$).[16]

Different methods[19,20] are known for the estimation of the formation of mixed ligand complexes. In this respect, Sigel's Δlog K_M value (the constant due to the equilibrium $MA + MB \rightleftharpoons MAB + B$)[19] cannot be calculated, since the complex with 1:1 ratio is not formed in measurable concentrations in the Cu(II)-Hisha system (see Table I). log X (the constant due to the equilibrium $MA_2 + MB_2 \rightleftharpoons 2MAB$)[20] can be calculated, and the appropriate constants are given below.

Equilibrium[1]	log X
$[MA_2H_2]^{2+} + [MB_2H_2]^{2+} \rightleftharpoons 2[MABH_2]^{2+}$	1.74
$[MA_2H]^{+} + [MB_2H]^{+} \rightleftharpoons 2[MABH]^{+}$	1.73
$[MA_2] + [MB_2] \rightleftharpoons 2[MAB]$	2.53

It seems that all the above log X values are somewhat larger than expected on a statistical basis (0.6). This means that the formation of mixed complexes is favoured in this system.

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[1] Stability constants for Cu(II)-His complexes;
log $\beta_{MB_2H_2} = 27.13$; log $\beta_{MB_2H} = 23.63$; log $\beta_{MB_2H_2} = 17.82$ (Ref. 16).

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