Complex Formation Equilibria between 2-Amino-*N*-hydroxyacetamide and 2–Amino-*N*-hydroxypentanamide and Cobalt (II), Nickel(II), Copper(II), and Hydrogen Ions in Aqueous Solutions

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The formation constants of the complexes formed between H^+, Co^{2+}, Ni^{2+}, and Cu^{2+} and 2-amino-*N*-hydroxyacetamide (aha) and 2-amino-*N*-hydroxypentanamide (ahp) have been measured at 25 °C and I = 0.5 mol dm^{-3} (KCl) using potentiometric techniques. Their acid–base and metal–ligand reaction stoicheiometries have been determined, and the equilibrium constants of the corresponding proton and metal ion association constants have been calculated from potentiometric data with the aid of the program SUPERQUAD. The equilibrium chemical models are selected on the basis of a critical evaluation of the least-squares results and of a statistical analysis of the weighted residuals. Interpretation of the results was facilitated by visible spectrophotometry of solutions containing metal ions (M), and aha or ahp (HL) at various pH. All metals form the mononuclear ($[ML]^+$ and $[ML_2]$) and hydroxo complexes with both ligands, whereas with copper(II) polynuclear species are also present. The ligands are bound to the metals through co-ordination of the aminohydroxamate moiety, *via* the N atom of the amino group, and by the deprotonated NHO^- group; the square-planar complexes are probably held together by quite strong intermolecular hydrogen bonds involving the unco-ordinated ketonic oxygen atom.

This paper is a part of a series relating the stability and structure in solution of metal chelates to biological activity either of the chelate itself or of the ligand, presumed to be acting biologically *via* metal complex formation. Hydroxamic acids are generally potent and specific inhibitors of urease activity [1] and have become important as therapeuticals in the treatment of hepatic coma.[2] In addition to the trace elements that are required for many forms of life and the essential elements, there are other elements such as nickel and cobalt whose biological and nutritional roles are not fully clear. Although the mechanism of the clinical action of the metal–ligand complex is not completely understood there is reason to suspect that the interaction of these ligands with metal ions is significant. Several investigations have shown that albumin is the principal Ni^{II}-binding protein in human, bovine, rabbit, and rat serums.[3,4] In the case of metalloenzymes, it has been shown that Jack bean urease contains nickel and other metals in stoicheiometric amounts, which raises the question as to whether the mechanism of action of this enzyme necessarily involves the metal atom. A current fundamental approach to investigating the role of metal ions in biological systems involves computer simulation of the equilibria between these and low-molecular-weight ligands, including those which occur naturally and those administered as medications.[5–7] The data required for such studies comprise the specific stoicheiometric identities of the metal complexes that coexist in equilibrium together with their formation constants. In order to advance these investigations the work described in the present paper, on aqueous solution equilibria of 2-amino-*N*-hydroxyacetamide (aha) and 2-amino-*N*-hydroxypentanamide (ahp) with the metal ions Cu^{2+}, Ni^{2+}, and Co^{2+}, was undertaken.

Experimental

Reagents.—The ligands aha and ahp were obtained from Sigma (St. Louis) and their purity was checked potentiometrically. Doubly distilled and deionized water was used throughout, and all titrations were carried out under an atmosphere of purified nitrogen. Concentrations of stock solutions of bivalent metal chlorides (AnalaR products) were determined by inductively coupled plasma (i.c.p.) atomic emission spectrometry. All other chemical reagents employed were of the highest grade available and were used as previously described.[8a–10] High purity potassium chloride (Merck) was used as supporting electrolyte.

Potentiometric Measurements.—The potentiometric measurements were performed by using a Metrohm Titroprocessor E 636. The electrode pair consisted of a H 268 glass electrode (Schott-Jena glass) and a B 343 reference electrode (Schott-Jena glass). The solution in the titration vessel was stirred by means of a mechanical stirrer. A stream of nitrogen, presaturated with water vapour by bubbling it through a 0.5 mol dm^{-3} KCl solution, was blown over the surface of the solution. The alkalimetric titrations were carried out at 25 ± 0.1 °C and I = 0.5 mol dm^{-3} (KCl) as previously reported [8,9] for solutions of binary systems containing copper(II), nickel(II), cobalt(II), and/or ligand (aha or ahp) at different molar ratios. Small amounts (0.05 cm^3) of base (KOH) were added with the use of a Metrohm Dosimat E 635 autoburette (volume 5.0 cm^3). E.m.f. readings and titration curves were recorded graphically by using a E 636 automatic titrator and a thermo-printer. The solutions employed (25 cm^3) were thermostatted to 25.0 ± 0.1 °C using a water-circulation pump. The base used for e.m.f. measurements was carbonate-free potassium hydroxide (0.2891 mol dm^{-3}) and was standardized using the different procedures given below.

Spectrophotometric Measurements.—Absorption spectra in the region 430—700 nm were obtained on a Jasco Uvidec-505 spectrophotometer. Solutions containing ligand and metal ion, prepared and maintained under purified nitrogen with ionic strength 0.5 mol dm^{-3} (KCl), were scanned at a series of pH from 4.0—12.0 at 25 °C using 5-mm cells.

Calculations.—Great care has been taken in the calculation and critical evaluation of some parameters relating to potentiometric calibration curves using different mathematical

Table 1. Evaluation of equivalence point (v_e/cm^3), N (normality of KOH), K_w (ionic product) from thirteen potentiometric titrations of HCl (0.2969 mol dm^{-3}) with KOH at 25 °C and I = 0.5 mol dm^{-3} (KCl) both in acidic and basic media using the NBAR program

	v_e			N/mol dm^{-3}		
	Acid	Basic	v_e *	Acid	Basic	$10^{14}K_w$/mol^2 dm^{-6}
Mean with standard deviation	2.055(1)	2.052(2)	2.061(5)	0.288 93(16)	0.289 42(24)	1.941 1(823)
Variance	1.14×10^{-6}	3.23×10^{-6}	2.09×10^{-5}	2.48×10^{-8}	5.82×10^{-8}	0.006 77
Standard error	2.96×10^{-4}	4.99×10^{-4}	1.27×10^{-3}	4.37×10^{-5}	6.69×10^{-5}	0.023

* Equivalence point calculated following the Metrohm method.

procedures. In the potentiometric experiments the standard potential ($E^{\ominus}$), the coefficients of the correction terms for the effects of both liquid junction potential in acid (A_j) and in basic (B_j) solution, the concentration of the potassium hydroxide solution (N), the equivalence point (v_e), and K_w were determined before and after each experiment by dynamic titration of a known amount (*ca.* 2.0 cm^3) of hydrochloric acid (0.2969 mol dm^{-3}) in 0.5 mol dm^{-3} KCl at 25 °C with potassium hydroxide solution, according to Gran's method[11] using different calculation procedures. In the dynamic titration the total number of measuring-points with a variable increment in volume (Δv) means that at each point on the titration curve the amount of added KOH (Δv) is inversely proportional to the last difference (ΔE) in the electromotive force (e.m.f.). First, starting from the Nernst equation, the NBAR program[12] was used to calculate the standard electrode potential ($E^{\ominus}$) and the coefficients of the correction terms for the effect of liquid-junction potentials in acidic and basic solution obtained by a least-squares method. Finally, the equivalence point (v_e) and the normality of the alkali solution (N) were evaluated, following the principles of Gran's procedure,[11-13] by a least-squares method based on the same unequally spaced points (v, E), in acidic and basic media, previously used. The ionic product (K_w) was obtained from the basic region of the same calibration curve by using NBAR and varying its value until the average $E^{\ominus}$ in alkali media equalled that in acid solution. The equivalence point (v_e) was also calculated with Metrohm interpolation, applied by the Titroprocessor E 636 using, at the most, 9 pairs of experimental data (v, E) about the equivalence point, for which the mathematical method is not precisely established. From the results obtained it is possible to verify excellent agreement between the parameters ($E^{\ominus}$, v_e, and N) calculated for acidic solution and those calculated for alkali solution. The statistical analysis of the results shows how the parameters (v_e and N, Table 1) obtained from the two sets of the same titration curves are practically indistinguishable. At the same time the differences in the values of the parameters (v_e and N) are not significantly different from the mean values: even the estimated standard deviations are almost equal.

The differences obtained in the values of K_w are significantly different from one experiment to another. This could be due to various factors: a non-linear function of the electrodes in the experimental range of pH (7.0—12.2), due to the appearance of the 'potassium error' which starts mostly only above pH 11.0 and increases with the ionic strength; moreover the strongly alkaline buffer solutions are very unstable due to CO_2 absorption from the atmosphere. When the data of each experiment are treated separately, and then the results are averaged and assessed, if one of the calibrations is affected by some particular error, the values of the parameters (N, v_e, *etc.*) should be significantly different from the mean values and should allow the identification of the source of error. In addition, this procedure is recommended because it gives a more reasonable measure of the dispersion of the errors. The stability constants (β_{pqr}), which are defined by equation (1) (charges are

$$pM + qH + rL \rightleftharpoons M_pH_qL_r \qquad (1)$$

$$\beta_{pqr} = [M_pH_qL_r]/[M]^p[H]^q[L]^r$$

omitted for simplicity), were refined by the method of rigorous least-squares using the computer program SUPERQUAD;[14] p, q, and r are the numbers of metal(II), proton, and ligand, respectively, in the complex $M_pH_qL_r$. The program SUPERQUAD calculates the values of the overall protonation or formation constants which minimize the sum of the squared residual between observed and calculated e.m.f. values, equation (2). The parameter Z is the total number of potentiometric data

$$U = \sum_{i=1}^{Z} w_i(E_i^{\text{obs.}} - E_i^{\text{calc.}})^2 \qquad (2)$$

and w_i is the weighting factor, defined by equation (3), where σ_E

$$w_i = \sqrt{1/[\sigma_E{}^e + (\partial E_i/\partial v_i)^2\sigma_v{}^2]} \qquad (3)$$

(= 0.2) is the error in the e.m.f. and σ_v (= 0.005) the error in the volume used in the refinement. At first the protonation constants of the ligands were determined separately through the refinement of several sets of potentiometric data; the values obtained were introduced as constants into the refinement process of the complex formation constants for binary systems. All the calculations were performed on the CRAY X-MP/12 computer of the Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord Orientale, Casalecchio, Bologna, with financial support from the University of Parma. The compositions of the starting solutions for each potentiometric titration are quoted in Table 2.

Results and Discussion

The presence of likely metal–proton–aminohydroxamic acid (aha or ahp) species were tested for by using the following values: p = 1, 2, 3, 4; q = 1, 2, 3, −1, −2, −3; r = 1, 2, 4, 5. The equilibrium model was selected in successive trials according to the best agreement between experimental and calculated data. The values of the standard deviations of the parameters, the agreement factor (σ^2), the goodness of fit statistic (χ^2), and the chemical significance of the species selected were taken into account for each hypothesis. The calculated protonation and formation constants (log β_{pqr}) of the two ligands are given in Table 3.

The ligands aha and ahp have two titratable protons in the studied pH range (5.0—10.0) which can be attributed to the hydroxide NHOH and the NH_3^+ groups. The presence of the α-amino group in aha and ahp increases the acidic character of the OH group in comparison with that of the related acids $CH_3CONHOH$ (log β_{011} = 9.342[15]) and CH_3CH_2-CONHOH (log β_{011} = 9.56[16]). Similarly, a comparison of log β_{011} for aha and ahp with that of glycine [log β_{011} =

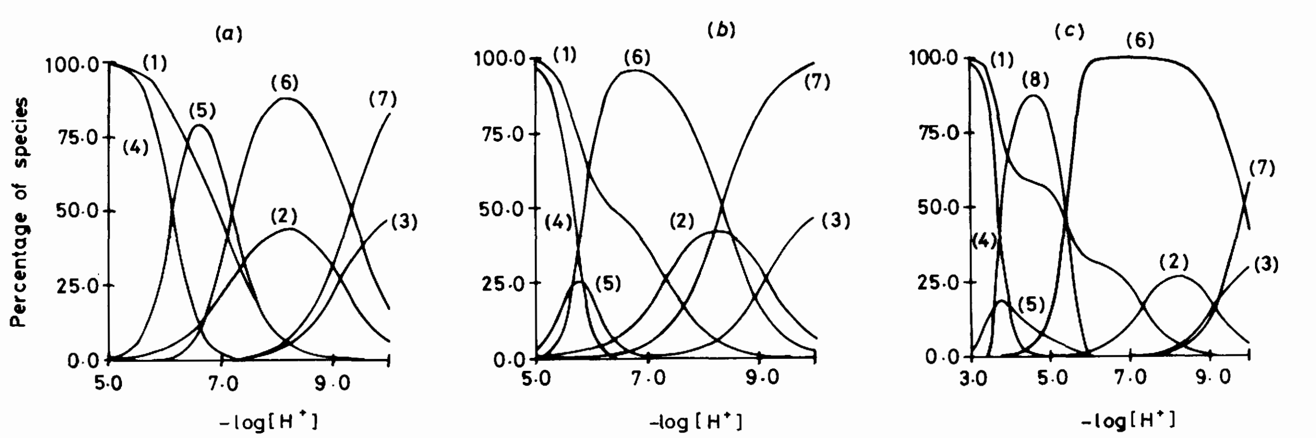

Figure 1. Typical distribution diagrams for M^{2+}–ahp systems. The percentage of each species has been calculated from the data of a hypothetical solution of metal ions (0.004 mol dm^{-3}) and ahp (0.012 mol dm^{-3}) by the HALTAFALL (N. Ingri, W. Kakalowicz, L. G. Sillén, and B. Warnqvist, *Talanta*, 1967, **14**, 1261) program, and using a PLOTTER Calcomp 936. The concentrations of the species not containing metal were calculated as percentages of the total ligand, those containing metal as percentages of the total metal: (*a*) Co^{2+}–ahp, (*b*) Ni^{2+}–ahp, (*c*) Cu^{2+}–ahp; (1) H_2L^+, (2) HL, (3) L^-, (4) M^{2+}, (5) $[ML]^+$, (6) $[ML_2]$, (7) $[M(OH)L_2^-]$, (8) $[Cu_4L_5]^{3+}$

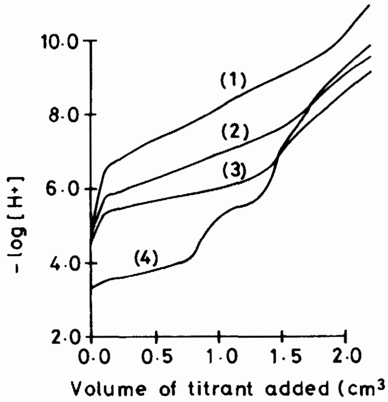

Figure 2. Titration curves of pH as a function of the volume of KOH added, calculated by the HALTAFALL program, and using a PLOTTER Calcomp 936. Initial concentrations of solutions: c_H = 2.4 × 10^{-2}, c_L = 1.2 × 10^{-2}, c_M = 4.0 × 10^{-3}, c_{KOH} = 0.2891 mol dm^{-3}, v_0 = 25 cm^3: (1) ahp, (2) Co^{2+}–ahp, (3) Ni^{2+}–ahp, (4) Cu^{2+}–ahp

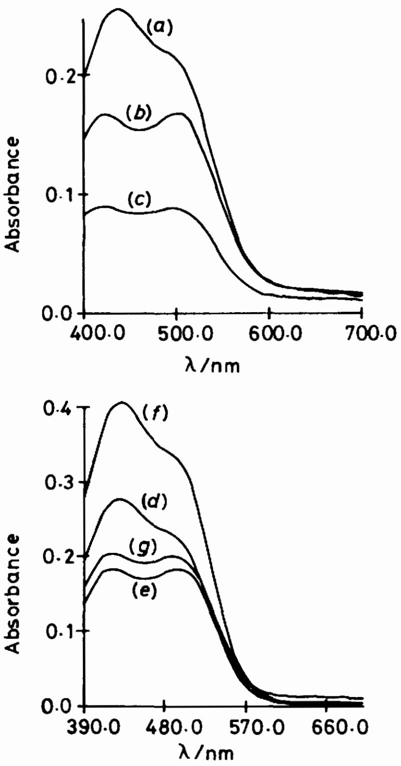

Figure 3. Plots of experimental absorbance data *versus* wavelength for some solutions of Ni^{2+}–aha and Ni^{2+}–ahp systems using the program VISION with the PLOTTER Calcomp 936. For Ni^{2+}–aha system: (*a*) pH 9.97, $[H_2L^+]$ = 1.598 × 10^{-2}, $[Ni^{2+}]$ = 6.563 × 10^{-4} mol dm^{-3}; (*b*) pH 8.60, $[H_2L^+]$ = 1.542 × 10^{-2}, $[Ni^{2+}]$ = 6.337 × 10^{-4} mol dm^{-3}; (*c*) pH 7.82, $[H_2L^+]$ = 1.509 × 10^{-2}, $[Ni^{2+}]$ = 6.201 × 10^{-4} mol dm^{-3}. For Ni^{2+}–ahp system: (*d*) pH 11.29, $[H_2L^+]$ = 1.093 × 10^{-2}, $[Ni^{2+}]$ = 2.649 × 10^{-3} mol dm^{-3}; (*e*) pH 8.13, $[H_2L^+]$ = 1.053 × 10^{-2}, $[Ni^{2+}]$ = 2.550 × 10^{-3} mol dm^{-3}; (*f*) pH 11.36, $[H_2L^+]$ = 1.086 × 10^{-2}, $[Ni^{2+}]$ = 3.945 × 10^{-3} mol dm^{-3}; (*g*) pH 6.76, $[H_2L^+]$ = 1.037 × 10^{-2}, $[Ni^{2+}]$ = 3.768 × 10^{-3} mol dm^{-3}

9.54(1) [17]] and DL-norvaline [log β_{011} = 9.186(2) [13]] shows that substitution of an NHOH group for the OH group of a carboxyl lowers the protonation constant (log β_{011}) in accord with the electron-withdrawing character of the NHOH group. Using the stability constants given in Table 3 and the protonation constants of the ligands under the same experimental conditions, the percentage of each complex involving H^+ or OH^-, metal ion, and ligand has been calculated.

Representative species-distribution diagrams for M–ahp systems are reported in Figure 1. Some general observations about the behaviour of the various systems are as follows. (*a*) The species distribution curves show that complexation begins at low pH values (*ca.* 3.0 for Cu^{2+}, 5.0 for Co^{2+} and Ni^{2+}) with formation of species $[ML]^+$ corresponding to the displacement of two protons; the complex $[ML]^+$ reaches a maximum concentration of 78% total cobalt at pH 6.75, 26% total nickel at pH 5.75, and 18% total copper at pH 3.8; (*b*) $[CoL_2]$ reaches 88% at pH 8.2, $[NiL_2]$ has a maximum of 96.5% at pH 6.8, while $[CuL_2]$ reaches a peak of 99.9% at pH 6.75; (*c*) above pH 7.0, one hydroxyl species was detected; (*d*) in the presence of Cu^{2+} the formation in acidic media of polynuclear species $[Cu_4L_5]^{3+}$ has been observed, which reaches a maximum concentration of 87% total metal at pH 4.6. In fact the titration curve (Figure 2) of the protonated ligand (H_2L^+) in the presence of Cu^{2+} is

Table 2. Protonation and complex-formation constant determinations. Initial concentrations (T_L, T_M, T_H/mmol) of the reagents* for the alkalimetric titration of 2-amino-*N*-hydroxyacetamide and 2-amino-*N*-hydroxypentanamide with divalent metal ions at 25 °C and I = 0.5 mol dm^{-3} (KCl)

Run	System	T_L	T_M	T_H	pH
1	H^+–aha	0.334 63		0.669 26	6.20—10.17
2		0.278 98		0.557 95	6.25—10.02
3		0.446 66		0.893 31	6.21—9.98
4		0.334 63		0.669 26	6.16—10.14
5		0.301 38		0.602 77	6.21—10.05
6	Co^{2+}–aha	0.559 12	0.028 45	1.116 90	5.03—9.69
7		0.559 12	0.014 23	1.116 90	5.08—9.54
8		0.559 12	0.007 11	1.116 90	5.17—9.60
9		0.447 29	0.056 91	0.893 52	5.44—9.78
10		0.447 29	0.085 36	0.893 52	4.74—9.64
11		0.335 47	0.056 91	0.670 14	4.90—9.45
12	Ni^{2+}–aha	0.447 29	0.073 51	0.893 52	5.57—9.88
13		0.447 29	0.036 75	0.893 52	4.72—9.90
14		0.335 47	0.073 51	0.670 14	4.67—9.72
15		0.447 29	0.018 38	0.893 52	4.90—9.97
16		0.223 65	0.073 51	0.446 76	4.66—9.17
17		0.335 47	0.014 70	0.670 14	4.98—9.94
18	Cu^{2+}–aha	0.447 30	0.050 91	0.893 52	3.31—10.03
19		0.223 65	0.050 91	0.446 76	3.43—9.85
20		0.335 47	0.033 60	0.670 14	3.45—9.96
21		0.335 47	0.018 33	0.670 14	3.68—10.21
22		0.447 30	0.040 73	0.893 52	3.36—10.11
23		0.559 12	0.050 91	1.116 90	3.27—9.97
24	H^+–ahp	0.303 39		0.606 78	5.92—10.01
25		0.265 47		0.530 93	5.99—9.98
26		0.379 24		0.745 84	5.78—10.01
27		0.333 73		0.667 46	6.20—9.97
28		0.348 90		0.697 80	5.84—9.85
29	Co^{2+}–ahp	0.303 39	0.113 81	0.606 78	3.84—11.36
30		0.303 39	0.071 13	0.606 78	3.88—11.50
31		0.303 39	0.184 95	0.606 78	4.06—11.43
32		0.265 47	0.071 13	0.530 94	4.06—11.43
33		0.303 39	0.142 27	0.606 78	3.90—11.39
34	Ni^{2+}–ahp	0.303 39	0.073 50	0.613 43	5.15—9.67
35		0.303 39	0.110 26	0.613 43	5.05—9.30
36		0.303 39	0.139 66	0.608 74	5.22—8.61
37		0.265 47	0.073 50	0.537 58	5.20—9.58
38		0.227 54	0.036 75	0.461 74	5.66—9.46
39		0.341 31	0.036 75	0.689 28	5.26—9.62
40	Cu^{2+}–ahp	0.303 39	0.101 83	0.613 43	3.13—11.14
41		0.303 39	0.152 74	0.613 43	3.04—11.34
42		0.303 39	0.050 91	0.613 43	3.28—10.96
43		0.455 09	0.050 91	0.920 15	3.14—11.30
44		0.379 24	0.076 37	0.766 79	3.14—10.52
45		0.265 47	0.091 64	0.536 75	3.14—11.35

* T_L = mmol of ligand, T_M = mmol of metal, T_H = mmol of hydrogen ion in the titration vessel.

clearly different from those of the protonated ligand alone or in the presence of Co^{2+} and Ni^{2+}. These curves reveal an appreciable complexing capacity in the acidic media, but for the Cu^{2+}–ahp system showed two distinct buffer zones separated by a sharp equivalence point between them that would exactly correspond to a 1.25 molar ratio (moles of base added per two moles of metal ion). Thus, complexation occurs with the formation of a mononuclear $[ML]^+$ species with release of two protons. For the Ni^{2+} systems the general pattern of the i.r. spectra [18] and the *X*-ray crystallographic studies [19] support preferential co-ordination *via* the nitrogen atom of the amino group and the nitrogen atom of the deprotonated NHO^- group, as previously reported for nickel complexes of glycinehydroxamic (aha) and serinehydroxamic acids. The solution electronic spectra (Figure 3) of both the Ni^{2+}–aha and Ni^{2+}–ahp systems over a wide pH range suggest a square-planar configuration of the $[NiL_2]$ species in solution as well as in the solid state.[19] Really the solution electronic spectra provide confirmation of this configuration since both systems show two bands, one in the range 425—435 nm and one in the range 490—500 nm assigned respectively as $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions in square-planar symmetry by comparison with observed spectra of different Ni^{2+} complexes of confirmed square-planar configuration.[20] The majority of these complexes, as in the present case, exhibit a strong absorption band (ε 50—400 dm^3 mol^{-1} cm^{-1}) in the visible region in the range 667—400 nm, and in many cases a second more intense band at 435—335 nm (ε 100—400 dm^3 mol^{-1} cm^{-1}). Therefore the probable structure consists of a square-planar Ni complex with *trans* geometry and co-ordination of the amino nitrogen atom and, surprisingly, of the N atom of the NHO^- group, with intermolecular hydrogen bonds between a CO group of one molecule and the unco-ordinated oxygen atom of an adjacent NHO^- group.

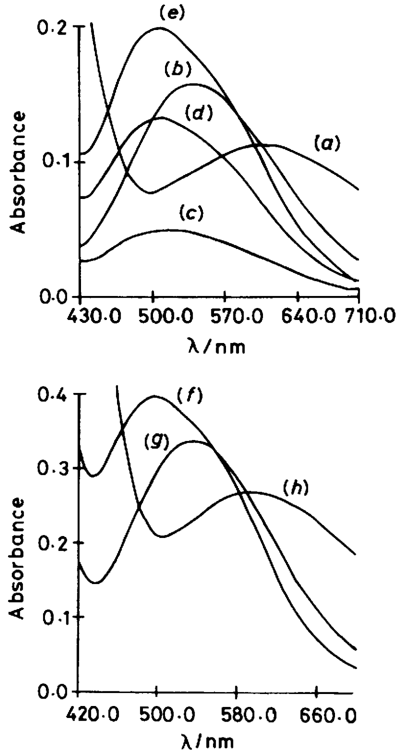

Figure 4. Plots of experimental absorbance data *versus* wavelength for some solutions of Cu^{2+}–aha and Cu^{2+}–ahp systems using the program VISION with the PLOTTER Calcomp 936. For Cu^{2+}–aha system: (*a*) pH 4.82, $[H_2L^+] = 1.458 \times 10^{-2}$, $[Cu^{2+}] = 1.659 \times 10^{-3}$ mol dm^{-3}; (*b*) pH 5.7, $[H_2L^+] = 8.059 \times 10^{-3}$, $[Cu^{2+}] = 1.835 \times 10^{-3}$ mol dm^{-3}; (*c*) pH 11.97, $[H_2L^+] = 1.157 \times 10^{-2}$, $[Cu^{2+}] = 6.320 \times 10^{-4}$ mol dm^{-3}; (*d*) pH 10.86, $[H_2L^+] = 1.218 \times 10^{-2}$, $[Cu^{2+}] = 1.220 \times 10^{-3}$ mol dm^{-3}; (*e*) pH 11.12, $[H_2L^+] = 8.299 \times 10^{-3}$, $[Cu^{2+}] = 1.889 \times 10^{-3}$ mol dm^{-3}. For Cu^{2+}–ahp system: (*f*) pH 11.14, $[H_2L^+] = 1.095 \times 10^{-2}$, $[Cu^{2+}] = 3.676 \times 10^{-3}$ mol dm^{-3}; (*g*) pH 6.20, $[H_2L^+] = 1.068 \times 10^{-2}$, $[Cu^{2+}] = 3.585 \times 10^{-3}$ mol dm^{-3}; (*h*) pH 3.97, $[H_2L^+] = 1.024 \times 10^{-2}$, $[Cu^{2+}] = 3.435 \times 10^{-3}$ mol dm^{-3}

The only colour variation observed for nickel(II)–aminohydroxamic acid systems is from pink-orange, in acidic solution, to gold-yellow in basic media, showing an intermediate colour (pink-yellow) in the neutral region. When the pH is increased, small bathochromic and high hyperchromic shifts are observed

Table 3. Cumulative and stepwise protonation complex-formation constants of 2-amino-*N*-hydroxyacetamide (aha) and 2-amino-*N*-hydroxypentanamide (ahp) with divalent metal ions at 25 °C and $I = 0.5$ mol dm^{-3} (KCl). Standard deviations (σ values) are given in parentheses

	aha				ahp			
	H^+	Co^{2+}	Ni^{2+}	Cu^{2+}	H^+	Co^{2+}	Ni^{2+}	Cu^{2+}
log β_{011}	9.096(1)				9.125(1)			
log β_{021}	16.580(2)				16.465(2)			
log K_2^{H} [a]	7.484(2) [b]				7.340(2)			
log β_{101}		6.493(14)	6.768(7)	10.682(16)		6.185(15)	6.825(12)	10.609(18)
log β_{102}		11.144(11)	13.378(4)	19.772(12)		10.593(17)	13.948(5)	19.699(11)
log β_{1-12}		1.708(16)	5.061(9)	10.064(22)		1.266(21)	5.620(11)	9.838(20)
log β_{405}				61.763(21)				62.616(22)
log K_2		4.651(13)	6.610(6)	9.090(14)		4.408(16)	7.123(9)	9.090(15)
Z [c]	206	377	312	330	213	239	253	354
U	2.662×10^1	2.547×10^3	3.051×10^2	4.348×10^3	3.737×10^3	2.334×10^3	1.186×10^3	2.561×10^3
χ^2 [d]	12.33	10.57	11.18	14.02	7.51	12.45	11.82	13.44
σ^2 [e]	0.37	2.56	1.0	3.66	0.43	2.67	2.18	3.55

[a] $\log K_n = \log \beta_{0n1} - \log \beta_{0n-11}$. [b] $\sigma(\log K_n) = \{[\sigma^2(\log \beta_{0n1}) + \sigma^2(\log \beta_{0n-11})]/2\}^{\frac{1}{2}}$. [c] Total number of data points used in the refinement. [d] Observed χ^2; calculated value (degrees of freedom, 6, confidence coefficient, 0.95) should be 12.6. [e] $\sigma^2 = \sum_{i=1}^{Z} w_i(E_i^{obs.} - E_i^{calc.})^2/(Z - m)$; m is the number of parameters to be refined.

from 425 to 435 nm, while a shoulder appears in place of the band at 490—500 nm. For the Cu^{2+} systems, the previous i.r. and magnetic results of Fe^{3+}–aha,[21] and also the visible spectra and the stability constants reported in the present paper, suggest that the co-ordination pattern probably involves the α-amino group and the oxygen atom of NHO^-.

The spectra for Cu^{2+} systems are shown in Figure 4 for the pH range 3.9—11.9. The highest limiting value of $\lambda_{max.}$ for the Cu^{2+}–aha system is *ca.* 610 nm whereas for the Cu^{2+}–ahp system $\lambda_{max.}$ reaches 600 nm, suggesting that even in the mononuclear $[CuL]^+$ species the mode of co-ordination of aha is almost the same as that of ahp. The increase in absorption and shift to smaller wavelengths with increase in pH indicates greater complexation, and above pH 7.0 both $\lambda_{max.}$ and $\varepsilon_{max.}$ change further, consistent with formation of the $[CuL_2(OH)]^-$ species which predominates in this range.

Associated with the shift of the unique band in the 610—495 nm region is the change of colour from intense green to purple in acid media, while for pH >7.0 the colour changes from purple to reddish purple. Because of the relatively low symmetry of the environments in which the Cu^{2+} ion is characteristically found, detailed interpretations of the spectra are somewhat complicated. Addition of ligands to aqueous solutions of $[Cu(H_2O)_6]^{2+}$ leads to the formation of complexes by successive displacement of water molecules, but it must be kept in mind that two of the water molecules are further from the metal atom than the other four. Because of the Jahn-Teller effect, the Cu^{2+} ion does not bind the fifth and sixth ligands strongly. Such complexes[22,23] give rise to one absorption band in the visible region near 625 nm; the band often exhibits a broad 'tail' into the near-i.r. region. The present ligands as well as amines (*e.g.* NH_3, $H_2NCH_2CH_2NH_2$) produce a stronger ligand field than does $[Cu(H_2O)_6]^{2+}$, which causes the absorption band to move from the far red to the middle of the red region of the spectrum. Therefore, we suggest a d_{xy} ground state for the copper(II)–aminohydroxamate systems with square-planar geometry. Interestingly, square-planar complexes of Cu^{2+} are sensitive to axial perturbation, and similarly the copper(II)–aminohydroxamate spectra show a marked red shift in aqueous solution indicative of co-ordination by H_2O molecules in axial positions. A maximum near 600 and 610 nm for Cu^{2+}–ahp and Cu^{2+}–aha respectively is tentatively assigned to the d_{xy}–$d_{x^2-y^2}$ transition.

The above observations correlate well with the values for stability constants reported in Table 3. In particular the cumulative and stepwise formation constants for the 1:1 and 1:2 metal–aminohydroxamic acid complexes follow the Irving-Williams order. The larger log β_{101}, log β_{102}, and log K_2 values for aha compared to those for ahp presumably reflect the greater basicity of the NHOH group (log K_2^H) of aha compared to that of ahp. This is not the case for the Ni^{2+} systems where this trend is reversed. In addition, the logarithm of the second stepwise formation constant (log K_2) for the Ni^{2+}–ahp system is appreciably greater than that of the first, log β_{101}. This is contrary to earlier findings[24—27] using a method of calculation based on the erroneous assumption that the formation of ML is effectively complete before $[ML_2]$ begins to be formed. Other ligands have also been found to give the sequence, log β_{101} < log K_2, in their metal complexes.[28,29]

The explanation of this behaviour may lie in the ability of Ni^{2+} to form square-planar complexes with co-ordination of the aminohydroxamic acids *via* the N atom of the amino group and from the deprotonated NHO^- group. It also demonstrates that individual five-membered rings in the complex $[NiL]^+$ are more stable than six-membered rings ($[CoL]^+$, $[CuL]^+$); when a second ligand is bonding facially in a bidentate manner the two five-membered rings in the complex $[NiL_2]$ are much more stable than six-membered rings formed by other metals (for Co^{2+}–aha, log β_{101}/K_2 = 1.84; for Co^{2+}–ahp, log β_{101}/K_2 = 1.78; for Cu^{2+}–aha, log β_{101}/K_2 = 1.59; for Cu^{2+}–ahp, log β_{101}/K_2 = 1.52; for Ni^{2+}–aha, log β_{101}/K_2 = 0.16; for Ni^{2+}–ahp, log β_{101}/K_2 = −0.30) but the differences are not great enough to alter the fact that both log β_{101} and log K_2 follow the Irving-Williams series.

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