Mixed-metal Complexes in Solution. A Potentiometric and Spectrophotometric Study of Copper(II)–Nickel(II)–δ-Hydroxylysine Complexes in Aqueous Solution†

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Binary and ternary complexes (homo- and hetero-polynuclear) formed in the system copper(II)–nickel(II)–δ-DL-hydroxylysine have been studied by potentiometry at different temperatures and by visible spectrophotometry. In the presence of both copper(II) and nickel(II) a quite complicated complexation scheme has been observed, with the participation of the acid and aminoethanol moieties of the ligand molecule and the consequent formation of mono- and poly-nuclear species: $[ML]^+$, $[M(HL)]^{2+}$, $[M(HL)_2]^{2+}$, $[ML_2H]^+$, $[NiLH_2]^{3+}$, $[NiL_2]$, $[NiL_3]^-$, and $[M_2L_2H_{-2}]$, $[M_3L_2H_{-2}]^{2+}$, $[Cu_2L_2H_{-1}]^+$, $[Ni_2L_2]^{2+}$ (with M = Cu^{2+} or Ni^{2+} and L^- = anion of δ-hydroxylysine). In addition to the above binary complexes, the mixed-metal species $[CuNiL_2H_{-2}]$ and $[Cu_2NiL_2H_{-2}]^{2+}$ have been found in solution. Structures in solution of relevant species have been proposed, both on the basis of visible spectra calculated for each copper(II) complex and upon thermodynamic parameters obtained by potentiometric measurements at different temperatures.

It has been shown that ligands having two or more co-ordinating centres quite easily form homo- and hetero-polynuclear complexes.[1–9] Some biofunctional ligands have been studied in order to ascertain their ability to form polynuclear species and in some cases it has been found that heterobinuclear species are formed, and furthermore that this is favoured on statistical grounds. For example, for some citrate[1,6] or DL-isoserine[9] mixed transition metal complexes the stability is significantly higher than that of the corresponding homobinuclear species. The possibility of forming heterobinuclear species has been attributed to a series of factors, among which are the presence of two complexing sites of different 'softness' in the ligand and the presence of well separated co-ordinating centres. Nevertheless, no general rules have been found to predict the formation of heteropolynuclear complexes in solution, except the obvious observation that a statistical factor is always to be taken into account, so that when homopolynuclear species are formed it is quite probable, for similar metal ions, that formation of heteropolynuclear species occurs as well.

The study of mixed-metal complexes in solution shows at least two interesting aspects: advance in the knowledge of co-ordination chemistry, as well as the possibility of applying these results to the speciation of natural multicomponent systems.

Among the polyfunctional ligands that form heterobinuclear complexes in solution, are amino acids such as L-histidine,[2] dipeptides such as β-alanyl-L-histidine[3] and L-histidylglycine,[8] a catechol amino acid 3-(3,4-dihydroxyphenyl)alanine (L-dopa),[4] a hydroxypolycarboxylate ligand (citrate),[1,6] and a hydroxyamino acid DL-isoserine.[9]

In the literature there are some interesting reports which emphasize the behaviour of the ethanolamino group in co-ordination chemistry.[10–14] For these reasons we have studied a second hydroxyamino acid ligand, DL-δ-hydroxylysine (D,L-2,6-diamino-5-hydroxyhexanoic acid, H_3L^{2+}) which should form heteropolynuclear species in solution, although structurally different from DL-isoserine. We find two well separated co-ordination centres, one able to bind metal ions in an α-amino acid-like mode, the other in an ethanolamino-like mode.

Our investigation was first carried out by pH-metric measurements with the ligand in the presence of copper(II), nickel(II), or copper(II) and nickel(II), at different temperatures. Then the characterization of the binary and ternary systems was improved by visible spectrophotometric measurements and consequent estimation of the visible spectra of complexes formed in solution.

Experimental

Materials.—DL-5-Hydroxylysine was a Fluka puriss. product, used without further purification; its purity, checked by alkalimetric titrations, was >99.5%. Copper(II) and nickel(II) nitrate (Fluka) stock solutions were standardized by ethylenediaminetetra-acetate (edta) titrations. Nitric acid and sodium hydroxide standard solutions were prepared by diluting concentrated ampoules; their concentrations were determined against 2-amino-2-hydroxymethylpropane-1,3-diol (tris) and potassium hydrogenphthalate respectively. Sodium nitrate, used to adjust the ionic strength to 0.15 mol dm^{-3}, was a Fluka product, used without further purification. Grade A glassware and twice distilled water were employed throughout to prepare all solutions.

Apparatus.—The free hydrogen-ion concentration (c_H) was measured by two different potentiometric systems: (*a*) a model E600 Metrohm potentiometer and (*b*) a semiautomatic home-made potentiometer, built with an Analog Devices millivoltmeter, Printel printer, and Mosteck logic circuits, in order to add a pre-fixed volume of titrant and to print the corresponding e.m.f. value. The potentiometers were coupled with glass and saturated calomel electrodes supplied by Metrohm. In both cases the instrumental resolution was ±0.1 mV. The titrant sodium hydroxide solution was delivered by a model 882 Amel dispenser (minimum reading 0.001 cm^3). The electrode couples were systematically calibrated, in $-\log c_H$ units (pH), by titrating nitric acid (5—10 mmol dm^{-3}) with standard sodium hydroxide, under the same experimental conditions (temperature and ionic strength) as the solution under study. The

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† *Supplementary data available* (No. SUP 56759, 2 pp.): experimental details of potentiometric measurements. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Thermodynamic parameters for protonation of DL-δ-hydroxylysine, at I = 0.15 mol dm^{-3} (NaNO$_3$)

	$\log \beta_j^{H}$ ($\log K_j^{H}$)^{a,b}						
j	18	25	37	47 °C	$-\Delta G_j^{\circ\,c}$	$-\Delta H_j^{\circ\,c}$	$\Delta S_j^{\circ\,c}$
1^a	9.956(14)^d	9.744(8)	9.462(8)	9.207(15)	55.61(5)	44(1)	39(3)
2^a	18.94(3)	18.561(10)	17.908(10)	17.39(2)	105.9(1)	91(2)	49(6)
3^a	21.05(5)	20.66(2)	19.98(2)	19.44(5)	117.9(2)	95(3)	76(9)
2^b	8.98	8.82	8.45	8.18	50.3	47	10
3^b	2.11	2.10	2.07	2.05	12.0	4	27

[a] β_j^{H} : jH$^+$ + L$^-$ $\longrightarrow$ [H$_j$L]$^{j-1}$. [b] K_j^{H} : H$^+$ + [H$_{j-1}$L]$^{j-2}$ $\longrightarrow$ [H$_j$L]$^{j-1}$. [c] ΔG° and ΔH° in kJ mol^{-1}; ΔS° in J K^{-1} mol^{-1}; 25 °C. [d] The errors in parentheses are $\pm 3\sigma$ in the last significant figure(s).

measurements cells (50 cm^3) were thermostatted at $T \pm 0.2$ °C. During the titrations magnetic stirring was employed. All the titrations were carried out whilst bubbling purified nitrogen through the solution. Further details are available as SUP 56759.

Spectrophotometric measurements in the visible region were recorded by a model Spectracomp 601 Carlo Erba spectrophotometer, from 400 to 800 nm, at 25 °C. The solution being examined was transferred from the potentiometric to an optical cell by circulation from a peristaltic pump.

Procedure.—An aqueous solution containing H$_3$L^{2+} (protonation constant measurements), H$_3$L^{2+}, and copper(II) or nickel(II) (binary complexes), or H$_3$L^{2+}, copper(II), and nickel(II) (mixed-metal complexes) was titrated with standard sodium hydroxide until precipitation occurred (20—50 experimental points). When studying binary complexes the concentration of metal ion ranged from 2.5—15 mmol dm^{-3}, with metal-to-ligand ratios from 1 : 1 to 1 : 3. The ternary system was investigated by considering copper(II) : nickel(II) : ligand concentration ratios of about 1 : 1 : 2 and 2 : 1 : 3, with the ligand concentration ranging from 6—10 mmol dm^{-3}. For determination of the protonation constants, an excess of strong acid was added to the solutions to ensure complete protonation of the ligand, in order to calculate directly the internal standard electrode potential, E°_{int} (E°_{ext} is the corresponding value calculated by independent calibration). The mean of the differences $E^{\circ}_{ext} - E^{\circ}_{int}$ is not higher than 0.5 mV and gives a measure of the reliability of the experimental system. For spectrophotometric determinations, after accurate measuring of pH, the solution was transferred to the optical cell. Spectra were recorded against sodium nitrate solution.

Calculations.—Calculations related to the determination of E°_{int} and protonation constants were performed using the non-linear least-squares computer programs ACBA,[15] ESAB,[16] and/or ESAB2M.[17] The values of stability constants were expressed by: $\beta_{pqrs} = [\mathrm{Cu}_p\mathrm{Ni}_q\mathrm{L}_r\mathrm{H}_s]/[\mathrm{Cu}]^p[\mathrm{Ni}]^q[\mathrm{L}]^r[\mathrm{H}]^s$. Calculations relating to the determination of binary and ternary complex-formation constants (β_{pqrs}) were performed using the non-linear least-squares computer program SUPERQUAD.[18] Throughout the paper, the errors reported are three times the standard deviation (3σ) in the parameters.

By taking into account that visible spectra were recorded at known values of total reagent concentrations, pH, and stability constants, the analysis and refinement of spectrophotometric data were made using the MOLEX program,[19] which calculates the values of molar absorption coefficients (ε_λ, dm^3 mol^{-1} cm^{-1}) of the species present in solution.

Results

Potentiometric Measurements.—The thermodynamic parameters related to protonation of the ligand are collected in Table 1. Due to the molecular structure of δ-hydroxylysine, the complexation scheme resulting from the interaction of H$_3$L^{2+} with Cu^{2+} or Ni^{2+} is quite complicated. By using the computer program SUPERQUAD and the model selection method proposed by Vacca and Sabatini,[20] in solution the following species were found: [M(HL)]$^{2+}$ and [M(HL)$_2$]$^{2+}$ (M = Cu or Ni), in which it seems likely that the ω-amino group is protonated; [ML]$^+$, [ML$_2$H]$^+$, and [NiL$_2$] which arise from the above species by dissociation of the protonated ω-amino group and its eventual participation in co-ordination; dimeric [Cu$_2$L$_2$H$_{-1}$]$^+$, [M$_2$L$_2$H$_{-2}$], and [Ni$_2$L$_2$]$^{2+}$ which additionally show co-ordination of the ethanolamino group; and the very interesting trinuclear complexes [M$_3$L$_2$H$_{-2}$]$^{2+}$. Additionally [NiLH$_2$]$^{3+}$ and [NiL$_3$]$^-$ are observed.

The thermodynamic parameters calculated for the different complexes by means of potentiometric measurements at four temperatures (18, 25, 37, and 47 °C) are collected in Table 2.

Information about the relevance in solution of the above species can be obtained by calculating the species distribution *vs.* pH: [M(HL)]$^{2+}$, [M(HL)$_2$]$^{2+}$, and [M$_2$L$_2$H$_{-2}$] species are the most favoured for both the metal ions studied here.

Evidence for mixed metal complex formation was obtained by comparing the experimental titration curves obtained with solutions containing Cu^{2+}, Ni^{2+}, and the ligand with those calculated on the assumption that no heteronuclear species are present in solution. It was found that the trend of experimental curves is not explained except by assuming mixed-metal complex formation. The stoicheiometry of the heteronuclear species is the same as found for polynuclear binary species, *i.e.*, heterobinuclear [CuNiL$_2$H$_{-2}$] and heterotrinuclear [Cu$_2$NiL$_2$H$_{-2}$]$^{2+}$.

The values of the thermodynamic parameters for the mixed-metal complexes are listed in Table 3. An example of species distribution in the copper(II)–nickel(II)–δ-hydroxylysine ternary system is reported in Figure 1: the relevance of ternary [CuNiL$_2$H$_{-2}$] at higher pH values is noticeable.

Spectrophotometric Measurements.—Visible spectra recorded at different pH values with the Cu^{II}–H$_3$L^{2+} system are shown in Figure 2(*a*). Comparison of these spectra with those obtained with the Cu^{2+}–Ni^{2+}–H$_3$L^{2+} ternary system [Figure 2(*b*)] shows an interesting shift towards shorter wavelengths after addition of Ni^{2+} to a solution already containing Cu^{2+} and the ligand. This fact may be considered as further evidence of heteronuclear complex formation, in addition to that obtained on the basis of potentiometric measurements. All the visible spectra were interpreted by using the complexation schemes proposed above. By introducing into the calculation the stability constant values of Tables 1—3 the visible spectrum of each complex was obtained. For Ni^{2+}, for all the species low ε values (< 10 dm^3 mol^{-1} cm^{-1} per Ni^{2+}) were found, indicative of octahedral co-ordination. When refining the spectrophotometric data obtained with the ternary system, the ε values estimated for

Table 2. Thermodynamic parameters for the formation of Cu^{2+}– and Ni^{2+}– δ-hydroxylysine binary complexes, at $I = 0.15$ mol dm^{-3} ($NaNO_3$)

		log β_{pqrs}						
Reaction	*pqrs*	18	25	37	47 °C	$-\Delta G^{\circ a}$	$-\Delta H^{\circ a}$	$-\Delta S^{\circ a}$
$Cu^{2+} + L^- \longrightarrow [CuL]^+$	1010	9.8(2)[b]	9.75(15)	9.58(7)	9.35(15)	55.6(9)	26(9)	98(30)
$Cu^{2+} + L^- + H^+ \longrightarrow [Cu(HL)]^{2+}$	1011	17.312(17)	17.040(14)	16.578(14)	26.16(2)	97.2(2)	67(2)	100(6)
$Cu^{2+} + 2L^- + H^+ \longrightarrow [CuL_2H]^+$	1021	24.39(4)	24.04(4)	23.46(4)	22.84(5)	137.2(3)	90(3)	159(10)
$Cu^{2+} + 2L^- + 2H^+ \longrightarrow [Cu(HL)_2]^{2+}$	1022	33.52(8)	32.95(5)	31.94(2)	31.08(4)	188.0(3)	143(4)	151(13)
$2Cu^{2+} + 2L^- \longrightarrow [Cu_2L_2H_{-1}]^+ + H^+$	202−1	15.0(2)	14.85(15)	14.62(7)	14.3(2)	84.7(8)	40(13)	150(30)
$2Cu^{2+} + 2L^- \longrightarrow [Cu_2L_2H_{-2}] + 2H^+$	202−2	7.8(2)	7.80(10)	7.78(7)	7.75(15)	44.5(6)	−3(6)	159(20)
$3Cu^{2+} + 2L^- \longrightarrow [Cu_3L_2H_{-2}]^{2+} + 2H^+$	302−2	12.26(11)	12.28(6)	12.31(6)	12.35(9)	70.1(4)	−5(6)	252(20)
$Ni^{2+} + L^- \longrightarrow [NiL]^+$	0110	5.86(12)	5.70(10)	5.39(6)	5.3(2)	33(1)	34(9)	−5(30)
$Ni^{2+} + L^- + H^+ \longrightarrow [Ni(HL)]^{2+}$	0111	14.633(18)	14.393(17)	13.975(17)	13.67(2)	82.1(1)	57(2)	85(5)
$Ni^{2+} + L^- + 2H^+ \longrightarrow [NiLH_2]^{3+}$	0112	19.2(2)	19.1(2)	18.89(16)	18.65(18)	109(2)	32(10)	258(35)
$Ni^{2+} + 2L^- \longrightarrow [NiL_2]$	0120	10.01(4)	9.88(3)	9.68(3)	9.33(5)	56.4(2)	39(3)	58(10)
$Ni^{2+} + 2L^- + H^+ \longrightarrow [NiL_2H]^+$	0121	19.74(3)	19.42(3)	18.89(3)	18.40(3)	110.8(2)	78(3)	109(10)
$Ni^{2+} + 2L^- + 2H^+ \longrightarrow [Ni(HL)_2]^{2+}$	0122	28.64(3)	28.14(2)	27.28(2)	26.53(3)	160.0(2)	123(2)	124(6)
$Ni^{2+} + 3L^- \longrightarrow [NiL_3]^-$	0130	11.8(2)	11.7(2)	11.6(2)	11.3(2)	67(1)	27(15)	133(50)
$2Ni^{2+} + 2L^- \longrightarrow [Ni_2L_2]^{2+}$	0220	14.14(9)	13.96(8)	13.76(7)	12.9(2)	80(1)	68(8)	40(25)
$2Ni^{2+} + 2L^- \longrightarrow [Ni_2L_2H_{-2}] + 2H^+$	022−2	−5.02(16)	−4.80(8)	−4.32(7)	−3.89(13)	−27(1)	−67(8)	134(25)
$3Ni^{2+} + 2L^- \longrightarrow [Ni_3L_2H_{-2}] + 2H^+$	032−2	−1.2(2)	−0.92(15)	−0.49(10)	0.23(8)	−5(2)	−82(9)	258(35)

[a] ΔG° and ΔH° in kJ mol^{-1}; ΔS° in J K^{-1} mol^{-1}; 25 °C. [b] The errors in parentheses are ±3σ in the last significant figure(s).

Table 3. Thermodynamic parameters for the formation of Cu^{2+}– Ni^{2+}– δ-hydroxylysine mixed-metal complexes, at $I = 0.15$ mol dm^{-3} ($NaNO_3$)

		log β_{pqrs}						
Reaction	*pqrs*	18	25	37	47 °C	$-\Delta G^{\circ a}$	$-\Delta H^{\circ a}$	$-\Delta S^{\circ a}$
$Cu^2 + Ni^{2+} + 2L^- \longrightarrow [CuNiL_2H_{-2}] + 2H^+$	112−2	2.76(6)[b]	2.83(4)	2.95(5)	3.04(4)	16.2(3)	−17(4)	110(15)
$2Cu^{2+} + Ni^{2+} + 2L^- \longrightarrow [Cu_2NiL_2H_{-2}]^{2+} + 2H^+$	212−2	10.42(11)	10.44(8)	10.45(7)	10.45(15)	60(1)	−2(7)	208(15)

[a] ΔG° and ΔH° in kJ mol^{-1}; ΔS° in J K^{-1} mol^{-1}; 25 °C. [b] The errors in parentheses are ±3σ in the last significant figure(s).

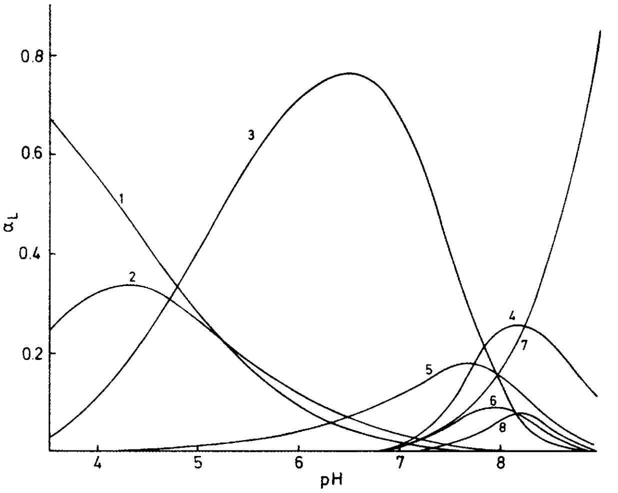

Figure 1. Species distribution α_L *vs.* pH for the ternary Cu^{II}–Ni^{II}–H_3L^{2+} system; $c_{Cu} = 4.99$, $c_{Ni} = 5.01$, $c_L = 9.96$ mmol dm^{-3}. Species: 1, $[H_2L]^+$; 2, $[Cu(HL)]^{2+}$; 3, $[Cu(HL)_2]^{2+}$; 4, $[Cu_2L_2H_{-2}]$; 5, $[Ni(HL)]^{2+}$; 6, $[Ni(HL)_2]^{2+}$; 7, $[CuNiL_2H_{-2}]$; 8, $[Cu_2NiL_2H_{-2}]^{2+}$ (only the species whose formation exceeds 5% were reported)

complexes of Ni^{2+}, although low, were taken into account. The spectra calculated for copper(II) binary and ternary complexes are shown in Fig. 3. The probable errors in ε values (3σ) are ±3—4% for $[Cu(HL)]^{2+}$, $[Cu(HL)_2]^{2+}$, $[Cu_2L_2H_{-2}]$, and $[CuNiL_2H_{-2}]$, ±8% for $[Cu_2NiL_2H_{-2}]^{2+}$, ±10% for $[Cu_3L_2H_{-2}]^{2+}$, and intermediate for the other species.

Discussion and Conclusions

As pointed out by some literature reports on the co-ordination chemistry of ethanolamino compounds,[10–14] alcoholic group dissociation is favoured in the presence of metal ions. So we found in solution, at lower pH values, complex species formed only through the interaction with the amino acid part of hydroxylysine, but also species formed at higher pH, in which the deprotonated ethanolamino group is probably involved as well. All the complexes reported here can be interpreted by assuming: (*i*) co-ordination only by the α-amino acid group ($[M(HL)]^{2+}$, $[M(HL)_2]^{2+}$); (*ii*) dissociation of the ω-amino group ($[ML]^+$, $[ML_2H]^+$); (*iii*) the involvement of the amino-ethanolate moiety ($[Cu_2L_2H_{-1}]^+$, $[M_2L_2H_{-2}]$, $[M_3L_2H_{-2}]^{2+}$, $[CuNiL_2H_{-2}]$, and $[Cu_2NiL_2H_{-2}]^{2+}$). The trinuclear species were previously suggested by Nyberg and Cefola[12] and are necessary for the correct explanation of some titration curves.

The formation of heteronuclear complexes takes place by substitution of a copper(II) by a nickel(II) ion, but without change to the stoicheiometry of the corresponding binary complex, as we have found in the formation of several other mixed-metal complexes.[1,3,4,6,8,9]

Some indications of the structural features of the species under study can be inferred from the thermodynamic parameters and visible spectra. The stoicheiometry and the pH range of formation suggest that for the species $[M(HL)]^{2+}$ and $[M(HL)_2]^{2+}$ only a glycine-like bond is present (the protonated ω-amino group does not interact). The values of ΔH° for the reactions $M^{2+} + HL \longrightarrow [M(HL)]^{2+}$ and $M^{2+} + 2\,HL \longrightarrow [M(HL)_2]^{2+}$ are −23 and −54 kJ mol^{-1}, respectively, for Cu^{2+} and −13 and −36 kJ mol^{-1} for Ni^{2+}. These values are consistent with the above hypothesis (see, for example, ref. 21).

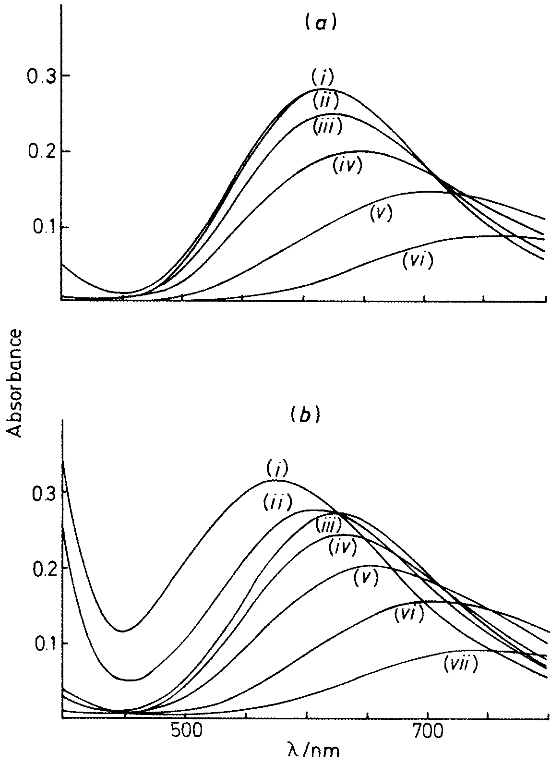

Figure 2. Visible spectra at different pH values: (*a*) 8.47 (*i*), 7.36 (*ii*), 6.17 (*iii*), 5.25 (*iv*), 4.19 (*v*), 3.13 (*vi*), c_{Cu} = 4.99, c_L = 9.98 mmol dm^{-3}; (*b*) 9.74 (*i*), 8.67 (*ii*), 7.15 (*iii*), 6.05 (*iv*), 5.08 (*v*), 4.10 (*vi*), 3.11 (*vii*), c_{Cu} = 4.99, c_{Ni} = 5.00, c_L = 9.99 mmol dm^{-3}, optical path length = 1 cm

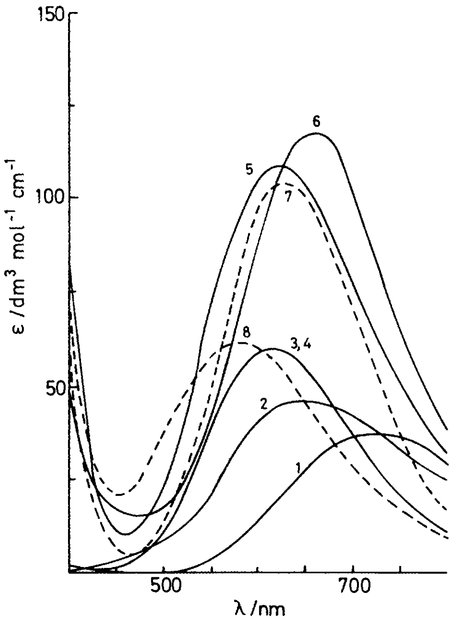

Figure 3. Visible spectra for the different species containing Cu^{II}: 1, $[Cu(HL)]^{2+}$; 2, $[CuL]^+$; 3, $[Cu(HL)_2]^{2+}$; 4, $[CuL_2H]^+$; 5, $[Cu_2L_2H_{-2}]$; 6, $[Cu_3L_2H_{-2}]^{2+}$; 7, $[Cu_2NiL_2H_{-2}]^{2+}$; 8, $[CuNiL_2H_{-2}]$

A further confirmation comes from comparison of the spectra of $[Cu(HL)]^{2+}$ and $[Cu(HL)_2]^{2+}$ [$\varepsilon_{max.}$ = 37, 59 dm^3 mol^{-1} cm^{-1}, $\lambda_{max.}$ = 727, 620 nm, respectively, Figure 3] with those calculated for mono- and bis-(alaninato) copper(II) complexes[22] ($\varepsilon_{max.}$ = 37, 57 dm^3 mol^{-1} cm^{-1}, $\lambda_{max.}$ = 723, 623 nm, respectively).

For $[CuL]^+$, both the log β value and the visible spectrum suggest a somewhat tridentate character. Since the interaction of Cu^{2+} with the ω-amino group is absent in the corresponding species with L-lysine[23] and the ΔH° value seems to exclude a second nitrogen donor atom, the tridentate character might derive from an interaction with the undissociated alcoholic group. For the corresponding nickel complex however, the observed ΔH° value does suggest involvement of the second nitrogen atom in $[NiL]^+$.

The coincidence (within the probable error) of the spectra calculated for $[Cu(HL)_2]^{2+}$ and $[CuL_2H]^+$ suggests a simple dissociation step in the reaction $[Cu(HL)_2]^{2+} \longrightarrow [CuL_2H]^+ + H^+$. Comparison between the ΔH° values estimated for the formation of these two complexes is in agreement with this assumption.

Among the dimeric species $[M_2L_2H_s]^{(2+s)+}$ those of the type $[M_2L_2H_{-2}]$ are the most relevant. Their probable structure involves co-ordination of both the acid and aminoethanol moieties of the ligand molecule, with deprotonation of the alcoholic group, since neither L-lysine nor L-ornithine[23] is able to form the same type of species.

The spectrum calculated for $[Cu_2L_2H_{-2}]$ exhibits $\varepsilon_{max.}$ = 109 dm^3 mol^{-1} cm^{-1}, $\lambda_{max.}$ = 621 nm, consistent with a bis(N,O) co-ordination for both metal ions {the value of $\lambda_{max.}$ being the same as that found for the amino acid-like $[Cu(HL)_2]^{2+}$ complex and only slightly different from that obtained for bis-(alaninato)copper(II)}. The scarcity of enthalpy values available in the literature[14] for reactions of the type Cu^{2+} + R–CHOH–$CH_2NH_2 \longrightarrow [Cu(R\text{-}CHO^-\text{-}CH_2NH_2)]^+ + H^+$, and the structural differences between the ligands previously studied (all having an alcohol group which can participate at the same time in two different chelating rings) limit the use of the thermodynamic data for structural elucidation. It is clear, however, that since four nitrogen atoms are involved in the formation of $[Cu_2L_2H_{-2}]$ and $[Ni_2L_2H_{-2}]$, alcohol group deprotonation reactions are highly endothermic and significantly more so than the corresponding reactions of aminoethanol compounds such as isoserine or 1,3-diaminopropan-2-ol.[14]

It seems likely that the formation of trinuclear complexes occurs through opening of the dimer structure and a successive addition of the third metal ion, with a transition from two four co-ordinated to one four-co-ordinated and two two-co-ordinated copper(II) ions. The small or negligible enthalpy change for the reaction $[M_2L_2H_{-2}] + M^{2+} \longrightarrow [M_3L_2H_{-2}]^{2+}$ might confirm the above suggestion, since the groups involved in co-ordination should be the same in both $[M_2L_2H_{-2}]$ and $[M_3L_2H_{-2}]^{2+}$. Although the low concentration of $[Cu_3L_2H_{-2}]^{2+}$ present in solution limits the estimation of a reliable visible spectrum for this complex ($\varepsilon_{max.}$ 115 dm^3 mol^{-1} cm^{-1}, $\lambda_{max.}$ = 650 nm), the spectrophotometric data indicate an intermediate situation between an (N,O) two-co-ordinated ($\lambda_{max.}$ = 723 nm and a bis(N,O) four-co-ordinated copper(II) ($\lambda_{max.}$ = 620 nm) and so are not in contrast with the structure proposed above.

The value of the enthalpy change estimated for $[CuNiL_2H_{-2}]$ suggests a structure similar to that proposed for $[M_2L_2H_{-2}]$. The spectrum expected for this complex should have a value of $\lambda_{max.}$ not very different from that for $[Cu_2L_2H_{-2}]$ with a rough halving of the $\varepsilon_{max.}$ value (with respect to the same dimeric species). However it is found that the calculated $\lambda_{max.}$ (581 nm) is significantly lower. Since no species of copper(II), formed by (N,O) donor bidentate ligands in aqueous solution has been characterized with a $\lambda_{max.}$ = 581 nm, it seems likely that the presence of Ni^{2+} in the heterobinuclear complex $[CuNiL_2H_{-2}]$ significantly affects the spectral behaviour of Cu^{2+}, as we have already suggested for the similar heteronuclear citrate complex $[CuNi(cit)_2H_{-2}]^{4-}$.[24]

For $[Cu_2NiL_2H_{-2}]^{2+}$, both the value of ΔH° and the calculated visible spectrum can be considered only as fair estimates of the true values. Neither however are inconsistent with a structure similar to that of $[Cu_3L_2H_{-2}]^{2+}$, with the substitution of one two-co-ordinated copper(II) by nickel(II).

Acknowledgements

This work was performed with the financial support of the Centro Nazionale delle Ricerche (Rome) and Ministero della Pubblica Istruzione.

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Received 29th September 1988; *Paper* 8/03867H